

Abstracts

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Plenary Speaker

Plenary Speaker

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Drilling the Chicxulub impact crater to understand planetary evolution and mass extinction

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Content

The most recent of Earth's five largest mass extinction events occurred 66 Ma, coeval with the impact of a ~14 km asteroid into what is today the Yucatán Peninsula, México, producing the ~200 km-wide Chicxulub crater. This impact, by some estimations, drove the extinction of 75% of life on Earth at the genus level. The mass extinction event marks the boundary between the Cretaceous and Paleogene. Proposed kill mechanisms include thermal effects caused by the reentry of fast ejecta into Earth's atmosphere, dust and sulfate aerosols reducing Earth's solar insolation, ocean acidification, and metal toxicity due to the chemical make-up of the impactor. The magnitude and duration of these processes is still debated, and further evaluation of the proposed kill mechanisms requires an understanding of the mechanics of the Chicxulub impact as well as the resulting global environmental perturbations.

In April and May 2016, the International Ocean Discovery Program, with co-funding from the International Continental Scientific Drilling Program, successfully cored into the Chicxulub impact crater with nearly 100% recovery. These cores include the first-ever samples of the transition from an intact peak ring through post-impact sediments. A peak ring is a discontinuous ring of mountains observed within the central basin of all large impact craters on rocky planets. Newly drilled cores include the uplifted target rocks, melt-rich impactites, hydrothermal deposits, a possible settling layer, and the resumption of carbonate sedimentation. The discovery that Chicxulub's peak ring consists of largely granitic crust uplifted by ~10 km calibrates impact models, allows for observation of impact processes, and for a first-order assessment of the environmental consequences of the impact ("kill mechanisms"). These cores provide an unprecedented opportunity to study the relationship between the kill mechanisms, the mass extinction event, and the initial recovery of life.

Interplay Between Magmatic, Tectonic and Hydrothermal Processes at Oceanic Spreading Centers

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Content

Significant progress has been made in recent years in understanding the interplay among the geological processes that produce the characteristics of oceanic spreading centers with different spreading rates. Along fast-spreading ridges, extension is mostly accommodated by magmatism. Magma supply is high resulting in frequent volcanic eruptions and relatively smooth seafloor topography. In contrast, at intermediate- and slow-spreading ridges, faulting with only intermittent volcanic activity accommodates a significant portion of the extension. In fact, the low magma supply at slow and ultraslow spreading ridges results in crustal accretion that is characterized by asymmetric exhumation along large-offset normal (detachment) faults and the formation of oceanic core complexes that expose lower crust and upper mantle rocks.

Hydrothermal circulation at oceanic spreading centers is driven by heat from crystallization of magma and cooling of young oceanic lithosphere. At fast-spreading ridges, axial magma chambers at depths of 1-2 km result in relatively shallow depths of hydrothermal fluid circulation, but as spreading rate decreases, fluids focused along large faults can reach depths of perhaps 5 to more than 8 km. The role of faulting is most extreme at ultraslow-spreading ridges where permeability becomes increasingly important as a secondary control on hydrothermal vent field frequency.

Despite the large variations observed in the chemical compositions of vent fluids discharging at mid-ocean ridges and at back-arc spreading centers, there are similarities in the fundamental processes — fluid-mineral equilibria, phase separation, magma degassing, interactions with overlying sediments — that contribute to vent fluid chemistry. Seawater entrained in deep-sea hydrothermal systems may chemically react with various rock types, ranging from mafic (basalt, gabbro) and ultramafic rocks (peridotite) at mid-ocean ridges to more felsic volcanic rocks (andesite, dacite, rhyolite) at back-arc spreading centers due to proximity to the subducting slab. Phase separation can occur at depth within the basement, resulting in the partitioning of chemical species and volatiles into different fluid phases. In some cases, particularly in back-arc settings, magmatic degassing that can add volatiles and metals to the circulating fluids. This complex interplay between magmatic, tectonic and hydrothermal processes facilitates the cycling of heat and mass between the Earth and the oceans.

New discoveries on the Origin of Life: Darwin's Warm Little Pond revisited

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Content

Darwin first postulated, 145 years ago, that life might have originated in "...some warm little pond with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc. present, that a protein compound was chemically formed, ready to undergo still more complex changes...". However, the 1970's discovery of black smokers and their rich vent fauna, together with evidence from the mitochondrial tree of life, led to the currently prevailing view that life got started at deep sea vents.

But it turns out that the energy required for polymerisation of organic molecules from simple amino acids comes from expelling a water molecule. In addition, the cytoplasm of cells from all three branches of life have K⁺/Na⁺ ratios more aligned with fresh water than seawater, and that certain key elements (B, Zn, Mn) required as catalysts for polymerisation are hard to concentrate in a marine environment. Thus, the oceans, or any permanently wet environment, is not suitable for prebiotic chemistry and a land-based environment undergoing wet-dry cycles is required for an Origin of Life setting.

What kind of environment?

Previous authors have suggested a desert with occasional rain, or a river flowing over komatiitic crust as possible sites for the Origin of Life. But these cold-water environments lack the capacity for compositional complexity and highly reactive interfaces.

Recent discoveries from an ancient analogue site in Western Australia's Pilbara region provide support for an Origin of Life in terrestrial hot springs. The 3.48 Ga Dresser Formation is well known as hosting some of Earth's oldest convincing evidence of life (stromatolites, fractionated stable isotopes, putative microbial remains), all within an active volcanic caldera characterised by voluminous hydrothermal fluid circulation. Previously, the depositional environment was considered as shallow marine, but the recent discovery¹ of geyserite and other siliceous sinter deposits containing biosignatures and spatially associated with stromatolites, point to a thriving terrestrial hot spring setting with wet-dry cycles. A parallel, key discovery is of concentrations of the key prebiotic elements (B, Zn, and Mn), arising from hot water-rock interactions. These discoveries are leading to a developing model for the Origin of Life in terrestrial hot spring fields, and have implications for Astrobiology and the search for life elsewhere in the Solar System.

¹ Djokic, T. et al. (2017). Nature Communications 8:15263

Nonclassical nucleation and crystallization

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Content

In recent years, research on nucleation and crystallization has revealed alternative pathways to the classical ones known from the textbooks of crystallization. These so called nonclassical pathways allow for a better understanding of so far difficult to understand crystallization processes as observed for example in Biomineralization. In addition, they open up entirely new possibilities for the control of crystallization processes and therefore crystals, which would be impossible to synthesize by classical methods.

The presentation will start with nonclassical nucleation processes for the example of CaCO_3 . It can be shown that so called prenucleation clusters of ca. 40 ion pairs in size exist in equilibrium with the ions and ion pairs. These clusters are highly dynamic polymers which constantly form and dissociate. Their formation is entropically driven by the release of hydration water. Increasing the overall ion concentration leads to a decrease in their dynamics and a phase transition in form of binodal demixing to nanodroplets. These coalesce and form larger droplets which solidify and form amorphous CaCO_3 , which finally crystallizes. This multi-step nucleation scenario is not only relevant for CaCO_3 , but also other minerals like calcium oxalates or phosphates.

Once nanocrystals are formed, they are expected to grow layer by layer according to the textbook knowledge. However, they are also able to interact with each other and form crystallographically aligned superstructures of individual nanoparticles combining the properties of nanoparticles with those of crystals. These structures are called mesocrystals. For the example of CaCO_3 Biominerals like a sea urchin spine, it will be shown that Nature is using this highly interesting crystalline structure for the generation of crystals with improved mechanical properties. For the example of calciumsilicate hydrate – the binder in cement – it will be demonstrated that such structures can be mimicked synthetically leading to fracture resistant cement outlining the technological potential of such nonclassical structures.

The Rise of the Andes: Growth of an Orogen and Climate Change

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Content

The Andean plateau is the 2nd largest active orogenic plateau on Earth, with over 600.000 km² of topography located at >3 km above sea level. Over the last decade, the formation of this spectacular feature has been linked to global and regional climate change, and increased South American biodiversity. The processes related to high-elevation plateau formation include not only deep seated lithospheric scale geodynamic processes, but also interactions between climate, tectonics, and topography. In this plenary lecture, I address the seemingly simple question of 'How, when, and how fast did the Andean Plateau rise?'. To answer this question, thermochronology, structural geology, and stable isotope paleoaltimetry observations are integrated with atmospheric general circulation model simulations to quantify the timing of the Andean Plateau width and height formation. For example, low-temperature thermochronometer data from across the Andes provide valuable constraints on the timing of exhumation. When combined with balanced cross-sections at different latitudes these observations provide insight into the timing of plateau width and proximal fold-and-thrust belt formation. Stable isotope paleoaltimetry techniques applied to carbonate nodules in paleo soils have recently emerged as a powerful tool for reconstructing the elevation history of orogens. However, the interpretation of paleo-elevations from this technique are sensitive to not only surface uplift, but also climate change that occurs in response to surface uplift. In this talk, I integrate stable isotope paleoaltimetry data with atmospheric general circulation models to provide a significantly revised, and controversial, interpretation of the elevation history of the Andean plateau. When considered together, the plateau width and height observations presented here suggest a slow and steady rise of the Andes over the last 40 Ma, and new insights into how the lithosphere and atmosphere interact over geologic time scales.

Session 1.1: Geohazards in time and space: Poster

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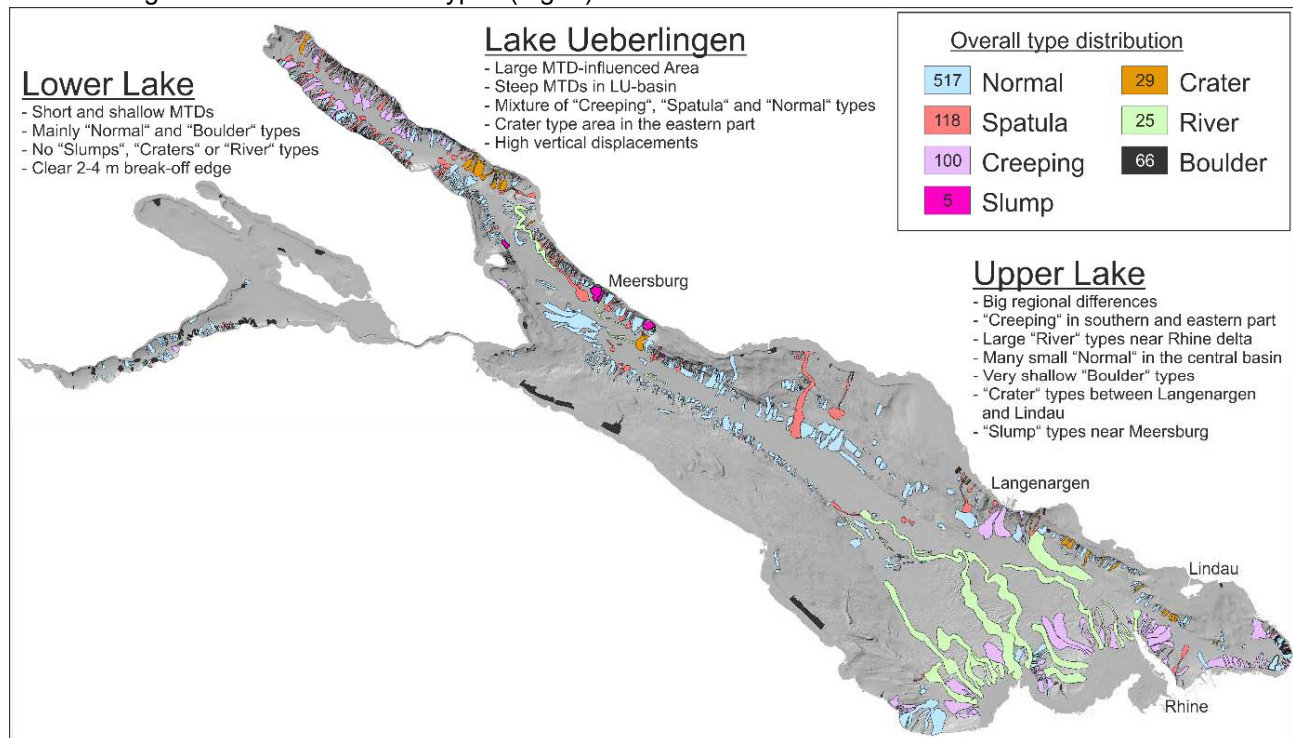
Distribution and mechanisms of mass transport deposits in Lake Constance, central Europe – discoveries from high-resolution hydroacoustic data

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Content

In 2013 and 2014, the largest German lake has been re-surveyed. The transnational project "Tiefenschärfe", funded by the European Union (INTERREG IV) and Switzerland (Schweizerische Eidgenossenschaft), delivers a detailed digital elevation model (DEM) of the lake floor. GIS analyses reveal a large amount of mass wasting events occurring on all slopes and influencing large parts of the lake floor. Within the geomorphologic investigation a manual picking of mass transport deposits (MTD) as well as a digital reconnaissance were carried out. The latter is based on the visual appearance of mass transport deposits and elevation-derived morphometric parameters. In total, we could identify more than 800 MTD and were able to assign them to several MTD-types (Fig01).



Distribution of MTD-types in Lake Constance.

The abundance and distribution of identified "river" type events verify the dependence on Rhine associated hydrodynamic patterns and the reduction of its erosional potential since the "International Rhine Regulation" (1900). Additionally, "crater"-shaped initiations of events co-occurring with aligned pockmarks possibly

indicate new locations of groundwater-leakage and the joint mechanism of groundwater intrusion, gas bearing of sediments and remnant Alpidic, sub-bottom faulting. The evaluation of the pre-conditioning of Lake Constance' slopes reveal the affinity of surficial sediments to distribute littoral sand and silt into the basins via turbiditic debris flows. This may be the result of high clay/sand ratios and potential hydroplaning enhancement.

Long-term relationship between landslide occurrence and precipitation in southern Lower Saxony and northern Hesse

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Content

No other natural hazard is in such a way present and common in the uplands in Germany as landslides. In the geohazard research this term is used for a downslope and rapid displacement of soil and rock material as well as rockfall processes.

In context with the evaluation of climate impact on soil water content it is known that the occurrence and the frequency of landslides is correlated with short- or long-term positive anomalies of soil moisture. These are significantly controlled by heavy precipitation and/or periods of distinct moisture. It implies that slope stability is determined at first by the basic susceptibility given by the characteristics of relief and soil and at second by a variable susceptibility controlled by weather conditions.

A dataset for southern Lower Saxony and northern Hesse with information of 400 landslide events occurring between 1901 and 2016 is used for the evaluation of their temporal distribution. Landslide data are compared with monthly and yearly precipitation records of a synthetic precipitation series as representative for the study area. The synthetic data series is generated with precipitation records from 17 stations. The relationship between the occurrence of landslide events and the precipitation is to be evaluated and explained for the entire period. Furthermore, the seasonal distribution is discussed.

The temporal distribution of landslides shows an increasing linear trend in which phases of high and low landslide activity alternate. The correlation with the annual precipitation predominantly shows a more frequent occurrence of landslides in more humid years. These lay within periods in which the seasonal distribution of precipitation is primarily characterized by wetter summers and drier winters. First, an accumulation of events in the winter months (Jan. - Mar.: 30 %) can be identified for the entire period. A second peak appears in the summer months (Jun. - Aug.: 33 %). In general the seasonal landslide distribution follows the annual course of precipitation. Particular seasonal distributions are apparent where periods of increased landslide activity do not coincide with winter and/or summer precipitation trends. In these periods the seasonal distribution does not follow the annual precipitation trend.

Rock Garden - a supercritical accretionary ridge at the Hikurangi margin, New Zealand

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Content

Submarine landslides are important geological hazards for seafloor facilities and may generate tsunamis that can cause substantial coastal damage. Numerous studies have hypothesized that gas hydrates play a major role in controlling slope failure initiation and mass movement processes, but the issue remains controversial. To gain a better understanding of the controlling factors of slope destabilization, i. e. especially the interaction of tectonic steepening and gas hydrate transformation, we investigated the frontally accreted ridge at Rock Garden of the Hikurangi subduction zone east of New Zealand's North Island during the RV SONNE expedition SO247. The frontally accretionary ridge Rock Garden, the exceptional steepness of which has been caused by the subduction of a seamount, is located in about 600-800m water depth. A bathymetric map with a grid size of 8-13 m was generated based on EM710 data. Combined EK60 system data, a single beam scientific echosounder, 11 different gas flares were directly observed at Rock Garden. In Rock Garden, we took 22 gravity cores with a length of 1-6.5 m and drilled altogether three MeBo200 sites with a length of 37 m on average. During cruise SO247, shipboard measurements of sediment physical properties were restricted to undrained shear strength, moisture and density measurements (MAD) and magnetic susceptibility. In the XRF-laboratory Bremen we measured the light elements Al, Si, S, K, Ca, Ti, Mn, Fe and the heavier elements Sr, Rb, Zr, Br with a resolution of 1 cm. From the light elements we see paleoclimate changes during sedimentation. From the heavier elements it is possible to detect the visible tephra layers and also cryptothepras. With the MSCL (Multi-Sensor Core Logger) we measured the magnetic susceptibility, gamma density and the p-wave velocity. The results are being used to undertake sediment-tectonic investigations to understand why chemical and physical properties of the two MeBo-cores from the top of Rock Garden, which are only 2 km apart from each other, differ so significantly. Geochemical investigations of the core material GeoB20824-4 suggest that we drilled through a fault. The high lithium content in the sediments of the GeoB20824-2 below 18m indicates warm source fluids with temperatures about ~80°C with a geothermal gradient of 40°C/km. We are using quantitative morphometric tools to understand the fault zones of Rock Garden. The results will be compared with those of scaled sandbox experiments.

The superposition of Mesozoic to Cenozoic structural elements in the SW-German North Sea and their influences on fluid migration through barriers

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Content

Sedimentary and structural elements in the Mesozoic to Cenozoic deposits, such as tunnel valleys, polygonal fault systems, faults and salt structures, may have high impact on barrier integrity of sediments in which they are hosted. Especially in regions where these structures are in superposition to each other, they may form network-like fluid pathways connecting deeper reservoirs and the seafloor. Moreover, a hypothetical genetic dependency of such a superposition of structural elements, e.g. between tunnel valleys and salt diapirs as well as between salt diapirs and polygonal faults has been discussed in literature. However, within the German North Sea sector a comprehensive (mapping) study dealing with these linked topics is missing so far.

Within the present study, which is embedded in the project TUNB at the Federal Institute for Geosciences and Resources (BGR), we aim to characterize the superposition and possible (genetically) interaction of glaciogenic erosional structures with underlying connected structural elements, such as crestal fault systems of diapirs, step faults, polygonal faults as well as sediment bodies of a delta system in the SW-German North Sea sector. To achieve this, all structural elements are mapped based on a comprehensive 2D-seismic data set, and subsequent surface modeling is accomplished. Based on this, the following attribute maps are compiled: i) regions, where tunnel valleys intermesh with crestal faults, ii) regions, where tunnel valleys are in contact to faults/step faults within Cenozoic sedimentary successions, iii) regions, where tunnel valleys are in contact to faults/step faults within Cenozoic to Mesozoic sedimentary successions, iv) regions, where polygonal faults are penetrated by faults affecting the Cenozoic and v) regions, where polygonal faults are penetrated by faults affecting the Cenozoic to Mesozoic. Thereby we will identify regions of increased connectivity of glaciogenic structures with older structures below. On type localities we will also evaluate the possible impact of the superposition of structural features on the barrier integrity of rock units affected by those features, e.g. possible fluid pathways formed by interconnection of such structural features. The results of the present study may contribute to a future, high detailed structural 3D model and to a qualitative evaluation of the influence on barrier properties.

Session 1.1: Geohazards in time and space: Talk

Session 1.1: Geohazards in time and space: Talk
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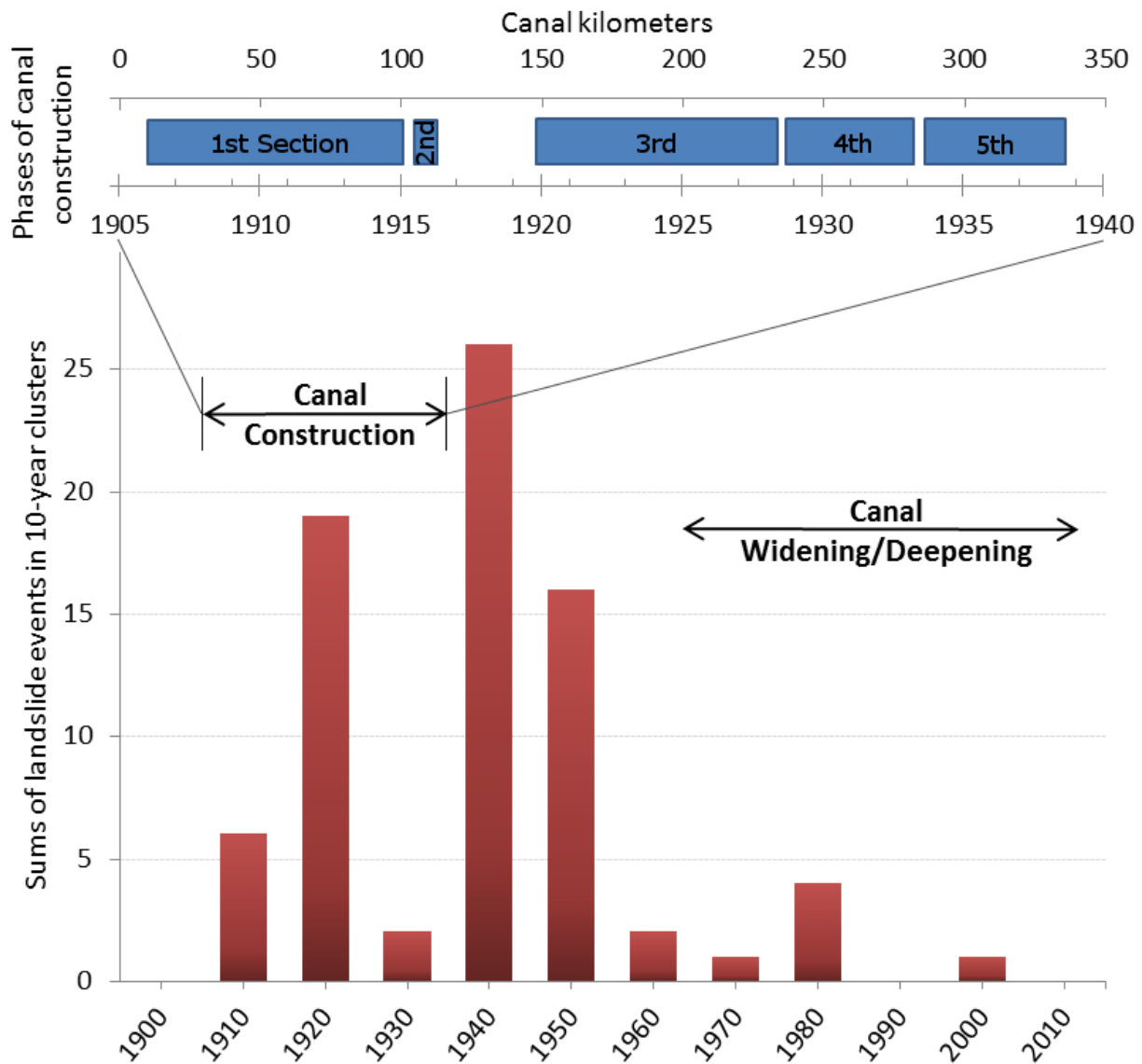
Case histories for post-construction landslides – examples from the Mittelland Canal (Germany)

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Content

The Mittelland Canal in Central Germany is the one of the important waterways within Germany connecting the Elbe River in the East with the Rhine River in the West. With a total length of 324,4 km it is the longest artificial waterway in Germany. The construction of the canal took 42 years and was divided into several sections with successive opening of the canal [1]. Construction phases were locally accompanied by landslide events involving medium to large volumes (up to 150 000 m³) which postponed the opening and increased construction costs. 77 landslide events spanning the last 120 years are extracted from the German landslide database [2]. Most information within the database is gathered by means of archive studies from inventories of emergency agencies, state, press and web archives, company and department records as well as scientific and (geo)technical literature. The information includes material characteristics, repair and mitigation measures as well as resultant costs.



Sums of landslide events in 10-year-clusters along the Mittelland Canal since construction with timeline of canal construction

From landslide clusters three case histories are developed. 88% of landslide events occurred in the first half of the 20th century between construction phases (1906 to 1938) and canal widening/deepening in mid-1960s (figure 1). During reconstruction of the canal (mid-1960s) the profile of the canal was locally changed by implementing steel pilings [1].

The main cause of slope failures are material characteristics of Mesozoic over-consolidated fine-grained sediments which destabilize due to bulging and shrinking respectively dynamic stress (construction and/or diapirism) [3]. Construction engineers were not able to detect unstable slope areas prior to construction but mitigation for slope stabilization was evolved contemporary [4]. Subsequently only few landslides occurred, which are concentrated at tributary canals. At former landslide hotspots, slopes are still moving though, today in a creeping movement.

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Combining surface and subsurface analyses for the reconstruction of landslide dynamics

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Content

Conducting landslide research in areas where the data basis is limited or sparse requires great effort in data acquisition. Therefore, a common approach is to develop representative case studies in order to learn more about the characteristics of a specific region. The application of relatively cost-effective methods thereby improves the process of data collection. In areas, which are commonly affected by landslides, these information have great value in order to provide the base for a landslide vulnerability assessment.

This study is situated in the State of Veracruz (Mexico) as damaging landslide events occur annually and detailed data on causes and triggers are not yet available. The present case study aims to improve the knowledge concerning characteristics of landslides and their internal structure and further to identify involved movement processes in order to gain a better understanding of the process dynamics in the study area.

The case study is located in the Palma Sola-Chiconquiaco Mountain Range, a volcanic massif, situated in the eastern part of the Trans Mexican Volcanic Belt, in the State of Veracruz. The geology in the research area is characterized by a Late Tertiary volcano-sedimentary succession, which is dominated by claystones, siltstones, basalts, and andesites. The steep slopes are mainly formed by basalts and partially by andesites. The more moderate inclined slopes are covered by massive, inhomogeneous slope deposits (thickness up to 50 m), which often correspond to instable zones.

Aerial photographs were collected by an unmanned aerial vehicle (UAV) in order to generate 3D-models, using the Structure from Motion workflow. The resulting digital elevation model served as basis for further geomorphological investigations. To obtain reliable information on the subsurface composition, electrical resistivity tomography (ERT) as well as seismic refraction tomography (SRT) were combined.

The investigations reveal a good agreement of ERT and SRT and the geophysical results support the geomorphological observations very well. Geophysical investigations reveal the presence of a large earlier landslide, which indicates that the landslide event from 2013 corresponds to a reactivation process. The thickness and internal structure of the slide mass can also be determined. This methodological approach enables a far-reaching visualization of complex landslide bodies and strongly supports the reconstruction of internal structures and process dynamics.

Data acquisition methods for landslide proxies.

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Content

It is generally known that data acquisition for landslide inventories is a time consuming task. For inaccessible landslides or for data which can not be reconstructed through field investigations proxies like administrative archives, news reports, etc. are the only alternatives to get information [1]. Furthermore, many proxies point to locations of unknown landslides. Over time many different proxy source formats have been established which carry information about landslides [2]. Lately, digital sources present the possibility to automatically search and extract information and facilitate faster information acquisition [3]. The aim of this work is to facilitate comparability by presenting a standardized set of acquisition methods for historical and contemporary landslide proxy data. Archives which are not digitally available demand intensive manual work to search through. Therefore, data selection processes begin before the data is sighted. Contrarily, digital data for machine learning processes is almost effortlessly acquired and thus the selection process is applied after the sighting of data. It is found that the availability of pictures and the overall quantity of proxy sources increased over time. Machine learning methods for digital sources generate many false positives. Best results are obtained by ranking sources to manually work through them. In conclusion, the amount of different proxy sources requires a common methodological approach for comparability. Digital sources increase acquisition speed and information content due to overlapping coverage and respective pictures. Validation of all found information is usually mandated, but can often be done by remote sensing methods.

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Lahar hazard at Colima volcano caused the 2015 Hurricane Patricia investigated by repeated drone surveys and time lapse cameras

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Content

Colima is one of the most active volcanoes in Latin America, with frequent dome building eruptions and pyroclastic flow hazards. In July 2015 Colima had a new climax of eruptive activity, profoundly changing the summit morphology and redistributing volcanic ashes to the lower volcano apron. These unconsolidated ashes are prone to be mobilized by rainfall events, and therefore required close monitoring. A major hurricane then had landfall in western Mexico in October 2015, accumulating c. 450 mm of rainfall at a meteorological station at Nevado de Colima (3461 m) and immense lahar and ash deposit mobilization from Colima Volcano. Hurricane Patricia was the largest ever recorded category 5 storm, directly crossing the state of Colima. Due to the successful scientific advice and civil protection no human losses were directly associated to this lahar hazards.

We have conducted drone overflight in profound valleys that directed the pyroclastic flows and lahars two days before and three days after the hurricane. Over 8,000 close range aerial photographs could be recorded, along with GPS locations of ground stations. Images were processed using the structure from motion methodology, and digital elevation models compared. Erosion locally exceeded 10 m vertically and caused significant landscape change. Mass mobilization unloaded the young pyroclastic deposits and led to significant underground heat loss and water boiling in the affected areas. We also firstly report the use of camera array set-ups along the same valley to monitor lahar deposition and erosion from different perspectives. Combining these photos using photogrammetric techniques allow time series of digital elevation change studies at the deepening erosional ravines, with large potential for future geomorphic monitoring. This study shows that photo monitoring is very useful for studying the link of volcano landscape evolution and hydrometeorological extremes and for rapid assessment of indirect volcanic hazards.

Pyroclast-forming Submarine Volcanism: Mechanisms and Hazard Potential

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Content

The vast majority of volcanic activity takes place under submarine conditions. Since we know that subaerial volcanic eruptions had, and in future will have, the potency to influence the global climate, and thus the whole biosphere of earth, the question arises what might be the impact of a major submarine volcanic eruption. The key factors that determine the impact of an eruption are the mass eruption rate (i.e. the output of magma per unit time), the total mass of magma erupted, and the coupling to the environment (i.e. the flux rate of heat, gases, and particles), which is dominated by explosive magma fragmentation. Even during a large eruption, the impact on the environment can be no more than minor if no significant magma fragmentation occurs. We know little about large-scale submarine eruptions, however, insight from numerous submersible expeditions and seafloor sampling operations revealed the existence of much more volcanoclastic material than expected (White et al., 2003). Are such deposits products of explosive volcanism and in what amounts are they produced? So far, only a few experimental studies on the thermal interaction between magma and water under subaqueous conditions exist (Oddson et al. 2016, Zimanowski et al., 2015). These experiments demonstrate a dramatic increase of the heat-flux into the surrounding water, if magma fragmentation occurs. On a large scale, this might lead to the formation of a very large thermal plume, which then might have a major impact on the oceanic circulation and the atmosphere, causing something like a volcanic “Super El Niño” or even the “Kiss of Death” (Kerr, 2005).

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Statistical landslide susceptibility assessment in zones of rapid urban development: case study Lanzhou city

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Content

Statistical landslide susceptibility assessment (LSA) is being extensively applied in landslide prone areas to support disaster risk management activities. Generally, in statistical LSA the assumption of model stationarity is made to enable causal reasoning from incomplete datasets. In particular, this works well in slow-evolving natural systems. However, in zones of rapid development, urbanization may significantly affect the landscape violating the presumption of model stationarity. This set new challenges for the statistical LSA. The evaluation of consequences on the conventional statistical LSA in zones of rapid urbanization and possible adaptation strategies are important topics that are investigated in the framework of the project "Landslide Hazard and Risk Assessment Lanzhou (LHARA)". This cooperation project is implemented by the China Geological Survey (CGS), China Institute of Geo-Environment Monitoring (CIGEM) and the Federal Institute for Geosciences and Natural Resources (BGR) of Germany. The current study introduces conditions of the Lanzhou area and presents an approach to estimate the evolution of the landslide susceptibility patterns mainly caused by man-made activity. Therefore, data of different origins representing different temporal states were compiled to a multitemporal dataset covering historical and recent land use data, landslide inventories, geomorphological change detection, and digital elevation models. Based on this dataset, statistical assessment based on generative Bayesian approach was applied. As a result, three landslide susceptibility maps depicting the landslide susceptibility patterns for the years 2000, 2012 and 2016 were generated.

The results show that the evolution of the susceptibility pattern is mainly influenced by geomorphological reshaping activities due to leveling of mountainous areas prior to construction of new infrastructure facilities. Although artificial irrigation can also be assumed as a serious factor for slope destabilization in the loess environment, its impact is difficult to assess reliably due to missing quantitative data and accurate patterns for irrigated areas in the past. Generally, the understanding of the causal relations between human activity and landslide susceptibility will allow the elaboration of scenarios for spatial planning of new city development areas and adapted strategies for mitigation of the risks associated with landslide events.

Session 1.2: Archives of Quaternary climatic and environmental changes: Poster

Session 1.2: Archives of Quaternary climatic and environmental changes: Poster A-583

Applying different statistical methods on high-resolution geochemical data of Lake Stymphalia (Greece)

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Content

X-ray fluorescence analysis (XRF) is a useful method to obtain continuous, high-resolution climate records. Here, we present new geochemical data for Lake Stymphalia, covering the last 5,000 years BP, and propose different statistical methods to gain meaningful proxies for the palaeoenvironmental interpretation of the dataset.

XRF scanning analysis of lacustrine sediments can provide a very high temporal resolution and thus has an enormous potential to be compared with archaeological data and further local and regional palaeoenvironmental data. This study presents new interpretation on geochemical data of sediment cores from Lake Stymphalia (Peloponnese). While the palaeoenvironmental record spanning the period 15,000-5,000 cal BP has already been published (Heymann et al., 2013), we here present new data covering the archaeologically interesting last 5,000 years BP.

We use our XRF and sedimentological proxies in combination with Bayesian age-depth-modeling of ¹⁴C dates, thereby testing and comparing different modeling tools (OxCal, Clam and Bacon). The Rb/Sr ratio as a proxy for chemical weathering indicates different oscillations and pronounced transition phases, especially around 1,400 cal BP, corresponding to a phase described by Büntgen et al. (2016) as Late Antique Little Ice Age. The Ca/Sr proxy may be used to reconstruct evaporation and likewise shows a pronounced peak around 1,400 cal BP, pointing towards colder climate conditions. We investigate the potential of different correlation analyses (grouped correlations, sliding window correlations, correlation matrices) in finding variations and coupling effects between different elements over time. Principal Component Analysis (PCA) adds a new and more complex interpretive approach to the dataset. While PC1 seems to provide information on the source and origin of the sediment, PC2 seems to reflect the change between oxic and anoxic conditions in Lake Stymphalia over time as do the chemical elements Mn and Fe. As a next step, investigations on the complex interplay between natural and anthropogenic forcing of landscape change shall be carried out to identify appropriate proxies for the human impact on the landscape.

The geochemical data from Lake Stymphalia is the starting point for a more detailed and comprehensive environmental reconstruction using lacustrine sediment data from the surrounding of the Gulf of Corinth.

Coastal landscape evolution in NW Sri Lanka linked to variations in the SW monsoon intensity during the last deglaciation

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Content

The intensity of the Indian summer monsoon varies over decadal to millennial time scales and is reflected in changes in surface processes, terrestrial environments, and marine sediment records. In Sri Lanka, the sedimentary record of coastal dunes provides evidence for repeated changes of aeolian deposition and fluvial erosion or ferrallithic red soil formation in response to a change of climatic conditions from dry to wet during the last deglaciation. Yet, these environmental shifts are poorly resolved because there is largely a lack of age constraints. Facies analysis of a lithological section at the Point Kurdimalai sea cliff in the Wilpattu National Park reveals, however, a striking resemblance to the stratigraphic succession associated with the Teri Red Sands in southeastern Tamil Nadu (S India), which is fairly well dated. This allows for regional litho- and climate stratigraphic correlations across the Gulf of Mannar and links the landscape evolution at Point Kudrimalai to variations in monsoon circulation.

Ecological responses from the northeast of Brazil since the Last Interglacial inferred from palynomorphs analyses

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Content

Changes in the ocean circulation have strong influences on Earth's climate due to the properties of ocean currents in heat transfer. Palaeoceanographic studies correlate the oceanic and atmospheric dynamics with climate changes. The palynology (using terrestrial pollen, spores and marine dinoflagellate cysts) is an excellent tool to determine the development and dynamics of the terrestrial (flora, fauna, temperature changes and rainfall) and oceanic (sea level fluctuations, sea surface temperature and salinity as well as ocean currents intensity) environments.

During the long sequence of Quaternary ice ages the climate was cooler and drier, the last glacial also had the highest sequence of warm climate events (Rasmussen et al., 2014), it had directly affected the biodiversity in the Northern Brazil and even the patterns of atmospheric and oceanographic local circulation. Those climatic influences will be directly reflected in the pollen and dinocysts analysis. This work aims to do palynological studies on a sediment core from continental shelf of Barreirinhas Basin, is located in the Northeastern Brazil, respectively.

Palynological analyses of the ocean core aims to elucidate (based on occurrence and concentration interchange of terrestrial and marine palynomorphs and its quality) how this atmospheric and oceanic teleconnections works on environmental responses like the Amazon River and Parnaíba River flow force during the last glacial and its oscillating climatic events (HS and D-O). The variability in sea surface temperature (SST) of these currents also modulates the position and intensity of the Inter Tropical Convergence Zone (ITCZ) (Burckel et al., 2015), an atmospheric stream that controls the climate ecological response in South America Northern Northeastern which increases the amount of water available in the water systems of the area. Understanding the response of terrestrial vegetation and palaeoproductivity front of the wide range of climatic mechanisms is essential to determine the ecological response to current abrupt climate change.

Paleoenvironmental investigations on peat sediments from Vankervelsvlei in the Year-Round-Rainfall Zone of South Africa

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Content

Lake sediments as well as peat deposits provide excellent archives to investigate past environmental and climate variability. Vankervelsvlei, a fen at the southern cape coast, in the Year-Round-Rainfall Zone (YRZ) of South Africa, located 152 m above mean sea level is one of the scarce environmental archives in this region. From this fen a 15 m long sequence was retrieved and analysed using a multi-proxy approach. The wetland has previously been described as a 'Schwingmoor' (floating bog), based on the assumption of a water column between the sediments and a floating vegetation mat. In this study, the recovery of a continuous sediment sequence from the surface of the wetland down to dune sediments forming the bedrock has resulted in revision of the 'Schwingmoor' hypothesis.

The chronology is based on 13 radiocarbon ages and reveals a basal age of 37,720 +940/-1,160 cal BP. A rather dry phase from 37,720 +940/-1,160 to 28,520 +375/-450 cal BP is followed by a hiatus (28,520 +375/-450 – 8,360 +730/-810 cal BP) likely reflecting the driest conditions of the record. This is likely caused by an increase in the Antarctic sea ice extent which resulted in an equatorward shift of the Westerlies, blocking the tropical easterlies which resulted in dry conditions at the south coast. A mean annual insolation maximum at 34 °S potentially increased the evapotranspiration at Vankervelsvlei and in turn contributed to the desiccation of the fen and decomposition of previously accumulated peat.

During the Early Holocene reworked soil and subsequent resumed peat formation at 6,820 +305/-365 cal BP in Vankervelsvlei point to moister climatic conditions. This is potentially driven by the contraction of the Antarctic sea ice and a poleward shift of the Westerlies during the Holocene. In general Vankervelsvlei appears to be an evapotranspiration controlled system, in which wind seems to be the dominant driver compared to temperature.

Patagonian Ice Sheet Geometry & Dynamics in South-Western Chile during the Last Glacial Period

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Content

During the last glacial cycle the Patagonian Ice Sheet (PIS) extended approx. 1800 kms along the Andean Cordillera. Whilst a number of detailed geochronological constraints exist for the horizontal and vertical dimension of the PIS during the last glacial, all but two chronologies focus on the former eastern terminating margin. In order to better understand glacier-climate dynamics in southern Patagonia comprehensive chronologies of glacier expansion and recession along longitudinal transects are needed. During Polarstern cruise 97 (ANT-XXXI/3) erratic boulders and bedrock samples were collected along the western margin of the Chilean Fjords (52-55°S) namely at: Islas Cabo de Hornos, Londonderry & Narborough. Cosmogenic surface & Optically Stimulated Luminescence exposure dating is being used on the geological samples to establish the extension and/or vertical dimension of the former PIS along its western margin. In addition IRD records from marine cores collected west of the terrestrial sample sites are developed to ascertain glacier-ocean-climate interactions during the last glacial period in southern south America.

Quaternary's subsidence anomaly in the North Sea, NW offshore Germany – a consequence of lower crustal flow?

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Content

The uppermost seismic units in the North Sea covering the Entenschnabel area, NW offshore Germany, have been studied systematically based on industrial multichannel 2D and 3D seismic data sets. As a result of these investigations, depth and thickness maps have been derived which are used in combination with well data for quantitative subsidence analyses.

The present-day depth of the Quaternary surface attains a maximum of 1050 m in the NW offshore Germany. The resulting subsidence rate of up to 380 m/Ma, indicates a more than ten-fold Quaternary increase in subsidence relative to average Cenozoic rates. In this study we consider a number of possible mechanisms explaining the observed Quaternary subsidence. With exception of isolated top diapir faults no significant indications for tectonically induced fault structures and extensional deformations are visible in our seismic profiles. Thus, a renewed tectonic activity and the development of pull-apart basins as origins for the Quaternary subsidence anomaly are excluded. Calculated subsidence values from sediment loading explain 400–500 m, reflecting half of the total Quaternary's subsidence pattern. During the Quaternary the area generally was characterised as subaerial or shallow marine, thus a major contribution from water-load is unlikely the case. Previously intraplate stress driven lithosphere buckling has been also suggested as a mechanism providing additional accommodation space for Quaternary sediments. However, the present-day compressional stress field in the central North Sea is mainly trending in a NNW-SSE direction. The Quaternary depocentre follows an axis consistently to this direction, questioning a causal relationship. Our preferred explanation links the Quaternary subsidence anomaly is a combination of sediment-load induced subsidence, enhanced by flow of ductile middle/lower crust beneath the North Sea basin. The observed Quaternary's deposition center fits well the location of sediment source area, which changed direction from East to Southeast during the Quaternary. This resulted in an increased sedimentation, about 50 km offset from the German part of the Central Graben. We suggest that the Quaternary sedimentation phase triggered enhanced subsidence and also crustal flow away from the area, resulting in supplementary accommodation space for further sediment supply. It might be speculated that at least portions of the mobile crust supports coincident uplift in surrounding onshore areas.

Sedimentary architecture and late Holocene dynamics of a polar gravel spit (King George Island, Antarctic Peninsula)

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Content

Sedimentary architecture and late Holocene development of a polar bay-mouth gravel spit system are presented based on ground-penetrating radar data, historical aerial images and radiocarbon dating. The spit is situated at the mouth of a tributary fjord formed by a tide water glacier and developed under the circumstances of an overall sea level fall. The system comprises two distinct marine terraces, situated below 0.8 m and at 3 to 5.7 m above present mean sea level. The upper terrace developed around 0.4 ka cal BP. It comprises several beach ridges formed by packages of seaward-dipping beds delimited by erosional unconformities. Beach ridges situated towards the more exposed western part of the spit facing the main fjord are internally characterized by convex aggradational bedding pattern. The lower terrace is located inside the bay in a more sheltered situation and comprises several curved beach ridges internally characterized by seaward-dipping beds delimited by erosional unconformities. The upper terrace is nowadays subjected to erosion and an up to 5 m high cliff developed towards the main fjord. There is a distinct shift in the direction of spit progradation through time, which we see as a reaction to intensified wave action at the beach and the retreat of the adjacent tide-water glacier. Furthermore, the lower terrace showed accelerated progradation during the last decades, probably in reaction to a reduction in annual sea-ice coverage, a lowering of the rate of glacioisostatic uplift and the subsequent stabilization of sea level, and an increased sediment availability.

The '4.2 ka BP event' and its influence on the paleo-environment and past human societies in the Western Mediterranean.

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Content

The Mediterranean is known as being very sensitive to climatic changes and, especially, suffering from aridity. Recently, this is of particular interest due to the ongoing global warming. In the Mediterranean area the '4.2 ka BP event' can be characterized as a drought, affecting mainly the monsoonal influenced eastern and central areas. Archaeologists have been shown that this event also caused severe crises in past human societies. The extent of this drought into the Atlantic-climate influenced Western Mediterranean remains unclear, since climate reconstructions in this area are sparse and the existing ones show contrary results and mostly have a rather low resolution. Nonetheless, contemporaneous and profound crises in human societies are known from this area and raise the question of a climatic influence.

This study tries to show whether this drought is evident in the Western Mediterranean and how it possibly affects the terrestrial vegetation as well as human societies. For this purpose, high-resolution marine sediment core ODP-161-976A from the Alboran Sea is studied for changes in precipitation (δD of terrestrial n-alkanes), Sea Surface Temperatures (U^k_{37} derived from alkenones), and C4 plant distribution ($\delta^{13}C$ of terrestrial n-alkanes) between 3 to 5 ka BP. This approach is new for the entire Mediterranean. The preliminary results, indeed, confirm the '4.2 ka BP event' and, moreover, indicate the presence of rather two distinct events.

Session 1.2: Archives of Quaternary climatic and environmental changes: Talk

Session 1.2: Archives of Quaternary climatic and environmental changes: Talk A-672

3D microfabric analysis of progressive, polyphase subglacial deformation beneath the late Weichselian Baltic Ice Stream (Scandinavian Ice Sheet, Europe)

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Content

We present the results of a detailed micro- and macrostructural study on the Late Pleistocene subglacial tills exposed in the sea cliffs at Jasmund on the Island of Rügen, northern Germany. These deposits form part of a major thrust and fold complex which developed as a result of glaciotectonism associated with the highly dynamic Baltic Ice Stream, which drained the Scandinavian Ice Sheet during the Weichselian. The island of Rügen is located on the southwestern Baltic Sea coast and was situated at the southern marginal zone of the Scandinavian Ice Sheet during the late Weichselian. Sediment-landform associations and flow-direction criteria derived from a variety of glacial deposits have been used to reconstruct successive glacial advances and retreats of this highly dynamic ice sheet across the Island of Rügen.

The microfabrics developed within the tills have been studied by means of a three-dimensional analysis based on the microstructural mapping methodology [1], enabling the identification and interpretation of the successive generations of fabrics in terms of a progressive, polyphase deformation history. The data sets derived from three perpendicularly oriented thin sections taken from 10 block samples, were used to construct detailed 3D models of the planar and linear microfabrics developed within the tills. The cross-cutting patterns of the microstructural domains which define these fabrics have been used to reconstruct a temporal succession of deformation events which occurred in response to ductile shearing imposed by the overriding ice. Three successive generations of microfabric have been identified: S1 (oldest) is a heterogeneously developed, up-ice-dipping, planar foliation (S fabric); whereas S2 is represented by a locally well-developed, down-ice-dipping linear fabric (L fabric); and S3 (youngest) is an anastomosing, variably developed subvertical fabric which probably formed as a result of the dewatering of the till during final stages of the shear event and the “locking” of the subglacial shear zone.

Shear-sense indicators, including asymmetrical S-C fabrics and C'-type shear bands, present within the tills are used to reconstruct the direction of ice flow responsible for subglacial deformation. This evidence, coupled with the orientation and relative age relationships displayed between the microfabrics have enabled the construction of a detailed 3D model of subglacial deformation beneath the Baltic Ice Stream.

Advancing mass spectrometry imaging of sediments: molecular stratigraphy with sub-mm resolution.

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Content

Marine sediments harbor specific molecular biomarkers that serve as recorders of past ecosystems because their source organisms slightly modify their molecular structure in response to environmental conditions. After sedimentation, the information archived in these molecules originally produced in the water-column is preserved over geological time-scales. Retrieval of this information by conventional analysis, i.e. molecular stratigraphy, is labor-intensive and requires relatively large samples that limit temporal resolution. To achieve unprecedented spatial (and thereby temporal) resolution in molecular proxy analysis, we propose a Mass Spectrometry Imaging (MSI) approach. It is based on matrix assisted laser desorption ionization (MALDI) coupled to ultra-high resolution mass spectrometry, avoids wet-chemical sample preparation and enables analysis directly on sediment sections at ~100- μ m-scale resolution. In 2014 we demonstrated the feasibility of this technique, and provided a fine-scale image of archaeal GDGT distribution on an undisturbed sediment [1].

The overarching goal of our dedicated ZOOMEULAR project is the interrogation of suitable archives, primarily laminated and dated sediment cores, for subannual to decadal climatic and environmental variations, and to investigate the nuances of the spatial distribution of biomarkers in their sedimentary context. Thereby we aim to advance molecular stratigraphy to a new level, regarding both the resolution of records and the understanding of proxy formation.

The most pressing requirements for advancing this technology to the routine level were to develop protocols for sample preparation and to extend the spectrum of analyzable compounds. Here we present an optimized sample preparation pipeline, which preserves sedimentary structure and provides thin sediment slices ideally suited for biomarker MSI and congruent sub-mm elemental mapping. This sample preparation, target-specific instrumental settings and the choice of a suitable matrix to aid ionization now allow the detection of additional biomarkers, such as long-chain diols and alkenones, or sterols. Long-chain alkenones and associated SST estimates are useful to complement GDGT-based data, as evidenced in the first μ m-scaled molecular stratigraphy records that are being generated for laminated sediment archives known to harbor rich paleoenvironmental information such as Cariaco Basin and Santa Barbara Basin.

[1] Wörmer et al. (2014) PNAS 111, 15669–15674.

Continuous ice surface lowering during the last glacial cycle, Fitz Roy Massif, Argentina

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Content

Southern South America is the only continuous landmass intersecting the southern westerly winds (SWW), which dominate the climate of the southern hemisphere and significantly influence global circulation patterns. Studies focusing on shifts in SWW location and/or strength during the last glacial period are still providing contradictory results. A tighter grid of proxy studies are needed to refine the regional palaeodynamics of the SWW.

The glacial geomorphology and geochronology is presented from three mountain valleys east of the Fitz Roy massif, southern Patagonia (49°S, 72°W). Boulders perched on bedrock, as part of glacier drift or on lateral moraines are used to build a vertical chronology of ice surface elevation limits through time utilizing cosmogenic surface exposure dating. Results provide information on the existence of glacier cover at the end of the last interglacial, progressive ice surface lowering during MIS3 and reduced ice surface elevations during the globally defined glacial maximum. Glacier-climate interactions will be discussed with focus on palaeoprecipitation changes in southern Patagonia.

Effect of different sediment components on the detectability of lipid biomarkers via spatially resolved, laser-based mass spectrometry

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Content

Recent technical and methodological advances in matrix assisted laser desorption ionization (MALDI) coupled to ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) have significantly increased the spatial resolution of lipid biomarker detection in geological sample material. Unlike the conventional analytical approach in organic geochemistry, this groundbreaking technology enables detection of organic molecules directly on the surface of intact sediment core sections. However, the impact of sedimentary components, including mineral composition and organic matter content, on the laser-based ionization process remains unclear. In this study, a laboratory experiment was designed, involving amendments of pure lipid biomarkers on pure minerals, to investigate the ionization efficiency during laser desorption ionization in a controlled system. Long chain n-alkanes were selected as lipid targets in this study due to their proxy-potential for the reconstruction of paleo-vegetation. By analysis on an aluminum plate as reference material, the analyte suppression effect and matrix suppression effect were clearly shown in concentration gradients of both target compound and artificial matrix. The chemical composition and structure of minerals had significant impacts on the signal responses of different n-alkanes under a given LDI condition, and on their ionization with varying laser powers. Collectively, these results suggest that mineral composition in the sediments may influence the lipid detection in LDI FTICR-MS. Ongoing experiments focus on the assessment of n-alkane detection in geological samples and the assessment of the proxy potential of n-alkane distributions measured at sub-millimeter scales.

High-altitude peatlands of the central Andes as sentinels of Holocene environmental changes

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Content

The high-altitude cushion-plant peatlands of the Central Andes are a typical element of the high-Andean vegetational belt at altitudes of 4000-5000 m a.s.l. The main peat-accumulating species of these soligenous peatlands are the juncaceae *Distichia muscoides* and *Oxychloe andina*, which are adapted to the harsh environmental conditions at these altitudes.

High-Andean peats are effective collectors of organic and inorganic components, which can be used for the reconstruction of their development and of paleoclimate. They have the quality to be very sensitive towards environmental changes and are well-suited for the application of a variety of methods that can be used for the reconstruction of palaeoclimates. The strengths of these geoarchives are their comparability over climatic gradients, their high accumulation rates and the high quality of their peat deposits to be precisely ¹⁴C-dated.

In the past, the peatlands used to recover from climatic oscillations. Nowadays, most Andean peatlands are heavily degraded by human interventions. The loss of the protective vegetation cover within the water catchment areas due to dry periods and/or overgrazing, leads to an increased input of sediment and the expansion of alluvial fans upon the peat deposits. In the past, sediment layers were rapidly accumulated by the peat-forming vegetation. Only if there is heavy degradation of the vegetation cover, coupled with increased discharge, the peat deposits become susceptible to erosion and incision. If these processes continue in the future, the high-mountainous ecosystems will lose their unique water storing and regulating capacity.

Nd, Pb, and Sr isotope composition of organic materials, guano and fishmeal, from upwelling waters off Chile and Peru

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Content

The eastern boundary upwelling system along the Pacific coast off Chile and Peru is well known for its enormous biological productivity that e.g. sustains a large population of colonial, coastal seabirds that mainly feed on small schooling fish (preferentially anchovy). Their once economically important guano-deposits are preserved along the arid section of the Chilean and Peruvian coast since at least 2.5 Ma. We investigated Nd, Pb, and Sr isotope composition of modern and fossil guano from North Chile and anchovy fishmeal off Peru. Heavy isotopes do not substantially fractionate in the trophic chain and hence transfer the composition of the involved water masses through the distinct feeding levels. The guano deposits on land are prone to additions from continental sources. Seawater Sr isotope signature is an excellent tracer for such additions, that are absent or very small in modern and more variable but still close to seawater in fossil samples. The ϵ Nd compositions of guano from an active (sampled 2014) nesting place in North Chile and of anchovy fishmeal (catch 2014) from off Peru plot both around -8. Slightly older modern and fossil guano from North Chile consistently show ϵ Nd between +2 to -2. This comparable radiogenic signature coincides with that of near surface, northward moving coastal seawater of the Humboldt Current system at -34° S [1]. Seawater from -3 to -17° S (ϵ Nd from -6 to -1; sampled 2008/9 [2]) provides the composition of potential confluence with water from the North, but this composition is not obvious in the analysed materials. ϵ Nd of the fishmeal (2014) from the same latitude and the youngest guano (2014) resembles the unradiogenic ϵ Nd of Antarctic intermediate water or compositionally similar East Pacific water masses around -8 [3,4].

Pb has short residence times in ocean water. The analysed Pb isotope signatures of guano and fishmeal show no significant influx of anthropogenic Pb and largely resemble compositions of the expected regional continental runoff including the shelf deposits.

Radiogenic isotopes in marine organic materials allow monitoring the composition of their source areas and especially the guano opens a window into past compositions.

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Quantifying shale weathering by Li isotopes

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Content

Lithium isotopes have emerged as powerful tools for investigating abiotic weathering processes because isotopic fractionation is controlled by silicate weathering depending on the weathering rate. In this study, we explore Li isotopes as a proxy for shale weathering in the well-characterized Susquehanna Shale Hills Critical Zone Observatory (USA), a first-order catchment in a temperate climate in the Appalachian Mountains. Groundwater, soil, and stream water vary significantly in $\Delta 7\text{Li}$ (14.5 to 40.0‰), a range that is controlled primarily by kaolinite and vermiculite formation. Parental shales, bulk soils, and stream sediments have average $\delta 7\text{Li}$ values of -0.6‰, 0.5‰, and -0.3‰, respectively, which is in the typical range for shales dominated by structural-bound Li and consistent with high Li retention. An isotope mass balance approach suggests that Li is virtually quantitatively exported by erosional weathering from the system whereas the dissolved flux is very small. This result is consistent with a high depletion of Li together with clay minerals in soils whereas both are enriched in stream sediments. Overall silicate weathering at SSHCZO is dominated by illite and chlorite weathering forming kaolinite through intermediate phases under highly incongruent weathering conditions followed by preferential loss of fine-grained weathering products, a process which is likely an important mechanism in the modern global Li cycle.

Reconstruction of the deglaciation history in the Fremont Lake-Titcomb basin, Wind River Range, Wyoming, using ^{10}Be exposure dating

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Content

The history of glacier retreat in a mountain range is controlled by the climate history responsible. Terminal or recessional moraine ridges are ideal to document changes in glacier length over time. With the application of cosmogenic radionuclide (CRN) exposure dating, moraines have been targeted frequently to assess the timing and duration of maximum glacier extent and to determine the onset of glacier retreat. Yet, the limitations are obvious as moraines do only record a single time step in the history of glacier retreat. The dating of glacially-polished bedrock surfaces overcomes this limitation and provides the opportunity to extract the history of deglaciation at several time steps. We document the deglaciation history in the Fremont Lake – Titcomb basin in the Wind River Range, Wyoming. This site is exceptionally well-suited as a comprehensive record of more than 30 ^{10}Be ages from the terminal and a recessional moraines already exists (1,2). We augment this dataset with new ^{10}Be measurements from glacially-polished bedrock surfaces and 2-D numerical glacier modeling to characterize the deglaciation history. In our 2-D glacier model, we apply different deglaciation scenarios, which are driven by equilibrium line altitude (ELA) histories. The model predicts the expected ^{10}Be concentration for each cosmogenic sampling site, which we in turn compare to the measured values. We explicitly use ELA histories that account for characteristic paleoclimatic events such as the Heinrich I event to evaluate the possible influence on the deglaciation ages. We obtain ^{10}Be ages from glacial polish ranging between 17 ka at roughly 35 km downvalley from the range crest and about 5 km upvalley from the moraine to 12 ka in the upper part of the catchment. Our highest sample, which we took only 5 km downvalley from the range crest, has an age of ~16 ka. We interpret the latter age to reflect inheritance due to insufficient erosion during glacial occupation, which leads to the preservation of the cosmogenic production zone. Combining our ages with the recalculated ages by Gosse et al. (1,2), it appears that deglaciation initiated around 19 ka. Based on our glacial modeling we find that the retreat occurred with a monotonic ELA rise and without any major glacier readvances. Only the recessional moraine in the Titcomb basin, upvalley from our last ^{10}Be sampling site, may reflect a short readvance or stillstand during retreat.

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Southern Hemispheric Westerlies: reconstructing their intensity and position based on multiproxy investigations of sediments from Laguna Azul (Southern Patagonia, Argentina)

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Content

Temperature, precipitation and wind intensity of South America respond to the air-pressure gradient between polar and subtropical latitudes as well as to sea-surface temperatures of adjacent oceans, the extent of sea-ice and continental ice masses but most of all to the pathway of the Southern Hemispheric Westerlies (SHW). Sedimentary proxies record the resulting variations of the regional hydrological balance and offer an opportunity to reconstruct position and strength of SHW, which are one of the main drivers of global climate. Investigations of Holocene sediments from Laguna Azul (52°S) document the climatic control. Position and strength of the SHW affect semiarid southeastern Patagonia and overprint ontogenetic effects that also influenced the sedimentary record of this young, closed lacustrine system. SHW influence local evaporation, precipitation and insolation with impacts on stratification of the water column and on lake-level fluctuations. These influences could lead to internal feedbacks on algal communities and trophic conditions as well as on authigenic mineral formation.

Based on sedimentology, geochemistry, stable isotopes, pollen and diatoms we present a radiocarbon-dated environmental reconstruction documenting a millennial-scale hydrological variability for the Holocene. According to this multiproxy dataset, lake internal and external processes characterize hydrological fluctuations. These include influences of the shrinking and expanding littoral zone as well as changes in lacustrine productivity, salinity and patterns of water-column circulation. Driest conditions of the record correspond to high wind speeds resulting in a low lake level and higher salinity that caused the rare occurrence of an ectogenic meromixis. Together with anoxic conditions in the hypolimnion, methanogenesis and high salinity were recognized for the early Holocene between 10,400 and 8,600 cal. BP. We relate this period to highest intensities of SHW occurring at the latitude of Laguna Azul.

Between 8,000 and 4,000 cal. BP a moister period followed with less intense SHW. After ~4,000 cal. BP conditions started to become more variable with a tendency towards drier conditions and stronger SHW. Only during the past two centuries, human impact obscured the climatic signal, as evidenced by eutrophication, increased precipitation of authigenic calcite, spreading of neophytic plants like *Rumex* and dominance of the diatom *Stephanodiscus parvus* in lake sediments.

Sr-isotopic signatures in modern and Holocene catfish otoliths and bivalve shells along the NW African coast - Potential proxies for freshwater discharge

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Content

The nature and timing of the mid- to late Holocene aridification of NW Africa continue to be subjects of considerable debate. A growing body of evidence suggests a rather gradual and spatially heterogeneous transition, in contrast to early marine sedimentary records indicating a relatively abrupt change to the modern hyper-arid climate at around 5.5 ka BP. In this context, fish otoliths and bivalve shells retrieved from shell-middens have been shown to provide valuable information to further constrain Holocene monsoonal activity in NW Africa, primarily through ontogenetic stable oxygen isotope ($\delta^{18}\text{O}$) analyses. Pre-depositional cooking of fish and mussels, however, can evidently alter their original chemical signatures, imposing a considerable uncertainty to $\delta^{18}\text{O}$ - based water temperature and salinity estimates.

In order to improve paleoenvironmental reconstructions based on archaeological samples, we therefore explored the use of strontium (Sr) isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) as an alternative approach for the identification of Holocene freshwater discharge patterns. Based on the observation that global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values are remarkably consistent (ca. 0.70917), any significant deviation from the marine end-member in biogenic carbonates is expected to reflect a substantial influx of freshwater to the organism's habitat. To test this assumption, we analysed bulk $^{87}\text{Sr}/^{86}\text{Sr}$ in modern catfish (*Arius parkii*) otoliths sampled in different estuarine systems along the N-S monsoon precipitation gradient of NW Africa using thermal ionisation mass spectrometry. Furthermore, we evaluated the applicability to archaeological samples by measuring $^{87}\text{Sr}/^{86}\text{Sr}$ in modern hard clams (*Mercenaria campechiensis*) that have been subject to different pre-historic cooking methods. Finally, we analysed mid- to late Holocene catfish otoliths and bivalve shells (*Senilia senilis*) from shell-midden deposits in a large paleo-estuary east of the Banc d'Arguin, Mauritania, to assess bulk $^{87}\text{Sr}/^{86}\text{Sr}$ analyses in light of existing high-resolution $\delta^{18}\text{O}$ records.

The isotopic dance of the Monsoon/Environment couple in a Holocene speleothem from Vietnam

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Content

Speleothems are well-suited for exploring the response of the environment to climatic forcings because they contain multiple proxies that enable the reconstruction of climate and environment at the same time. As these proxies are tied to the same (precise and absolute) chronology they are perfect for identifying leads and lags between climatic and environmental change.

Up to today, there is a notable lack of high-quality palaeo-datasets from the tropics beyond the speleothem records from China. To help close this gap and to investigate the evolution of the EASM (East Asian Summer Monsoon) during the Holocene and its impact on the environment in the tropical West Pacific, we have analysed a well-dated stalagmite from a cave in Northern Vietnam for stable isotopes, trace elements and fabrics.

The overall positive trend of speleothem $\delta^{18}\text{O}$ ($\Delta = 2 \text{ ‰}$) suggests a long-term reduction in monsoonal rainfall amount consistent with statistical analyses of GNIP (Global Network for Isotopes in Precipitation) rainwater samples [1] and with decreasing NH summer insolation due to changes in the Earth's orbit [2]. Speleothem $\delta^{13}\text{C}$, as a proxy for vegetation density and/or composition as well as soil zone biological activity, also features a long-term positive trend. Both isotope records show a remarkably similar behaviour over the main part of the 8000 years record, being closely coupled to one another.

However, there appear to be several centuries-long periods with multi-decade leads and lags in this otherwise straightforward relationship. Even more intriguingly, the $\delta^{13}\text{C}$ environment signal seems not only to lag behind the $\delta^{18}\text{O}$ monsoon signal but, at times, it even seems to lead. This implies that the environment has, in turn, somehow influenced the local hydrogeology.

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Session 1.3: Controlling factors of surface evolution: Poster

Session 1.3: Controlling factors of surface evolution: Poster

A-574

Cosmogenic ^{10}Be derived denudation rates of a former partially glaciated catchment in the Southern European Alps.

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Content

INTRODUCTION

Cosmogenic nuclides measurements from river sands have been widely used to assess denudation rates at the catchment scale. We present here ^{10}Be derived denudation rates from present-day sediments of the Var river (Southern Alps, 2 800 km², mean elevation 1 250 m, maximum elevation 3 200 m and slope of 23°) as well as its main tributaries.

GOAL OF STUDY

In situ ^{10}Be measured in sediments sampled at the mouth of a river are often used to derive catchment wide denudation rates. If a catchment has heterogeneous lithology and topography, erosion may however be affected by significant spatial variations. We investigate here such potential variations studying the Var catchment in the Southern European Alps. For this, we sampled the Var and four of its biggest tributaries (Tinée, Vésubie, Estéron, and Coulomp) before and after each confluence. This approach allows us to calculate individual denudation rates for each subcatchment and estimate their relative contribution to the spatially average denudation rate. While most of the catchment consists of Mesozoic and Cenozoic rocks (Estéron and Coulomp valleys) with variable quartz contents, Paleozoic external crystalline quartz rich massifs are found in the northeast part of the catchment (Tinée and Vésubie valleys).

MATERIAL AND METHODS

A total of 20 sediment samples were collected from active riverbeds of the Var River and its tributaries. In order to test the impact of the granulometry, samples were sieved in two fractions: 50-100 μm and 100-250 μm and their respective quartz contents were isolated. Quartz samples have then been prepared and processed to extract their in situ ^{10}Be nuclides following the standard protocols used at CRPG and CEREGE. $^{10}\text{Be}/^9\text{Be}$ ratios were then measured by the ASTER CEREGE LN2C AMS.

EXPECTED RESULTS

From the ^{10}Be measurements, we will determine spatially constrained denudation rates for the four tributaries of the Var and compare those values to the catchment wide denudation rates. We also will propose new insights about the influence of the quartz granulometry (50-100 μm vs 100-250 μm) on the in situ ^{10}Be concentration.

Foreland basin evolution records the effects of plate reorganization, surface evolution and crustal deformation on mountain building

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Content

Due to a wealth of geological and thermochronology data the northern foreland basin of the European Alps is an ideal natural laboratory for understanding the dynamics of foreland basins and their interaction with surface and geodynamic processes. We present a new compilation of thermochronological data from the Molasse Basin that shows no correlation between inferred cooling and exhumation rates and elevation, relief or tectonics. We quantified cooling and exhumation rates in the basin by combining published and new vitrinite reflectance, apatite fission track and U-Th/He data with a new inverse burial and thermal history model. We compare derived temperature histories to exhumation estimates based on the retro-deformation of Molasse basin and the Jura mountains, and to exhumation caused by drainage reorganization and incision. Drainage reorganization can explain at most 25% of the observed cooling rates in the basin. Tectonic transport of the basin's sediments over the inclined basement of the alpine foreland as the Jura mountains shortened can explain part of the cooling signal in the western part of the basin. However, overall a substantial amount of cooling and exhumation remains unexplained by known tectonic and surface processes. Our results document basin wide exhumation that may be related to slab roll-back or other lithospheric processes. The timing exhumation remains largely unconstrained. Uncertainty analysis shows that thermochronometers can be explained by cooling starting as early as the Miocene or as late as the Pleistocene. New (U-Th)/He data close to the Alpine front may provide better constraints on the timing of exhumation.

Geological and thermochronological context of a rapid lithospheric collision (Grampian orogeny, Ireland)

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Content

The Connemara region is a world-class example of a regional-scale, high-temperature metamorphic terrain. Its rock record documents formation of a bi-vergent orogenic wedge and associated calcalkaline magmatism in an arc–continent collisional setting (Grampian orogeny), for which a protracted evolution was inferred based on a >75 Ma spread in U–Pb, Rb–Sr, and K–Ar mineral ages. In contrast, geological field observations imply a simple relationship between syntectonic magmatism, bi-vergent deformation, and Barrovian-type metamorphism. We explore the significance of the spread in apparent cooling ages using ⁴⁰Ar/³⁹Ar mica thermochronometers of varying grain sizes and composition, collected across metamorphic grades ranging from staurolite to upper sillimanite. We integrated geological and previously published geochronological evidence to identify a 32 Ma range (ca. 475–443 Ma) of permissible cooling ages and distinguished them from those dates not related to cooling after high-temperature metamorphism. Variations in ⁴⁰Ar/³⁹Ar dates at a single locality are ≤10 Ma, implying rapid cooling (≥6–26 °C/Ma) following metamorphism and deformation. A distinct cooling age variation (≥15 Ma) occurs on the regional scale, consistent with spatial differences in the metamorphic, magmatic, and deformational evolution across Connemara. This cooling record relates to a lateral thermal gradient (30 °C/km) in an evolving arc–continent collision, rather than to differential unroofing of the orogen. Our results imply that the large (≥50 Ma) spread in thermochronometers commonly observed in orogens does not automatically translate into a protracted cooling history, but that only a small number of thermochronometers supply permissible cooling ages. Based on the thermochronometers and their geological context, we propose a sequential geometric and kinematic evolution of the bi-vergent orogenic wedge at Connemara as a consequence of island-arc-continent collision followed by subduction polarity-reversal.

Geomorphological and geological evidences for glacial isostatic adjustment

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Content

Climate change and its accompanied growth and decay of ice sheets cause significantly vertical movement of the lithosphere, known as glacial isostatic adjustment (GIA). Glaciers are capable to subside the lithosphere with their mass; when ice masses are absent, the asthenosphere compensates the subsidence and Earth's crust recovers again. A peripheral forebulge surrounds the uplift area (Steffen and Wu 2011). These differential vertical crustal movements have a socio-economic impact at the coasts of the southern Baltic and North Sea.

GIA is responsible for the long-term viscoelastic strain-release and is, besides eustatic changes, an essential factor of relative sea level variability. In a period 9-7.5 cal. ka BP subsidence rates of ca 3.33 m/ka occurred in north-western Germany and ca 2.67 m/ka in the Netherlands (e.g. Vink et al. 2007). Paleo-shorelines are geomorphologically expressed as terraces in the SE part of the Baltic Sea (Rosentau et al. 2009) and are submerged below the present sea level in the SW part (Björk 1995). These characteristics of the southern Baltic Sea make mapping of the peripheral forebulge of Fennoscandia feasible. Thus, this study focuses on reviewing published data of reconstructed paleo-shorelines contributing to a sounder understanding of relative sea level change for coastal protection in the southern Baltic Sea. Furthermore, this study seeks to quantify the process of GIA in space and time. Geological evidences for GIA are evident in sea level index points along shorelines of the North and Baltic Sea (e.g. Vink et al. 2007, Steffen and Wu 2011). Remote sensing reveals evidences of recent geomorphological changes and shows current subsidence and uplift rates which occur at the southern Baltic Sea. The result contributes to the deeper understanding of the neotectonic activity in northern Europe since the last glacial maximum.

Primary fault activity, tectonic segmentation and deformation pattern of the western Himalaya on Ma timescales inferred from landscape morphology

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Content

The location and magnitude of the Himalayan active deformation has been debated for decades, but several aspects remain unknown. For instance, the spatial distribution of the deformation, shortening that ultimately sustains Himalayan topography, and the activity of major fault zones are not well constrained at Ma timescales. In this study, we address the spatial deformation pattern in the western Himalaya, a previously understudied region. We calculated catchment-averaged, normalized river-steepness indices of non-glaciated drainage basins between 5 and 200 km². We analyzed the relative change in their spatial distribution both along and across strike to gain information about the regional deformation pattern as well as of the activity of distinctive fault segments. For our study area, we observe some degree of a positive correlation of averaged ksn values with previously published exhumation rates derived from zircon U-Th/He data as well as with denudation rates based on cosmogenic nuclide dating. Our results indicate three orogenic segments with distinctive landscape morphology, structural architecture, and fault geometry along the western Himalaya: Garwhal, Chamba and Kashmir Himalaya (from east to west). Moreover, we observe distinctive fault segments showing an increased thrust activity along the Main Frontal Thrust (MFT), the Main Boundary Thrust (MBT) and the physiographic transition zone between the Lesser Himalaya and the High Himalaya (PT2). Therefore, we suggest that during the Quaternary primary fault zones in the Western Himalaya experienced out-of-sequence thrust activity and have accommodated some portion of crustal shortening.

The fate of forearc sediments at the Middle America Trench offshore Costa Rica - the role of bending, faulting, and mass transport processes at an erosive margin

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Content

The recycling of continental material at convergent margins influences the geochemistry of mantle and arc volcanism, and has a profound effect on the global amount of continental crust throughout the geological history. Forearc mass balance calculations for erosive subduction zones have been done, among others, by Vannucchi et al. (2016) for the Middle American Trench, who estimate sediment contribution from sediment thicknesses in the trench.

The estimates, however, pass over the fact that sediment from the shelf break over the slope arrives to the trench faster than plate convergence and margin erosion would cause it to. In northern Costa Rica, over 75% of sediment deposited on the shelf is seen to undergo downslope transport. Subduction erosion causes extensional faulting at the shelf edge, visible in multichannel seismic data. The resulting change in slope angle allows mobilization of sediments, documented by numerous gullies on the seafloor. Through these, debris flows and turbidites can move material towards the middle slope, where it is partly redeposited. Further trenchward, ultra-slow downslope movement along listric faults is documented in sediment echosounder data. Near the trench, sediment structure on the overriding plate appears destroyed by mass wasting.

In our contribution we highlight and document the above processes with examples of seismo-acoustic data. We discuss controlling factors for sediment transport such as slope angle and slab geometry, and illustrate how these may generally affect the fate of forearc sediments at erosive margins. The results provide a missing piece to the puzzle of mass balance estimates.

Session 1.3: Controlling factors of surface evolution: Talk

Session 1.3: Controlling factors of surface evolution: Talk
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Climatically driven morphodynamic stability / activity and applied soil erosion research

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Content

The role of biota for effective soil formation, producing easily erodible material, is increasingly acknowledged within the geosciences (Johnson et al. 2005). Equally recognized is the role of Quaternary sediments (loess, cover beds) as parent materials for soils in the temperate zone (Kleber & Terhorst 2013). The apparent contradictions in these two perspectives on soil genesis have fundamental relevance for applied research. Rohdenburg (1970) postulates climatically driven morphodynamic stability (pedogenesis) under closed vegetation cover and -activity (erosion/sedimentation) during phases of landscape degradation. However, soil erosion studies consider tolerable erosion rates, in balance with an assumed effective soil reproduction. If soils are not the results from in situ weathering of local rock, but mainly altered erosional products developed during previous phases of morphodynamic activity, soil reproduction and thus tolerance for erosion are almost zero.

The recently established research cluster “Erosion Through Time: Causes and Consequences” unites scientists from the fields of Paleo-Geoecology, Soil Science, Remote Sensing and Sustainable Land Management to combine fundamental research on soil formation with applied research on soil erosion. This contribution provides a conceptual overview and discusses examples for both perspectives on soil formation and erosion as well as implications for current land use practice.

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Geodynamics meets atmosphere: Reconstructing long-term surface elevation through stable isotope paleoaltimetry

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Content

The surface dynamics of large orogenic systems not only affect local (distribution of rainfall, biodiversity and climatic gradients) but also global environmental conditions e.g. through atmospheric teleconnections. Similarly important, the surface elevation history of a region is a key element in deciphering the competing roles of geodynamic processes in crust and mantle and erosion at the Earth's surface and, therefore, represents an important link in reconstructing the interactions among lithospheric and atmospheric processes. Stable isotope paleoaltimetry as a tool to recovering elevation histories of mountain ranges has gained significant momentum over the past decade mainly because such topographic histories of high elevation regions are otherwise largely elusive from the geologic record. Stable isotope paleoaltimetry based on oxygen ($\delta^{18}\text{O}$) or hydrogen (δD) isotopes in precipitation relies on the systematic decrease in the heavy isotope (^{18}O or D) of precipitation due to cooling of air parcels and associated condensation of water vapor during uplift. The resulting isotope-elevation relationships are commonly robust and permit to relate the stable isotopic composition of past rainfall to changes in surface elevation. Single-site records of $\delta^{18}\text{O}$ or δD in precipitation, however, can be affected by climatic and topographic parameters some of which may have magnitudes much larger than can be accounted for by changes in regional surface uplift alone. This is particularly troublesome in high-elevation plateau regions that have reached threshold dimensions such that atmospheric circulation patterns change through topographic forcing.

Here, we present examples from the North American Cordillera and the Turkish-Iranian plateau to document how surface topographies have developed over time and how determining relative changes in the isotopic composition of rainfall between low and high elevation sites eliminates some of the pitfalls typically encountered in stable isotope paleoaltimetry that ultimately feed back into our understanding of the impact of lithospheric dynamics on surface elevation.

Headwater catchment response in the Southern Pyrenees: Landscape transformation and surface process response to Late MIS 2 climate change in the Valle de la Fueva, Aragón, Spain.

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Content

Intramontane basins function as sediment traps and provide important insight into the sediment dynamics and erosion processes in mountain ranges. With the purpose of establishing the drivers and phasing of catchment erosion in the Southern Pyrenees, adjacent 10–100 km² drainage basins were investigated as to their morphogenetic evolution. The Valle de la Fueva is a highly erodible drainage basin, typical of the southern Pyrenean fold and thrust belt (SPFZ) with its shallow and deep marine strata, and synorogenic debris. It consists of a number of subcatchments in the Ainsa depression – a large Eocene piggy-back-basin in the SPFZ.

Morphogenetic mapping revealed three major complexes: high-lying talus slopes; extensive residual erosion surfaces; and "cut-in-fill" alluvial terraces in the ravines. They denote successive basin development stages: extensive surface denudation and sheet flooding; intense basin excavation, accompanied by large-scale sediment routing; and minor late-stage incision and terrace formation. ¹⁰Be exposure ages for the most prominent talus slopes and glacia in the Valle de la Fueva cluster between 18 and 45 ka (MIS 3–MIS 2), testifying to a lasting cold-climate genesis of the denudation plains and the present talus surface levels. The lower complex developed during intense late MIS 2 climatic warming. Preliminary ¹⁰Be results indicate the termination of intense catchment erosion already during Early Holocene (8–12 ¹⁰Be-ka), followed by relative quiescence during Middle-Late Holocene.

Preservation of distinctive cold and warm climate features, and inconsistent gradients and incision magnitudes among the local rivers, show that the Valle de la Fueva is a transient landscape. Trends and distribution of stream profile knickpoints further indicate that headward propagation of fluvial incision is a function of catchment size and runoff, and initiated by base level lowering at the basin outlet (i.e. Cinca River junction). However, pedimentation in the Valle de la Fueva is delayed with regard to the base level lowering at the outlets. Pedimentation phases seem internally triggered and directly linked to the local paleoclimatic conditions and precipitation levels in the Valle de la Fueva. Confined, non-glaciated mountain catchments have high preservation potential for (at least) the latest landscape rejuvenation cycle and they could play a key role in assessing the direct impact of major climate transitions on landscapes and surface processes.

How is the western Himalayan topography sustained and where is plate convergence accommodated?

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Content

The Himalaya is an orogenic wedge formed by a stack of thrust sheets scraped off India as it subducts beneath Tibet. All primary fault systems within the wedge sole into a main basal décollement, called the Main Himalayan Thrust (MHT). Competing hypotheses suggest that Himalayan topography is sustained and the plate convergence is accommodated by deformation either solely along the basal décollement, rupturing the surface along Main Frontal Thrust (MFT) or through more broadly-distributed deformation across multiple thrust faults such as the Main Boundary Thrust (MBT) and others.

For the western Himalaya (73°E to 79°E), we present a summary of published and new studies including catchment-averaged, normalized river-steepness indices, new ¹⁰Be-ages of displaced fluvial terraces levels and zircon (U-Th)/He thermochronologic data with thermo-kinematic modeling (PECUBE). We argue that to a first order normalized-steepness indices can be used as proxy for detecting tectonic deformation on millennial to Pleistocene timescales. These data yield information about the spatial distribution of deformation and shortening. We document (1) along-strike variation in fault activity of primary fault systems, and (2) we are able to distinguish between three 100-150 km wide tectonically decoupled mountain front segments with discrete topographic and fault geometric characteristics. Furthermore, we propose in addition to the MFT other primary fault zones in the Himalaya are still active and have accommodated some portion of crustal shortening on Quaternary or longer timescales.

These observations based on digital topography are supported by our recent field- and numerical modeling studies. More specific, along the central segment of western Himalaya new low temperature thermochronologic data and thermo-kinematic models reveal that the MBT form a steep-seated fault ramp that has uplifted the Dhauladhar range since at least the Late-Miocene. Million-year mean MBT slip rates range between ~2.6 and 3.5 mm.a⁻¹ which corresponds to a horizontal shortening of ~1.7-2.4 mm a⁻¹. Out-of-sequence faulting along the Jwalamukhi Thrust constrained by ¹⁰Be surface-exposure ages accommodates 6 - 8 mm a⁻¹ faulting leading to ~40-60% of shortening within the northwest Sub-Himalaya since 10 ka. From these results we infer that in the western Himalaya only a portion of the total crustal shortening is accommodated by the frontal MFT, contrasting with central Himalayan segments in Nepal.

Imaging and structural analysis of the Geyser field, Iceland, from underwater and drone based photogrammetry

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Content

The Geyser thermal area, southwestern Iceland, name giving for all geysers in the world, is composed of a large number of individual thermal springs, geysers and hot pots that are roughly elongated in a north-south direction. Located in a shallow valley, the Geyser field is located on the eastern slope of a hill. No detailed analysis on the spatial distribution and structural relations of the Geysers have been carried out yet. By use of high resolution unmanned aerial vehicle (UAV) based optical and radiometric infrared cameras, we are able to identify over 290 distinct thermal spots distributed in three main areas. Close analysis of their arrangement yields a preferred direction with azimuth 023° , therefore consistent with the assumed tectonic trend in the area. Furthermore by using thermal isolated deep underwater cameras we are able to obtain images from the two largest geysers at depths up to ~20 m. Near to the surface, the conduit of the geysers are near circular, but at a depth of 8-11 m the shape changes into a crack-like elongated fissure. The elongation direction of these deep cracks is consistent with the identified thermal expression at the surface, highlighting a structural or even tectonic control at the Geyser thermal area.

Reconstructing the Thakkhola graben exhumation history: detrital apatite (U-Th-Sm)/He and Apatite FT from the Mustang area (central Nepal)

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Content

The Nepal Himalaya represents an ideal setting to investigate the interactions between tectonics, surface and climate processes. For this reason, data from several thermochronometers were gained in the past to quantify uplift and exhumation rates. However, most of these studies focus on the range front along the main Himalayan ramp, where the link between tectonics and climate appears more dramatic. Fewer studies focus towards the interior of the orogen, due to both inaccessibility and scarcity of datable minerals. In this study, we present the results of low-temperature thermochronology from the Kali Gandaki river along the orogen-perpendicular Thakkhola-Mustang Graben, draining, amongst others, the Mustang Granite. Both, the Thakkhola Graben and Granite are situated within the Tethyan Himalaya. The main objective is obtaining the exhumation history north of the South Tibetan Detachment Zone (STDZ). For this purpose, we applied in situ dating of the Mustang Granite and detrital thermochronology to sediments of the Kali-Gandaki river, using apatite (U-Th-Sm)/He (AHe) and Fission Track (AFT). The granite, which was emplaced at 24 Ma [1], yielded AFT and AHe dates of ~20 and 14 Ma, implying rapid initial exhumation during the Early Miocene, and subsequent slower cooling during the Late Miocene. Rapid post-intrusion cooling is also suggested by detrital AFT dating, which yielded a single age group overlapping within error with the granite's emplacement age. Emplacement and rapid Early Miocene exhumation are temporally coeval with the activity along the STDZ, which ceased around 18-20 Ma, implying that exhumation of the Mustang Granite was driven by the STDZ activity. The detrital signal from AHe thermochronology shows stronger variations than the AFT data, suggesting periods of enhanced cooling at ~14 to 13 Ma and around 8 Ma. We interpret these data as reflecting initiation and main activity of normal faulting along the orogen-perpendicular Thakkhola Graben and thus the switch from south-directed thrusting to orogen-parallel extension. The timing of this switch, which we place at ~14 to 13 Ma, is in good agreement with previous studies from the Greater Himalaya [2]. Our data also suggest that the Early to mid Miocene exhumation history of the Tethyan Himalaya seems to be controlled by its structural evolution and thus by tectonic processes.

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Spatial patterns of erosion in the central Menderes Massif (Western Turkey) revealed by cosmogenic ^{10}Be – Landscape evolution during active continental extension

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Content

In extensional tectonic settings erosion and normal faulting constitute key processes to rock exhumation, however, the relative importance of both processes is often difficult to quantify and has rarely been constrained. The central Menderes Massif in Western Turkey – which encompasses two mountain ranges that are separated by the E/W-trending Küçük Menderes Graben – is bound by the low-angle Gediz and Büyük Menderes detachment faults and provides an ideal region to study the relative contribution of normal faulting and erosion to exhumation in an extensional setting. Here we present spatially-averaged and local ^{10}Be erosion rates for 36 catchments and 10 ridge crests, respectively, in order to resolve the spatial pattern of erosion across the massif and link it to landscape evolution. Erosion rates for catchments located in the footwall of the Gediz detachment range from 40 to 220 mm/kyr, indicating that the thick (20–50 m) cataclasites associated with this detachment fault have protected the footwall from significant erosion. However, catchments that drain southward into the Küçük Menderes Graben erode ~ 3 times faster and cause an asymmetric erosion pattern on this mountain range. Chi-map analyses further imply a northward migration of the drainage divide, indicating that particularly the eastern part of the range is in a transient state. In contrast, erosion rates for catchments in the footwall of the Büyük Menderes detachment are generally higher (140–400 mm/kyr), which is consistent with the observation that the respective catchments expose mechanically weak mica schists or phyllites and have rather steep hillslopes. Along with the fact that the Büyük Menderes detachment is associated with a relatively thin layer of fault gouge and cataclasite, this explains why the Büyük Menderes detachment is less well preserved than the Gediz detachment despite the contemporaneous activity of both detachments [1] [2]. In combination with thermochronological data, our results reveal that normal faulting played the dominant role for rock exhumation at both detachments, although the relative contribution of erosion to exhumation is higher at the Büyük Menderes detachment. Finally, local erosion rates derived for ridge crests are by a factor of 3–2 lower than catchment-wide erosion rates, indicating that the relief of the central Menderes Massif is currently increasing.

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Sri Lanka: a prototype for the development of micro-continents?

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Content

Sri Lanka represents a micro-continent that is composed primarily of Precambrian basement rocks. The Phanerozoic history of the island is poorly constrained. Only a small patch of Jurassic strata and some Neogene sediments are preserved in NW Sri Lanka.

The landscape of the island is divided into three distinctive physiographic provinces: lowlands, uplands and highlands. Early workers suggested telescope-like uplift of the central highlands, while most recent studies interpret the high relief as the remnant of a single geomorphic block that was faulted and uplifted prior to 130 Ma. The morphological high was then reduced to the island's interior by polycyclic downwearing or rapid escarpment retreat, potentially by the weathering contrast between charnockitic and granitic or meta-sedimentary rocks.

Here we combine petrographic and thermochronological techniques to develop a model of regional long-term landscape evolution and, more generally, of medium-scale continental fragments. The Jurassic deposits of W Sri Lanka consist of poorly sorted feldspatic sandstones and mudstones. Feldspars of four samples are variably altered, detrital micas are corroded and partly replaced by clay minerals, and pore spaces are filled with kaolinite and illite-like clay minerals. XRD and infrared spectroscopic data confirm a homogeneous mineral composition of kaolinite, illite/smectite mixed-layer minerals, quartz and goethite.

Five detrital apatite fission-track (AFT) sample ages of 222–351 Ma are substantially older than the Jurassic stratigraphic age, and are associated with short mean track lengths (MTL) of 11.4–11.9 µm. Petrographic, mineralogical and AFT data commonly refer to post-Jurassic temperatures of 90°–110°C. The basement adjacent to the Jurassic strata yields much younger AFT ages of 62–189 Ma and MTL of 11.3–13.6 µm. Thermal history modelling indicates post-Jurassic basement heating to temperatures >100°C followed by rapid early Cenozoic cooling.

Thermal histories of both sedimentary and basement rocks are not compatible with any of the predicted landscape evolution scenarios. Instead, they require Jurassic – Cretaceous diffuse crustal extension and burial of the W Sri Lanka lowlands within a 3–5 km thick sedimentary basin. Focussed continental rifting between India and Sri Lanka commenced in the latest Cretaceous, triggered the opening of the Palk Strait and basin inversion on W Sri Lanka, and was compensated isostatically by the uplift of the central highlands.

Testing monsoonal controls on bedrock river incision in the Himalaya and Eastern Tibet with a stochastic-threshold stream power model

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Content

10Be-derived catchment average erosion rates from the Himalaya and Eastern Tibet show different relationships with normalized channel steepness index (ksn), suggesting differences in erosional efficiency of bedrock river incision. We used a stochastic-threshold stream power model (SPM) to explore to what extent this observation can be explained by differences in the mean and variability of discharge between the two regions. Based on the analysis of 199 daily discharge records (record lengths 3-45 years; average 18.5 years), we parameterized monsoonal discharge with a weighted sum of two inverse gamma distributions. During both high- and low-flow conditions, annual and inter-annual discharge variability is similarly low in each region. Channel widths for 36 rivers indicate, on average, 25% wider streams in Eastern Tibet than in the Himalaya. Because most catchments with 10Be data are not gauged, we constrained mean annual discharge in these catchments using gridded precipitation data sets that we calibrated to the available discharge records. Comparing 10Be-derived with modeled erosion rates, the stochastic-threshold SPM explains regional differences better than a simple SPM based on drainage area or mean annual runoff. Systematic differences at small ksn values can be reconciled with ksn-dependent erosion thresholds, whereas substantial scatter for high ksn values persists, likely due to methodological limitations. Sensitivity analysis suggests that changes in the duration or strength of summer monsoon precipitation have the largest effect on erosional efficiency, while changes in monsoonal discharge variability have almost no effect. The modeling approach presented in this study can in principle be used to assess the impact of precipitation changes on erosion.

The imprint of Weichselian glacitectonism on the recent morphology of Jasmund (Rügen Island, NE Germany)

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Content

Glacitectonic deformation in the Weichselian Pleniglacial led to the tectonic framework of large-scale folds and displaced thrust sheets of Maastrichtian (Late Cretaceous) chalk and Pleistocene glacial deposits in the southwestern Baltic Sea region. The involved processes shaped the characteristic morphology of today's Jasmund Peninsula, which is best visible in digital elevation models (DEM).

The Jasmund Glacitectonic Complex represents a small-scale fold and thrust belt including transitions from detachment folds over fault propagation folds to fault bend folds with hanging-wall anticlines and footwall synclines. Those structures have a surface expression in the form of sub-parallel ridges and elongated valleys in between. DEM analyses suggest a division into two structural sub-complexes – a northern part with morphological ridges striking NW–SE and a southern part with SW–NE trending ridges.

A wide spectrum of methods has been compiled to unravel the structural evolution of Jasmund. Geological cross sections from the eastern coast are constructed and restored using the software *Move*TM and the complementary module *2D Kinematic Modelling*TM. Landform analyses show, how the structural framework influences the morphology of Jasmund. They provide an insight into the chronology of sub-complexes formation and help to find a consistent terminology for the tectonic setting. The northern part is suggested to have been generated before the southern one, considering the partly truncated northerly ridges and their superimposition by the southern sub-complex. Furthermore, the term *push moraine* used for Jasmund in many papers, is no longer recommended. Based on our investigation results and taking into consideration modern classifications of glacitectonic complexes [1] the morphological ridges are better described as *composite ridges*.

Although there is a high number of scientific publications on the glacitectonic evolution of Jasmund, the presented models often lack a consistent theory for the development integrating all parts of the 100 sq km large complex. Therefore, the currently applied spectrum of methods provides the possibility to come up with a more self-consistent genetic model for the entire Jasmund Glacitectonic Complex.

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The Seymchan Basin and the Okhotsk-North America plate boundary: why is it so hard to see what's going on here?

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Content

The geomorphological expression of the Seymchan Basin, bounded by the clearly active trace of the Okhotsk-North America plate boundary, is spectacular. It is also relatively young (Oligo-Miocene onwards). The basin is a 120kmx40km depression cut into a region of high relief due to Paleo-Neogene, regional “back-arc” extension, and later Neogene, “pull-apart” tectonics. As such, it appears to act as an “attractor” for regional drainage. Most prominent are the Kolyma river, and its major, mid-course tributary, the Buyunda river. Both cross the same plate boundary fault (Ulakhan) as they enter the basin, their intersections occurring about 50km from each other. The interaction of the two rivers with the fault is remarkable in how different their response is. The Buyunda river has built a major alluvial fan and created relief, whereas the Kolyma river incises the basin floor today. Incision of the Kolyma river upstream of the basin is intense and appears to have involved multiple phases of incision, backfilling, and reincision.

We present new age dating results for river sediments in abandoned and cut off meanders of the Kolyma, and for sediments on a neotectonic pressure ridge formed by the Ulakhan fault on the western edge of the now abandoned Buyunda fan. We also present an analysis involving the joint interpretation and georeferencing of an aerial photo mosaic along the fault trace with an 0.4 arc second tandem-x digital elevation model. Whilst we are able to trace back probable old courses of the rivers, within the incised part of the Kolyma, and to some degree the Seymchan basin itself, an obvious relationship to tectonics (the plate boundary is thought to slip at 5mm/yr) is not easy to identify. Nor is the possible influence of glaciation related, eustatic sea-level change. A subset of the glacio-eustatic effects is that of transient adjustments of equilibrium profiles to different perturbations, which can potentially be constrained by river erosion/sediment transport models. Finally, we ask the question of the influence of the rivers on the fault. Substantial (100's km³) volumes of sediments have been removed from adjacent to the fault which is trans-lithospheric and vertical. Age data suggest the final removal occurred within a matter of 10Ka. This is fast enough and large enough to have a flexural isostatic response, which we calculate. Where is this to be found in the current erosional/depositional behaviour of the major rivers?

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Poster

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Poster

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First results from kinematic analyses and structural restoration of the Schillgrund Fault (eastern main boundary fault of the German Central Graben)

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Content

This study intends to better constrain the structural evolution of the eastern German Central Graben by seismic interpretation of Late Permian to Cenozoic intervals along lines approx. perpendicular to its eastern flank and main boundary fault (Schillgrund fault, SGF).

Based on seismic interpretation and interim results from structural restoration and kinematic analysis we can draw the following (preliminary) conclusions: The depth of the base Zechstein indicates that the German part of the Central Graben forms a „structural high“, compared to its Danish and Dutch counterparts. The total vertical displacement across the Schillgrund fault is of 2-3 km (base Zechstein), but major rollover structures in post-Zechstein strata suggesting locally even higher displacement values. Generally, all interpreted sections show a dominant dip-slip character of the fault. In contrast, some faults to the west which are oriented parallel to subparallel to the SGF, show a distinct strike-slip component. The latter might be related to a reactivation of older Paleozoic to Mesozoic elements.

Inversion movements along the SGF occurred during the middle Upper Cretaceous, but main inversion occurred in Campanian to Early Maastrichtian times. After that inversion movement was slowly waning, but persisted until the Palaeocene. Inversion movement shows a distinct increase from NE to SW associated with frequent changes in the structural style of the hanging wall and is not restricted to the main boundary fault but is also evident along structures in the inner part of the graben. Compared to other parts of the Central European Basin System, the direction of inversion (ESE/SE) is rather atypical along the SGF. Based on preliminary kinematic modelling, we can decipher the total amount of shortening to be between 650 m and 1000 m (without decompaction and depending on kinematic algorithm used (flexural slip unfolding, trishear or fault parallel flow) and geometry of constructed detachment fault in the deeper parts of the SGF (listric or listric with local flat-ramp-flat geometry)).

In subsequent steps we will perform retro-deformation and decompaction analyses along interpreted lines aiming to: (i) investigate the subsidence history; (ii) better constrain the timing of deformation along the Schillgrund fault during Mesozoic extension/rifting and contraction/inversion and (iii) investigate the influence of Zechstein salt mobilisation on the deformation style in the Post-Permian strata.

New insights on the exhumation history of the Sierra de San Luis (Sierras Pampeanas, Argentina) from low-temperature thermochronological data

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Content

This study presents low-temperature thermochronological data and K Ar fault gouge ages from the Sierra de San Luis in the Eastern Sierras Pampeanas (Argentina) in order to constrain its low-temperature thermal evolution and exhumation history.

Thermal modelling based on (U-Th)/He dating of apatite and zircon and apatite fission track dating show that exhumation of the analysed section of the Sierra de San Luis started during the Carboniferous. Our data point to the Middle Permian and the Triassic / Early Jurassic as main cooling/exhumation phases, equivalent to ca. 40-50 % of the total exhumation recorded by the applied methods. Cooling rates are generally low to moderate, varying between 2-10 °C/Ma during the Permian and Triassic periods and 0.5-1.5 °C/Ma in post-Triassic times. Slow cooling and, thus, persistent residence of samples in partial retention / partial annealing temperature conditions strongly influenced obtained ages.

Thermochronological data indicate no significant exhumation after Cretaceous times, suggesting that sampled rocks were already at or near surface by the Cretaceous or even before. As consequence, Cenozoic cooling rates are low, generally between 0.2-0.5 °C/Ma which is, depending on the geothermal gradient used for calculation, equivalent to a total Cenozoic exhumation of 0.6-1.8 km. The final structural relief and present topography of the Sierra de San Luis has been achieved as a result of Neogene regional crustal shortening and consequent differential uplift of surfaces which were already exhumed during Late Paleozoic and predominantly Mesozoic times.

K-Ar fault gouge data reveal long-term brittle fault activity. K-Ar fault gouge and thermochronological data reveal that crustal deformation and associated exhumation during the main exhumation phase were related to main tectonic processes. The Carboniferous evolution could be related to the development of the southeasternmost Paganzo Basin, whereas Permian exhumation is here associated with basin inversion during the San Rafael Orogeny. Crustal extension and rifting, in turn, gave rise to Triassic deformation and exhumation. Fault gouge ages constrain the end of ductile and onset of brittle deformation in the Sierra de San Luis to the Late Carboniferous/Early Permian. Youngest K-Ar illite ages of 222-172 Ma are interpreted to represent the last illite formation event, although fault activity is recorded up to the Holocene.

Postintrusive thermal evolution of the Lower Cretaceous alkaline complex of Jacupiranga, Brazil

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Content

The aim of the ongoing research is the quantification of the post-intrusive thermal history of the alkaline complex of Jacupiranga which is located 200 km southwest of the state of São Paulo, Brazil. The alkaline complex intruded the Neoproterozoic metamorphic basement at 131 ± 3 Ma (Rb/Sr,[1],[2]). Apatites of 22 rock samples were analysed by using the fission-track technique. Two thermal evolutionary models were extracted from published geological data and then tested against the thermochronological data set by using the software code HeFTy ([3],[4]).

AFT-ages of the intrusive rocks range from 98.4 ± 6.3 Ma to 76.4 ± 7.4 Ma. Apatites of two alkaline dykes revealed ages of 58.4 ± 5.1 Ma and 52.3 ± 4.3 Ma, respectively. One Neoproterozoic gneiss sample taken close to the intrusion exhibits an AFT-age of 69.1 ± 4.9 Ma.

Model 1: 90 °C was reached at 120 Ma. The cooling rate would have been 51°C/Ma. The fast cooling is interpreted as cooling of the intrusion temperature to the surrounding crustal temperature. Thereafter, very slow constant cooling reached about 40 °C at about 20 Ma. The cooling rate would be 0.5 °C/Ma.

Considering a constant surface temperature of 20°C and a constant geothermal gradient of 30 °C/km, an exhumation rate of 0.02 mm/a was calculated. Surface temperature was reached at 1-2 Ma.

Model 2: The AFT-data set allowed to reach surface temperature at about 55 Ma. Thereafter, a minor reheating up to 40 °C and cooling to surface temperature again followed.

Assuming an intrusion temperature of 600 °C at 130 Ma and no to minor erosion until 120 Ma, the 90°C might represent the overall temperature of the Neoproterozoic basement and, therefore, an intrusion depth of 3 km is calculated by using 20 °C surface temperature and a geothermal gradient of 30 °C/km. From Lower Cretaceous to Miocene, about 2 km of rock column was eroded. The final erosion took place since the Miocene. Testing the second model provided the information that a reheating up to 40 °C would have been possible. As the existing data set does not allow to distinguish between the two thermal models, apatites and zircons are analysed for their (U-Th-Sm)/He behaviour and fission-track dating on zircons is done.

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Quantifying the thermal evolution of early passive margins formation and its consequences on the structure of passive margins

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Content

Many large-scale dynamic processes, from continental rifting to plate subduction, are intimately linked to metamorphic reactions. This close relation between geodynamic processes and metamorphic reactions is, in spite of appearances, yet poorly understood. For example, during extension processes, rocks will be exposed to important temperature, pressures and stress changes. Meanwhile less attention has been paid to other important aspects of the metamorphic processes. When reacting rocks expand and contract, density and volume changes will set up in the surrounding material.

While several tectonic models are proposed to explain the formation of extensive basins and passive margins (simple shear detachment mantle exhumation) a single thermal model (McKenzie, 1978), as a kind of dogma, is used to understanding and modeling the formation and evolution of sedimentary basins. The study of the thermal evolution, coupled with other tectonic models, and its consequences have never been studied in detail, although the differences may be significant. And it is clear that the petrological changes associated with changes in temperature conditions, influence changes reliefs.

Constrained by the new field data of north Pyrenean basins on thermal evolution of pre-rift and syn-rift sediments, we explore the petrological changes associated to different thermal evolution and the consequences on the subsidence of the basins. We will also present numerical models quantifying mineralogical and physical changes inside the whole lithosphere during rifting processes. In the light of these models, we discuss the consequences of different thermal evolution on the subsidence processes as well as on gravimetry and seismic velocities signature of passive margins.

We are able to distinguish two types of margins according to their thermal evolution:

- An Alpine-type basin in which the temperature rise is 50 to 100 Ma older than the tectonic extension, leading to the "cold" opening of the ocean.
- A Pyrenean type basin in which temperature changes are synchronous with basin formation, leading to a crustal boudinage and to the formation of a "anomalous" geophysical layer at the OCT

Sensitivity analyses of the effect of variable thermal rock parameters on the thermal structure of the lithosphere - new insights on the thermal evolution of the Brazilian South Atlantic passive continental margin

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Content

The aim of the research is to quantify the long-term evolution of the western South Atlantic passive continental margin (SAPCM) in SE-Brazil. Excellent onshore outcrop conditions and extensive pre-rift to post-rift archives between São Paulo and Laguna allow a high precision quantification of exhumation and rock uplift rates, influencing physical parameters, long-term acting forces, and process-response systems. The research integrates published ([1]) and partly published thermochronological data from Brazil, and tests lately published new concepts on causes of long-term landscape and lithospheric evolution in southern Brazil.

Six distinct lithospheric blocks (Laguna, Florianópolis, Curitiba, Ilha Comprida, Peruibe and Santos), which are separated by fracture zones ([1]) are characterized by individual thermochronological age spectra. Furthermore, the thermal evolution derived by numerical modeling indicates variable post-rift exhumation histories of these blocks. In this context, we will provide information on the causes for the complex exhumation history of the Laguna block. Following up on the latest publication ([2]) regarding the effect of variability in rock thermal conductivity on exhumation rate estimates we performed a sensitivity analysis to quantify the effect of variable thermal rock parameters on the thermal evolution of the Laguna block versus exhumation rates estimated from modelling a uniform crustal block.

We furthermore present results from a sensitivity analysis concerning the effect of varying salt thicknesses on the thermal structure of the lithosphere in a case study of Santos Basin, Brazil.

The long-term landscape evolution models with process rates were computed with the software code PECUBE ([3],[4]).

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Structural restoration of 2D geological cross-sections through the Paleozoic Ellesmerian and Cenozoic Eurekan fold belts in SE-Ellesmere Island, Canadian Arctic.

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Content

The superposition of two fold-and-thrust belts, a Paleozoic (Ellesmerian) and a Cenozoic (Eurekan) one, determine the structural evolution along the NE coast of Ellesmere Island. Geological investigations in this still poorly understood region are complicated by the absence of reflection seismic and well data, as well as the present day large extent of glaciation, hampering detailed kinematic and structural field investigations. In such cases, i.e. the absence of geophysical constraints for structural interpretations, structural and kinematic restoration and modelling techniques applied to existing structural interpretations may provide valuable insights in their viability and admissibility.

We tested existing conceptual structural models of this region by using sequential restoration techniques on two representative, NW-SE oriented regional cross-sections compiled by Piepjohn et al. (2008), putting together the state of knowledge on the architecture, structural style, and kinematics of the Paleozoic to Cenozoic fold-and-thrust belt in NE Ellesmere Island. The cross-sections were restored stepwise to a pre-Ellesmerian stage, deciphering the amount of shortening caused by Eurekan and Ellesmerian deformation events and, in this way, provide constraints for a better plate tectonic reconstruction.

The sequential restoration shows that minimum values for total shortening (for both Eurekan and Ellesmerian deformation) are in the range of 43 % (34 km) for the northern section (section 1) and 35 % (35 km) for the southern one (section 2). The amount of Ellesmerian shortening can be constrained to about 18 % (14 km) along section 1 and 8 % (8 km) along section 2. In contrast, the Eurekan deformation produced significant stronger deformation in the eastern coastal region of Ellesmere Island, with a total shortening of about 30 %. For section 1 and 2 this accounts for 24 % (19 km) and 27 % (27 km), respectively. The structural and kinematic inventory of the Ellesmerian deformation to be characterized by large scale blind thrust systems is related to fault-bend folding and local detachment horizons in the Kennedy Channel and Cass Fjord Formation. In contrast, the Eurekan deformation is characterized by large scale thrust systems, which are branching off a postulated reactivated basal detachment in ca. 8 km depth and passively carried Ellesmerian structures towards the foreland, suggesting flat laying stratigraphic units for the footwall of these thrust systems.

Tectonic evolution of the Horn Graben

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Content

The Horn Graben, located 50–100 km off the western coast of Denmark and Germany, is a comparably unexplored area with regard to other parts of the North Sea such as the Central Graben. This up to ten kilometers deep-reaching, NNE–SSW to NNW–SSE trending rift structure transects the Ringkøbing-Fyn-High and is in most parts a westward dipping half-graben. Only three wells intersect the sediments within the graben. Two of the wells end in the Triassic. Due to the lack of wells in this area, seismic interpretations are challenging and different approaches are required.

Previous studies mainly focused on the Mesozoic evolution of the graben. In comparison, the initial Paleozoic history was not very much in focus of scientific research in the past. Moreover, previous studies were carried out separately for the Danish and the German part of the Horn Graben.

In this study, started in the end of 2016 as part of the joint project TUNB (“Subsurface Potentials for Storage and Economic Use in the North German Basin”, project period from 2014-2021), we analyze the Danish and the German area of the Horn Graben based on high resolution 2D seismic data in order to obtain a detailed structural model. We carefully interpret faults, salt structures and various seismostratigraphic units of the German and Danish part of the Horn Graben. The seismic interpretations are guided by existing seismostratigraphic concepts of the Triassic, the Cretaceous and the Tertiary of the German North Sea, established in the TUNB project. The main objective of our work is to clarify the initial tectonic history of the Horn Graben and the possibly tectonically influenced sedimentation of the Upper Paleozoic. The precise understanding of the tectonic evolution of this graben structure from the initial phase in the Paleozoic up to the main halotectonic movements in the Middle to Upper Triassic may help us to explain tectonic processes of other comparable intraplate rift structures and their early tectonic evolution such as of the Glückstadt Graben. Furthermore, we will analyze the interaction of Mesozoic halotectonics, sedimentation and subsidence history of the Horn Graben. The linkage of these mechanisms will be estimated and verified by testing different restoration and balancing techniques.

The compressible adjoint equations in geodynamics: derivation and numerical assessment

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Content

The adjoint method is a powerful means to obtain gradient information in a mantle convection model relative to past flow structure. While the adjoint equations in geodynamics have been derived for the conservation equations of mantle flow in their incompressible form, the applicability of this approximation to Earth is limited, because density increases by almost a factor of two (Dziewonski and Anderson (1981)) from the surface to the Core Mantle Boundary. Here we introduce the compressible adjoint equations for the conservation equations in the anelastic-liquid approximation. Our derivation applies an operator formulation in Hilbert spaces, to connect to recent work in seismology (Fichtner et al (2006b)) and geodynamics (Horbach et al (2014)), where the approach was used to derive the adjoint equations for the wave equation and incompressible mantle flow. We present numerical tests of the newly derived equations based on twin experiments, focusing on three simulations. A first, termed Compressible, assumes the compressible forward and adjoint equations, and represents the consistent means of including compressibility effects. A second, termed Mixed, applies the compressible forward equation, but ignores compressibility effects in the adjoint equations, where the incompressible equations are used instead. A third simulation, termed incompressible, neglects compressibility effects entirely in the forward and adjoint equations relative to the reference twin. The compressible and mixed formulations successfully restore earlier mantle flow structure, while the incompressible formulation yields noticeable artifacts. Our results suggest the use of a compressible formulation, when applying the adjoint method to seismically derived mantle heterogeneity structure.

Thermal history and long-term landscape evolution of the lower cretaceous Poços de Caldas alkaline massif and surroundings in southeastern Brazil

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Content

The thesis presents apatite fission-track data (AFT), first zircon fission-track (ZFT), and first apatite and zircon (U-Th-Sm)/He (AHe; ZHe) data to be undertaken in the Lower Cretaceous Poços de Caldas alkaline massif and surroundings. The Alkaline massif (~83 Ma intrusion age) is a semi-circular feature built of a nearly flat plateau with an average elevations of about 1300 m.a.s.l.. Almost all borders of the plateau are surrounded by topographic ring features that reach more than 1600 m.a.s.l.

The study constrains the pattern and exhumation history of the Poços de Caldas alkaline massif and surrounding area since the Neoproterozoic. AFT samples of the alkaline massif range from 69.0 (4.4) Ma to 42.7 (3.4) Ma in age and one AFT sample of a Neoproterozoic foliated granite provide an age of 101.3 (5.4) Ma. Color selected zircon concentrates of the granite and the Lower Cretaceous Botucatu sandstone revealed ZFT-ages between 254.9 (19.4) Ma and 424.2 (39.6) Ma. ZHe-ages cover the age range between 534.0 (42.7) Ma and 83.5 (3.8) Ma. AHe-ages are in the range of 47.1 (5.8) Ma to 84.1 (4.4) Ma. Application of system filters lead to a reliable AHe age of 47.1 (5.8) and ZHe-ages of 293.6 (1.3) Ma for the Neoproterozoic foliated granite. The Botucatu sandstone provided a reliable ZHe-age of 78.7 (0.4) Ma. Two samples of the alkaline massif revealed each two reliable zircon grains with an age range from 89.1 (7.1) Ma to 83.6 (6.7) Ma. The thermochronological cooling history of rocks exposed in the Poços de Caldas alkaline massif reveals that the faster cooling and main exhumation process occurred shortly after the intrusion of the alkaline magma (83 Ma) and lasted for about 11 Myr until about 72 Ma. This very fast cooling is partly contributed by the heat dissipation of the hot magmatic rocks to the surrounding colder Neoproterozoic foliated granite (~ 100 °C around ~80 Ma ago) and an erosion of about 2,000 m of volcanic and subvolcanic rocks. These erosion leads to topography with elevation differences of about 200 m in the Poços de Caldas alkaline massif. During the Late Cretaceous (~ 70 Ma) and Early Paleogene (~45 Ma) the exhumation almost stopped. The presented thermochronological data set do not support the formation of the “South American Planation Surface” during the Late Cretaceous to Early Paleogene.

Visualizing time on interregional geological maps

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Content

The color spectrum on maps relates to geological time. Who does not know that certain shades of green stand for Cretaceous time? Put a geological map in front of a geologist and she will read from the book of time for hours without end, although there are no words on the map, just colored patches in a certain arrangement. The geologist immediately associates the colored arrangements with geological eras, systems, series, or stages representing hundreds of, tens of, or millions of years, respectively. Yet, even more information resides in the maps regarding the earth's time record, which puzzles the eye of the untrained reader. The goal of our work is to visualize the geological maps' "hidden temporal information," to explore alternative ways of how the untrained eye may perceive time on these maps. We used the International Geological Map of Europe at a scale of 1 : 5 000 000 (Asch 2003). We tested the results on geologists trained in reading geological maps and on dozens of students and geoscientists unfamiliar with the traditional geological color scheme. We first showed traditional geological maps to the untrained proponents and asked them to point to the largest time gap in the rock record (hiatus or unconformity) on the map. Impossible! Blank stares at the maps and minute-long silence resulted. We then applied diverging color schemes to display 4,6 billion years and asked the same question again. Answers sprout within fractions of a second as to the correct location of the largest hiatus on the map! At this time, geologists shout in protest that "nothing" can be seen on the map any longer, because "all the colors are now the same." On the map of Europe, this statement refers to the vast region of Cenozoic and even Mesozoic units that appear nearly-mono-colored when placed in a 4500 m.y. linear time frame. We use up to three diverging schemes to illustrate regions younger than 1000 m.y. and 250 Ma, respectively. After a few minutes of studying such maps, most spectators get excited about the map, and express that they "had not realized that that's what can be seen on maps." Diverging color schemes are useful to understand time, to visualize changing rates of formation and deformation of the earth's surface rock record, but traditional color schemes remain essential to visualize the geometric patterns of the geological record. GISs are an excellent tool to analyze time on geological maps.

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Talk

Keynote speaker

A-832

Impacts of the Icelandic Plume on the North Atlantic Geological Record

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Content

Onset of rifting in the North Atlantic coincided with the arrival of the proto-Icelandic plume head. Large volumes of basaltic volcanism were emplaced across a ~2000 km wide area stretching from Baffin Island across to western Scotland. This igneous activity continues to the present-day, with elevated crustal thicknesses observed both in Iceland and down the Reykjanes mid-oceanic spreading ridge. Dynamic support associated with the plume results in elevated oceanic residual depth anomalies and uplift of the fringing continental margins. Transient thermal perturbations within the plume conduit have generated V-shaped ridges of thickened crust and ephemeral landscapes on the surrounding continental shelves. These hot ripples of plume material uplift oceanic gateways at the Denmark Straights and Faroe-Shetland Ridge, periodically cutting off Arctic deep-water currents and reducing sedimentation rates in the ocean basin. Multiple strands of evidence illustrate that the Icelandic plume continues to exert a profound influence on lithospheric architecture, sedimentation, geomorphology, seismicity, oceanic circulation and climate in the North Atlantic region.

Evolution of structures, pressure and temperature in the footwall of large scale overthrusts – Oman's passive continental margin during obduction orogeny

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Content

The Oman Mountains are world famous for their exceptionally well-exposed Cretaceous ophiolite sequence. During obduction the overridden sedimentary basin was forced to deep burial. Localization of most plate-collisional deformation at the Makran subduction zone, which evolved parallel further north, resulted in preservation of the embryonic stage of a collisional orogen immediately after ophiolite obduction in the Oman Mountains. Eurasia-Arabia collision in the Cenozoic led to large-scale dome structures, which have subsequently been incised by steep valleys exposing the entire passive margin sequence. Past studies focused on the tectonic evolution of the orogen (e.g. Glennie et al., 1973; Loosveld et al., 1996), the initial subsea obduction and its associated metamorphism (El-Shazly and Sisson, 1999; Hacker and Mosenfelder, 1996), and reconstruction of the obducted nappes (Béchenec et al., 1988; Searle, 2007). Few studies address the associated sedimentary basin, its response to obduction on the passive continental margin (Boote et al., 1990; Cooper et al., 2013) or the tectonically induced fault and fracture geometries (Hilgers et al., 2006; Holland et al., 2009; Virgo et al., 2013). Even though, we lack a comprehensive understanding of how obduction manifests itself in the structural record and how it influenced the evolution of pressure and temperature. In particular, relative timing of obduction related shearing and burial related veins, obduction influences on hydrocarbon generation and tectonically driven migration are still unknown. This knowledge is required for understanding both, obduction dynamics, and consequences of rapid burial of a sedimentary package during early phases of mountain building.

Here, we focus on the Jebel Akhdar Anticline, one of three tectonic windows in the Oman Mountains. We present combined results of meter-scale structural mapping with thermal reconstructions of peak burial (solid bitumen reflectance, Raman spectroscopy), exhumation (zircon (U-Th)/dating), pressure reconstruction (fluid inclusion thermometry) as well as 2D numerical basin modeling. Peak burial temperatures of 225-260 °C for Natih rocks reflect peak burial of about 8-10 km, prior to platform exhumation which was active 49-39 Ma. Moreover, we quantify related pressure evolution and show how ophiolite obduction initiated overpressure cells forcing tectonically expelled fluid migration.

**Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Talk
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Geodynamics of passive margins: insights from the DFG Schwerpunktprogramm SAMPLE for the South Atlantic and beyond

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Content

The DFG Priority Program SAMPLE (South Atlantic Margin Processes and Links with onshore Evolution: <http://www.sample-spp.de/>), which is to be completed 2016, has studied the evolution of the South Atlantic from its Cretaceous inception to the present day. The program has an explicit interdisciplinary focus, drawing on constraints from deep Earth geophysics, lithosphere and basin dynamics, petrology, landscape evolution and geodesy, thus linking processes that are commonly studied in isolation. Starting from the premise that passive margins are first-order geo-archives, the program has placed the South Atlantic opening history into an observational and theoretical context that considers seismic imaging, plate motion histories, uplift and subsidence events, magmatic and surface evolution, together with models of mantle convection and lithosphere dynamics. A primary lesson is that passive margins are active, displaying a range of vertical motion, i.e. dynamic topography, events, apparently correlated with plate motion changes, that do not conform to traditional rifting models of passive margins. I will summarize some observational results of the program, and place them into a geodynamic context.

Influence of mechanical stratigraphy and fault kinematics on the development of massively dilatant faults – insights from scaled physical models and outcrop data from Iceland

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Content

Dilatant faults are major fluid pathways and therefore of interest for many applications such as groundwater flow, hydrocarbon production or geothermal energy. Dilatant faults form in cohesive rocks near the surface where overburden stress is low, or at depths at elevated fluid pressures. Our work focuses on dilatant faults near the surface, as found around mid-ocean ridges or in sandstones or carbonates. Work has been done on the surface geometry of these faults, but we still lack detailed understanding of the 3D structure and connectivity at depth and their evolution. The geometry of the transition zone between tensile and shear failure, as well as the extent until which dilatancy occurs at depth is unknown. We combine detailed structural mapping of dilatant faults in northern and southwestern Iceland with scaled physical models to gain insights on their 3D geometry and the parameters controlling it.

In the field we derive high resolution (5-8 cm per pixel) digital elevation models (DEM) from UAV (unmanned aerial vehicle) imagery of faults of several kilometers length with tens of meters throw and dilatant openings of several meters. These allow mapping of fault parameters in high detail. Images of basalt walls combined with ground truthing provide information on the heterogeneous and anisotropic mechanical stratigraphy. A variety of materials filling the dilatant faults such as sand, water, ice, lava and rocks which influences the mechanical properties of a fault. We propose a model for the effects of mechanical stratigraphy and fault mechanical properties on fault evolution.

We then use scaled analog models to study the 3D geometry of massively dilatant faults with mechanical stratigraphy and fault obliquity. We use hemihydrate powder and sand-powder mixtures as modeling materials with known cohesion, tensile strength and friction angle. In a first series of experiments we vary the position and thickness of a weaker layer. A second series of experiments investigates the effect of syn-depositional faulting. A third series finally tests the effect of fault obliquity on the 3D geometry. Cutting vertical slices through the experiments allows for investigating the 3D structure of faults at depth, and removal of the hanging wall material provides insights into the fault plane structure. Combining field and experimental data results in a model for the evolution and geometry of dip-slip and oblique massively dilatant normal faults.

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Talk
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Mantle convection models constrain central Neo-Tethys Ocean reconstructions

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Content

A striking feature of the Indian Ocean is a distinct geoid low south of India, pointing to a regionally anomalous mantle density structure. Equally prominent are rapid plate convergence rate variations between India and SE Asia, particularly in Late Cretaceous/Paleocene times. Both observations are linked to the central Neo-Tethys Ocean subduction history, for which competing scenarios have been proposed. Here we evaluate three alternative reconstructions by assimilating their associated time-dependent velocity fields in global high-resolution geodynamic Earth models, allowing us to predict the resulting seismic mantle heterogeneity and geoid signal. Our analysis reveals that a geoid low similar to the one observed develops naturally when a long-lived back-arc basin south of Eurasia's paleo-margin is assumed. A quantitative comparison to seismic tomography further supports this model. In contrast, reconstructions assuming a single northward dipping subduction zone along Eurasia's margin or models incorporating a temporary southward dipping intra-oceanic subduction zone cannot sufficiently reproduce geoid and seismic observations.

New insights on the Neoproterozoic to recent geological evolution of the continental margin of Southeastern Brazil derived from zircon and apatite (U-Th-Sm)/He and fission-track data

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Content

Passive continental margins are important geoarchives related to mantle dynamics, the breakup of continents, lithospheric dynamics, and other processes. The main concern yields the quantifying long-term lithospheric evolution of the continental margin between São Paulo and Laguna in southeastern Brazil since the Neoproterozoic. We put special emphasis on the reactivation of old fracture zones running into the continent and their constraints on the landscape evolution. In this contribution, we represent already consisting thermochronological data attained by fission-track and (U-Th-Sm)/He analysis on apatites and zircons. The zircon fission-track ages range between 108.4 (15.0) and 539.9 (68.4) Ma, the zircon (U-Th-Sm)/He ages between 72.9 (5.8) and 427.6 (1.8) Ma whereas the apatite fission-track ages range between 40.0 (5.3) and 134.7 (8.0) Ma, and the apatite (U-Th-Sm)/He ages between 32.1 (1.52) and 92.0 (1.86) Ma. These thermochronological ages from metamorphic, sedimentary and intrusive rocks show six distinct blocks (Laguna, Florianópolis, Curitiba, Ilha Comprida, Peruibe and Santos) with different evolution cut by old fracture zones.

Furthermore, models of time-temperature evolution illustrate the differences in Pre- to post-rift exhumation histories of these blocks. The presented data will provide an insight into the complex exhumation history of the continental margin based on the existing literature data on the evolution of the Paraná basin in Brazil and the latest thermochronological data. We used the geological model of the Paraná basin supersequences (Rio Ivaí, Paraná, Gondwana I-III and Bauru) to remodel the subsidence and exhumation history of our consisting thermochronological sample data. First indications include a fast exhumation during the early Paleozoic, a slow shallow (northern blocks) to fast and deep (Laguna block) subduction from middle Paleozoic to Mesozoic time and a extremely fast exhumation during the opening of the South Atlantic (Cretaceous time). This enables a possible interpretation of the southeastern Brazilian margin being an outer part of the Paraná basin and even the possible source area for the Ordovician to Carboniferous sediments. Further on, we try to research the newly gained exhumation history models for indications on the evolution and movement of the lithosphere of the southeastern Brazilian mantle.

On the observability of epeirogenic movement in current and future gravity missions

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Content

Next generation gravity missions are expected to improve the accuracy of temporal gravity models significantly. The periodic signals and trends retrieved by these missions are induced by mass redistribution in the Earth system, carrying essential information on dynamic processes in the atmosphere, cryosphere, continental hydrosphere, the oceans and the solid Earth. While temporal gravity signals induced by deep Earth's processes are commonly thought to lie below the observational threshold of satellite gravity missions, as one assumes them to be small in amplitude and restricted to the longest spatial and temporal scales, there exists evidence from the geologic record for rapid uplift and subsidence events at regional scales, especially along passive continental margins, related to flow in the underlying mantle. Here we explore novel mantle flow retrodictions for geodynamically plausible, compressible, high resolution Earth models with ≈ 670 million finite elements. These time-dependent Earth models link to geologic observables in the late Paleogene that can be tested independently, while at the same time indicating mantle flow induced geoid rates on the order of $5 \mu\text{m}/\text{year}$, at spatial scales of 1000 km . We assess the signal retrievability of the modeled rates in closed-loop numerical simulations, with different satellite gravity retrieval mission assumptions, including GRACE, GRACE-FO and a next generation gravity mission. We find the modeled deep Earth signal to be on the edge of detectability, but coming into the range of detectability in future temporal gravity field solutions, suggesting the use of satellite gravity data to validate geodynamic Earth models. Importantly, the application of forward modeled dynamic mantle signals seems to be essential for improved de-aliasing and signal separation in future gravity missions.

Post-breakup burial and exhumation of passive continental margins: Seven propositions to inform geodynamic models

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Content

The processes involved in the post-breakup development of passive margins remain poorly understood. Integration of apatite fission track analysis (AFTA) and stratigraphic landscape analysis (SLA) at a number of margins has provided new insights into the development of elevated passive continental margins (EPCMs) [1].

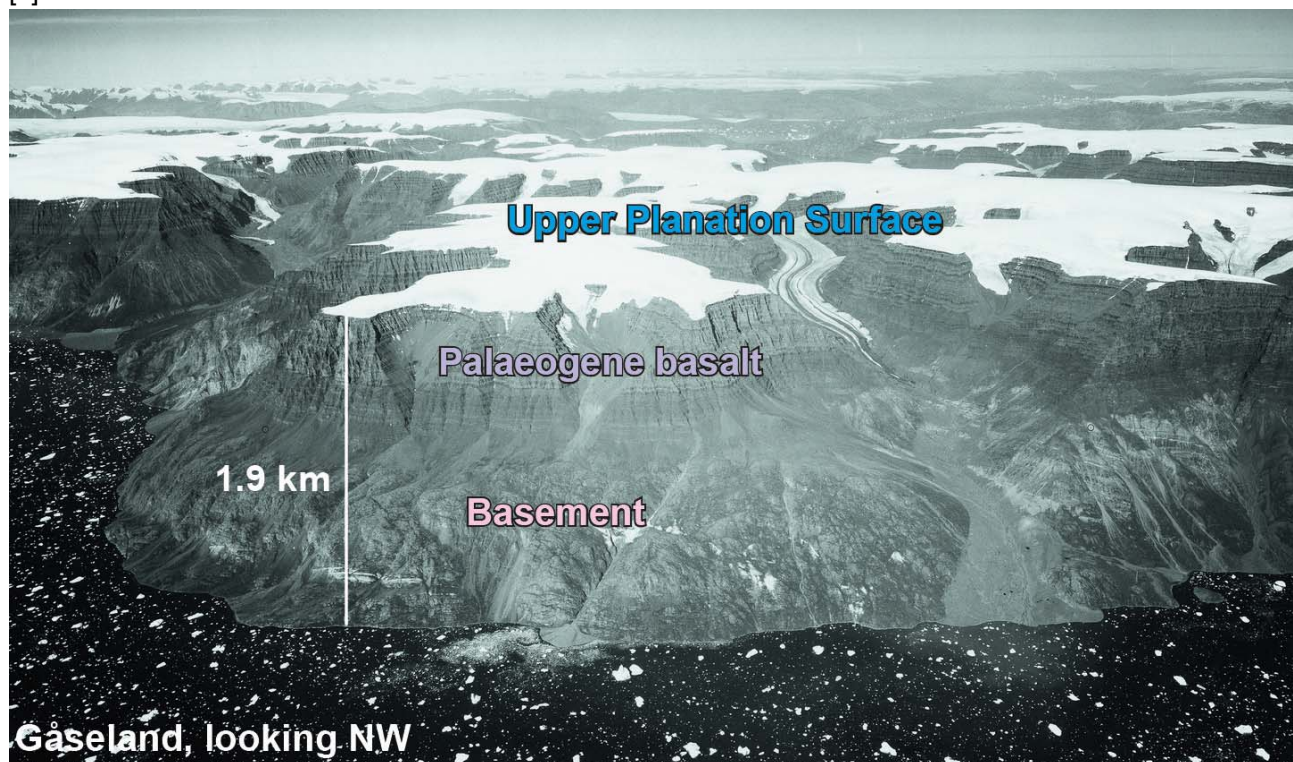


Figure 1. East Greenland (70°N) looking north-west across the extensive plateau representing an uplifted peneplain (Upper Planation Surface, UPS) that cuts across Eocene basalts and Precambrian basement at elevations around 1.9 km a.s.l.

In particular, by integrating evidence from the preserved rock record and landscape [2] with information on the deposition and erosional removal of rock units which are no longer present ("missing section") these studies have highlighted the importance of episodic positive and negative vertical km-scale crustal movements.

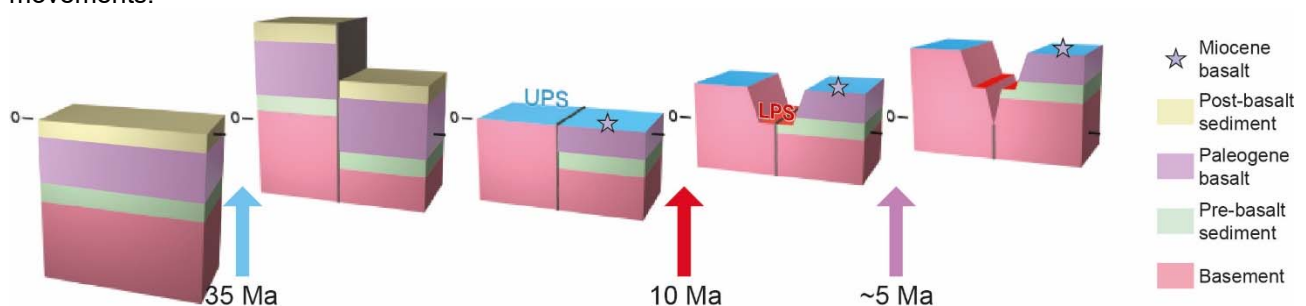


Figure 2. Block diagrams illustrating the development of the East Greenland margin from maximum burial at the end of the Eocene to the formation of the present-day landscape with two elevated plains, UPS and LPS (Upper and Lower Planation Surface).

Based on these studies we present seven propositions regarding the formation of EPCMs and the nature of the controlling processes [3]. These propositions imply that positive and negative vertical motions at passive margins are controlled by plate-scale processes. Another key conclusion is that present-day elevation alone provides no clue to the earlier history of a margin. Many of the key aspects of these propositions are absent from current geodynamic models of passive-margin development. Understanding the processes that control vertical movements at passive continental margins requires development of realistic geodynamic models that honor these propositions.

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Retrodictions of Mid Paleogene mantle flow and dynamic topography in the Atlantic region from compressible high resolution adjoint mantle convection models: Sensitivity to deep mantle viscosity and tomographic input model

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Content

Abstract

Although mantle convection at Earth-like vigor is a chaotic process, it has been shown by conceptual studies that one can constrain its flow history back in time for periods comparable to a mantle overturn, ≈ 100 million years, if knowledge of the tangential surface velocity field and estimates on the present-day heterogeneity state are available. Such retrodictions, enabled through computationally demanding adjoint methods, are a promising tool to improve our understanding of deep Earth processes, and to link uncertain geodynamic modeling parameters to geologic observables. Here we present the first mantle flow retrodictions for geodynamically plausible, compressible, high resolution Earth models with ≈ 670 million finite elements, going back in time to the Mid Paleogene. Our retrodictions involve the dynamic effects from a low viscosity zone (LVZ) in the upper mantle, assimilate a past plate motion model for the tangential surface velocity field, and probe the influence from uncertain modeling parameters by using two different estimates for the present-day heterogeneity state of the mantle as imaged by two recent seismic tomographic studies, and two different values for deep mantle viscosity. Focusing on the African hemisphere, we find that our retrodictions produce a spatially and temporally highly variable asthenosphere flow with faster-than-plate velocities, and a history of dynamic topography characterized by local doming events, in agreement with considerations on plate driving forces, and regional scale uplifts reported in the geologic literature. Our results suggest that improved constraints on non-isostatic vertical motion of Earth's surface — provided, for instance, by basin analysis, seismic stratigraphy, landform studies, or the sedimentation record — will play an important role in our understanding of the recent mantle flow history.

Role of the Inherited Wadi Ghoweiba Oblique Half-Graben on the Gulf of Suez Rift Development, Egypt

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Content

The northwestern onshore side of the Gulf of Suez (GOS) shows dissipation of the rift over a vast area with concomitant changes in its structural-sedimentary style. The surface exposures of this area were studied and mapped in detail with analysis of processed satellite images and interpretation of 2D-seismic and well data. Tying together the surface and subsurface geology revealed the existence of an inherited major E-W-trending half-graben system called Wadi Ghoweiba (WG). The half-graben initiated as a Jurassic basin during the rifting phases associated with the opening of the Tethys and it represents the southern limit of marine Jurassic sediments in the Eastern Desert of Egypt. In later times, the WG half-graben continued to subside and accommodated a 2500-4000m-thick sedimentary column of dominant marine facies relative to 1400-1500m-thick sediments in its footwall block, represented by the Northern Galala Plateau. During the Late Cretaceous wrenching tectonics of the Syrian-Arc system, the northern side of the half-graben was affected by E-ENE-trending strike-slip faults associated with en échelon fold culminations. These folds persisted as intra-basinal highs and sub-aerial ridges in the succeeding Early Tertiary basin. Early Oligocene fluvial sediments filled the depression of WG half-graben and were followed by Late Oligocene volcanics on its western side. The Oligocene clastics were possibly derived from the GOS side.

In Late Oligocene time, the northern gulf area was dominated by deep-seated faults and fold culminations, structurally-induced physiographic highs and lows and drastic sedimentary thickness variations. The northward propagating GOS rift encountered these highly oblique inherited fabrics and consequently the rifting stress dissipated over a vast area. This resulted in termination of both the rift border fault and rift shoulder, deviation of the GOS towards the NE-direction through achievement of a coastal fault of less displacement, and development of swarms of faults across the entire width of the north Eastern Desert. These faults are mainly of extensional-type, follow the GOS NW-trend and form elongated horsts and grabens. The E-ENE-striking deep-seated faults, activated by oblique divergence, formed arrays of E-W, ENE- and WNW-trending oblique-slip fault segments. The latter faults act as transfers between the NW-trending horsts and grabens, thin-skinned, and rooted at depth onto the inherited Syrian-Arc strike-slip faults

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Talk
A-852

The Paleocene-Eocene evolution of the onshore margin southeast Brazilian using Apatite Fission Track and (U-Th)/He ages

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Content

The Serra do Mar (SM) mountain range on the southeast Brazilian continental margin is related to a complex tectono-magmatic evolution since the break-up of Western Gondwana and opening of the South Atlantic Ocean in Early Cretaceous. Alkaline magmatism in the Late Cretaceous, and Paleogene Continental-rift reactivation of Precambrian basement structures uplifted a proto-SM. Related erosion provided siliciclastic sediments to the Santos basin. The paleogene Southeastern Brazilian Continental Rift (SBCR) was associated with eruption of ankaramitic flows in the Volta Redonda and Itaboraí basins at 48 Ma. The Santos basin presents similar tectonic reactivation.

In order to clarify the intensity and duration of tectonic and geomorphological processes that formed the SM we have undertaken a low temperature thermochronology study of crystalline basement from south Rio de Janeiro and São Paulo states. Apatite fission track (AFT) and (U-Th)/He (AHe) dates are combined with geologic information to generate precise thermal histories. AFT ages range from 145 to 53 Ma and AHe ages range from 75 to 37 Ma. Forward modeling using QTQt confirms the Late Cretaceous-Paleocene cooling pulse identified earlier. The episodes are seen across the region at ~80 Ma, and at 40-50 Ma. Early Miocene cooling affected the SM southern rim and surrounding of the Volta Redonda basin in Rio de Janeiro state. The Neogene cooling phase is not observed everywhere. We assume that the proto and actual SM follow the complex cooling history phase of the Paleocene-Eocene were normal re-activation with faulting uplifted flanks in this section of the SM.

THERMOCHRONOLOGICAL CONSTRAINTS ON THE CAMBRIAN TO RECENT GEOLOGICAL EVOLUTION OF THE ARGENTINE AND URUGUAYAN PASSIVE CONTINENTAL MARGIN

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Content

“Passive” continental margins are valuable geo-archives that store geological information of pre- syn-, and post-rift tectonic and thermal history processes. The elevation of “passive” continental margin along the South Atlantic varies from more than 1,000 m a.s.l. to less than 50 m a.s.l. Causes of such strong variations in topography are still in debate and under examination. Whereas the South Atlantic “passive” continental margins (SAPCM's) in Brazil, Namibia, and South Africa are mainly high-elevated margins (up to 2,000 m a.s.l.), the SAPCM in Argentina and Uruguay is of very low elevation. Low-temperature thermochronology has been applied at the two NW-SE-trending mountain ranges Sierras Septentrionales and Sierras Australes in Argentina and along the SAPCM of Uruguay.

In Argentina, the low-temperature thermochronological (LTT) data (< 240 °C) indicated that the Upper Jurassic to Lower Cretaceous opening of the South Atlantic has not completely thermally reset the surface rocks (Kollenz et al., 2016). The LTT archives apatite and zircon still revealed information on the pre- to post orogenetic history of the Gondwanides and the Mesozoic and Cenozoic South Atlantic geological evolution. The corresponding t-T models report a complex subsidence and exhumation history with variable rates since the Ordovician. Based on the LTT-data and the numerical modeling we assume that the NW-SE-trending mountain ranges received their geographic NW-SE orientation during the syn- to postorogenetic history of the Gondwanides.

Along the uruguayan coast the Apatite fission-track (AFT) ages indicate cooling phases during Permian to Jurassic time. Whereas further inland the thermochronological data closer to the Parana Basin show ages of the Early Paleozoic up to Late Paleozoic time. The AFT-data of Uruguay do not indicate a significant Post-South Atlantic-rift reactivation of onshore Precambrian to Palaeozoic fault and shear systems as has been happened in Brazil and Argentina (Karl et al., 2013), Franco-Magalhaes et al., 2010, Kollenz et al., 2016). However, pre-rift tectonic movements along the Precambrian fault and shear systems could be proven. Furthermore, computer based numerical modelling using the software code HeFTy tests the influence of a possible Parana magmatic event with volcanic rocks reaching towards the recent coast. The t-T evolution of all samples allows a magmatic volcanic sheet of up to 1.5 km on top of the Precambrian basement.

**Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Talk
A-422**

Timing and spatial patterns of Cretaceous and Cenozoic inversion in the Southern Permian Basin

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Content

Mesozoic extensional and intracontinental basins of the Southern Permian Basin system became inverted from Late Cretaceous time onwards. There is a consensus that a first “Subhercynian” pulse of contractional deformation and basin uplift occurred in Late Cretaceous time, but views on the later evolution differ: Either inversion is taken to have been continuous into the Cenozoic, or several distinct Cenozoic inversion events are invoked. In the second scenario, the oldest of these pulses is the “Laramide” event of Paleocene age (about 60 Ma). The Laramide event coincides with the termination of chalk deposition and widespread regression around the North Sea Basin which continued to subside. The spatial extent of these effects is far too wide to be compatible with inversion by folding and reverse faulting, and they occur indiscriminately across Mesozoic grabens and older inversion structures. The width of the uplifting and subsiding regions was even too large to be consistent with folding of the entire lithosphere under tangential compression. There appears to be no unequivocal evidence of discrete folds or faults formed or reactivated in the Laramide event. By contrast, a well-documented inversion event of approximately Late Eocene to Late Oligocene or Early Miocene age is recorded in the region from the Celtic Sea to the western Netherlands. The associated deformation is substantially weaker than that caused by Late Cretaceous inversion. The shortening direction is rotated slightly counterclockwise to N-S from the Late Cretaceous NNE-SSW shortening direction. Cretaceous and Eocene to Miocene inversion spatially overlap only in the southern North Sea. Structural inversion of the SPB thus comprised only two events clearly separated in time and mostly also in space.

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Keynote speaker

Session 1.4: From rifts to passive continental margins: mantle-, and lithosphere-basin dynamics, and long-term landscape evolution: Keynote speaker

A-662

Stratigraphic framework for the plume mode of mantle convection

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Content

Mantle convection is a fundamental planetary process. Its plate mode is well established and expressed by plate tectonics; its plume mode is equally well established and expressed by interregional-scale geological patterns; I developed a stratigraphic framework to translate the surface effects predicted by the plume mode, which also serves as a methodology to analyze continent-scale geological maps based on unconformities and hiatuses. The surface expression of ascending plumes lasts for tens of millions of years and leaves a distinct record, not only as a > 1-km-high dome above the plume center, but also above the plume head margins and in distal regions (> 1200 km). Regional-scale erosion of the uplifting dome dominates prior to arrival of the plume head at the base of the lithosphere, and is followed by extensional collapse and flood-basalt eruption. A nearly complete sedimentary record may be preserved in distal regions, which did not experience any plume-related uplift. The marginal section of the uplifted dome is the most complex, because it undergoes multiple episodes of uplift and erosion followed by subsidence and sedimentation, and renewed outward-directed uplift and erosion as the plume head collapses and spreads laterally. Thus, marginal regions contain regional-scale “double-unconformity-bounded” stratigraphic successions. Complete global stratigraphic synthesis of plate interiors requires integration of plate- and plume-stratigraphic frameworks. This plume-stratigraphic framework is event-based, interregional, but not global, with time-dependent amplitudes that are significantly larger than global eustatic sea-level fluctuations.

Session 1.5: High latitude geodynamic and environmental evolution: Poster

Session 1.5: High latitude geodynamic and environmental evolution: Poster
A-308

Cretaceous magmatism along the Canadian Arctic margin related to the High Arctic Large Igneous Province (HALIP) – an overview

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Content

Onshore occurrences of Cretaceous igneous rocks related to the High Arctic Large Igneous Province (HALIP) are scattered today around the Arctic Ocean. They can provide important information about the tectonic evolution of the Arctic. Key areas of HALIP-related magmatism in the Canadian High Arctic were studied by the BGR in the frame of the CASE program (Circum-Arctic structural events) since 1997.

Cretaceous magmatism in the Canadian High Arctic took place majorly during three stages: 130 – 120 Ma (Stage I), 105 – 95 Ma (Stage II), and 85 – 75 Ma (Stage III).

Stages I and II are represented by dominantly tholeiitic continental flood basalt magmatism with lava flows, sills, and dykes. Stage II includes tholeiitic felsic volcanism at the north coast of Ellesmere Island and mildly alkaline flood basalts in northeast Ellesmere Island. Stage III is characterised by rift-related, alkaline, bimodal intrusive and extrusive magmatism at the northwestern coastal region of Ellesmere Island.

The three stages of magmatism are closely related to the opening and evolution of the Arctic Ocean. Stage I accompanies the formation of the Canada Basin. Stage II is linked to the formation of Alpha Ridge and probably to the opening of Makarov Basin. Magmatism of stage III is controlled by pre-existing E-W trending fault zones parallel to the continental margin that were reactivated by early extension of the future Eurasia Basin. Renewed (hydro-) thermal activity during the Eocene Eurekan deformation (c. 50–45 Ma) led to resetting of Ar–Ar ages.

Timing and magnitude of submarine landslides in high-latitude trough-mouth fans of the SW Barents Sea

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Content

Trough-mouth fans (TMF) in high-latitude continental margins of the SW Barents Sea contain a climatically controlled heterogeneous sediment archive that is driven by glacial advances and retreats to and from the shelf edge. The fundamental control that such TMF exert on continental slope stability is exemplified by large and numerous submarine landslides located mainly at TMF flanks. To understand the factors driving this instability, frequency-magnitude relationships of landslide events in the Storfjorden, Kveithola and Bj  rn  ya TMF are investigated within a PhD project issued by the University of Troms   (UiT) and funded by the Western Norway University of Applied Sciences (HVL, Sogndal). The investigated submarine landslides point at deglaciation-associated deposits (mainly meltwater plumites) as a primary gliding horizon within the glacial-interglacial cycle. Contrarily, former till deltas that have been pushed over the shelf break and deposited as glacial debris flows in glacial times make up large parts of rather stable, central TMF areas and can therefore be clearly distinguished from landslide events. Both findings jointly reveal a climate control on arctic continental slope stability.

Session 1.5: High latitude geodynamic and environmental evolution: Talk

Session 1.5: High latitude geodynamic and environmental evolution: Talk

A-435

Actively evolving subglacial conduits and eskers initiate ice shelf channels at an Antarctic grounding line

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Content

Meltwater beneath the polar ice sheets drains, in part, through subglacial conduits. Landforms created by such drainages are abundant in areas formerly covered by ice sheets during the last glacial maximum. However, observations of subglacial conduit dynamics under a contemporary ice sheet are lacking. We present results from ice-penetrating radar to infer the existence of subglacial conduits upstream of the grounding line of Roi Baudouin Ice Shelf, Antarctica. The conduits are aligned with ice-shelf channels, and underlain by esker ridges formed from sediment deposition due to reduced water outflow speed near the grounding line. In turn, the eskers modify local ice flow to initiate the bottom topography of the ice-shelf channels, and create small surface ridges extending onto the shelf. Relict features on the shelf are interpreted to indicate a history of these interactions and variability of past subglacial drainages.

Eskers beneath a contemporary ice sheet have not yet been observed, and our analysis provides novel insights for interpreting their existence in areas where ice sheets have since retreated. Because ice-shelf channels are loci where intense melting occurs to thin an ice shelf, these findings expose a novel link between subglacial drainage, sedimentation, and ice-shelf stability.

Aerogeophysical survey over the Forster Magnetic Anomaly and its implications for revealing the tectonic evolution of central Dronning Maud Land

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Content

The ice-covered and remote Polar Regions are still insufficiently known. Within a long-standing collaboration between Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research (AWI) and the Federal Institute for Geosciences and Natural Resources (BGR), one of the scientific aims is to investigate the sub-ice crustal architecture and tectonic evolution of East Antarctica with main emphasis on Dronning Maud Land between Wohlthat Massif and Lützow-Holm Bay. Here, a prominent NE-SW trending magnetic lineament, the Forster Magnetic Anomaly (FMA), is of major interest.

The FMA was first identified during aerogeophysical surveys carried out by the AWI between 2001 and 2005, and lies well to the south of isolated mountainous outcrops that do not directly help to identify the anomaly source.

One hypothesis suggests that the FMA represents a major suture between rocks with African affinities and Archean to Mesoproterozoic ages in the West and juvenile Early Neoproterozoic rocks of the recently defined TOAST (Tonian Oceanic Arc Super Terrane) in the East. Consistent with this idea, satellite gravity data have recently revealed that a major change in lithospheric thickness coincides with the FMA.

Polar 6 operated in 2015/16 and 2016/17 out of Neumayer and Kohnen stations to focus on the densification of existing survey profiles over the FMA from 10 km to 5 km spacing. Interpretation of these data will help sharpen our understanding of the final amalgamation of Gondwana and provide a better image of the FMA itself.

**Application of very high spatial resolution satellite imagery to the study of Arctic geology:
an example from the Wootton area, Ellesmere Island, Arctic Canada**

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Content

The geological studies in the Arctic face a number of challenges due to the remote location, hostile climate conditions, lack of infrastructure etc. In this respect, the use of aerial and satellite imagery is beneficial to assist in the geological mapping, tectonic studies and mineral exploration activities in the Arctic regions (e.g., Bedini, 2011). Digital Globe's WorldView-2 satellite provides panchromatic imagery with a nominal spatial resolution of 0.46 m. It also acquires multispectral imagery in 8 spectral channels in the visible to near infrared wavelength range (0.42-0.95 μm) with a nominal spatial resolution of 2 m. This study used WorldView-2 imagery for lithologic and tectonic mapping, and detection of hydrothermal alteration zones in the eastern part of the Wootton Peninsula of the Ellesmere Island, Arctic Canada. In the study area, the satellite image analysis mapped metasedimentary units and granitic gneisses of the Pearya terrain, sediments of Kulutingwack and Danish River formations etc. Within the Pearya terrain on both sides of the Mitchel Point Fault Zone igneous rock units that belong to the Wootton Intrusive Complex (Estrada et al., 2003) were distinguished. In addition, based on the spectral reflectance properties in the visible to near infrared wavelength range of goethite and hematite, a map of the iron-stained zones in the study area was obtained. The iron-stained zones are often related to the lithology (e.g., rhyolites) or with faults. The remote sensing results were used as an auxiliary layer of information from the BGR Polar Research group carrying out geological field activities in the northern Ellesmere Island, Arctic Canada. The study indicates that the very high spatial resolution satellite imagery can be used to improve existing geological maps, map tectonic features and contribute to the mineral exploration activities in the Arctic regions.

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Exhumation of the High Arctic Eurekan Belt during the Eocene – implications for sediment deposition and glaciation in the Arctic

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Content

The Eocene was a time of profound change in the Arctic realm, with the initiation of sea floor spreading along the Gakkel Ridge, presumably first continental glaciation and sea ice formation, and the formation of the Eurekan deformation belt. The latter results from northward movements of Greenland as an independent microplate, thereby colliding with Ellesmere Island (Canadian High Arctic) and the Svalbard archipelago. Recent studies even suggest that Eurekan deformation has propagated further north across the Arctic Ocean, causing an Eocene hiatus or strongly condensed section as observed from the sedimentary record on top of the Lomonosov Ridge.

For this study, we investigate the exhumational response to Eurekan deformation across Ellesmere Island using low-temperature thermochronology. Data on exhumation do not provide direct evidence for the topographic evolution, but it gives an indirect measure, as relief formation is usually associated with enhanced exhumation. Our data show a dramatic difference between the exhumation history of South vs. North Ellesmere Island. South Ellesmere Island experienced only minor Eurekan exhumation, even when sampling close to the Eurekan deformation front. North Ellesmere, by contrast, was affected by km-scale exhumation (>5-7 km) during the Eocene, slowing down at the beginning of the Oligocene. This suggests that erosion was focused in the north of the Eurekan belt, making it likely that the Eurekan orogeny in deed led to a hiatus in the central Arctic sedimentary sequence. Furthermore, our data imply a high latitude belt of pronounced topography. Recent studies show that strongly enhanced topography (as compared to the present) is a prerequisite for Eocene continental glaciation of Greenland. We suggest that this glaciation nucleated in the area of the Eurekan belt. Furthermore, we suggest that detritus from the Eurekan orogen may be the source of the ice rafted debris observed in Eocene sediments of the Arctic Ocean and the North Atlantic.

From subduction to rifting: low-temperature cooling signatures along the Pacific margin of West Antarctica: Insights from apatite thermochronology

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Content

West Antarctica is a collage of several crustal blocks which were amalgamated along an active margin in Palaeozoic and Mesozoic times forming the Gondwana supercontinent. Subsequent extension since the mid Cretaceous led to continental break-up and the initiation of the West Antarctic Rift System (WARS), one of the largest rift systems on earth. Along this 3000 km long large-scale continental structure within the Antarctic continent several crustal blocks - e.g. Marie Byrd Land, Thurston Island block- are being separated again. Due to a perennial ice cover, the precise location, geometry, and tectonic evolution of the WARS are, however, still poorly constrained and understood. Continental break-up was most-likely associated with a period of pronounced erosion and rapid exhumation, hence apatite thermochronology provide an ideal measure to monitor and constrain the shallow crustal tectonic processes active at that time and thus enhance the understanding of the WARS.

Thermal models including apatite fission-track and apatite (U-Th-Sm)/He data of (meta-) plutonic rocks of the Marie Byrd Land and Thurston Island crustal blocks indicate a relatively isochronous cooling episode in the mid to Late Cretaceous. This demonstrates that large portions of the eastern Gondwana margin underwent regional exhumation while crustal convergence was progressively replaced by extension and rifting.

Mantle exhumation and ocean basement formation in the Nansen Basin, Arctic Ocean

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Content

We study the transition from the North Barents Sea margin into the southern Eurasia Basin based on two multichannel seismic data (MCS) profiles, which were acquired during ice-free conditions with a 3,600 m long streamer. Additionally, we acquired gravity and magnetic data. The seismic data resolves the up to 5,000 m thick sedimentary section as well as several kilometers of crustal structures. The profiles cover 120 km and 170 km of the southern Nansen Basin, respectively. The seismic data show large faulted and rotated basement blocks probably made up of exhumed and serpentinized mantle. Gravity modeling indicates a thin basement with a thickness of 1-3 km and a density of $2.8 \cdot 10^3 \text{ kg/m}^3$ between the base of the sediments and the top of the mantle, which supports the interpretation of exhumed and serpentinized mantle. The change from thick continental crust on the North Barents Sea margin to thin crust in the Nansen Basin is quite abrupt and is explained by an initial transform movement of the Lomonosov Ridge along the North Barents Sea margin and subsequent near-orthogonal initial opening of the Nansen Basin. This process brought mantle material to the surface where it was serpentinized. Subsequent faulting produced the basement blocks. The size and shape of the blocks in our data are quite similar to blocks visible in previously acquired data closer to the present-day active spreading center, the Gakkel Ridge. The Gakkel Ridge is characterized by an amagmatic or sparsely magmatic sector in prolongation of the seismic data. We propose that mantle exhumation is active since the opening of the Eurasia Basin and the basement is entirely formed by exhumed and serpentinized mantle only with minor magmatic additions.

Middle Miocene magmatic activity in the Sophia Basin, Arctic Ocean – evidence from dredged basalt at the flanks of Mosby Seamount

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Content

The area to the northwest of Svalbard was affected by repeated tectono-magmatic processes starting from the Cretaceous formation of the High Arctic Large Igneous Province, to Late Cretaceous/early Cenozoic birth of the Eurasian Basin towards the establishment of a full seafloor-spreading regime along the Lena Trough/Fram Strait in Middle Miocene. These processes also affected the Sophia Basin located in-between the Yermak Plateau and the northern Svalbard Shelf. In 2013 a little piece of basalt could be dredged from the southern flank of the Mosby Seamount, the central landmark within the Sophia Basin. Geochemical analyses support our assumption that the rock fragment has a local origin and that it was not rafted towards the sample site by ice. The trace element composition implies that the basalt had incorporated marine sediments and also Fe-Mn crusts or nodules. According to geochronological data the basalt erupted ~13 Ma, contemporaneous to incipient seafloor spreading in the nearby Lena Trough and volcanic activity in northern Svalbard. Assuming a link of the dredged basalt with seismic indication of sediment covered lava flows and sill intrusion around Mosby Seamount, its middle Miocene age can be used to better constrain the regional seismo-stratigraphy.

Numerical Modelling to Evaluate the Impact of Paleo-bathymetry and Basin-Fill Processes on Source Rock Distribution in the Hammerfest Basin, Barents Sea.

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Content

In basin modelling, the paleo-bathymetry and distribution of organic matter within the source rock are important properties yet they are uncertain and are often be considered as constant or homogeneous. In this study, high resolution 3D models are produced with their heterogeneities of paleo-bathymetries, basin-fill processes and source rock distributions, employing numerical modelling for the three most important source rock intervals; the Early-Mid Triassic, the Late Jurassic, and the Early Cretaceous, in the Hammerfest Basin. More importantly, the study attempts to further analyse the factors controlling the source rock distribution by linking the paleo-bathymetry and basin-fill processes. The models are validated by sand fraction (SF), total organic carbon (TOC) and hydrogen index (HI) data. The three source rock intervals show distribution models with diverse values for each parameter. The paleo-water depths vary from 2200 m to 50 m, while the sedimentation rates are between 1 and 48 cm/ka with siliciclastic dominated deposition, and thus reflect different basin-fill processes and tectonic development through time. As a result, the source rocks are composed by various organic matter source types, from marine organic matter to terrigenous and residual organic matter. The source rocks have a range of quantity (TOC from 0.1 to 14 wt%) and quality (HI from 24 to 344 mgHC/gTOC) with poor to very good source rock potential. In general, the Late Jurassic Interval is the best source rock in the study area with good to very good source rock potential. The main reason identified is very high primary productivity with favourable basin-fill process and depositional environment for source bed deposition. With these selected examples, it is demonstrated how the paleo-environment controls the distribution of the source rock properties.

Paleo-Current Activity in the Eastern Arctic Ocean - Evidence from Sediment Waves and Drifts

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Content

Four stages of deposition regime on the southeastern Lomonosov Ridge and its Eurasian side have been detected on high-resolution seismic reflection profiles.

First, old Mesozoic strata on the Lomonosov Ridge, its faulted flanks and the initial Amundsen Basin were covered and filled with syn-rift sediments of Paleocene-early Eocene age. Small vertical faults indicate differential compaction of probably anoxic sediments deposited in the still isolated Eurasian Basin.

The second stage comprises the Eocene and Oligocene Epoch, and likely the formation of a high-amplitude-reflector sequence (HARS) indicating a time of widespread changes in deposition realm. The stage is associated with the gradual opening of the Fram Strait and ongoing subsidence of the LR which posed no longer an obstacle. Episodic incursions of water masses from the North Atlantic probably were the consequences and led to the deposition of sediments of strongly different lithology. Likely the HARS is indicative for the hiatus detected on the central LR, and consists of sediments deposited during this span.

The third stage is marked by uniform reflection characteristics in the upper sedimentary succession on the ridge and in the basin, which implies widespread and pelagic sedimentation since earliest Miocene.

Sediment waves in the upper units in the AB are evidence for paleo-bottom current activity and the onset of an ocean circulation system. The southeastern slope of the LR is structured into three terraces, indicating fault-controlled sediment drifts arisen since the early Miocene on formerly rifted crustal blocks. These drift bodies constrain the onset and intensification of current circulation during Miocene in the EB. Since that time the advanced deepening of the Fram Strait must have enabled an effective exchange of water masses between the North Atlantic and Arctic Ocean. Continuous sagging of the ridge, reactivation of former faults and bottom currents passing along the LR may shape the steep sediment free flanks of the terraces in addition.

At least, the uppermost seismic unit forms a continuous regional drape of high-amplitude reflectors and likely marks the transition to large-scale glaciation of the northern hemisphere in early Pliocene. A pronounced high-amplitude reflector, parallel to the seafloor and described as BSR in earlier studies, turned out to be an artefact.

Polyphase structural evolution of northern Victoria Land (Antarctica) in the light of Gondwana break-up and the development of the Australia-New Zealand-Antarctica plate fragments (ANZAPF)

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Content

The Australia-New Zealand-Antarctica plate fragments (ANZAPF) evolved as consequence of break-up and fragmentation of Gondwana since the late Early Jurassic. Antarctica occupied the centre of Gondwana, and it thus holds a key position for any plate tectonic reconstruction. Northern Victoria Land (NVL) is located at the Pacific end of the Transantarctic Mountains, a high-elevation mountain chain that stretches for >3500 km from the Atlantic to the Pacific oceans across the entire Antarctic continent. The modern Transantarctic Mountains represent the uplifted western shoulder of the Cenozoic West Antarctic Rift System. The main uplift commenced around the Eocene-Oligocene boundary due to inversion of a wide mid-Jurassic to early Paleogene sedimentary basin ("Mesozoic Victoria Basin"). The basement rocks of the Transantarctic Mountains formed by orogenic processes due to subduction of the Palaeopacific Ocean beneath East Gondwana during the ?latest Ediacaran to early Palaeozoic Ross Orogeny. This long-lasting geological history of NVL produced a highly anisotropic crust, which is very much susceptible to repeated reactivation. Here, we present multi-methodological evidence for the polyphase structural evolution of NVL after initial break-up of Gondwana in this region indicated by the ca. 180 Ma Ferrar volcanic event. A post-34 to 30 Ma old, predominantly Neogene NW-SE striking dextral strike-slip belt with local transtension and transpression has overprinted and in parts obliterated older structures and controls the present structural architecture of NVL. It may be interpreted in terms of dynamic response to intra-oceanic fracture zone arrays between Australia and Antarctica reaching into the NVL crust and extending further into the Ross Sea. Structural and geophysical evidence indicates that dextral strike-slip overprints two older increments with (i) WNW-ESE striking sinistral strike-slip and (ii) ENE-WSW directed crustal extension. They are related to the late Mesozoic to early Cenozoic fragmentation of the ANZAPF region involving the formation of a left-lateral transform margin between Australia and Antarctica in the middle/late Cretaceous to ?early Paleogene and followed by large-scale extension of NVL continental crust possibly linked to the Adare Trough spreading event (ca. 43-27 Ma: Cande et al. 2000).

Cande, S.C., Stock, J.M., Müller, R.D. & Ishihara, T. (2000), *Nature*, 145-150.

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A temperature profile through paleo-oceanic crust (Wadi Gideah transect, Oman): Application of the REE-in-plagioclase-clinopyroxene thermometer

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Content

The crystallization temperatures of gabbroic rocks over crustal depths can help to gain insight into accretion and cooling mechanisms of the oceanic crust. Typical end member models for the crustal accretion from fast-spreading ridges are the gabbro glacier and the sheeted sill model. For the first model, heat extraction mainly takes place within the shallow axial magma chamber, with subsiding crystal mush to the central axis flanks. For the second model, the accretion by many injection sills of crystal mushes a higher heat extraction within the deep crust is needed. Hybrid models will show low temperatures where subsiding material from the magma chamber and the upflowing crystal mush encounter each other, leading to variation of other signals (e.g. trace element geochemistry, mineral chemistry, isotope geochemistry, crystal preferred orientation) over the crustal depth profile obtained for the Wadi Gideah transect (Semail Ophiolite, Oman).

Partitioning of incompatible elements, especially REE between plagioclase and clinopyroxene is affected by temperature, pressure and water content of the parental melt. While the pressure is low and water content insignificant in a typical MOR setting, temperature is the main controlling factor of partitioning. Therefore, REE partitioning between plagioclase and clinopyroxene can be used as near solidus crystallization temperature tracer.

Here we present first LA-ICP-MS mineral data of coexisting plagioclase and clinopyroxene of gabbros throughout the crustal reference profile of the Wadi Gideah transect and apply the new REE+Y partitioning thermometer by Sun (2017). Our data shows significant changes in REE partitioning behaviour over depth, especially for the HREE. The resulting temperature profile will be used to test thermal models (e.g. MacLennan et al., 2005) and the conceptual models of crustal accretion.

MacLennan, J., Hulme, T., and Singh, S.C., 2005, Cooling of the lower oceanic crust: *Geology*, v. 33, no. 5, p. 357, doi: 10.1130/G21207.1.

Sun, C., 2017, A REE-in-plagioclase–clinopyroxene thermometer for crustal rocks: *Contributions to Mineralogy and Petrology*, v. 172, no. 4, p. 20, doi: 10.1007/s00410-016-1326-9.

Constraints on cooling of the lower ocean crust from epidote veins in the Wadi Gideah section, Oman Ophiolite

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Content

Timing, depth and extent of high-temperature hydrothermal alteration in the ocean crust is key to understanding how lower oceanic crust is cooled after accretion. We report data of epidote veins from the Wadi Gideah section in the Wadi Tayin block of the Oman Ophiolite, which is a reference section for alteration pattern of the lower crust formed at a fast oceanic spreading center. Epidote veins ($X_{Fe} = 0.05 - 0.33$) were collected in reoccurring zones of intense alteration of the lower crustal Wadi Gideah section and the root zone of sheeted dykes at Wadi Amadhi extending the transect. $^{87}Sr/^{86}Sr$ ratios feature a narrow range from 0.70429 to 0.70512, while O isotope compositions vary between -0.7 and +4.9 permil in $\delta^{18}O_{SMOW}$. These compositions indicate uniform water-rock ratios between 1 and 2 and formation temperatures in the range of 300 to 450°C. There is no systematic trend in Sr and O isotope compositions down section. Fluid inclusion entrapment temperatures for a subset of samples linearly increase from 338°C to 465°C in the lowermost 3 km of crust of the Wadi Gideah section and record 340°C for the Wadi Amadhi basal sheeted dike sample. Salinities are uniform throughout and scatter closely around seawater values (3.2 ± 0.2 wt%).

Previously proposed thermal models assumed hydrothermal cooling down to the base of the crust within 5 km off the ridge axis. These models, however, come with conductive reheating in the more distal flanks after off-axis circulation shut down. There is no evidence for prograde metamorphic reactions in the samples we studied (or other hydrothermally altered oceanic gabbros). We developed a numerical model to assign possible crustal ages to the thermal gradients observed. A model, in which axial cooling down to 2 km (i.e. depth of melt lens) is assumed for the first 0.1 Ma is followed by less vigorous hydrothermal cooling ($Nu=20$ (< 0.5 km); $Nu=4$ (0.5-3 km); $Nu=2$ (3-7 km)) down to the mantle-crust transition, for 1 Ma. This distribution predicts a thermal gradient for the lower crust that matches the observed one for ages between 1 and 3 Ma. A plausible explanation for the origin of the epidote veins is that they formed in off-axial hydrothermal systems that reach the base of the crust within 50-150 km off axis. This deep circulation provides an efficient mechanism for mining heat that escapes the crust in the young flanks of mid-ocean ridges where >75% of the global oceanic hydrothermal heat flux is expected to take place.

Contrasting styles of hydrothermal activity in the Southern Kermadec Arc

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Content

Island arcs volcanoes are fed by volatile-rich magma, which is affected by the influx of water and other volatiles from the subducting slab into the melting regime in the mantle wedge. These magmas degas huge quantities of water, carbon dioxide, and sulfur dioxide, in addition to volatile metals and metalloids. Roughly 7000 km of intra-oceanic island arcs globally feature hundreds of submarine volcanic centers, many of which are hydrothermally active. The water-rock interactions and associated hydrothermal mass transfers in these hydrothermal systems differ strongly from those in mid-ocean ridge settings. These differences relate to the more felsic host rock compositions, the greater variability of water depths, and – most notably – the influx of magmatic fluids. Rates of magma degassing are highly variable on small temporal and spatial scales, which causes a geochemical diversity in fluid composition and hydrothermal mineralization in submarine island arc volcanoes that greatly exceeds the variability seen at mid-ocean ridges.

During the RV Sonne cruise SO253 in Dec/Jan 2016/17, we sampled rocks as well as hydrothermal precipitates and fluids from hydrothermal vents in four volcanic centers in the Southern Kermadec Arc: Macauley Cone, Huangaroa, Brothers, and Rumble III. The styles of hydrothermal venting varied from acid-sulfate at Macauley and Brothers to near-neutral pH fluids at Brothers and Huangaroa to diffuse venting at Rumble III. The hydrothermally active Brothers volcano is a prime example of a complex arc volcano, with its main caldera and two prominent cone-shaped resurgent cones (de Ronde et al., 2011, Min Dep 46: 541-584). Both the caldera wall and the cone sites host hydrothermal vents. The cone sites emitted low temperature (<100°C), acidic, gassy fluids, with very low H₂(aq) concentrations and extraordinary high Mg and sulfate concentrations.

The north-west caldera site at Brothers features high temperature (up to 305°C), gas-poor, SiO₂-rich black-smoker type fluids with the typical depletions in Mg and sulfate. We found a new hydrothermal site on the southern flank of a volcanic peak decorating the rim of the NW caldera wall with spectacular, up to 20m high chimney structures issuing fluids as hot as 311°C. In many areas of the 600-m wide NW caldera site, slope collapse has exposed stockwork zones underneath active hydrothermal vents, with pervasive altered volcanic rocks that are cut by pyrite/chalcopyrite vein network.

Geochemical variation of the sheeted dike complex in the Troodos Ophiolite, Cyprus

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Content

The Troodos Massif, exposed on the island of Cyprus, is one of the best-preserved ophiolites in the world. The plate tectonic setting of the Troodos Ophiolite is unclear but the composition of the rocks indicates an origin above a subducting slab. The enrichment of fluid mobile elements varies in the lavas that have been studied and indicates several stages and/or positions of the ophiolite above the slab. The composition of the pillow lavas ranges from tholeiitic to boninitic. The largest portion of the ophiolite consists of the sheeted dike unit but little is known about the tectonic and magmatic evolution during the spreading phase. Here we present whole rock data from several locations of the sheeted dike complex of the Troodos Ophiolite in order to define the geochemical variation of this unit. Additionally, we study the geochemical variation with increasing distance from a proposed Solea Rift spreading axis.

The data set consists of about 50 samples from the sheeted dike unit that are compared with published data. We analysed major and trace elements as well as Sr and Nd isotope ratios. The composition of the sheeted dikes ranges from basalt to dacite, with an average Mg# of 49, and most rocks lie on a tholeiitic fractional crystallization trend. All sheeted dike samples show an enrichment in fluid mobile elements (e.g. Ba, Pb, Sr) as well as a depletion in HFSE (i.e. Nb, Ta, Zr, Hf), with Nb/Yb values between 0.3 and 0.5 and Zr/Yb between 5.4 and 20.6. The chondrite-normalized Ce/Yb ratios are depleted in light rare earth elements and range between 0.3 and 0.8. Two groups can be defined with (Ce/Yb)_N higher and lower than 0.5, possibly indicating partial melting of different mantle sources. La/Sm values lie around 0.9 for most samples, showing only little difference to N-MORB ratios. We study geochemical trends with increasing distance from the assumed fossil spreading centre of the Solea Rift. The group with high (Ce/Yb)_N shows increasing ratios with distance from the Solea Rift, whereas values of the second group decrease. The composition of the sheeted dike rocks overlaps with that of the tholeiitic lavas but we did not find dikes with boninitic composition. We conclude that the ophiolite formed by spreading above a subducting slab from variably depleted mantle but that the boninites formed at a later stage after spreading ceased.

Hydrothermal venting at the ultraslow-spreading Gakkel Ridge, 87°N, 55°30'E

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Content

The Gakkel Ridge is an 1800km long ultra-slow spreading ridge (spreading rates from <6mm - 13mm/y) in the Eastern Arctic. Despite the low spreading rate, the Gakkel ridge shows a higher hydrothermal plume incidence than previously expected from the low magma budget. Here we present results on the physical and geochemical characteristics of a hydrothermal plume located at 87°N, 55°30'E based on CTD measurements along with water sampling used for chemical analyses.

To infer the vertical and horizontal extent of the hydrothermal plume, the instrument package was either lowered and heaved in a seesaw manner while the ship drifted slowly with the ice, or was kept at plume level as the ship drifted to obtain horizontal plume transects. During these transects the stratified plume was persistently observed in the depth range between 2600m and 2800m with little temporal variability in its spatial position. The buoyant plume is characterized by pronounced Eh and potential temperature anomalies while turbidity increases in the non-buoyant plume relative to the ambient and the freshly vented water. This indicates an intermediate temperature (~300 °C) source fluid with particle ingrowth during plume dispersion. A positive linear relationship between potential temperature anomaly and CH₄ abundance in all samples affirms that plume waters derive from a single source fluid. Further, a high CH₄ to ³He ratio strongly indicates that the hydrothermal plumes emanates from a serpentinizing system.

Reaction-induced porosity and low-temperature carbonation of abyssal peridotites from the Mid-Atlantic Ridge

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Content

The occurrence of abyssal peridotites is common at slow-spreading oceanic ridges. Hydrous alteration of peridotites at the seafloor leads to formation of serpentinites, which - compared to their unaltered precursor rocks - show significant changes in both chemical composition and physical properties. Besides hydration, serpentinites are also prone to carbonation reactions.

We performed a detailed study of serpentinites from the uppermost section of ODP Leg 209 Site 1270D (Mid-Atlantic Ridge at 14°45'N). A sample taken from 0.75 meters below seafloor reveals a high degree of serpentinization with only a few relicts of orthopyroxene and spinel. Olivine is completely replaced by serpentine ($X_{Mg} = 0.95-0.97$) and magnetite in mesh textures. A common observation is that mesh centers consist of empty space or of highly porous serpentine aggregates. Larger voids feature a thin inner lining of Fe-oxides/hydroxides. Scanning electron microscope observations as well as X-ray microtomography confirm the presence of these voids throughout the sample. Furthermore, it can be shown that the voids are connected by a network of thin ($< 15 \mu m$) aragonite veins, pointing to a connection between carbonation and the porosity-forming reactions.

The development of porosity is interpreted to result from dissolution of brucite and/or olivine. These dissolution reactions in conjunction with changing alkalinity lead to precipitation of carbonate. The fact that the pore space is only partially filled with carbonate indicates that under static condition low-temperature carbonation leads to clogging of fluid pathways and thus to reduction of permeability. Iron released from dissolving brucite and olivine is oxidized and now contained within Fe-rich precipitates on the inner walls of open voids. Thermodynamic computations show that this process may be a source of catabolic energy for microorganisms inhabiting serpentinites. Hence, this study provides an example of the dynamic interactions between lithosphere, hydrosphere and biosphere in abyssal serpentinites.

Shallow mantle controls sulfide differentiation in slow-spreading ridge magmas

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Content

Cooled lithosphere that occurs near fracture zones at the slow-spreading ridges is known to trigger subcrustal crystallization of silicate minerals from a MORB-like melt. Although cooler lithosphere may also affect the sulfide crystallization and the metal budget of the lower and upper crust, the related sulfide behavior is poorly understood.

Here, we use chalcophile elements to trace sulfide crystallization in a suite of MORBs erupted at the Kane Megamullion south of the Kane Fracture Zone along the Mid-Atlantic Ridge (Dick et al., 2008). The basalts display a Cu trend that contrasts with the global MORB trend: between 8.3–6.0 wt.% MgO, Cu increases linearly from 60 to 100 ppm with a coefficient of determination (R^2) of 0.90, whereas non-plume-related MORBs from the global reference data set of Jenner and O'Neill (2012) show the Cu concentrations decreasing from 80 to 60 ppm over the same MgO range (Fig. 1). The increasing Cu trend in the Kane Megamullion MORBs is matched by increasing Zn, As, Pb, Tl, Sb, and Ga. Chalcophile elements thus behaved incompatibly during the differentiation of the Kane Megamullion MORBs, implying that this occurred under sulfide-undersaturated conditions.

Although sulfide-undersaturated MORBs are unusual, we argue that primary MORB melts can be depleted in sulfur and chalcophile elements by early crystallization of sulfides during reaction of percolating melts with the mantle. To be efficient, this process requires a thin crust and shallow cool serpentinized lithospheric mantle.

Dick, H.J.B., Tivey, M., and Tucholke, B.E., 2008, Plutonic foundation of a slow-spreading ridge segment: Oceanic core complex at Kane Megamullion, 23°30'N, 45°20'W: *Geochemistry Geophysics Geosystems*, v. 9, Q05014, doi:10.1029/2007GC001645.

Jenner, F.E., and O'Neill, H.S.C., 2012, Analysis of 60 elements in 616 ocean floor basaltic glasses: *Geochemistry Geophysics Geosystems*, v. 13, Q02005, doi:10.1029/2011GC004009.

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Circulation of seawater-derived fluids beneath fast-spreading mid-ocean ridge: Insights from IODP Site 1256

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Content

Circulation of seawater-derived fluids through newly formed oceanic crust at mid-ocean ridge (MOR) has important effects on crustal accretion and alteration. It partly controls extraction of magmatic heat, and thus influences differentiation and crystallization of MOR basaltic magmas prior to their eruption out of axial melt lens (AML) to form lavas and dikes. It also controls the mass transfer between ocean and lithosphere, especially for volatiles (H₂O, CO₂, S, F and Cl) and fluid-mobile elements, forming particular ecosystems on the MOR seafloor. Drilling at the IODP Site 1256 provided coherent crustal samples including lavas, sheeted dikes and intrusive rocks in the dike-gabbro transition. Petrological and geochemical studies have been performed to track seawater-derived fluids and to shed new light on their roles in magmatic and hydrothermal processes associated with processes in the AML. Thermodynamic modeling of mineral evolution trend suggests that the main process for magma evolution is differentiation, producing evolved gabbros, diorites and tonalites, with parental melts containing water contents as low as 0.1~0.2 wt%, in accordance with the rare existence of magmatic amphibole. Such low water contents imply that the AML roof rocks cannot be highly enriched in H₂O. Detailed investigations on apatite in the differentiated intrusive rocks show that the core of apatite usually contain much higher Cl but lower F than the rim, and rare earth element concentrations decreasing from core to rim with decreasing Cl. Our calculation based on Cl-OH exchange partitioning between apatite and melt suggests that the high-Cl melt should have assimilated high-density Cl-rich brine, which is most likely a product of enhanced phase separation of seawater-derived fluids when heated by underlying AML. Another compensating product with a much greater amount is low-density vapor that then migrates back to seafloor, which dominates the hydrothermal leaching and alteration above AML. As the intrusive rocks experienced on-axis magma intruding and subsequent off-axial cooling and alteration, the original high-Cl feature resulted from brine assimilation recorded in apatite core has been strongly erased by leaching and alteration, as evidenced by fluid inclusions in hydrothermal minerals, which is the main source of Cl in the bulk rocks. However, brine assimilation in the AML has the potential for significantly elevating Cl concentration in erupted MOR basaltic magmas.

Dissolved-particulate exchange in the proximal hydrothermal plume at the Aurora vent field, Gakkel Ridge, Arctic Ocean

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Content

The Aurora vent field (82° 53.83' N 6°15.32' W) is located on a volcanic mount at the western edge of the ultraslow-spreading (0.6–1.3 cm yr⁻¹) Gakkel Ridge in the Arctic Ocean, which is the slowest spreading mid-ocean ridge on Earth. Here, hydrothermal activity has first been documented by Edmonds et al. (2003; Nature) based on water column anomalies in light scattering intensity, temperature, and elevated manganese concentrations. Fallout of mineral particles from the hydrothermal fluid occurs as soon as it cools upon mixing with seawater, often already within the ocean crust, but latest upon discharge at the seafloor. The hydrothermal plume can rise several hundreds of meters until it reaches a level of neutral buoyancy and can travel many km off the vent site, depending on the currents. The Aurora Seamount was revisited in 2014 during RV Polarstern cruise PS86. We report chemical data on the distribution of the proximal hydrothermal plume and its fallout particles in the water column and the surrounding sediments.

Deviations from element ratios dissolved in the plume water samples indicate the presence of hydrothermally sourced particles. Fe, Mn, $\delta^3\text{He}$, and CH₄ show distinct enrichments in the plume samples relative to the samples from the background sites. Large volume pumps were deployed to sample plume particles, which were collected on filters and analyzed to deduce sources and partitioning of elements in the plume. Al is predominantly detrital and not influenced by hydrothermal particle fallout. Thus, we use the Element/Al ratio as a reference for its behavior in the plume water. We observed elevated Fe/Al ratios in plume particles due to Fe particles that form within the hydrothermal plume. Mn does not show these elevated concentrations, as the Mn/Al ratios in the particle samples are identical to those of the background sites. We conclude from these data that Fe, but not Mn, forms particles in the plume. Moreover, elevated concentrations of these elements were detected in surface sediment samples in close proximity to the active vent. The surface sediments were characterized by Cu concentrations of up to 8225 mg kg⁻¹. Cu concentrations in sediment core tops a few km off the vent site are only approximately 50 mg kg⁻¹.

From the ratios of element enrichments in the hydrothermal plume we conclude that Aurora is chemically to the peridotite hosted Rainbow vent field and that it deposits significant amounts of Cu in the immediate proximity of the vent.

Evidence for intense hydrothermal alteration associated with flood basalt volcanism during the birth of the Azores Plateau

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Content

During RV Meteor cruise M128 in July of 2016, a stratigraphic section comprising >1000 m of upper crust in the Princess Alice Bank (PAB) of the western Azores Plateau was sampled using ROV MARUM Quest 4000m. Twenty-two samples were recovered between 2484 and 1439 m water depth from a near-vertical wall, which represents the northern master fault of a NW-SE striking rift zone within the PAB. These samples were investigated for whole-rock major element, trace element, and Sr isotope compositions. In addition, thin sections of these samples were examined for secondary phase assemblages and mineral compositions.

Our new results show that all samples, except one at 2201 m water depth, are pervasively altered. The deeper part of the section (up to ~1750 m water depth) was altered under greenschist-facies conditions to assemblages that include epidote, chlorite, albite, titanite, and actinolite. These rocks show $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.7036 and 0.7050. The topmost section was altered under lower metamorphic grades to chlorite/smectite-quartz-anatase. These rocks show severe losses of Ca and Sr, and gains in Mg, Li, and B, with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as high as 0.708. These geochemical signatures indicate an intensity of hydrothermal exchange between seawater and crust that is unmatched by any in situ section of upper ocean crust sampled by ocean drilling to date.

Recognizing the implications of the intense hydrothermal exchange in the studied crustal section for global crust-seawater exchange budgets requires us to consider the geological evolution of the PAB. Based on immobile element ratios of whole rocks and REE characteristics of relict clinopyroxene in the only incompletely altered sample, an E-type MORB primary composition of the basalts can be reconstructed. Our data suggest that the degrees of mantle melting were much higher than during extrusion of the <4 Ma old alkali-basalts recovered from the top of PAB (Beier et al., 2015, doi:10.1130/2015.2511(02)), and even higher than modern MORB at the adjacent mid-Atlantic Ridge.

These results lead us to suggest that the deeper sections of the PAB formed during the initial stages of flood basalt activity. The extreme hydrothermal alteration may hence be directly linked to the prolonged magmatic period during which excess melting produced a ~13-km thick igneous crust. Our results indicate that marine plateau-forming events may cause transient highs in hydrothermal flux rates.

Fluid geochemistry of cold seeps and hydrothermal vents in the Guaymas Basin, Gulf of California

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Content

We present geochemical data from pore fluids and gases that were sampled at cold seeps and hydrothermal vents in the Guaymas Basin during RV Sonne cruise 241. The Guaymas Basin is a unique environment where magma intrudes into thick sequences of organic-rich sediments, thereby maturing host rocks and releasing large amounts of hydrocarbons. Geochemical measurements performed on samples from a recently discovered high-temperature vent field (Berndt et al., 2016) clearly support this paradigm. ³He/⁴He ratios agree with that of excess He from the southern part of the Guaymas Basin and suggest the same general MORB source, while isotopic data of hydrocarbon gases largely indicate a thermogenic, sedimentary source. Heat flow measurements performed in the vicinity of the smoker site are extremely high, exceeding 10 W/m², indicating that hydrocarbon gas production is related to magmatic activity near the hydrothermal vents.

Cold seeps are located up to some tens of kilometres off the rift axis and their occurrence has been related to sill intrusions. Seismic records typically show evidence for sediment mobilization in the deeper subsurface and blanked zones due to gas accumulations directly beneath the seeps. Despite these visual and geophysical indications for deep-sourced heat-driven fluid flow, pore water data do not indicate geochemical reactions taking place at elevated temperatures. In addition, heat flow values do not deviate from regional averages. Overall, these findings do not support the hypothesis of a recent, sill-driven hydrothermal system feeding seafloor seepage sites in larger distance to the spreading axis (Lizarralde et al., 2010). A preliminary interpretation is that fluid and gas mobilisation from sill activity has currently ceased and mainly biogenically formed methane migrates upward along pre-existing fluid pathways.

Berndt, C., Hensen, C., Mortera-Gutierrez, C., Sarkar, S., Geilert, S., Schmidt, M., Liebetrau, V., Kipfer, R., Scholz, F., Doll, M., Muff, S., Karstens, J., Planke, S., Petersen, S., Böttner, C., Chi, W.-C., Moser, M., Behrendt, R., Fiskal, A., Lever, M.A., Su, C.-C., Deng, L., Brennwald, M.S. and Lizarralde, D. (2016) Rifting under steam -How rift magmatism triggers methane venting from sedimentary basins. *Geology*, 44, 767-770.

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Geodynamic constraints from glass geochemistry in the Troodos ophiolite

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Content

Ophiolites represent fragments of oceanic crust formed at spreading ridges and have been used to infer on the processes at mid-ocean ridges in the past. Many ophiolites were suggested to have formed in a 'supra-subduction zone' environment indicated by the characteristic enrichment in fluid-soluble elements relative to Rare Earth Elements compared to mid-ocean ridge basalts (MORB). But the precise tectonic is still debated. Here, we present microanalytical measured major and trace element data along with Sr and Pb isotopes of fresh volcanic glasses from traverses through the pillow lava sequence of the Troodos ophiolite. Glasses from the northern margin of the Troodos ophiolite display a large range in trace element and isotope composition. The range from tholeiitic basalts to andesitic and dacitic lavas that all have relatively low Pb/Ce ratios (0.13) indicating a subtle subduction zone component. They are also more depleted compared to normal depleted MORB ($\text{Sm/Yb} = 0.87$). The other Troodos glasses form a continuous array from less depleted tholeiitic to strongly depleted boninitic lavas ($\text{Sm/Yb} = 0.24$) that display greater influence from a subduction zone fluid component ($\text{Pb/Ce} = 0.77$). This source has subsequently been re-enriched by small degree sediment melts (high $\text{Nb/La} = 2.94$). Strontium and Pb isotope ratios increase with decreasing Sm/Yb and increasing Pb/Ce and Nb/La . The most depleted lavas with the highest subduction zone input occur south of the Arakapas Transform Fault suggesting that the former subduction zone was situated south of the present-day southern margin of the Troodos ophiolite. The paleo-spreading direction (east-west) was not parallel to the subduction zone and may represent a back-arc spreading ridge that propagated into arc crust. These observations seem to preclude an origin for the Troodos ophiolite during subduction initiation. Further detailed profiles through the Troodos lava pile are currently under work to test this hypothesis.

Hydrothermal and (fluid-) flow related heat flow values in the Guaymas Basin, Gulf of California

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Content

In this study, we present nine seafloor heat flow data sets measured during RV Sonne cruise SO241 in the vicinity of cold seeps and a recently discovered hydrothermal vent field located in the northern trough of the Guaymas Basin [1]. The Guaymas Basin is situated in the central part of the Gulf of California, which is a remarkable example of a sedimented, young spreading centre. In this region, magma intrudes into thick sequences of organic-rich sediments driving a seafloor hydrothermal circulation system. The seafloor temperature was measured using up to five miniaturized temperature data loggers [2] mounted either on a six meter long gravity core or on a five meter long lance. Thermal conductivity was measured on recovered sediment cores using the needle probe technique. By using the information of the temperature and thermal conductivity of the seafloor the geothermal heat flow was calculated. The presented heat flow data show evidence of conductive heat transfer as well as concave up and concave down sediment temperature profiles which is a clear indication of advective energy transport processes by fluids (recharge and discharge of seawater) or gases. The observed heat flow values in the northern trough of Guaymas Basin with a maximum of 10835.0 mW/m² are much higher than previously published values for this region (e.g. [3], [4]). Measurements indicate seawater recharge at most sites across the rift valley while discharge of hot seawater was predominantly measured on sites in the direct vicinity to the hydrothermal ridge. However, pore water geochemistry data from locations with advectively dominated temperature profiles do not support advective fluid transport. This enigmatic observation is contrary to published model calculations [5] which show that pore water geochemistry is a much more sensitive indicator for fluid seepage rates rather than temperature profiles. Active gas flow is observed in the northern trough of Guaymas Basin, but if this gas flow is responsible for the advective sediment temperature profiles remains questionable.

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Impact of ridge flank hydrothermal systems on the Li and $\delta^7\text{Li}$ composition of seawater

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Content

Low-temperature ridge flank hydrothermal systems (RFHS) transport huge amounts of water through the oceanic crust. Hence, the fluid-rock exchange in RFHS has a major impact on the global Li cycle. The $\delta^7\text{Li}$ value of seawater ($\sim 31\text{‰}$) is distinctly heavier than that of the sources of Li to the oceans ($\sim 15\text{‰}$). A preferential removal of ^6Li at the seafloor is hence required to solve the oceanic Li isotope budget. One major removal process of ^6Li from seawater is the uptake by low-temperature altered oceanic crust. But there is also a preferential incorporation of ^6Li by marine sediments. The relative roles of the two sinks in the global oceanic Li budget are not known. The major aim of this study is to directly assess the effect of RFHS on the $\delta^7\text{Li}$ composition of seawater. This goal is achieved by measuring Li contents and isotopic composition of discharging fluids in an active RFHS. The results allow us to discern between ^6Li uptake by crustal alteration and by sediment diagenesis.

Uptake of Li (and relative enrichment of ^6Li) by altered rock has been documented repeatedly, but it is very difficult to upscale these results to global fluxes. To date, no study has used the compositions of ridge flank fluids, although upscaling is much simpler, due to the well-established global hydrothermal heat flux in RFHS ($\sim 8\text{ TW}$). In this study we present first Li isotope data of fluids actively venting from a discharge zone of a RFHS. These fluids vented at 12°C from the Dorado outcrop, located in 23-Ma old crust of the Cocos Plate. Dorado is believed to be highly representative of typical RFHS, and the fluids venting there offer a unique opportunity for estimating mass fluxes and the magnitude of isotopic exchange associated with RFHS.

The fluid samples from Dorado outcrop show the expected decrease in Li concentrations relative to seawater. The magnitude of Li loss from circulating seawater ($\Delta\text{Li}_{\text{SW-fluid}} \sim 1.2\text{ }\mu\text{mol Li/kg}$) can be merged with a water flux of $6 \cdot 10^{15}\text{ kg/yr}$ (corresponding to 8 TW of heat carried by seawater heated from 2 to 12°C) to estimate a Li sink flux rate of $7.6 \cdot 10^9\text{ mol Li/yr}$. At the same time, the fluids are enriched in ^7Li relative to seawater ($\Delta\delta^7\text{Li}_{\text{SW-fluid}}$ of $0.73 \pm 0.34\text{ (}2\sigma\text{) ‰}$). This increase in $\delta^7\text{Li}$ implies a ^6Li uptake by the crust in RFHS that represents $\sim 12 - 30\%$ of the total sink flux required to explain the high $\delta^7\text{Li}$ of seawater. The remaining isotopic shift has to be caused by additional processes, like uptake of ^6Li by marine sediments.

Oman Drilling Project: Crystallographic preferred orientations as indicator for lower crustal formation at fast-spreading mid-ocean ridges – The Wadi Gideah transect

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Content

In order to provide a reference frame for the crustal drillings within the ICDP Oman Drilling Project, a transect through the complete lower crust of the Sumail Ophiolite (Sultanate Oman) was sampled (Wadi Gideah near Ibra). This project aims to provide constraints on the accretion and evolution of the Oman paleocrust with focus on depth logs with respect to (1) petrology, (2) major and trace element geochemistry on bulk rocks and minerals, (3) crystallographic preferred orientations (CPO), (4) the evolution of hydrothermal alteration and (5) the sulfur cycle. The collected samples cover the whole oceanic crust from the mantle/crust boundary up to the dike/gabbro transition zone. This enabled us to establish a coherent and comprehensive reference data set. Here, we present our results on CPO obtained by EBSD.

The EBSD technique helps to quantify CPO of minerals in a rock, using the J-index and the BA-index to quantify the shape of the crystal fabric. The BA-index was primarily calculated for plagioclase and is classified in three types: Axial-B fabric with a (010) point maximum and a [100] girdle (BA-index ≈ 0); P-type fabric with (010) and [100] point maxima (BA-index ≈ 0.5); Axial-A fabric with a [100] point maximum and (010) girdle (BA-index ≈ 1).

Plotted versus depth, both indices give evidence for a significant change in CPO and the crystal fabric of plagioclase between layered and foliated gabbro. Furthermore, a significant microstructural change between foliated and layered gabbro is observed. This is consistent with the geochemical evidence for a change in formation/differentiation processes between the layered and foliated gabbro sections. The BA-index between 0.1 and 0.6 gives evidence for magmatic deformation. A hybrid accretion model for crustal formation at fast-spreading mid-ocean ridges is consistent with EBSD and geochemical data: the genesis of the upper foliated gabbro can be better explained by the gabbro glacier model, while in-situ crystallization in the lower crust is plausible for sections below the upper foliated gabbro.

Significant changes within the layered gabbro at ~3200 meters above the crust mantle boundary (CMB) imply, that there is some kind of change in crystal growth in that crustal horizon and support the idea of the hybrid model with different crystallization processes in the upper foliated gabbro and the regions below, respectively.

Reactive transport in basalt: sulfate precipitation in flow-through experiments

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Content

Circulation of hydrothermal fluids within the oceanic lithosphere is a major factor in mass and heat transfer. Shallow parts of the crust are infiltrated by relatively cold and unaltered seawater, which may precipitate sulfates. Examples include anhydrite veins such as the ones in hydrothermal discharge zones, where seawater is entrained and anhydrite precipitates rapidly. Anhydrite also forms in hydrothermal recharge zones within the basaltic crust, but the time scales involved in this formation mode are poorly understood. To investigate anhydrite precipitation and related element transport we have conducted flow-through experiments of a gypsum solution in a pre-fractured basalt at 95, 110, 120 and 140°C. The run continued until the input tubing was clogged, usually after 2-8 weeks. Major element chemistry of fluid samples taken during the run was analyzed using ICP-OES. The basalt core was scanned before and after the experiment as well as every few days during the run, using X-ray tomography. Geochemical modeling with the EQ3/6 software package showed that in the starting solution, anhydrite was supersaturated ($SI=IAP/K$ of 2.5 or higher) in all cases upon heating.

Below 110°C, however, no anhydrite was observed. This could be due to sluggish kinetics. Instead, the lower temperature runs (95 and 110°C) contained hematite flakes and botryoidal Fe-rich structures containing up to 1 wt.% of S. Tomography images showed slightly closing pore spaces and the development of new fractures with time. This was not deemed related to crystallization pressure but to initial sample heterogeneity and stress localization upon dissolution and precipitation. The 120 and 140°C runs did show formation of anhydrite along with quartz in closed-off pores. In all experiments, Na, K, Si, Al as well as Mg and Fe were released from the basalt while Ca and S were taken up from the input fluid.

From this we conclude that anhydrite precipitation at temperatures below 120°C needs greater overstepping of its supersaturation and does not grow as fast in a basaltic substrate as is implied for hydrothermal chimney structures, where seawater is heated by mixing with hydrothermal fluids. Iron is redistributed but never travels far; it quickly precipitates as hematite or magnetite, being relatively immobile compared to the other released cations (Na, K, Mg and Al).

Thermal death of depleted melts biases the geochemical record of oceanic magmatism

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Content

Mantle melting results in compositionally diverse primary melts: low-degree high-pressure melts are incompatible element-enriched with respect to high-degree low-pressure melts. Correlations between isotope and trace element signals of enrichment show that source heterogeneity also contributes to melt variability, sometimes with an associated major element signal: on Iceland, where basalt addition to the mantle source region has been proposed, incompatible trace element-enriched melts are richer in Fe but poorer in Ca at any given MgO than incompatible trace element-depleted melts. Crucially, variations in the major element composition of basalts affects their solidus phase relations; primary melts from a single melting column will thus reach mineral saturation at different temperatures and form phases with different compositions. To isolate the effects of mantle-derived variability from the effects of temperature and pressure, we performed crystallisation experiments on synthetic analogues of depleted and enriched end-member eruptions from the Reykjanes Peninsula of Iceland. Our analogue of the depleted Háleyjabunga eruption is Fe-poor but Ca-rich whereas our analogue of the enriched Stapafell eruption is Fe-rich but Ca-poor. Experiments were performed in an internally heated pressure vessel at a pressure of 3 kbar, an oxygen fugacity near QFM+1 and temperatures of 1140 °C to 1300 °C. Although residual liquids generally follow differentiation trends defined by Icelandic basalts, enriched melts lose less mass (via crystallisation) per unit temperature decrease because plagioclase stability is suppressed in Ca-poor systems. Depleted melts therefore undergo thermal death (i.e., mass loss to the point of complete solidification) at higher temperatures than enriched melts. Thus, given that diverse depleted and enriched primary melts are supplied to the oceanic crust, the mean composition of surviving melts will be biased progressively towards enriched compositions as differentiation proceeds. Although numerous studies have explained the over enrichment of trace elements in mid-ocean ridge basalts and gabbros with respect to predictions from fractional crystallisation models by in situ crystallisation, reactive porous flow or repeated tapping and replenishment of steady state reservoirs, the preferential survival of enriched melts during crystallisation offers a simple alternative explanation that is independent of plumbing system geometries or dynamics.

Session 2.2: Intraplate volcanoes: evolution, processes and hazards: Poster

Session 2.2: Intraplate volcanoes: evolution, processes and hazards: Poster

A-804

Drone photogrammetry and thermal (IR) mapping of fumeroles, Vulcano, Italy

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Content

Vulcano is the southernmost active volcanic island of the Aeolian archipelago linked to back arc spreading of the Sicilian microplate. The four main eruptive phases over the last 120 ka are associated with recurrent hydromagmatic to explosive phases and have resulted in the present day La Fossa Cone crater. Fumaroles are active degassing sites linked to the underlying volcanic plumbing system. Their location, distribution and temperature have important implications for the state of the volcanic system and are often used as volcanic hazard indicators (Harris et al., 2000).

Data collected during this field campaign includes high resolution aerial drone imagery and handheld thermal IR camera data. The drone data was processed using Agisoft photogrammetry software to produce high resolution (2cm /pixel) mosaics and textured digital elevation models. The IR camera was used on more than 300 individual fumaroles. Data obtained in the field is limited to fumaroles on the crater rim and some easily accessible ones on the middle step within the crater. Preliminary mapping results show that the active fumaroles are concentrated in cm to m wide cracks in the northern part of the La Fossa Cone. Temperature variations are present between both a) fumaroles within the same crack (crack tip to centre and crack edge to centre) and b) different cracks in general. The IR data clearly shows a wide spectrum of temperatures ranging from ~100 °C to excess of 350 °C. Detailed mapping is still ongoing and will aim at linking surface features with the temperature distribution. In addition, comparison with previous thermal surveys (e.g. Harris & Stevenson, 1997 and Harris et al., 2000) will help to support models such as increased permeability or conduit sealing as mechanisms influencing the location and variability of gas and heat flux from active volcanic sites.

The juvenescence of the Walvis Ridge – evidence for recent submarine volcanism from hydro-acoustic data in the vicinity of Tristan da Cunha

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Content

The Walvis Ridge-Rio Grande Rise System is the only seamount chain in the Atlantic that is known being continuously active since the Cretaceous (130 Ma) and one of very few worldwide, that links an active hotspot (Tristan-Gough) with a continental flood basalt province (the Paraná-Etendeka province in South America and Africa). Previous work has documented age-progressive volcanism along at least parts of the Walvis Ridge and several initiatives acquired new geophysical and petrological data from seamounts of the Walvis Ridge and its southerly neighbours over the last decade.

The youngest stretch of the Walvis Ridge, the islands of Tristan da Cunha, was the focus of the ISOLDE project within the DFG priority program SPP1375 „South Atlantic Margin Processes and Links with onshore Evolution (SAMPLE)“. Temporary seismological and magneto-telluric measurements were carried out to characterize the upper mantle in the search for evidence of a mantle plume. Two expeditions with R/V MARIA S. MERIAN headed towards this remote area to install and dismantle ocean-bottom stations in 2012 and 2013, respectively. Hydroacoustic data were collected along the tracks and around the islands, allowing a first detailed bathymetric insight to the area, underpinned by backscatter and sediment echo sounder observations.

One unexpected outcome was the discovery of a new submarine volcano, Isolde Seamount, at the eastern flanks of Nightingale Island. Isolde lies very close to the assumed site of a submarine eruption in 2004, known only from floating pumice and seismicity. Further submarine volcanic centres could be mapped around the islands. Of interest are two volcanic fields, each about 20 x 40 km across, to the NW of Inaccessible Island, where small monogenetic volcanic cones and young lava flows were mapped.

Young volcanic activity seems to extend up to 250 km westwards from the Tristan group to about 14.8 W, where we mapped a small volcanic cone on top of old abyssal hills only 130 km east of the Mid-Atlantic Ridge. Further westward, normal seafloor fabric, with clearly defined abyssal hills, dominates the seafloor. Scattered volcanic activity is visible along and in close vicinity to the Tristan da Cunha Fracture Zone. The intraplate volcanic fields as well as the scattered probably monogenetic submarine volcanoes could indicate that the Tristan mantle plume (or at least part of it) currently sits to the west/southwest of Tristan da Cunha.

The Lower and Middle Cambrian volcanosedimentary succession in the vicinity of Ouanguigui (Ougnat Inlier, southeastern Morocco): facies, geochemical composition and geotectonic setting

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Content

The Moroccan Anti-Atlas experienced a multi-phased period of volcanism related to Neoproterozoic and Cambrian rifting at the northern edge of the West African Craton. We investigated a Lower to Middle Cambrian siliciclastic succession cropping out in the eastern Anti-Atlas around the village of Ouanguigui. The 1300 m thick shallow marine succession is exposed in a SSE dipping monoclinical block. The succession rests unconformably on Ediacaran volcanics. It is intercalated by lava and volcanoclastics and it is intruded by sills, laccoliths and volcanic necks.

Based on geological mapping, structural and petrographic analysis, the volcanic and subvolcanic rocks range in composition from basaltic to trachytic typical of an alkaline rift system. Four magmatic phases can be differentiated within the successions.

The first phase is present in the Lower Cambrian. It starts with coarse grained fan-delta deposits with a fining up trend. Hydroclastic deposits interfinger with the sediments. Scattered volcanic bombs within the sandstones also suggest synsedimentary volcanic activity. The succession is crosscut by a volcanic neck that displays partial reworking in the form of rounded volcanoclastic conglomerates.

The following Middle Cambrian sediments of the Tabanite Group feature two further magmatic phases. The siliciclastic deposits have been accumulated above fair weather wave base (presence of Scolithos) and they host widespread subaqueous to (sub-)emergent tachylitic volcanoclastites of basaltic composition. Ballistic bombs and accretionary lapilli indicate a partial subaerial emergence of the volcanic edifices. Some of the hydroclastic deposits contain numerous quartz grains presumably originating from the unconsolidated host of the volcanic vents. These conduits also led to the formation of volcanic necks and lava at the top of the succession. The basaltic lava flows have a brecciated base and an eroded top covered by reworked volcanic material displaying wave ripples.

Finally, porphyritic trachytic melts intruded within the Tabanite sandstones forming several sills and laccoliths. Uplift and fault structures in the sedimentary host indicate a late intrusion after consolidation of the sediments. The area has been affected by later Hercynian and Alpine faulting.

The Origin of Researcher Ridge (Central Atlantic Ocean)

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Content

Researcher Ridge (RR) is a 400 km long, WNW-ESE oriented chain of single and coalescent volcanic structures located on 20 to 40 Ma old oceanic crust on the western flank of the Mid-Atlantic Ridge (MAR) at $\approx 14^\circ\text{N}$. The origin of RR is completely unclear. Proposed models for its formation range from purely plate-tectonic driven, shallow processes (e.g., resulting from migration of a triple junction, Roest and Collette, 1986) to upwelling of a chemical heterogeneity in the upper mantle (as proposed for the South-MAR between the Ascension and Bode Verde Fracture Zones; Hoernle et al., 2011) to involvement of a deep mantle plume. Mid-ocean ridge basalts (MORB) sampled along the MAR axis in this area reveal an unusual geochemical anomaly. At the latitude where the RR axis projects to the MAR at $14^\circ\text{--}15^\circ\text{N}$, the ridge axis is bathymetrically elevated and characterized by geochemically enriched basalt, so called Enriched-MORB (E-MORB) (e.g., Hémond et al., 2006), suggesting a possible relationship of the geochemical/melting anomaly of the MAR and RR formation. In this study, we combine $^{40}\text{Ar}/^{39}\text{Ar}$ age dating with petrological and geochemical (trace element and Sr, Nd, and Pb double spike isotope analyses) studies of volcanic rocks dredged along an E-W profile of the RR during expedition POS 379/2 to reveal its elusive origin. Preliminary results show that RR lavas underwent high-pressure fractionation (with clinopyroxene as dominant phase), pointing towards deeper fractionation than normally occurring in MORBs. The depletion of heavy rare Earth elements and the enrichment of incompatible trace elements in RR lavas both indicate lower degrees of melting and at deeper depth (garnet stability field) than MORB. The isotopic composition of the lavas, however, largely overlaps with North Atlantic MORB, but the samples form a distinct trend towards the global HIMU (high time-integrated $^{238}\text{U}/^{204}\text{Pb}$) mantle end member.

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Volcanic evolution and new timing constraints on the Late Variscan Teplice Rhyolite (Altenberg-Teplice Caldera), Germany-Czech Republic

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Content

The waning stage of the Late Paleozoic Variscan orogeny was characterized by extensive magmatic activity in its eastern portion. This region is commonly referred to as the Central European Variscides and comprises parts of Germany and Czech Republic. The Altenberg-Teplice Caldera (ATC) is the oldest volcanic center of the Saxothuringian block and covers an area of about 35×17 km in the German-Czech border. The Teplice Rhyolite represents the filling sequence of this caldera and appears to record a step-wise volcanic evolution.

Lithofacies analysis indicates that the volcanic succession consists of a series of rhyolitic lavas and ignimbrites with variable contents of crystals and lithics, and different degrees of welding. The northern part (Germany) is dominated by rhyolitic lava domes/flows, which are intercalated with several rhyolitic ignimbrite sheets. On the Czech side, crystal-rich rhyolitic ignimbrites are the prevailing lithofacies and rhyolitic lavas are also present. Here, whole-rock chemical data in conjunction with gamma-ray maps (Th, Sedlák et al. under review) suggest the existence of a synclinal structure. Stratigraphically, the ATC eruptive sequence becomes progressively younger from north to south.

The age of the Teplice Rhyolite (and the ATC in general) has been controversial. To better constrain the age of the peak volcanic activity, three new U-Pb zircon ages from crystal-rich ignimbrites were obtained via LA-ICP-MS. The oldest age is 324.8 ± 1.5 Ma and corresponds to a sample collected in the northern part of the caldera. The other two ages are: 318 ± 4 Ma and 312 ± 4 Ma, which include the youngest eruptive units from the south. According to these data, the age of the Teplice Rhyolite varies ~325–312 Ma, older than previously published paleobotanical and radiometric ages (~308 Ma). Taking into account the timing of peak metamorphism in the Saxothuringian Zone (~340 Ma) and the intrusion of caldera collapse- and post-caldera-related plutons (~320–312 Ma) cutting the Teplice Rhyolite, it seems likely that the age for the Teplice Rhyolite is around 320 Ma.

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Session 2.2: Intraplate volcanoes: evolution, processes and hazards: Talk

Session 2.2: Intraplate volcanoes: evolution, processes and hazards: Talk A-252

Age relations, mineral-chemical and isotopic investigations on basaltic gem stone zircons from Eastern Germany

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Content

Abstract: In alkali basaltic rocks scarcely appear accessory minerals such as zircon and corundum. The origin of these mostly gem stone like mega-crystals is unknown and discussed controversial. Host magmas of the zircon mega-crystals are normally SiO₂ undersaturated (basanites and nephelinites). In several localities we could observe some zircon megacrystals and in a quarry in Saxony (eastern Germany) we collected about 40 crystals up to 15 mm in size in situ from the basanitic rock [1]. Zircons occur in agglutinates of lower crater facies of a scoria cone. The related lava flows are almost free of zircons and their Zr contents reaches up to 900 ppm [2]. There is a good correlation between Ar/Ar data of the basanites (30 to 31 Ma) and the zircon U/Pb data which show ages about 30.5 Ma.

First investigations indicate an alkaline source for zircons which origin possibly from intermediate alkaline melts. This is evidenced by zircon-typology, mineral chemistry and analyses of mineral inclusions and mineral paragenesis in the host rocks [3]. Preliminary in situ Hf-isotopic analyses of zircons indicate an origin from mantle melts. The crystals show an intensive magmatic corrosion in alkali basaltic rocks (including nephelinites), whereas zircons out of phonolites are mostly euhedral. CL images indicate a typical magmatic origin. Zircons in basaltic rocks have more or less evolved reaction rims, composed mostly of baddeleyite. Zr-contents in the rims of clinopyroxene phenocrystals decreases rapidly with the distance from the zircon inclusions. This indicates late entrainment of zircon crystals into the basanitic melt.

The age data of the zircons in relation to that of the host rocks as well as the mineral chemical and isotopic data imply a cogenetic development of both.

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Eruption at Fogo volcano, 2014-2015, crustal deformation and surface changes as observed by photogrammetry and InSAR

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Content

After 20 years of quiescence, Fogo volcano (Cape Verdes) initiated an eruption on 23 November 2014. The eruption had significant precursors, such as degassing and seismicity, and occurred at a similar location as in 1995. Lava flows rapidly propagated to inhabited regions, a significant part of the Islands' population has been replaced in the towns of Portela and Bangaeira. In a fast response action, scientist from GFZ started a coordinated field and remote sensing work. In an attempt to better understand the physics of this eruption, here we detail on ground deformation that is investigated using LiDAR, photogrammetry and the synthetic aperture radar interferometry method. LiDAR and field photogrammetry allows obtaining detailed views on the morphology changes associated with the eruption hazards. In addition, satellite data comes from the TerraSAR-X, interferometrically processed, and reveals significant displacements in the Cha das Caldeiras region. By using a Boundary Element Method we are able to model the data by applying a dike striking NE-SW, steeply dipping to the southeast. As the satellite data was acquired at different time increments we are furthermore able to image the location of the active dike changing in time and space. To explain this geometry, we compare the parameters of the dike to the topographic stress field and also discuss a possible reactivation of pre-existing structures. This work demonstrates a scenario where a magma pathway is reused in two consecutive eruptions that are 20 years apart, with important implications of the general volcano-tectonic framework and stress field of the island.

Late Paleozoic supereruptions in Central Europe: Anatomy of the Rochlitz caldera in northern Saxony

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Content

Numerous large, differentiated volcanic complexes have been active in Central Europe during late- to post-Variscan times (Timmerman 2008). Among these, the Early Permian North Saxony Volcanic Complex (NSVC) stands out for its volume and complexity (Repstock et al. under review). The NSVC is dominated by two large nested calderas, the Rochlitz Volcanic System (RVS; 294.4 ± 1.8 Ma) and the Wurzen Volcanic System (WVS; 289.3 ± 4.1 Ma; Hoffmann et al. 2013; Repstock et al. under review).

The trachydacitic to rhyolitic RVS ignimbrites, covering an area of c. 3100 km², formed during caldera collapse. Exploration wells reveal a minimum thickness of 400 m for the caldera fill, rendering the RVS a super volcano ($VEI \geq 7$). Welding compaction of the crystal clast-rich (35 – 40 vol. %) pyroclastic deposits yielded eutaxitic to parataxitic textures (fiamme aspect ratio 0.4 to 0.1).

As a novel approach we interpret the units that under- and overlie the RVS in the context of the overall NSVC caldera evolution. The RVS is partially underlain by the Kohren Fm. and partially overlain by the Oschatz Fm. The volcanics (lava, ignimbrites) and sediments (alluvial fan to fluvial plain and lacustrine) of the Oschatz Fm. we consider as post-climactic caldera fill. The rhyolitic Leisnig Porphyry (lateral extent 16 km, max. thickness 150 m), interpreted in previous studies as a lava complex belonging to the Kohren Fm., lacks textures typical for lava carapace. Instead, we contemplate a laccolithic nature for this body, and its emplacement below the RVS ignimbrites presumably caused resurgence of the RVS caldera. In fact, in the central part, the RVS ignimbrites are in direct depositional contact with the caldera fill units of the subsequent WVS.

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Magma plumbing during the 2014-2015 eruption of Fogo (Cape Verde Islands)

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Content

The latest eruption of Fogo (Cape Verde Islands), one of the world's most active oceanic island volcanoes, occurred from 23 November 2014 to 7 February 2015. It produced lava flows and tephra of basanitic composition, as well as minor phonotephrite at the early and late phases of the eruption. Zoned phenocrysts and mingled lavas in some samples indicate a magma mixing event that may have initiated the eruption. We have carried out thermobarometric investigations of a suite of samples to place constraints on the depths of pre-eruptive and syn-eruptive magma storage and transport. The samples cover all main stages of the eruption; their dates of emplacement have been determined from the date of incandescence of each sample site in high-resolution thermal infrared emissivity maps collected by satellite instruments (Landsat-8 OLI and EO-1 ALI) during the eruption. Phenocryst and groundmass compositions of basanites indicate equilibrium pressures of 540-740 MPa (average 640 MPa), equivalent to ca. 19-25 km depth, within the uppermost mantle. Phonotephrites yield slightly shallower depths. The data do not indicate systematic changes in equilibrium pressures during the course of the eruption. We suggest that this depth range reflects a magma reservoir system from which the eruption was fed. Fluid inclusions in clinopyroxene phenocrysts indicate a well-defined shallower depth range of 250-340 MPa (average 300 MPa), equivalent to ca. 9-13 km depth. This data is interpreted to reflect a section of lateral magma flow within the lower oceanic crust, plausibly in a short-lived storage subsystem that became filled prior to eruption. Remarkably, pre- and syn-eruptive seismic data do not reflect these depth ranges, as almost all events were at less than 5 km below sea level, mostly within the volcanic edifice rising above the ocean floor that is some 4 km below sea level. The bimodal depth distribution of our barometric data shows complete overlap with data from the preceding 1995 and 1951 eruptions, which suggests that similar magma storage systems and pathways in the uppermost mantle and lower crust are repeatedly used. The lack of pre-eruptive seismicity within the oceanic crust and uppermost mantle may reflect re-use of an existing magma conduit, with new dike propagation only taking place in the edifice itself.

**Mineral textures in ignimbrites of the Quaternary Aragats stratovolcano, western Armenia:
Implication for magma chamber dynamics**

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Content

The Aragats Volcanic Province (AVP) in western Armenia comprises a succession of Quaternary ignimbrites and fallout deposits ranging from trachyandesitic to rhyolitic compositions intercalated by various lava flows. Five units of crystal-poor and -rich ignimbrites are distributed in an area of more than 5,000 km²: (1) Qasakh, (2) Amberd, (3) Baghramyan, (4) Artik and (5) Gyumri units. In the framework of petrological and mineralogical investigations of the AVP ignimbrites, here we focus on mineral textures.

The modal mineralogy of phenocrysts typically consists of plagioclase, orthopyroxene and either clinopyroxene or amphibole, the predominant accessory minerals are members of the ilmenite-ulvöspinel-magnetite solid solution series. Subordinate microlites of apatite can mainly be reported in amphibole and plagioclase phenocrysts. In addition to normal and oscillatory zonation in plagioclase, the existence of reverse zonation, widespread coarse and fine sieve-texture suggests episodic stirring and indicates the interaction of different magma batches.

The appearances of either amphibole (magnesio-hastingsite, edenitic hornblende) or clinopyroxene (augite, diopside) as the predominant ferromagnesian silicates indicate different hydrous or anhydrous origins of each tapped melt. The co-existence of zoned amphibole together with clinopyroxene that is in disequilibrium with a trachytic and rhyolitic melt composition also suggest magma mixing processes and formation of the AVP ignimbrites from at least two different precursor magmas. Amphibole breakdown rim texture is formed during different decompression experiment scenarios and can be interpreted as a consequence of decompression during magma ascent. With a decrease in pressure, the reaction rim becomes fine grained and is composed of acicular crystals (i.e. needle-like shaped). The width and texture of the rim depend on the crystallization depth: a fine-grained rim is assumed to be grown in shallow magma chambers, whereas the coarse-grained one is formed in deeper parts of the magma reservoir (e.g. RUTHERFORD & HILL, 1993). Based on an estimation of local geothermal gradient of 5.5 °C per 100 m (BADALYAN, 2000), the magma reservoir was tracked down to depth to around 27 km.

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The Early Permian Wurzen Caldera of northern Saxony, Germany: Deciphering the pre-eruptive evolution and dynamics in the magma reservoir of a super volcano

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Content

The Wurzen Volcanic System of the North Saxon Volcanic Complex extends over an area of 2,111 km² to the east of Leipzig, Germany. The Artinskian climactic eruption formed a c. 52 x 40 km caldera edifice, nested in older caldera structures, and led to the deposition of voluminous and crystal-rich (up to 58 vol.-%) ignimbrites. This type of crystal-rich ignimbrites with 63 to 71 wt.-% SiO₂ are termed 'monotonous intermediates' and are known as products of super eruptions (VEI ≥ 7). The pyroclastic deposits are exceptionally well-preserved, in particular in comparison with other Permocarboniferous volcanic rocks of Central Europe.

The (trachy-)dacitic Wurzen ignimbrite hosts three different types of fiamme: (1) felsic fine grained, (2) mafic and (3) coarse porphyritic fiamme. Combining a study of mineral texture and chemistry by mineral liberation and electron microprobe analyses provides unique insights to reconstruct the magma dynamics. We use major and trace element chemistry and Nd isotopy on juvenile melt fragments (fiamme) in the intra-caldera ignimbrite and the related subvolcanics to constrain the lithospheric evolution of the magma reservoir. Feldspar, especially plagioclase, shows various degrees of susceptibilities to resorption and different growth textures. This demonstrates the interplay between decompression (e.g. patchy and sieve textures, granophyric intergrowths) and chemical fluctuations in the melt (e.g. oscillatory zonation). An-rich cores in plagioclase from the intra-caldera ignimbrite implies the influence of basaltic melt. The diversely pronounced albite-rich mantles indicate different retention times in SiO₂-rich melt. The presence of both augite and pigeonite in the caldera-fill ignimbrite can be explained by tapping of different Ca-rich and -poor anhydrous melts.

As the occurrence of pigeonite requires rapid cooling, this mineral reflects a superheated magma batch at 1010°C during the eruption. The presence of annite indicates the influence of a low temperature (~ 750°C) hydrous magma. Discrimination plots of calcic clinopyroxene and biotite suggest the evolution from alkaline and tholeiitic to calc-alkaline melts. By assuming a geothermal gradient for WVS of 34°C/km, the applied thermobarometers suggest a deep seated magma reservoir down about 40 km.

Pronounced negative Nb and Ta anomalies suggests a destructive plate margin setting, however, this signature may also be inherited by the basement. This was confirmed by a new Nd-data.

The juvenescence of the Walvis Ridge – evidence for recent submarine volcanism from hydro-acoustic data in the vicinity of Tristan da Cunha

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Content

The Walvis Ridge-Rio Grande Rise System is the only seamount chain in the Atlantic that is known being continuously active since the Cretaceous (130 Ma) and one of very few worldwide, that links an active hotspot (Tristan-Gough) with a continental flood basalt province (the Paraná-Etendeka province in South America and Africa). Previous work has documented age-progressive volcanism along at least parts of the Walvis Ridge and several initiatives acquired new geophysical and petrological data from seamounts of the Walvis Ridge and its southerly neighbours over the last decade.

The youngest stretch of the Walvis Ridge, the islands of Tristan da Cunha, was the focus of the ISOLDE project within the DFG priority program SPP1375 „South Atlantic Margin Processes and Links with onshore Evolution (SAMPLE)“. Temporary seismological and magneto-telluric measurements were carried out to characterize the upper mantle in the search for evidence of a mantle plume. Two expeditions with R/V MARIA S. MERIAN headed towards this remote area to install and dismantle ocean-bottom stations in 2012 and 2013, respectively. Hydroacoustic data were collected along the tracks and around the islands, allowing a first detailed bathymetric insight to the area, underpinned by backscatter and sediment echo sounder observations.

One unexpected outcome was the discovery of a new submarine volcano, Isolde Seamount, at the eastern flanks of Nightingale Island. Isolde lies very close to the assumed site of a submarine eruption in 2004, known only from floating pumice and seismicity. Further submarine volcanic centres could be mapped around the islands. Of interest are two volcanic fields, each about 20 x 40 km across, to the NW of Inaccessible Island, where small monogenetic volcanic cones and young lava flows were mapped.

Young volcanic activity seems to extend up to 250 km westwards from the Tristan group to about 14.8 W, where we mapped a small volcanic cone on top of old abyssal hills only 130 km east of the Mid-Atlantic Ridge. Further westward, normal seafloor fabric, with clearly defined abyssal hills, dominates the seafloor. Scattered volcanic activity is visible along and in close vicinity to the Tristan da Cunha Fracture Zone. The intraplate volcanic fields as well as the scattered probably monogenetic submarine volcanoes could indicate that the Tristan mantle plume (or at least part of it) currently sits to the west/southwest of Tristan da Cunha.

Session 2.3: Processes in layered mafic magma chambers and formation of associated ore deposits: Poster

Session 2.3: Processes in layered mafic magma chambers and formation of associated ore deposits:
Poster
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Lateral variations in the Unit 7-8 chromitite of the Rum Eastern Layered Intrusion, NW Scotland

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Content

Layered intrusions represent natural laboratories in which various magmatic processes like cumulate formation, magma solidification and post-magmatic re-equilibration can be interrogated. The ~60 Ma Rum Layered Suite is a particularly suitable example due to its relatively young age and small size, meaning it has not undergone significant post-emplacement alteration. The intrusion consists of 16 macro-rhythmic units of peridotite-troctolite ($\pm$ olivine gabbro), with 2-5 mm thick chromitite seams occurring at some of the unit boundaries. Recent studies (e.g. [1]) have proposed that chromitite seams formed *in-situ* by assimilation of troctolitic footwall cumulate by the replenishing picritic magma, highlighting the fact that the evidence for significant magma chamber processes are preserved in relatively narrow vertical intervals of cumulate. In this study we focus on the Unit 7-8 boundary to assess lateral variation in the presence, microstructural, and mineral chemical character of the chromitite and its immediate footwall and hanging wall, a new approach never tested before. The seam was mapped and sampled during a field campaign in several localities. We could show that although the Cr-spinel seam is continuous over almost 3 km, it is absent in large parts of the Rum Layered Intrusion. Three profiles of the Unit 7-8 contact including anorthosite lenses from the troctolitic footwall were sampled in three profiles, two with a Cr-spinel seam and one profile without. All profiles were investigated in great detail by electron microprobe and laser ablation ICP-MS measurements to trace chemical variations in olivine, plagioclase and chromite, data evaluation is pending. Taken together for the first time we could show that the chromitite is absent over significant areas of strike, implying that the proposed replenishment event had non-uniform effects on the footwall in different proportions of the Rum magma chamber.

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Magmatic origin of the Vergenoeg F - Fe - REE deposit, South Africa.

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Content

The Vergenoeg F–Fe–REE deposit is one of the largest fluorite deposit of the world and is situated in the Paleoproterozoic Bushveld Complex of South Africa. Despite the economic importance of the deposit its petrogenesis is controversial. Hydrothermal ore formation through fluids released from fractionated Bushveld granites or from carbonatite-related alkaline rocks has been postulated[2][3]. In another model ore formation is ascribed to separation of an immiscible Fe-rich magma from a parental felsic magma[1]. Recent experimental studies demonstrated the theoretical potential for this model but also indicate the necessity of late hydrothermal activity for the extreme F-enrichment[4]. The pipe-like deposit consists for three gradational units of fayalite, magnetite–fayalite and magnetite–fluorite from bottom to top. The pipe intruded into Paleoproterozoic rhyolites of the Rooiberg group which represents a large silicic igneous province. The aim of our study is to identify the source of F and REE enrichment in the deposit and to characterize the magmatic and metasomatic processes, related to the ore formation, including element mobilisation, transport and crystallization of the F and metal-bearing minerals.

We have studied the root zone of the deposit which is constituted by the fayalite rocks, as they are often unaffected by later overprints.

The rocks are dominated by megacrystic fayalite and comprise additional magnetite, ilmenite, apatite, and allanite. Mineral chemical investigations (EMP & LA-ICP-MS analyses) indicate a magmatic origin of the assemblage: Megacrystic fayalite is unzoned and close to the Fe-endmember (XMg: 0.92-0.98). REE elements show a strong enrichment of the HREE. Significant Li contents (20–40 ppm) suggests crustal assimilation. High Ti contents (up to 14 wt.%) and low Ni/Cr ratios of magnetite record its magmatic origin (Fig. 1). Zoned apatite shows a pronounced Eu anomaly and is F-rich, indicating F-enrichment in the melt. Based on the mineral chemical data and the textural relationships we interpret the fayalite rocks as mafic cumulate.

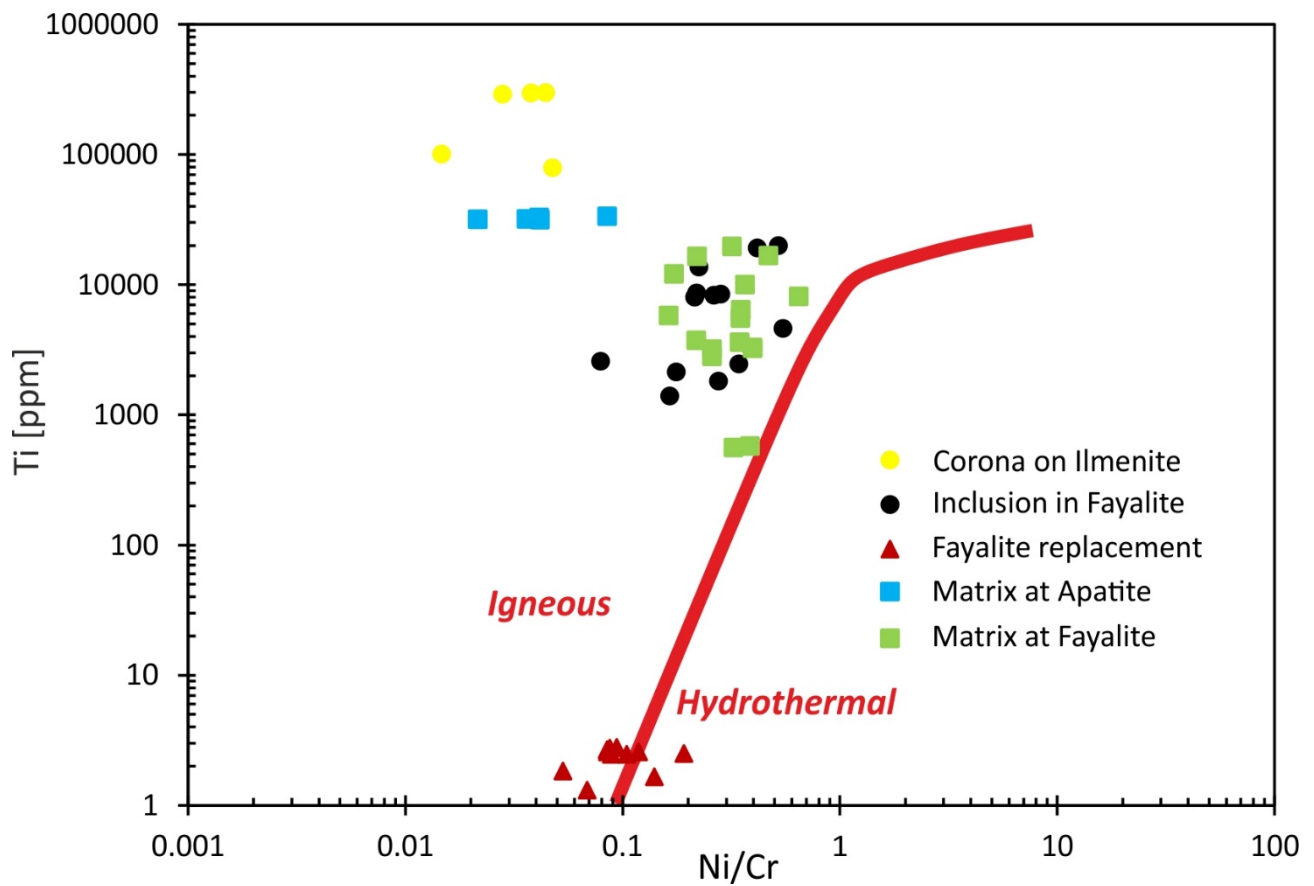


Fig. 1: Diagram of Ti [ppm] versus Ni/Cr (un-normalized) to discriminate between igneous and hydrothermal magnetite (after Dare et al., 2014).

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Mobility of Pt and Pd in the presence of organic complexes

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Content

Near-surface platinum group element (PGE) ores have much industry potential, however, PGE mobility and interaction with organic complexes, which may be necessary for beneficiation, has been poorly constrained so far. The goal of this study is to quantify the solubility of synthetic Pt- and Pd-tellurides and sulphides in aqueous solutions containing organic acids (represented by humic acids) under surface weathering conditions.

Long-term (several months) and short-term (several hours) leaching experiments employing synthetic Pd and Pt telluride and sulphide powders have been conducted in teflon containers at ambient temperatures. To mimic natural weathering conditions, the experiment was set up in stationary beakers with strongly diluted solutions of humic acid (0.1, 1, 10 ppm), which correspond to the natural concentration of humic acids sampled from soil horizons at the chromitite Thaba Mine, Bushveld Complex, South Africa. Sample aliquots were taken at irregular intervals and analysed by SF-ICP-MS.

Very little Pd (<5 µg/L) was liberated by humic acids from Pd tellurides during the experiment, although Te shows clear patterns of dissolution. However Pd and Pt were both liberated from sulphide, but show contrasting behaviour. Palladium increases throughout the duration of the experiment, whilst Pt increases in the beginning stages and after a few days of runtime, the Pt concentration decreases, indicating that it is removed from solution with time by adsorption or precipitation.

These results suggest (1) that Pd is generally more mobile in the presence of organic complexes than Pt under supergene weathering conditions, and (2) that the nature and composition of primary minerals which are exposed to weathering is crucial to understand the mobility of PGEs at supergene conditions. These data are consistent with natural observations suggesting higher Pd mobility and depletion in oxidised ores.

Small scale variations in mineral chemistry along the contacts of chromitite layers in the Bushveld Complex, South Africa

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Content

The study of layered intrusions is very important to understand basic processes of magma formation, evolution and migration and get insights into geochemical principles that can lead to e.g. ore formation and enrichment. The Bushveld Complex in South Africa is the largest layered intrusion and many studies have been performed to apprehend this enigmatic deposit and especially the stratigraphic unit called Rustenburg Layered Suite (RLS). The Critical Zone within the RLS comprises in general more than 10 chromitite layers which are the principle source for chromium and Platinum Group Elements (PGE) [1]. The formation of chromitite layers and PGE enrichment is still poorly understood. It is furthermore debatable, to what extent postcumulus processes such as interaction and migration of interstitial melt and the trapped liquid shift effect (TLSE), or subsolidus diffusion might have influenced the mineral chemistry.

In this study, we investigated changes in mineralogy, petrology and mineral chemistry at contacts between chromitite layers and adjacent host rock with focus on the main rock forming minerals chromite (chr), orthopyroxene (opx) and plagioclase (plag). Detailed petrographic investigations as well as electron microprobe measurements were conducted to identify small scale variations in texture and composition within the profiles. Additionally, Laser-Ablation-ICP-MS measurements were performed to obtain information about the trace element-composition of major mineral phases.

Both, optical investigations and mineral chemistry measurements showed that abrupt changes at contacts are very pronounced. Strong shifts in Mg# regularly occur in chr and opx and chemical zonation was found in opx and plag along the contacts. Generally, the concentration of incompatible trace elements was found to be lower in minerals within chromitite layers.

The characteristics of studied profiles hint to interactions of an already existing crystal mush with a newly intruding magma. Mineral chemistry and texture of the cumulate crystal mush may have been overprinted by interaction with percolating interstitial melt. Our data however does not support the TLSE as a major cause of mineral chemistry variation. This study demonstrates the power of small scale investigations to reconstruct physicochemical processes within the system that are overlooked by only analyzing overall medium to large scale compositional trends along the layers.

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Small-scale chemical and isotope variations through the UG2 in the eastern Bushveld Complex, South Africa: implications for post-magmatic processes

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Content

A detailed study of the Sr- and O- isotopic composition of minerals in the Upper Group 2 (UG2) unit of the eastern Bushveld Complex revealed significant variations in the pegmatoidal footwall pyroxenite and the UG2 chromitite layer itself. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Sri) of intercumulus plagioclase in the footwall rocks are significantly higher than in adjacent rocks of the Critical Zone. The $\delta^{18}\text{O}$ values of plagioclase-pyroxene and plagioclase-chromite mineral pairs in footwall pyroxenite and chromitite are consistent with oxygen isotope exchange from crystallization temperatures down to 700 °C and 800 °C, respectively, whereas in other parts of the UG2, plagioclase and pyroxene $\delta^{18}\text{O}$ values are consistent with O isotope equilibration at liquidus crystallization temperatures of approximately 1150 °C.

We propose that the higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ of plagioclase in the UG2 chromitite and the footwall pyroxenite reflects infiltration of fluid derived from dehydrating country rocks beneath the Bushveld Complex. Solution of this fluid in the Bushveld magma above the crystallizing cumulus mush layer induced partial melting of pyroxene and plagioclase supplying Cr and Al to the melt, thus invoking chromite formation. This dissolution-reaction front propagated from the top of the mush downwards replacing pyroxenite by chromitite. The pegmatoidal UG2 footwall constitutes the reaction front-line, which recrystallized to a coarse-grained rock upon cooling, reduced crystallization temperatures and favoured oxygen isotope re-equilibration during cooling to temperatures as low as 700 °C.

This study emphasizes the role of late- and post-magmatic processes in layered intrusions taking place at subsolidus temperatures, whereby isotopic and chemical compositions may be significantly changed.

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The sulfide mineralogy of the layered Ilímaussaq complex (South Greenland)

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Content

We investigated the Ilímaussaq complex (South Greenland), the type locality for layered magmatic complexes, with respect to its main sulfide mineralogy and their compositional variations. The investigated rocks include syenites, nepheline syenites, a granite and late hydrothermal veins.

The sulfide inventory systematically changes with rock type: In the more primitive syenites, Fe-sulfides (troilite, pyrrhotite and pyrite) are common and occur with minor chalcopyrite and sphalerite. In the more evolved nepheline syenites, granites and hydrothermal veins, Fe-sulfides are rare or absent, while sphalerite and galena are dominant and unusual phases like loellingite, djerfisherite and several TI-sulfides can be observed. Locally, sulfides are enriched in mafic layers of the intrusion and an immiscible sulfide liquid was formed in the early stages of the intrusion. The sulfide liquid is now partially preserved as inclusions of pyrrhotite or troilite in olivine, magnetite or clinopyroxene. This may have implications for possible sulfide deposits related to evolved magmatic complexes.

The occurrence of troilite (FeS) in Ilímaussaq has been reported before (Karup-Møller, 1978). We compared pyrrhotite stoichiometry and oxygen fugacity of four alkaline complexes and found a correlation between pyrrhotite stoichiometry and oxygen fugacity. Galena and sphalerite are usually rare in magmatic systems, but present in the investigated rocks. This is attributed to a combination of the geochemically enriched character of their magma sources (lithospheric mantle), melt degree during magma formation and differentiation history of the magmas.

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Trace element constraints on the differentiation of the Skaergaard intrusion

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Content

New major and trace element analyses of plagioclase and clinopyroxene in gabbros from the Skaergaard intrusion are used to understand the mechanisms of crystallization in the main magma body and in the crystal mush. Crystal cores show a continuous chemostratigraphic evolution in the Layered Series, with compatible elements (e.g. Cr and Ni in clinopyroxene) being progressively depleted bottom up, whereas incompatible elements (e.g. Sr, Ba, REE in plagioclase and clinopyroxene) become progressively enriched. We performed numerical models and showed that these trends can be explained by a simple process of fractional crystallization, except for the upper 20% of the intrusion where plagioclase and clinopyroxene trace element compositions depart fractional crystallization trends. At this stage of magma chamber solidification, fractional crystallization becomes less efficient and is replaced by a major component of in situ, equilibrium crystallization. Trace elements also show significant variations in interstitial overgrowths on plagioclase and clinopyroxene cumulus crystals. The evolution of compatible and incompatible elements indicates that the interstitial mush liquid dominantly solidifies through a process of fractional crystallization. However, incompatible elements, and especially REE, show a degree of enrichment in plagioclase rims (> 20 ppm Ce) that strongly exceeds the highest concentrations observed in plagioclase cores (up to 4 ppm Ce). Such a strong enrichment can hardly be explained by a simple process of fractional crystallization and is probably related to the development of silicate liquid immiscibility in the crystal mush or to delayed nucleation of apatite. After the crystallization of plagioclase and clinopyroxene overgrowths, diffusive re-equilibration during 0.1-0.25 Myr significantly changed of the original zoning profiles.

Session 2.3: Processes in layered mafic magma chambers and formation of associated ore deposits: Talk

Keynote speaker

A-475

A microstructural perspective on the role of compaction in the formation of the Skaergaard and the Bushveld adcumulates

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Content

The formation of adcumulates necessitates the loss of interstitial liquid and the continued growth of primocrysts down to low porosities. Gravitationally-driven compaction at the base of the crystal mushy layer on the magma chamber floor, driven by the weight of the mushy layer itself, is commonly suggested as a significant process acting to drive out interstitial liquid and promote adcumulate formation. Compaction necessitates viscous deformation, by either dislocation creep or diffusion-controlled processes such as pressure-solution: many studies suggest that the foliations preserved in cumulates are a consequence of recrystallization during compaction, completely overprinting primary magmatic fabrics. To test the compaction hypothesis, we are investigating microstructural evidence from two layered intrusions: the Skaergaard intrusion, East Greenland and the Bushveld Complex, South Africa.

A detailed examination of the Layered series gabbro from the Skaergaard intrusion, demonstrates only limited crystal plastic deformation, with no correlation between the extent of dislocation creep and the calculated volume fraction of trapped liquid left in the cumulates. While the evidence for diffusion-controlled deformation is often cryptic, there is an anti-correlation between apparent aspect ratio of plagioclase and the extent of adcumulate crystallization, contradicting previous hypotheses involving transposition of original magmatic fabrics by dissolution-reprecipitation. This is supported by the spatial distribution of compositional zoning in plagioclase which demonstrates that pressure-solution or related diffusion-controlled processes were insufficient to obscure primary magmatic fabrics. The Layered series adcumulates did not form by viscous compaction. Instead we suggest they formed by primary processes involving mass transport in a thin mushy layer.

Compaction is most likely to occur in slowly-cooled intrusions in which the bulk magma crystallises abundant dense minerals. Plagioclase crystals from Bushveld Upper zone samples show abundant evidence for plastic deformation such as localized recrystallisation and crystal plasticity. However, the evidence for dislocation creep in the Upper Zone of the Bushveld Complex is unambiguous, although deformation was insufficient to obliterate all traces of the primary magmatic fabrics and unlikely to have been sufficient to significantly reduce the volume of interstitial liquid.

Crystallisation temperature and the origin of the UG2 chromitite layer, Bushveld Complex, South Africa

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Content

Despite many years of extensive research there is still no consensus on the origin of chromitite layers in mafic layered intrusions and the relative roles of early, late, and post-magmatic processes in their formation. Our study of trace element distribution and variations of Sr and O isotope compositions in a vertical profile through the UG2 chromitite layer of the Bushveld Complex in South Africa provided estimations of equilibration temperatures between minerals in the layer and in silicate rocks immediately above and below.

We found that the $\delta^{18}\text{O}$ values of plagioclase-pyroxene and plagioclase-chromite mineral pairs in footwall pyroxenite and chromitite are consistent with oxygen isotope exchange down to 700 °C and 800 °C, respectively, whereas in other parts of the UG2 the values are consistent with O isotope equilibration at crystallization temperatures of about 1150 °C. Temperature estimations based on the two-pyroxene REE thermometer calibrated by Liang et al. (2013) provided similar results.

To account for the calculated low equilibration temperatures between minerals at the footwall contact of the UG2 layer we propose that the UG2, as well as other chromitite layers of the Bushveld Complex, formed by remelting of earlier formed cumulates at the bottom of the magma chamber due to injection of volatile components brought by hydrous melt/fluids generated by dehydration of marine sediments underlying the Bushveld complex. Such a mechanism of chromitite formation offers at least partial solutions to several long-standing problems related to the origin of the layers. (1) Formation of chromite by replacement of orthopyroxene helps resolve the Cr budget problem because Cr content in orthopyroxene is several times higher than in parental melt. (2) The proposed model offers an explanation for the absence of chromitite layers from the Lower Zone of the Bushveld Complex, which may have formed before the sediments had reached the dehydration temperature. (3) The narrowly localized radiogenic Sr isotope anomalies associated with chromitite layers can be explained by entrapment of crustal components brought by fluids in the remelting zone. (4) The ubiquitous occurrence of potholes in footwall contacts of chromitite layers can be explained as areas of more aggressive chemical erosion and propagation of the melting front.

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**Orthopyroxene oikocrysts in the MG1 chromitite layer of the Bushveld Complex:
Implications on cumulate formation and recrystallisation**

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Content

Despite the long history of research, magmatic layering in layered intrusions, with its complex successions of magmatic cumulate formation, solidification processes and post-magmatic textural and chemical re-equilibration, is incompletely understood and the subject of vigorous debate. Oikocrysts can contribute to our understanding of these processes, due to their ubiquitous occurrence in cumulate rocks in layered intrusions and their ability to preserve different stages in the genesis of magmatic layers. We investigated orthopyroxene oikocrysts in the Middle Group 1 (MG1) chromitite layer of the Western Bushveld Complex, using an integrated textural and geochemical approach by EBSD, electron microprobe and LA-ICP-MS measurements.

The MG 1 chromitite shows two typical mineral textures: (1) one characterised by abundant orthopyroxene oikocrysts; and (2) granular chromitite characterised by 120° triple junctions and smooth curved grain boundaries between chromitite grains, and only minor amounts of interstitial material. Oikocrysts occur as clusters of several crystals aligned parallel to the layering. The oikocrysts typically have subhedral, almost chromite-free, cores that contain remnants of olivine. The cores are surrounded by poikilitic aureoles containing subhedral chromite. EBSD mappings confirm and extend our petrographic observations: chromite grains display no preferred crystal orientation, whereas orthopyroxene grains forming clusters share the same crystallographic orientation. Mineral chemistry analyses reveal clear differences in composition of orthopyroxene cores and poikilitic rims: cores have lower Mg# and higher concentrations in incompatible trace elements compared to the poikilitic rims. REE signatures of cores show that they are enriched compared to a postulated parental magma (B1) and could not crystallise in equilibrium with the surrounding minerals, whereas the composition of the poikilitic orthopyroxene is consistent with growth from such a postulated magma.

Our data suggest that the cores of orthopyroxene oikocryst in the MG1 chromitite layer formed via replacement of olivine through reaction with an upwards percolating, incompatible trace element enriched, melt. Poikilitic overgrowth on oikocryst cores must have occurred in equilibrium with a basaltic melt of B1 composition near the magma-crystal mush interface. Finally post-cumulus annealing of chromite crystals not protected by oikocrysts led to the formation of granular chromitite.

Platinum-group elements and platinum-group minerals in the weathered chromitites of the Lower and Middle Group chromitites of the Bushveld Complex

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Content

The mineralization of economically important platinum group elements (PGE) mainly occurs in mafic-ultramafic intrusions such as the Bushveld Complex. PGE are currently mined from the Merensky Reef, the Platreef and the UG-2 chromitite, which is the only chromitite layer mined for PGE, however, the Lower Group (LG) and Middle Group (MG) chromitites also contain significant PGE concentrations ranging from 0.5 to 9 g/t ([1]). In the pristine ores, PGE occur both as discrete platinum-group minerals (PGM) and included within sulfides ([2] [3]). Previous studies showed that in the LG-6 and MG-1/2, PGE-sulfides (cooperite-braggite, malanite, laurite) are the dominant PGM, followed by PGE-sulfarsenides, sperrylite and Pt-Fe alloys ([2] [3]). The rocks in the Bushveld Complex are strongly weathered down to 10 to 40 m below the surface. Near-surface chromitite seams of the LG and MG of the western Bushveld Complex at the Thaba Mine are studied by electron microprobe and LA-ICP-MS for the distribution of PGE. The analytical conditions employed for silicates were: 20 kV acceleration voltage, 120 nA beam current, focused beam, and up to 360 s measuring time. LA-ICP-MS measurements were carried out on a ThermoScientific Element XR (HR-ICP-MS) coupled with a femtosecond laser ablation system.

During weathering, sulfides and PGM are largely destroyed and PGE are mobilized and redistributed in the near-surface ores. Within the near-surface weathered chromitite seams, only relict PGM can be observed, which are observed within silicates or as inclusions in chromite. Former grains of PGM are observed in secondary silicates showing larger shapes but are locally redistributed along small cracks and Pt-Fe-(oxides) are observed as well, arguing for the neoformation of PGM. Secondary silicate minerals in weathered ores show concentrations of Pt and Pd in the 100s-ppm range. A good correlation can be observed with Ni and Pd, arguing for the weathering of pentlandite, which hosts Pd in the pristine PGE ore. Palladium and Ni partly remained and were incorporated into secondary silicates while S is largely lost.

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Stratigraphy and mineralogy of platinum-group elements within the Jurassic layered mafic Dufek Intrusion, Antarctica

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Content

To better describe the magmatic evolution of the well-differentiated Dufek Intrusion (Antarctica), we investigated the stratigraphic distribution and mineralogical siting of the platinum-group elements (PGE). The studied ~3.5 km thick sequence consists of gabbroic cumulates with minor interlayers of anorthosites, pyroxenites and magnetitites exposed in two petrogenetically related sections in the Dufek Massif and in the Forrestal Range (FR); the latter comprises the upper 1.7 km of the intrusion.

About 60 samples were analysed for their PGE (Ir, Ru, Rh, Pt and Pd) by ID-ICP-MS after NiS fire assay. The lithologically diverse rocks exhibit highly variable PGE totals (5 - 800 ppb) showing a marked fractionation between the individual PGE dominated by the Pt- over the Ir-PGE. Bulk-rock PGE do not vary systematically as a function of stratigraphy or modal rock composition; only magnetite-rich gabbros and magnetitites from the lower 300 m of the FR section exhibit significantly elevated PGE contents. In these magnetite-rich rocks, PGE totals and ratios as well as S and Cu concentrations are strongly variable but lack clear interelemental correlations.

By electron microprobe analysis, a variety of well-known platinum-group minerals (PGM) as well as a number of unnamed phases are found as small inclusions (< 1 - 25 µm) either hosted by base-metal sulfides, Fe-Ti oxides or silicates or occurring in altered areas or in cracks and along rims of Fe-Ti oxides. PGM are either Pt- or Pd-rich alloys with semimetals (e.g. As, Sb, Bi and Te) and a few mixed Pt-Pd phases. PGE sulfides are notably absent, there are no discrete phases of Rh, Ir, Os and Ru. Common base-metal sulfides and rare sulfarsenides do not incorporate PGE detectable by electron microprobe, except of Co-rich pentlandite containing up to 0.75 wt% Pd and 1.44 wt% Rh.

The PGE variations are ascribed to an extensive differentiation history under mainly S-undersaturated conditions resulting in PGE enrichment until the onset of late-stage Fe-Ti oxide crystallisation. This process triggered a delayed S-saturation and exsolution of small amounts of sulfide melt removing the PGE from the highly evolved tholeiitic magma. However, our results indicate that the PGE in most of the studied rocks are not solely controlled by base-metal sulfides but also by a variety of PGM. Thus, both high-temperature and sub-solidus redistribution processes influenced the present PGE distribution observed in the studied Dufek profiles.

Vanadium distribution in the Upper Zone of the Bushveld Complex: Constrains on fO_2

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Content

The Upper Zone of the Bushveld Complex (South Africa) is dominated by gabbros with intercalated layers of anorthosite, magnetite and nelsonite hosting major resources of vanadium. The 2 km-thick sequence of cumulates shows an overall fractionation trend towards the roof of the intrusion. However, multiple injections of plagioclase laden magmas occurred and produced successive cycles with compositional reversals at the base and upwards fractionation (Yuan et al., 2017). The late-stage magma evolution is also marked by the onset of silicate liquid immiscibility, a process that contributed to the formation of nelsonite layers (Fischer et al., 2016). Magnetite is variably enriched in V along the stratigraphic column and is of critical economic importance for South Africa. However, the relevance of important ore-forming processes such as magma replenishments, cooling/fractionation, immiscibility and oxygen fugacity have not fully investigated for the Upper Zone of the Bushveld Complex.

Samples for this study were collected in the Bierkraal drill-cores that cover the entire Upper and Upper Main Zone (UUMZ) of the western limb in the Bushveld Complex. We investigate ore-forming processes for magnetite layers occurring in two overlaying cycles in the UUMZ. The lower cycle is P-free and shows only magnetite rich (up to 35%) gabbros, whereas the other occurs directly after apatite saturation and contains several magnetite and nelsonite layers. We use the partitioning of the V, a multivalent element that occurs in Fe-Ti-oxides and clinopyroxene, to estimate the oxygen fugacity conditions during the crystallization of the two cycles. V in magnetite ranges from 30 to 6670 ppm, in ilmenite from 2 to 720 ppm and in clinopyroxene from 1 to 290 ppm. Using available data from experimental studies on V partitioning between various minerals and melt, we were able to estimate that the fO_2 varied between NNO and NNO -1 (NNO corresponds to the nickel-nickel oxide-buffer) in both investigated cycles during their crystallization.

V distribution, fractionation of magnetite and oxygen fugacity are closely linked to each other. Therefore, oxygen fugacity calculations for a continuous sample set, as provided in this study, can help to understand the influence of different parameters contributing to the ore-forming process, such as magma replenishment and fractionation.

Fischer, L.A. et al. (2016): Earth and Planetary Science Letters

Yuan, Q. et al. (2017): Journal of Petrology

Session 2.4: Compositional evolution, dynamics and physical properties of Earth's mantle: Poster

Session 2.4: Compositional evolution, dynamics and physical properties of Earth's mantle: Poster A-156

Anisotropy in textured Ca-Mg carbonates in subducting slabs

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Content

Constraining the amount of carbon that is reintroduced into the mantle via subduction is a critical parameter to quantify the deep carbon cycle [1]. Mg-Ca-Fe carbonates are believed to be the main host of carbonates in subducted oceanic crust [2]. Their stability at lower mantle condition has been documented by experiments and thermodynamic models [3] [4]. Yet, a better knowledge of their physical properties (namely seismic velocities and anisotropy) is required for the detection of carbonated lithologies by geophysical methods and for constraining the extent of carbon recycled within the deep carbon cycle. Previous measurements of sound velocities in Mg-Fe carbonates concluded that the seismic contrast between non-carbonated and carbonated lithology is within the resolution of seismic methods [4] [5] and anomalies associated to spin crossover in Fe²⁺ within the ferromagnesian carbonates could enhance the resolution of velocity contrast even further [6]. Whilst alternatively the large shear anisotropy of carbonates [5] may be the most diagnostic feature to identify carbonates at great depth the effect of textures affecting the propagation of the seismic waves is unknown. Here we present results of plastic deformation experiments performed on magnesite Mg(CO₃) and dolomite MgCa(CO₃)₂ up to 43 GPa employing synchrotron radial X-ray diffraction in diamond anvil cells. We show that the differential stress of magnesite is lower compared to most other minerals in subducting slabs but rapidly increases with pressure, while the preferred orientations in the crystals at low pressure persist at all investigated pressures. In this contribution we will present the analysis of measured data and discuss first results for the applications to the seismic identification of carbonates.

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Combined La-Ce and Sm-Nd Isotope Systematics and Implications for the Depleted Mantle

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Content

The Cerium (Ce) and Neodymium (Nd) isotopic systematics of mid ocean ridge (MORB) and ocean island basalts (OIB) reflect their time integrated La-Ce and Sm-Nd ratios, and hence the extent of light rare earth element (LREE) depletion or enrichment of their mantle sources. New high precision Ce-Nd isotope data of global MORB and OIB form a well-defined “mantle array” in ϵCe - ϵNd space, in good agreement with the sparse literature data. The slope, extent, and scatter of the ϵCe - ϵNd “mantle array” is sensitive to the nature, relative proportion, age, and melting behavior of the different mantle source materials.

Quantitative models using variable compositions and age of different source components –depleted mantle, recycled oceanic crust, and subducted upper and lower continental crust– are used to explore the effects of the various input parameters on the ϵCe - ϵNd in oceanic basalts.

We find that the extent and age of depletion of the depleted mantle has a key influence on the slope and extent of the ϵCe - ϵNd “mantle array”. The isotopic composition of the enriched source materials also greatly influences the overall extent of isotopic variability, but compared to the depleted mantle, their leverage on the slope of the ϵCe - ϵNd “mantle array” is relatively subordinate. With increasing amount of mantle depletion, the ϵCe - ϵNd isotope array becomes steeper and, importantly, also rotates away from the chondritic reference point at $\epsilon\text{Ce}=\epsilon\text{Nd}=0$.

The intersection point of the “mantle array” at $\epsilon\text{Ce}=0$ is at $\epsilon\text{Nd}>0$. This non-chondritic intersection point indicates that Earth’s mantle is pervasively depleted, and does not require an originally non-chondritic LREE composition of bulk silicate Earth, in good agreement with the ^{146}Sm - ^{142}Nd systematics of Earth and chondritic meteorites.

Imaging dislocations in a natural olivine by electron channeling contrast in a field emission SEM.

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Content

Observation of individual dislocations in minerals is indispensable for the understanding of the deformation mechanisms in rocks at sub-micrometre scale. Transmission electron microscopy (TEM) has been so far the main tool to observe individual dislocations in rock-forming minerals. On the other hand, the chemical etching and oxidation decoration method are often used for dislocation density measurements especially in Fe-bearing olivine, by using optical microscopy or scanning electron microscopy. Currently, electron channeling contrast imaging (ECCI) in a field emission scanning electron microscope (FE-SEM) is developing into an alternative tool to observe crystal defects in metallic alloy and ceramics containing relatively heavier elements in the material science fields. We are applying it much further into the mantle minerals. Here we report ECCI of individual dislocations in a naturally deformed olivine.

A natural olivine from the Finero lherzolite was examined in a FE-SEM equipped with electron backscatter diffraction (EBSD) apparatus. The bulk rock specimen was using a 0.25-1 μm -diamond paste followed by a 40 nm-colloidal silica suspension. The polished surface was coated with amorphous carbon. The FE-SEM was operated at 20 kV-acceleration voltage and ~ 9 nA probe current with a low convergent angle at 6.9 mm working distance. Backscattered electron (BSE) images were obtained with a large annular scintillator placed directly under the pole piece. The crystal orientations of a target olivine grain were determined by EBSD. The BSE image of a single crystal of olivine displays cross-hatched subgrain boundaries. The straight boundaries are nearly parallel to the (001) and (010) planes on the [100] projected image, which implies that the two slip systems were co-activated in the deformation. The ECCI of the olivine at a nearby (001) subgrain boundary is shown in Fig. 1. The right-side of the boundary in the image has a stronger channeling effect under the Bragg condition of the (004) plane. A few of bright line features are the [001] screw dislocations in plan-view. Many bright spots with a tail can be characterized as having a "comet"-like feature. The contrast is originated from inclined dislocations to the sample surface.

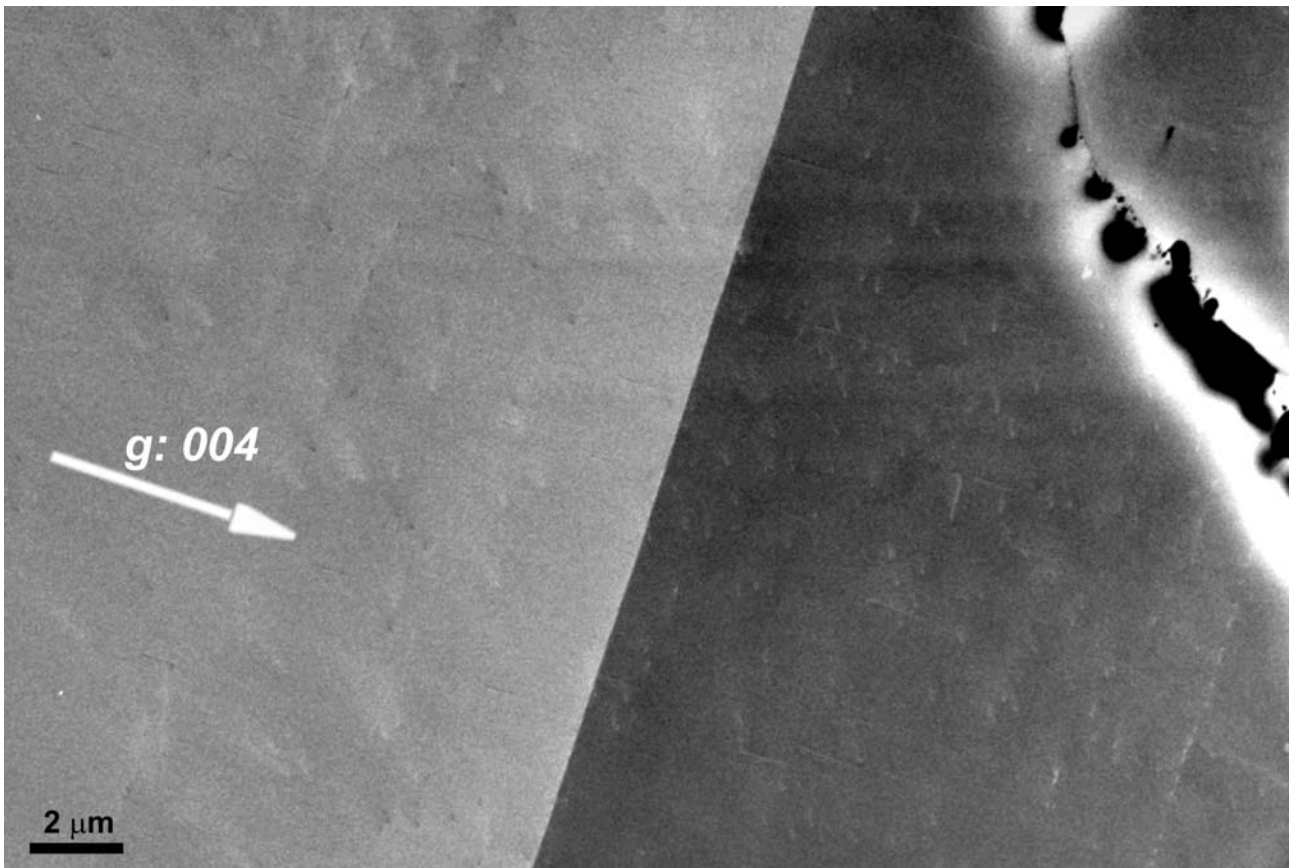


Fig. 1. ECI of individual dislocations in an olivine from the Finero lherzolite.

Plastic deformation in aluminous stishovite and implications for mantle heterogeneities

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Content

Information on the elasticity and plasticity of candidate minerals in the Earth's interior assists in understanding mantle flow and the underlying geodynamic processes at depth when compared with seismic observations. Seismic signals from mid-mantle depths (~ 800 to 1850 km) provide evidence for negative shear wave anomalies of 2 to 6% in the vicinity of subduction zones [1] [2] [3] [4], including a new discontinuity at ~1000 km [5]. A possible explanation for these anomalies could be the presence of remnant unmixed basaltic crust, where stishovite (rutile structure) transforms into post-stishovite (CaCl₂ structure) under pressure. This transition is accompanied by shear softening that could explain the low velocity anomalies [6]. However, additional information on the physical properties of deformed stishovite due to mantle flow is required to understand the origin of seismic anomalies and mantle heterogeneities. Here we present results from plastic deformation experiments on aluminium-bearing stishovite containing 5 wt% Al₂O₃ up to 37 GPa along isotherms at 873, 1073, 1323 and 1473 K. Experiments were conducted using synchrotron radial x-ray diffraction at PETRA III beamline P02.2. The samples were loaded in x-ray transparent boron gaskets in a Mao-Bell-type diamond anvil cell, equipped with graphite heaters [7]. Our preliminary data shows that the lattice strain supported by the sample is comparable to that of pure SiO₂-stishovite and that differences in the strength arise from the effect of aluminium in the elastic properties [6]. We will further discuss the implications of these results and the effect of textures on mantle deformation and heterogeneities.

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Session 2.4: Compositional evolution, dynamics and physical properties of Earth's mantle: Talk

**Session 2.4: Compositional evolution, dynamics and physical properties of Earth's mantle: Talk
A-315**

Carbonate-silicate reactions under mantle conditions and the role of carbonates as possible trace-element carriers in the deep Earth

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Content

Carbonates play a key role in the chemistry and dynamics of our planet. They are prevalent on Earth and are directly connected to the CO₂ budget of our atmosphere. Moreover, it is believed that more than 90% of the planet's carbon content is stored in the Earth's deep interior [1]. Recent studies have shown that carbonates are stable at mantle conditions [2,3], where they may react with silicates [4] to form new phases. These reactions will redistribute elements, such as carbon and other trace elements, which are carried by the carbonates. Investigating the processes that stabilize and preserve carbonates in the mantle is thus important to better understand the carbon cycle and associated transport of trace elements in the deep Earth. Laser-heated diamond anvil cell experiments are used to study carbonate-silicate reactions at high pressure and high temperature. First experiments were performed with Sr/REE-doped CaCO₃ and olivine or enstatite as starting silicates. Structural changes of the samples are monitored with X-ray diffraction (XRD). Changes in trace element distribution are followed by X-ray fluorescence (XRF) analysis. XRD and XRF mapping before and after heating of the sample material showed transformation of the starting silicates into Mg,Fe-perovskite (e.g. bridgmanite) + MgO and redistribution of the trace elements. Additional (optical) fluorescence spectroscopy and TEM analyses on the recovered sample material indicated a decomposition of the carbonate during heating. Furthermore, distribution of Sr into the newly formed perovskite phase was observed. These first findings provide further insights into the stability of carbonates in presence of mantle silicates and indicate that carbonates may have an impact on the trace element budget of the Earth's mantle.

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Geochemistry and Evolution of Peridotite Xenoliths from the Eger Graben

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Content

The subcontinental lithospheric mantle (SCLM) is a very old reservoir that can be sampled in ultramafic massifs or as xenoliths in alkaline magmas. The chemical composition, the age, the formation and the relationship to the crust are still poorly understood.

We studied the SCLM along the NE-SW trending Eger Rift, Germany with highly precise and accurate trace element methodologies, augmented by detailed petrographic investigations. The Eger Rift is located on the boundary between the Saxothuringian and Moldanubian zones of the Variscan basement of the Bohemian Massif and represents part of the Cenozoic Central European Volcanic Province. The alkaline lavas that erupted both along the rift axis and its shoulders contain abundant mantle xenoliths of spinel peridotites. The major and trace element and the REE concentrations of pyroxenes, olivine, and spinel of xenoliths from a number of locations within the Eger Graben show a very wide range in mineral composition, variable degrees of melting and an unexpected variability within single xenolith samples.

The studied xenoliths are all spinel lherzolites and harzburgites that experienced different degrees of partial melting from ~7 to 21 % based on Cr# in spinel. Individual mineral grains are homogeneous, but different grains in a sample show a significant variation on a small-scale. Interestingly, the REE concentrations and pattern in the clinopyroxenes indicate a significant melt influence although the Al₂O₃ and Mg# concentrations in orthopyroxene and clinopyroxene show restitic signatures. We suggest that the clinopyroxenes in the xenoliths are mostly of restitic origin, but experienced melt interaction that led to elevated contents of incompatible elements. Our data therefore reveals a very complex history of the SCLM below the Eger Graben.

Germanium coordination >6 in compressed amorphous GeO₂ above 50 GPa by valence-to-core X-ray emission spectroscopy

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Content

The density contrast between minerals and melts within the Earth's mantle determines whether melts are buoyant, sinking or gravitationally stable with respect to their surrounding. Knowledge about viable atomic scale compaction mechanisms can be a basis for predictions on the existence of ultra-dense melts in the Earth's lower mantle. The most important compaction mechanism at depths beyond the transition zone is the increase in coordination of silicon from six to above six oxygen neighbors.

Compressed amorphous GeO₂ is investigated as an analogue to SiO₂, which is the most important component of silicate melts in the Earth's mantle. For the time being, solid amorphous material is investigated as structural analogues to melts.

The application of valence-to-core X-ray emission spectroscopy to DAC experiments is a developing field of research, which allows direct insight into the pressure evolution of electron binding energies.

We compressed amorphous GeO₂ up to 101 GPa in diamond anvil cells (DAC) and measured germanium valence-to-core X-ray emission spectra. A new approach allows us to interpret the spectra in terms of Ge-O bond distance and germanium coordination.

The 6-fold coordination is reached at 20 GPa. At about 50 GPa, a further coordination increase is observed, and the average coordination reaches seven at 100 GPa. As coordination transitions in germanate phases commonly precede those in silicate phases by few tens of GPa at most, this observation points to the possible existence of very dense silicate melts with coordination above six near the core-mantle boundary.

The effect of pressure on the oxidation state of iron in silicate melts at a fixed oxygen fugacity

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Content

As terrestrial planets formed their silicate mantles equilibrated with core forming iron metal, resulting in a mantle oxygen fugacity that would have been below the iron-wüstite oxygen buffer. The oxygen fugacity of at least the accessible portions of the Earth's upper mantle, however, have been throughout Earth's history 4-5 orders of magnitude higher than this. The origin of the rapid increase in the redox state of the mantle soon after core formation is unclear. Here we test the possibility that a deep magma ocean, that would have likely existed towards the end of accretion, would develop a gradient in oxygen fugacity for a fixed ferric-ferrous ratio as a result of the effect of pressure on the stability of iron melt components. In a multianvil press we have equilibrated an andesitic melt with a Rh-RhO₂ buffer between 5 and 24 GPa. Further experiments were performed on the same melt in equilibrium with iron metal. The recovered melts were then analysed using Mössbauer spectroscopy to determine the ferric/ferrous ratio. The results show that for the Rh-RhO₂ buffer at lower pressures, the ferric iron content decreases with pressure, due to a positive volume change of the reaction $\text{FeO} + 1/4\text{O}_2 = \text{FeO}_{1.5}$. However, above 15 GPa this trend apparently reverses and the ferric iron content increases with pressure. This reversal in pressure dependence would drive the oxygen fugacity of a deep magma ocean with a fixed ferric/ferrous ratio down with increasing depth, creating a redox gradient. As a result the magma ocean could potentially be in equilibrium with metallic iron at its base but more oxidised in its shallower regions. Crystallization of this magma ocean could render an upper mantle oxygen fugacity similar to that in the Earth's accessible mantle today.

What is the origin of ULVZs?

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Content

The core-mantle boundary region is complex. In addition to large regions with reduced shear velocities (LLSVPs), there are small areas with shear velocities up to 30% lower than surrounding material, the so-called ultralow velocity zones (ULVZs). Although these heterogeneous regions are small (10 to 100 km), they have featured in speculation regarding an ancient global magma ocean, magnetic pole positions during reversals, core-mantle material exchange and the source of mantle plumes. Mineral physics provides important constraints in understanding the nature of ULVZs through the comparison of seismic data with experimental and computational studies of the relevant phases. Shear wave velocities are particularly important, and nuclear inelastic scattering (NIS) offers the attractive possibility to measure these velocities for iron-containing minerals in the laser-heated diamond anvil cell through direct measurement of the partial density of states (DOS). Complementary determination of the partial DOS using density functional theory (DFT) has shown the potential to identify experimental features that impact the velocity determination as demonstrated by our recent study on bridgmanite. We performed first-principles calculations to determine the iron partial DOS for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{SiO}_3$ post-perovskite. We calculated Debye sound velocities (which are closely related to the shear wave velocities) using the same approach as for experimental NIS data, and obtained velocities for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{SiO}_3$ post-perovskite that are consistent with literature values for MgSiO_3 and FeSiO_3 post-perovskite also calculated using DFT. In contrast, literature data on the Debye sound velocity determined experimentally using NIS is 35% lower than our calculated value, which led to previous suggestions that ULVZs originate from regions containing iron-rich post-perovskite. Our results show, however, that the lower NIS velocities in post-perovskite data likely arise from a similar artefact as the NIS bridgmanite data. The velocities derived from the DFT DOS of both bridgmanite and post-perovskite are consistent with seismic velocities of the bulk lower mantle, suggesting that ULVZs are likely not caused by iron-rich post-perovskite. Instead we favour previous suggestions that dense melts are a more plausible explanation.

Session 2.5: Subduction zone magmatism and crustal evolution: Poster

Session 2.5: Subduction zone magmatism and crustal evolution: Poster
A-288

Chollay Plutonic Complex: the roots of the Andean Triassic Arc?

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Content

The western border of South America has been proposed like periodically active margin since the Paleozoic, with a period of diminished or arrested subduction during the Permian-Triassic (Pre-Andean Cycle). The magmatism generated during this period has been explained by crustal melting in a continental rift context, however recent field, petrological and geochemical data show that this magmatism was probably created within an active margin.

The largest pre-andean intrusive unit cropping out in the High Andes of Chile (28°30'S – 30°S) is the Chollay Plutonic Complex (CPC). The CPC has a wide compositional variety, ranging from gabbros to granites being the granodiorites and granites the most common lithologies, all of them with hydrated mafic minerals. This complex was incrementally constructed between 249-234 Ma intruding Paleozoic metasedimentary and plutonic units, now exposed within the batholith, specifically in its western border, as elongated NE-SW strips. Mylonite bands along the western margin of the CPC indicate active deformation during its emplacement. The general disposition of the inner lithological pulses of CPC and its host rocks is subvertical. In its eastern flank, a Lopingian–Carnian dacitic to rhyolitic volcanic and volcanosedimentary sequence is in close spatial and temporal relationship to the CPC, and partially intruded by it.

In this work we present new field, petrographic, geochemical and isotopic data from the CPC and its host rocks in order to evaluate the source and the petrogenetic processes responsible of this magmatism. The geochemistry indicates a calcalkaline nature, an enrichment of LILE in relation to HFSE and negative anomalies of Nb-Ta, Ti and P, characteristics of a magmatism controlled by fluid induced melting of a depleted asthenospheric mantle, in an active subduction context, with variable contribution from a crustal source. A revised model for the Permian-Triassic evolution of the Andean margin is proposed in light of these results, suggesting a protracted subduction with the development of an extensional framework in the overriding plate during the Triassic-Jurassic period. This model fits recent reconstructions of global plate boundaries.

Dynamics of melting in the Valu Fa-Lau Basin backarc

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Content

Subduction zones are the regions of significant mass transfer between the Earth's crust and mantle. The dynamics of melting and composition of melts in island arcs differ from those observed at divergent plate boundaries where melting is solely driven by adiabatic decompression. Fluids from the subducting slab and variable depletion of the mantle wedge impact on the erupting island arc melts. Recent advances in subduction zone research suggest that a significant portion of melting in island arcs may however be due to adiabatic decompression. Uranium series disequilibria provide a unique tool to test between these competing models. Adiabatic decompression melting generally results in ²³⁰Th-excess while fluid flux melting in arcs displays excess of ²³⁸U.

The Valu Fa-Lau Basin backarc spreading centre is situated at increasing distance from the trench ranging from 175-325 km and increasing Benioff zone depth from 40-250 km. Here, we use a new sample set along with literature data to determine the processes of melting underneath the backarc. We can show that fluid mobile element ratios such as Ba/Nb decrease with increasing distance to the trench while trace element ratios sensitive to mantle wedge depletion (e.g., Nb/La) suggest a decreasing degree of depletion with increasing distance. A single samples more than 300 km distant from the trench and at Benioff zone depths of ~250 km displays ²³⁰Th excess, low Ba/Nb (<10) and relatively high Nb/La (~0.55). In contrast, samples closer to the trench (at 170-270 km) display a significant excess of ²³⁸U that is best explained by addition of fluids from the subducting slab. We note however, that these are not correlated with fluid mobile element ratios suggesting that the Uranium series disequilibria may require an alternative explanation. We test a model in which the ²³⁸U excess in the backarc may best be explained by adiabatic decompression melting of an oxidized mantle that has previously been depleted by melting underneath the arc. This depleted mantle has subsequently been transported towards the backarc due to slab rollback of the Pacific Plate.

Indications for tungsten mobility during oceanic crust alteration

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Content

A better understanding of the global W cycle between the Earth's geochemical reservoirs is of great importance for many petrological and geochemical models, e.g. for correctly interpreting the ^{182}Hf - ^{182}W age of core formation. So far, the geochemical behaviour of tungsten in different tectonic settings, such as in the continental crust or subduction zones has already been studied. However, it is yet still uncertain, whether all processes that have the potential to affect the tungsten geochemical cycle, i.e., fractionating W/Th, W/U and W/Ta ratios in the different geochemical reservoirs have already been fully identified. Due to similar incompatibility of the elements involved, these element ratios have long been regarded as being constant in most silicate reservoirs.

In contrast to this long standing view, W enrichments relative to Th and Ta in many arc lavas have been recently found and were explained by fluid-controlled W-enrichment in the subarc mantle wedge [1]. However, very little is known, as to whether hydrothermal alteration of the oceanic crust could already trigger W redistribution and enrichment of W in distinct portions of the oceanic crust. This can be tested by measuring W together with similarly incompatible elements like U, Th or Ta in sections from the oceanic crust.

Here, we present high-precision W-Th-U-Ta data obtained for samples from the oceanic crust by isotope dilution, using the Thermo Neptune MC-ICPMS at Cologne-Bonn. Our sample suite covers well characterised samples covering all major alteration styles within the upper as well as the uppermost part of the lower oceanic crust, drilled during several IODP/ODP campaigns at IODP Hole 1256D. This IODP hole is the first in-situ borehole comprising a complete intact section of upper oceanic crust down to gabbros [2]. Our first results indicate that systematic fractionation of W from Th, U and Ta within the altered oceanic crust is clearly resolvable, pointing towards a progressive enrichment of W in the Lava and Sheeted Dike Complex sections of Hole 1256D.

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Lithium isotope signatures of Central Andean Palaeozoic basement and Cenozoic volcanic rocks from arc and back-arc

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Content

The Cenozoic Central Andes of South America are the prototype of non-collisional orogen building at an active continental margin and include a variety of crustal domains with Proterozoic to Mesozoic formation-ages. The formation of thick continental crust from this variety of materials and potential foundering of dense lower lithosphere triggered the uplift of the Altiplano - Puna high Plateau. This study investigates the Li isotope and elemental composition of late Cenozoic volcanic rocks from arc and back-arc and the underlying Palaeozoic basement rocks in the southern Altiplano – Puna Plateau. All samples were previously characterized by their radiogenic isotope and trace element composition, and the Palaeozoic magmatic metamorphic basement is the principal crustal component in the Ordovician sedimentary basement and all younger magmatic rocks. Furthermore, basement and andesite samples (arc) were studied for B systematics ([1] ; [2]). The more mafic samples, mainly basaltic andesite (back-arc) were thought to represent magmatism related to young lithospheric delamination ([3]).

Li content of the andesite (arc) range from 11 to 37 ppm and $\delta^7\text{Li}$ from -1.5 to 6.1 ‰; respective ranges of the basaltic-andesite (back arc) are Li from 8 to 29 ppm and $\delta^7\text{Li}$ from -3.5 to 6.7 ‰. Palaeozoic high-temperature metamorphic - magmatic basement rocks vary in $\delta^7\text{Li}$ from ~ -1 to 3.7 ‰ with elevated Li concentrations of 45 ± 7 ppm. Ordovician sedimentary rocks show $\delta^7\text{Li}$ between ~ -3.3 and 7.3 ‰ and Li concentrations between 28 and 74 ppm.

The new Li data address the potential across arc variation of Li isotope ratios in the Cenozoic volcanic rocks that is known to be present or absent in other subduction settings. In addition, volcanic rocks and Palaeozoic basement are important source rocks of the economically first class Li enrichments in the salars of the Puna.

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**Volcano-tectonics at the northern tip of the Liquine-Ofqui Fault Zone, Argentina (37.5°S):
The Copahue Volcano**

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Content

Copahue volcano is one of the most active volcanoes in the Southern Volcanic Zone of the Andes and is spatially associated with a number of prominent structural discontinuities. The volcano is located close to the northern terminus of one of the most prominent intra-arc fault zones on Earth, the Liquine-Ofqui Fault Zone (LOFZ). Moreover, Copahue is situated at the western margin of the 20 x 15 km Agrio caldera, which is part of the 90 km long Callaqui-Copahue-Mandolegüe volcanic zone, a prominent NW-SE-trending volcanic zone in the SVZ. Copahue volcano is spatially also associated with the NE-striking Lomín Fault, a secondary dextral strike-slip fault of the LOFZ, and the N-striking Antinir-Copahue thrust system. Thus, Copahue may be an ideal target to study the interaction between deformation and volcanism at the South Chilean convergent plate margin.

A key objective of our study is to find out to what extent any of the mentioned structural discontinuities have influenced volcanic activity of Copahue. Previous studies concluded that the Agrio caldera and, thus, Copahue formed under transtension. This is at variance with the dextral transpressive character of the LOFZ recognized throughout the SVZ. We, therefore, aim at elucidating to which deformation regime volcano-tectonic structures of Copahue adhere to. We addressed this issue by lithological and structural mapping of the eastern flank of the volcano. Here, the towns of Caviabue and Copahue are, due to the presence of hot springs and winter tourism, of increasing economic importance, but are exposed to potentially severe volcanic hazards. This should not be underestimated as Copahue erupted 13 times in the last 260 years, 6 of which happened over the past 25 years.

Volcano-sedimentary strata found at the base of Copahue lavas, which postdate the last glaciation (ca. 30 ka), are moderately inclined toward the volcano. We interpret these strata as volcano-tectonic products filling half grabens separated by normal faults and possibly generated as a consequence of upper-crustal doming at an early stage of volcano formation in Pliocene time. We were unable to confirm the presence of normal faults apparently affecting Copahue lavas. Instead, we interpret prominent escarpments, disposed radially with regard to the volcano center, to have formed by glacial activity. We, thus, cannot confirm structural evidence by other workers suggesting that Copahue volcano formed under upper-crustal transtension.

Session 2.5: Subduction zone magmatism and crustal evolution: Talk

Session 2.5: Subduction zone magmatism and crustal evolution: Talk

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Back-arc magmatism of the southern Okinawa Trough

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Content

The Okinawa Trough is a back-arc basin located behind the Ryukyu subduction zone. The southernmost Okinawa Trough has rifted north-southward and has prolonged westward. The opening of the southern Okinawa Trough is closely related to the Taiwan orogenic belt whose northern end is adjacent to the western end of the Okinawa Trough. In other words, the current southern Okinawa Trough has started to open when the tectonic regime of the northern Taiwan orogen changed from plate collision to post-collision between the Philippine Sea Plate and the Eurasian Plate. The arc and back-arc volcanism almost coincide geometrically. There are three types of magmatism that can be observed in the southern Okinawa Trough: arc, back-arc and across-backarc magmatisms. In this study, we especially show the results from our deep-tow sub-bottom profiler and sidescan survey across the central depression of the southern Okinawa Trough. Our results show the Okinawa Trough rifting is very active. Furthermore, the Okinawa Trough crust is more brittle in both two margins than in the central trough. It seems that only the very early stage of backarc magmatism has accompanied the strong seafloor gas venting (gas emission).

Basement rocks of the Magallanes foreland basin, Tierra del Fuego; constraints from zircon Lu-Hf and O isotopes, and REE data

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Content

The Palaeozoic Tierra del Fuego Igneous and Metamorphic basement complex (TFIMC) of southern Patagonia plays a key role in any reconstruction of the southwestern part of Gondwana. It has been regarded as the missing link between two early Palaeozoic orogenic belts that represent tectonic activity associated with a convergent continental margin: the Pampean in Argentina and the Ross in East Antarctica. Here, we present a detailed study of zircon, including U-Pb geochronology, REE+Y+Ti, Lu-Hf, and O isotopic data of samples from the TFIMC in order to clarify its timing and evolution. Cambrian magmatism occurred between ca. 540 and 520 Ma, with the igneous zircons recording initial ϵ_{Hf} values ranging from +1.2 to -3.8, and $\delta^{18}\text{O} > 6.8\text{‰}$. These indicate a clearly uppercrustal (e.g. sedimentary) influence on the magma source, but also suggest that isotopic homogenization occurred early in the magma evolution. Zircon U-Pb, Lu-Hf and O isotopic data in combination with REE+Y+Ti analyses enable recognition of Permian metamorphic and magmatic zircon growth. Ti contents, U-Pb, O and Lu-Hf isotopes indicate that metamorphic zircon grew at ca. 265 Ma from aqueous fluids following homogenization. Lu-Hf isotopes in metamorphic overgrowths suggest that the aqueous fluids interacted with Grenvillian rocks (ca. 1000 Ma) before transport and crystallisation. U-Pb ages of inherited detrital zircon cores also indicate Grenvillian provenance (1100–950 Ma), as well as components of 640–590 Ma (and 520 Ma) and 2080–1850 Ma. Magmatism occurred at ca. 255 Ma arising from melting of Cambrian rocks, as confirmed by Lu-Hf and O isotopic data in Permian igneous zircons (initial ϵ_{Hf} values < -1 and $\delta^{18}\text{O} > 7.4\text{‰}$). Comparison of U-Pb zircon data, together with other geological considerations, indicates strong similarities between the Cambrian rocks of the TFIMC and those of the Pampean orogen of Argentina. Thus they represent the further continuation of the Pampean orogenic belt from the Sierras Pampeanas in Argentina to Tierra del Fuego. We suggest that southern Patagonia was involved in collision with southernmost Africa during the Guadalupian, as is recorded by the metamorphism and post-tectonic magmatism in Patagonia, synchronous with the stages of deformation observed in the Cape Fold Belt in South Africa.

**Crystallisation conditions of fore-arc basalts from the Izu-Bonin-Mariana island arc:
experimental constraints**

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Content

Subduction zone initiation is related to the sinking of an old dense oceanic lithosphere into the asthenosphere, with lithospheric upper mantle filling the gap above the sinking plate. Decompression melting of the ascending mantle leads to the formation of basaltic melts which are compositionally expected to be MORB-like lavas with arc-signature (termed fore-arc basalt, FAB). However, the formation and the magma storage conditions of FAB magmas are largely unknown. In this study we investigated samples from IODP Expedition 352. Petrological investigations of two drilling sites show that FABs are aphyric to sparsely plagioclase-pyroxene-phyric basalts and dolerites (bottom of the Hole U1440A). In general, most pillow glasses show relatively evolved compositions with MgO contents of 5–8 wt%. The anhydrous character of the FAB glasses is revealed by FTIR analyses of dissolved H₂O, which ranges from 0.1 to 0.8 wt%. Phase equilibria calculations show that some evolved lava units with Al₂O₃ and MgO enriched glasses cannot be produced by fractional crystallisation from more primitive units. On the other hand, primitive FABs with low TiO₂ concentrations cannot lead to less evolved magmas from other groups by fractional crystallization. We conclude that primitive FAB melts are not homogeneous, implying that source rocks and most probably melting and differentiation conditions differ for the different lava units. Experiments with pressures of 100–500 MPa, at nearly dry and low water activity (<0.05 wt% H₂O and ~0.6 wt% H₂O) and in the fO₂ range FMQ -2 to FMQ +0.5 were conducted to bracket the conditions of partial crystallization and potential magma storage conditions. The experimental liquid lines of descent are in general agreement with natural defined glass compositions. At 100 MPa, the observed natural phenocryst assemblage in FABs can be reproduced at ~1175°C for the most primitive samples and ~1150°C for the evolved samples. The natural mineral compositions are not always fully reproduced. Natural plagioclase are more calcic and clinopyroxenes are more magnesian for some units. This may indicate that fluids (higher aH₂O) played a role in the generation of some lava units (H₂O-rich Unit 13 with ~ 2% H₂O). The investigated FABs may trace the transition from very dry to fluid-assisted partial melting. Additional experiments at different pressures with boninitic compositions are planned to track the evolution from dry (FAB) to hydrous (boninite) mantle melting.

Electrical conductivity of aqueous HCl solutions at elevated temperature and pressure from impedance measurements in HDAC experiments

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Content

Aqueous fluids at elevated temperature and pressure are important agents of chemical reactions and transport processes in the Earth's continental crust. Magnetotelluric studies often detect areas of elevated electrical conductivity in the deep crust or below active volcanoes. Presently, it is difficult to decide whether these features are caused by silicate melts or by aqueous fluids, since electrical conductivity data for aqueous fluids under relevant P-T conditions are largely missing. HCl is likely to be a minor component particularly in fluids in subvolcanic systems, but due to the high ion mobility of the proton, it may have a disproportionally large influence on electrical conductivity.

We determined the electrical conductivity of 0.01, 0.1, and 1 mol/l aqueous HCl solutions in a modified Bassett-type hydrothermal diamond anvil cell up to 500 °C and 700 MPa. Full impedance spectra were measured at each P-T condition using a Solartron 1260 analyzer with alternating currents in the range of 1 to 107 Hz. Measured impedance spectra were modelled with an equivalent circuit to identify the respective electrical resistivity of a solution. Resistivity is then converted to electrical conductivity by determination of an individual cell constant at ambient conditions for each experiment. We determined pressure both from the equation of state of water according to the observed homogenization temperature of the fluid and from shifts in wave number of the ν_3 Raman band of zircon.

We observed that conductivity increases almost linearly with concentration, and increases exponentially up to about 300 °C with minor influence of pressure. For higher temperatures the electrical conductivity decreases as a function of fluid density and pressure, whereas lower pressures lead to stronger decrease. Our results from 0.01 mol/l aqueous HCl solution are consistent with existing conductivity data from experiments in conventional hydrothermal pressure vessels that are limited to 400 MPa. Further, our results from 0.1 mol/l HCl are in agreement with data acquired from experiments at shock wave pressures. We first successfully acquired conductivity from 1 mol/l HCl at elevated temperature and pressure. These data are essential for distinguishing fluids from silicate melts in the lower crust based on magnetotelluric measurements and a number of applications will be discussed in detail.

Evaluation of highly siderophile elements and stable Fe and V isotope systematics of ultra-mafic lavas from the complex Solomon Islands subduction zone, SW Pacific

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Content

Along the Solomon island arc, SW Pacific, the Indian-Australian plate is presently subducted beneath the Pacific plate. However, subduction of the Pacific plate underneath the Indian-Australian plate took place in the Solomon Islands region until ~5 million years ago. The active southern island chain of the Solomon island arc is marked by the occurrence of extremely ultra-mafic lavas with up to ~30 wt.-% MgO above the young (< 5 Ma) Woodlark Basin spreading center that is subducted beneath the central section of the island arc at the New Georgia Archipelago (NGA). Combined Pb-Sr-Nd-Hf isotope data and trace element abundances indicate a strong magma source overprint by subduction components in particular by slab melts (see [1] for an overview).

Subduction zone dynamics and the sources of the NGA ultramafic lavas were further investigated by combined analyses (with/without desilicification digestion steps) of the highly siderophile elements (HSE, including PGE, and Re), and stable Fe and V isotope signatures on a representative subset of (ultra-)mafic lavas from four NGA volcanic centers. The NGA lavas feature chondrite-normalized HSE patterns (with ranges for $\text{Ir}_N = 10^{-3} - 10^{-4}$, and $\text{Pd}_N/\text{Ir}_N = 6 - 60$) with a marked Re depletion (i.e., $\text{Re}_N/\text{Pd}_N = 0.02 - 0.6$). The $^{187}\text{Os}/^{188}\text{Os}$ compositions of the sample suite ranges from non-radiogenic to PUM-like ($^{187}\text{Os}/^{188}\text{Os} = 0.1264 - 0.1291$). The HSE abundances are, however, 10 % to a factor of 16 higher in the desilicified sample fractions, hence suggesting that the HSE are likely partly hosted by silicate phases. Stable $\delta^{56}\text{Fe}$ isotope signatures range from +0.03 to -0.21 ‰ and anti-correlate with FeO, thus indicating either an oxidation signature or alternatively a mixing process. The $\delta^{51}\text{V}_{\text{NIST}}$ values vary between -1.7 and -1.5 ‰, and are remarkably similar within a volcanic center.

In conclusion, and similar to lithophile element tracers (e.g., Ba/Th, La/Yb) and radiogenic isotopes (Sr, Nd, Hf, Pb, see [1]), the HSE data and ^{187}Os , stable Fe and V isotope compositions of several NGA volcanic centers give further, independent, evidence that the mantle wedge under the New Georgia Archipelago has been variably overprinted by slab fluids, and slab melts from the young Woodlark Basin oceanic crust.

[1] Schuth et al. (2009) *J. Petrol.* **50**, 781-811.

Ignimbrite magmatism related to the Central Andean subduction zone through space and time: compositions, magma production rates and net crustal growth

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Content

A compilation of 890 geochemical and ca. 1,200 geochronological data for 194 mapped ignimbrites from the Central Andes forms the basis to quantify eruption volumes through time and space. Using published Sr- and O-isotope data to estimate the mass balance between juvenile addition to the Andean crust vs. crustal melting and recycling, these volumes can be converted into net crustal growth rates. We document that so-called “ignimbrite flare-ups” represent pulses of magma addition from the mantle to the crust that is about twice as large as the typical arc magma flux (35 km³/km²*Ma). Ignimbrite trace element compositions change through time during the thickening Andean crust. Characteristic differences in trace element signatures are documented for the Eu anomaly, depletion of MREEs and variable enrichment in LREE.

Older (>14 Ma) plateau-forming ignimbrites in northernmost Chile and southern Peru are less depleted in HREEs and less radiogenic in Sr isotopes, indicating crustal contributions of up to only 25%. Younger (<10 Ma) Altiplano-Puna-Volcanic-Complex ignimbrites in the S have larger crustal contributions (up to 70%). These compositional variations indicate a relation to crustal thickening with a “transition” from plagioclase to amphibole and garnet residual mineralogy between 13 to 9 Ma. The spatial and temporal distribution of ignimbrites follows the N-S passage of the Juan-Fernández ridge and a flat-slab subduction regime. Slab steepening thus is the principal trigger of increased input of mantle magmas into the crust. However, ignimbrite “flares” also tend to follow (by a few Ma) pulses of crustal shortening. Their (different) isotope composition and crustal contributions then reflect the changing thermal state as a consequence of crustal thickening with time. Older ignimbrites in the N of the Central Andes are the consequence of input of mantle melt s into relatively thinner and colder crust. By contrast, while younger ignimbrites in the south were also triggered by increased mantle melting after slab steepening, the Andean crust had thickened but by that time (10 Ma later) was considerably hotter and thus “primed” for more intense crustal melting in response to the same input from the mantle wedge. This demonstrates that volume and composition of ignimbrites are controlled by the interplay of both, deep processes in the mantle wedge and processes of melting (and recycling) of the continental crust at shallower levels.

Lithospheric evolution at the Early Andean convergent margin, Chile

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Content

Classic models of tectonic evolution of the SW Gondwana margin suggest that in between two orogenic cycles, the Gondwanian (Late Paleozoic) and the Andean (Jurassic to Recent), continental subduction ceased during much of the Triassic period. In order to test this hypothesis, 50 new geochemical and isotopic data from igneous samples, mostly of Triassic units cropping out in northern Chile (24°30'-30°S), were studied and compared to available data of ~500 Late Paleozoic to Late Jurassic igneous rocks from north-central Chile/Argentina. The geochemistry suggests that the magma generation was invariably controlled by fluid induced melting of a depleted asthenospheric mantle source in a subduction setting. However, our data show systematic shifts in specific geochemical parameters that are linked to the extent of lithosphere in the magma sources as well as to crustal thickness. The ϵ_{Nd} decreases with time from Carboniferous (-8 to -2, >95%) to Jurassic (0 to +6, >95%), a variation that is coupled to Sr and Pb isotope data, although these systems are more prone to post-magmatic homogenization due to hydrothermal alteration processes which are common in the Andean rocks. The previous observations are supported by the LaN/YbN ratios that decrease from 4.0 at ca. 300 Ma to 1.5 at ca. 200 Ma. This shift suggests that the crust beneath the magmatic arc may have thinned from the Carboniferous to the Early Jurassic, involving loss of the lithosphere at some time during the Triassic. Either delamination of the arc roots or stretching of the lithosphere are likely scenarios. The Cordilleran geology (28°-29° S) indicates major tectonic changes during the Early Triassic, with evidences of extensional tectonics onset of extensional basins and large scale exhumation of basement and Early-Middle Triassic plutons, both covered by Late Triassic sequences. This large amount of uplift and exhumation processes relates to changes of buoyancy of the lithosphere triggered by partial delamination of lithosphere rather than crustal stretching.

Mélange formation at the slab-mantle interface as a key process in the generation of arc magmas: geochemical evidence

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Content

In subduction zones, sediments and hydrothermally altered oceanic crust, that together form part of the subducting slab, contribute to the chemical composition of lavas erupted at the surface to form volcanic arcs. In the classic models, transport of this material from the slab to the overlying mantle wedge is thought to involve discrete melts and fluids that are released from various portions of the slab.

However, recent studies of exhumed high-pressure mélange zones that represent the dynamic interface zone between the subducting slab and the overlying mantle have suggested that mechanical mixing of solid materials may play a key role in geochemical mixing. This newly formed mélange material is thought to be the source for the magmas produced in subduction zones [1].

This mélange hypothesis has recently gained significant support from our meta-analysis of geochemical data from eight globally representative arcs [2]. This analysis shows that melts and fluids from individual slab components cannot be responsible for the formation of arc lavas. Instead, the data is compatible with the mélange models that first invoke physical mixing of slab components and the mantle wedge, before arc magmas are generated.

[1] Marschall & Schumacher (2012), *Nature Geoscience*, 5: 862–867. [2] Nielsen & Marschall (2017) *Science Advances*, 3: e1602402.

The behaviour of Sn and In during mantle melting and crust formation

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Content

Among the moderately to highly volatile elements, Sn and In are particularly interesting because of their geochemical properties. Tin is prevalent in two oxidation states (2+ and 4+) and behaves like a lithophile element during partial mantle melting, being similarly incompatible as the MREE. Indium is more compatible than Sn, behaves chalcophile, and has a crust/mantle enrichment factor of three. Supposedly constant Sn/Sm of 0.32 and In/Y of 0.003 in mantle-derived basalts were considered representative of Earth's primitive mantle (1, 2) and were thus subsequently utilized in estimates of depleted and primitive mantle abundances (e.g., 3, 4). However, more recent Sn-In data for igneous rocks appear to indicate that these element ratios are fractionated during mantle melting with subduction zone processes causing the strongest fractionations.

We present a comprehensive dataset of high-precision Sn and In concentrations for well-characterized samples from Earth's major silicate reservoirs, including mantle peridotites, MORB, intraplate basalts, sediments, as well as a large suite of subduction zone basalts. Concentrations of Sn and In were obtained on the same digestions using isotope dilution and MC-ICP-MS, achieving 2RSD of $\pm 4\%$ for Sn and $\pm 0.5\%$ for In as estimated from replicate digestions of reference materials.

During partial mantle melting beneath mid-oceanic ridges, the Sn content correlates with the degree of partial melting of the mantle source, where Sn and In are mainly controlled by clinopyroxene. In subduction zones with sediment-dominated source enrichment (e.g., the Aegean arc), Sn enrichment is controlled by the magnitude of sediment contribution whereas In concentrations are virtually invariant. As such, the very high and variable Sn/In values of subduction zone basalts (Sn/In of 40-80 compared to 15 for BSE) correlate with their Sr-Nd-Hf isotopes compositions. Our preliminary results imply a rather uniform Sn/Sm of ~ 0.27 for the mantle source(s) of MORB, whereas Sn/Sm values in subduction zone basalts are indeed variable and become highly fractionated, to values as high as 1.

(1) Jochum et al., 1993; (2) Yi et al., 1995 (3) Salters & Stracke, 2004; (4) Palme & O'Neill, 2013

The budget of High Field Strength Elements in IBM forearc boninites and tholeiites, IODP Exp. 352

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Content

During IODP Expedition 352, a complete section of boninites and tholeiites was drilled in the Izu-Bonin (IBM) forearc, which is thought to represent the earliest phase of subduction initiation. Similar boninite-tholeiite associations are common constituents of ophiolites. Consequently, a detailed investigation of the IBM forearc can shed new light on ophiolite genesis. We performed high precision measurements of the extended HFSE-group (W-Nb-Ta-Zr-Hf) and Hf-Nd isotope data for 32 boninites and tholeiites from IODP Expedition 352, which in conjunction with conventional trace element and isotope data allows to study the mass transfer, mantle depletion processes, and HFSE mobility in subduction components.

The boninites and tholeiites are distinct in Hf-Nd isotope compositions, Zr/Hf and Zr/Nb, whereas both suites overlap in Nb/Ta (12-16), W/Th (0.073-0.70) and Ta/W (0.59-9.0). Our initial data suggests that the tholeiites originate from a severely more depleted mantle source, which is evident from lower Zr/Hf (~29) and more radiogenic Hf isotopes (ϵ_{Hf} of +20 to +24) than found in the boninites (Zr/Hf=32-34; ϵ_{Hf} of +13 to +18). As this appears in general contrast to current models of boninite petrogenesis, we argue that the generation of Exp. 352 boninites supposedly involved a higher contribution of slab components that refertilized their depleted mantle source. MORB-like Nb/Ta suggest a minor contribution of slab melts that typically exhibit more fractionated Nb/Ta (König et al., 2010; Münker et al., 2004). We regard slab fluids as a more important component during boninite genesis, consistent with higher Ba/Th and higher W/Th values of some boninites compared to the tholeiites. However, with increasing temperatures and pressures slab fluids can behave highly siliceous and transport significant amounts of HFSE and Th (Kessel et al., 2005) which are traditionally considered immobile.

Kessel et al. 2005. *Nature* 437, 724-727.

König et al. 2010. *GCA* 74, 684-704.

Münker et al. 2004. *EPSL* 224, 275-293.

Tonalite melts from mafic oceanic crust on Fiji: Analogues for Archean crustal growth?

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Content

The generation of felsic melts within modern oceanic crust is less voluminous than in the Archean, and it is debated whether such melts can serve as modern analogues for formation of Archean TTGs (e.g. [1]). Interestingly, voluminous felsic plutons from Fiji are calc-alkaline and show Archean TTG characteristics. We present combined trace element, high precision HFSE and Hf-Nd-Sr isotope data for felsic Fijian plutons. These tonalites are divided into LREE-enriched, LREE-depleted, and evenly REE-enriched suites. In line with their mafic host rocks, all tonalites exhibit “pacific” type Hf-Nd isotope compositions [2]. Zr/Hf range from 23-39, and Nb/Ta (9-16) decrease with increasing LREE. The LREE-enriched suite resembles Archean TTGs in its elevated Zr/Hf and low Nb/Ta (32-39 and 9-13; [3]). Petrogenetic modeling suggests that the LREE-depleted and evenly enriched tonalites represent products of fractional crystallization from island-arc tholeiitic (IAT) and tholeiitic melts, respectively. In contrast, the LREE-enriched rocks are produced by dehydration melting of IAT in the presence of amphibole. In general, formation of high volumes of tonalites via melting of thickened oceanic crust is still possible, even though some typical “Archean” traits are lacking, such as equilibrium with residual garnet or rutile (TTGs with high Nb/Ta).

[1] Willbold et al. (2009) EPSL 279, 44-52. [2] Todd et al. (2012) EPSL 335-336, 180-194. [3] Hoffmann et al. (2011) GCA 75, 4157-4178

Volcano-tectonics at the northern terminus of the Liquine-Ofqui Fault Zone, Southern Volcanic Zone, Argentina

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Content

Most magmatic arcs form at plate margins characterized by oblique convergence. Components of margin-parallel shear in the upper plate are resolved by distributed or localized deformation. The latter results in the formation of distinct faults characterized chiefly by strike-slip. Despite significant advances in our understanding of magmatic processes in obliquely convergent tectonic settings, it is unclear to what extent the local configuration of principal stresses as well as orientation, patterns and kinematics of faults drive volcanism. To better understanding these volcano-tectonic relationships, we investigate neo-tectonic deformation spatially associated with magmatic centers at the northern tip of the dextral transpressive Liquine-Ofqui Fault Zone (LOFZ) in the Southern Andean Volcanic Zone.

In particular, we examined the orientations of volcanic vents and the kinematics of mesoscopic shear faults spatially associated with Copahue Volcano. Copahue is located at the northern tip of the NE-striking Lomín Fault, a secondary dextral strike-slip fault connected to the northern LOFZ terminus. The shape of the volcano, its summit craters, hydrothermal vents and syn-glacial fissures are aligned in NE-SW direction, i.e., crudely parallel to the Lomín Fault. Near the volcano, this fault is characterized by a strong preferred orientation of mesoscopic brittle shear faults. Andesitic pillow lavas adhere to syn-glacial vents of the volcano.

Inversion of brittle shear faults at Copahue indicates that principal stresses are rather variable and at variance with the overall NE-SW directed stresses elsewhere at the LOFZ. Such heterogeneity of stress axes is known from experimental studies of stresses at fault termini. In case formation of Copahue Volcano is indeed associated with activity of the Lomín Fault, magma ascent may have been facilitated by brittle faults formed in front of the NE-ward propagating Lomín Fault. This volcano-tectonic scenario may also account for the NE-ward migration of hydrothermal zones, summit craters of Copahue, tremor epicenters and the 3.8 Mw earthquake epicenter of March 12, 2015. The scenario explains also the spatial concentration of NE-striking, syn-glacial (ca. 30 ka) vents characterized by basaltic pillow lavas and, last not least, for the NE-SW elongation of the volcanic edifice. Finally, the scenario provides an alternative explanation to Nakamura's (1977) hypothesis for the formation of topographically elongate volcanoes.

Session 2.6: High-resolution geochronology and isotope tracing of high-temperature geological processes: Poster

Session 2.6: High-resolution geochronology and isotope tracing of high-temperature geological processes: Poster

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Calcium isotope fractionation in ocean island basalts

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Content

Low-temperature mass-dependent Ca isotope fractionation in sedimentary rocks and calcareous organisms have become useful proxies for oceanic Ca budget reconstructions, trophic level indicators, nutrient cycling in soils, or biomineralisation processes. Calcium isotope fractionation at high temperatures is less pronounced, but up to 1‰ equilibrium isotope fractionation is observed between constituent minerals in silicate rocks. Moreover, stable Ca isotope ratio variability on the order of 0.5‰ in ocean island basalts may reflect recycling of ancient carbonates into the deep mantle, indicating that subduction of carbonate sediments may influence the global Ca and C cycles. However, owing to comparatively large equilibrium Ca isotope fractionation between mantle minerals, partial melting of mantle peridotite or eclogite may also contribute to the Ca isotope variability observed in oceanic basalts.

Here, we present bulk rock Ca isotope analyses on several ocean island basalts, including St. Helena, Gough, Tristan da Cunha, Iceland and the Cook-Austral islands as well as mineral separates of Iherzolite and eclogite mantle xenoliths, determined by double-spike thermal ionization mass spectrometry (TIMS) at the Westfälische Wilhelms-Universität, Münster, Germany. The mineral separates show inter-mineral fractionation, which is interpreted as function of Ca-O bond length of the respective phases, showing decreasing $\delta^{44/40}\text{Ca}$ with increasing bond length. Calcium isotopes of whole rock ocean island basalts range from 0.66 to 1.09‰ (relative to SRM 915a), in good agreement with previously reported data in oceanic basalts. Using our new inter-mineral fractionation factors for modeling, partial melting of mantle peridotite can account for 0.3‰ variability in Ca isotope composition of ocean island basalts. The remaining variability seen in the ocean island basalts is most likely related to magmatic differentiation or mantle source heterogeneities.

Compositional control on Pb-in-apatite diffusion: implications from LA-ICP-MS element mapping and LA-MC-ICP-MS U-Pb analysis for thermochronology

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Content

High temperature (>350°C) U-Pb thermochronometers utilise accessory minerals such as apatite and assume that daughter isotopes are lost by thermally activated volume diffusion while the parent remains immobile. Studies exploiting such behaviour have been successfully used to reconstruct thermal histories spanning several hundred million years. However, outliers in date (ID-TIMS) vs diffusion length space are frequently observed, and grains are found to be either too young or too old for expected thermal history solutions using the diffusion data of Cherniak et al. (2010). These deviations of single grain apatite U-Pb dates from expected behaviour can be caused by a combination of i) metamorphic (over-)growth, ii) fluid-aided Pb mobilisation during alteration/recrystallization, iii) parent isotope zonation, iv) metamictisation, and v) changes in diffusion length with time (e.g. fracturing). While some studies suggest that U distribution alters the effective diffusion length scale (e.g. in (U-Th)/He systematics, Farley et al., 2011), we observe in-situ apatite U-Pb profiles that cannot be fitted using a single set of diffusion parameters even if parent distribution is accounted for and under the assumption that volume diffusion controls the U-Pb dates. We present a large data set where we compare apatite U-Pb ID-TIMS-(TEA) data with LA-ICP-MS element maps and in-situ apatite U-Pb LA-MC-ICP-MS dates. We observe that the distribution of U and Th is very similar to the distribution of REE, but minor elements such as Mn and Fe have different distribution patterns. The investigated apatites are strongly enriched in Mn and Fe (up to 8000ppm and 4000ppm, respectively). The established diffusion parameters for Mn suggest that Mn-in-apatite has a higher (595°C) closure temperature relative to Pb-in-apatite (496°C) for a crystal with a radius of 100µm and a cooling rate of 10°C/Ma, with Mn occupying the same crystallographic position as Pb (Ca1 and Ca2 in apatite). High concentrations of Mn may therefore result in retarded Pb diffusion by creating barriers or zones which require more energy (effectively increasing ΔE) to facilitate ion exchange. We present LA-ICP-MS element maps of U, Th, Mn and Fe and U-Pb profiles from same grains to seek relationships between Mn and Fe concentration and U-Pb date relative to predictions from grain size (diffusion length scale) and parent distribution.

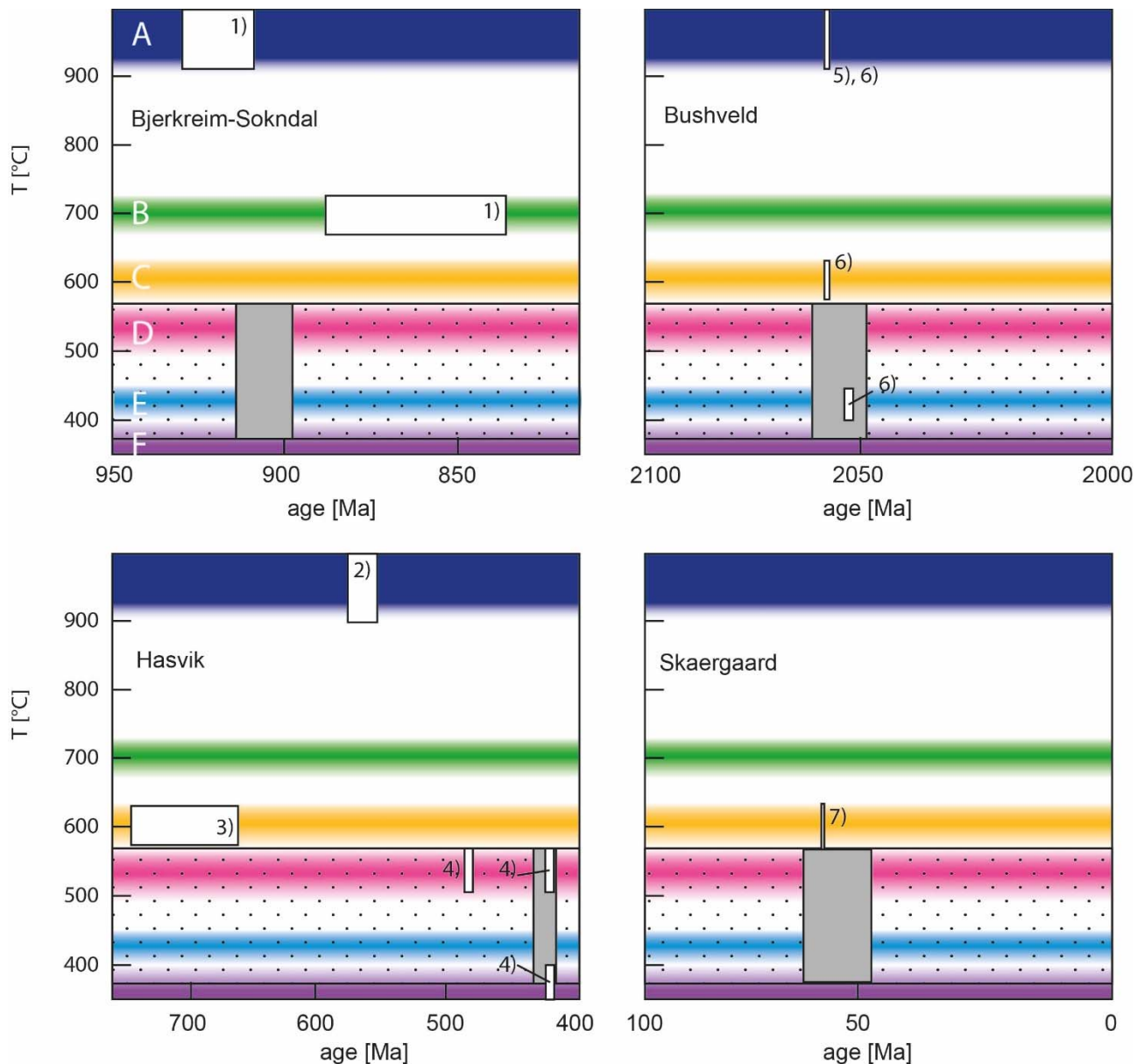
LA-Q-ICP-MS apatite U/Pb geochronology with application of Pb-isotopes in feldspar

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Content

Apatite geochronology is a versatile method for providing age constraints on the formation and metamorphic overprinting of rocks due to its low closure temperature. A widespread technique in U/Pb geochronology is LA-ICP-MS applied to a variety of minerals. Apatite U/Pb geochronology, in contrast to e.g. zircon, is compromised by variable amounts of common Pb incorporated into the crystal during growth. Therefore, the initial Pb isotopic composition needs to be estimated to obtain accurate and precise age information from apatite. Two approaches are common, one being the estimation of common Pb from a Pb evolution model and the other being the measurement of a coexisting mineral phase that tends to incorporate Pb but not U, e.g. feldspar. In this study we evaluate the application of quadrupole mass spectrometry for apatite U/Pb geochronology combined with Pb isotopic measurements in feldspar and compare the results with modelled initial Pb isotopic compositions. The resulting age information is accurate and precise despite using plagioclase rather than K-feldspar as is normally used to define initial Pb isotope compositions. We observe that LA-Q-ICP-MS for apatite U/Pb geochronology produces precise and accurate data, independent of the method applied for initial PbC – feldspar analyses or Stacey and Kramers calculation (Figure1).



Temperature-age (207Pb corrected) relations of the four investigated intrusions.

Analyses of feldspar for initial PbC is compromised by the feldspar composition. While measured Pb isotopes in K-feldspar are accurate at < 0.8% deviation from published values, analyses of plagioclase show a deviation from Stacey and Kramers model composition. Although measured initial PbC and calculated PbC deviate, neither the 207Pb-corrected age nor the anchored Tera-Wasserburg intercept age is affected and ages for the different initial PbC overlap within error. For samples in the age range between 400 and 900 Ma, the anchored Tera-Wasserburg intercept age is more accurate and precise. Geochronology of young samples like 90-22-467 from the Skaergaard intrusion can be compromised by weak variations of radiogenic Pb/common Pb ratios. Nevertheless, it should be noted that this does not limit the analytical technique to samples older than this (56 Ma) as we could produce an accurate and precise age for Durango apatite (31 Ma).

Laser ablation split stream (LASS) between three inductively coupled plasma mass spectrometers for zircon petrochronology

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Content

In laser ablation analysis the choice of which type of ICP-MS to use is dependent on the application. Chronometers requiring epsilon-level precision need to be measured with a multi-collector ICP-MS; for determination of the rare-earth elemental (REE) composition, a quadrupole-based instrument is sufficient. The development of LASS, where the laser aerosol is split between two ICP-MS instruments, has allowed two isotopic (or trace elemental) systems to be measured simultaneously from a single ablation site. A primary LASS application is zircon and monazite petrochronology, [1] for which two separate chronometers, U-Pb and Hf, and REE concentration are often collected. By determining both the chronometers and the elemental composition for a single ablation site, a direct link between each can be established.

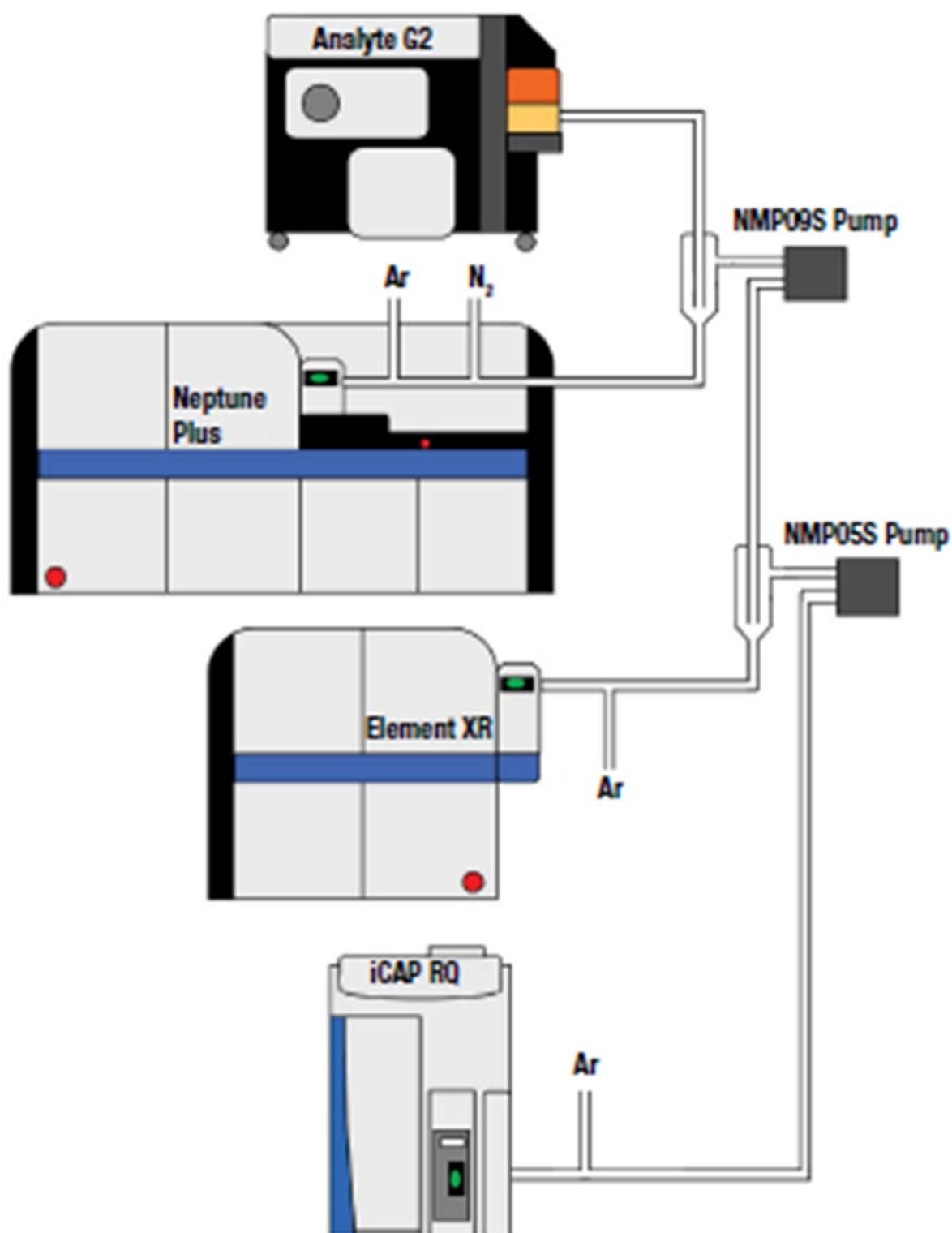


Figure 1 - Schematic of LASS to three ICP-MS systems.

Here the LASS analysis of common reference zircons combining three different ICP-MS instruments – Thermo Scientific™ Neptune Plus™ MC-ICP-MS (for Hf), Thermo Scientific™ Element XR™ HR-ICP-MS (for U-Pb), and Thermo Scientific™ iCAP™ RQ ICP-MS (for REE) – is reported. The laser ablation gas steam was split between the three ICP-MS, following the approach outlined by Frick *et al.*, [2] using small diaphragm pumps to control the amount of laser aerosol delivered to each ICP-MS system. The pumps are easy to use, cost effective, and widely available, and as such can be applied for routine LASS analysis. ¹⁷⁶Hf/¹⁷⁷Hf ratios were ≈ 100 ppm 1σ for the three sample reference (Plesovice, GJ-1 and Mud Tank) zircons measured. The corresponding U-Pb ages were accurate, within uncertainty, to the accepted values of the

reference zircons. The $^{206}\text{Pb}/^{238}\text{U}$ age of GJ-1 was better than 1.7% 2σ , and the Concordia age was better than 0.5% 2σ . REE concentrations could be measured to a precision level of better than 10% RSD and were in agreement with data from previously reported LASS configurations.

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Session 2.6: High-resolution geochronology and isotope tracing of high-temperature geological processes: Talk

Keynote speaker

A-205

Pb-loss in apatite and high temperature (>350°C) U-Pb thermochronology

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Content

Thermochronometers that utilise radioactive decay are founded on the assumption that daughter isotopes are lost by thermally activated volume diffusion. Previous studies support this assumption over laboratory time-scales, under controlled conditions. However, other authors suggest that the mechanisms that control isotope transport through crystal lattices over geological time-scales are dominated by aqueous fluid flow, and that thermally activated loss is subordinate. We present U-Pb isotopic data (ID-TIMS) from apatites extracted from Triassic acidic anatectites from northwestern South America. The apatites have variable grain sizes and are used to test the hypothesis that thermally activated volume diffusion over geological timescales controlled the loss of Pb. Confirmation of the hypothesis will establish the apatite U-Pb system as a reliable thermochronometer. Negation of the hypothesis would suggest that age variations may reflect interaction with aqueous fluids during retrogression or growth during prograde metamorphism, invalidating their use as a thermochronometer. Time(t)-Temperature(T) paths are generated by inverting ID-TIMS dates and grain sizes using the Pb-in-apatite diffusion parameters of Cherniak et al. (1991), and best fit models are sought from several million iterations. The accuracy of the best-fit models is tested by comparison with known geological models, as well as by comparing predicted and measured core-rim U-Pb date profiles (LA-MC-ICPMS). Many preferred models require re-heating, which is a consequence of the dispersion of single crystal dates and grain sizes, with respect to the maximum temperature reached. A secondary aim of this study is an investigation of the effects of parent isotope zonation on in-situ U-Pb dates and t-T solutions. Cores enriched in parent isotopes result in longer average diffusion lengths and higher bulk closure temperatures, which cause significant deviations in t-T solutions relative to homogeneous grains. We also investigate the influence of apatite composition and metamictisation on the diffusion properties of Pb in apatite, and thus t-T solutions. Thermochronological studies usually assume that mineral boundaries have a zero concentration of daughter isotope and thus represent an infinite reservoir. This assumption is tested by comparing predicted and measured in-situ U-Pb dates using boundaries that are in equilibrium with host phases according to a range of partition coefficients.

Calibration of suitable garnet reference materials for in situ lithium isotope analyses

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Content

Abstract

In situ measurements of the isotopic composition of lithium in natural garnet has so far not been carried out, because of the lack of suitable reference materials for in situ techniques, such as SIMS or LA-ICP-MS. A general issue with determining Li isotopic compositions is, how garnet major element composition influences the Li isotope instrumental mass fractionation in SIMS (chemical matrix effect). In this study we aim to establish a set of 15 homogeneous, Li bearing natural garnets from world wide localities. They cover a wide range of compositions from almandine to pyrope (Mg# 16-97) and are suitable for the calibration of Li isotope analyses by in-situ methods. We characterized all garnets for their major, minor and trace element compositions, by EPMA and LA-ICP-MS, as well as for their Li contents and Li isotopic homogeneity by SIMS. The Li isotopic compositions of the garnets were determined by solution MC-ICP-MS after chemical purification. We selected samples that were homogeneous in major elements better than ± 1 wt % (2 SD), and which showed a Li isotopic variability of less than ± 2 ‰ (2RSD). Our resulting calibration curve will be valid for garnets, composed of at least 85 % pyrope + almandine component. Since most garnets from peridotites and eclogites fall into this range, our calibration will be applicable for the investigation of zoned garnets and their Li and Li isotope profiles. This set of reference materials enables us, for instance, to unravel metasomatic events in the mantle and the metamorphic history of subducted slabs during subduction and exhumation.

Electron microprobe Th-U-Pb monazite dating of Devonian metamorphism in Münchberg and Frankenberg allochthonous units in the Saxothuringian Zone

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Content

The ages of metamorphism in the allochthonous domains of the Saxothuringian Zone (Erzgebirge, Münchberg Massif, Frankenberg Massif) are critical for resolving the complex Variscan geodynamic evolution. Especially in fine-grained metamorphic rocks, the geochronology is hampered by several methodological aspects. For such rocks, the in-situ chemical Th-U-Pb monazite dating by electron microprobe has demonstrated its high potential to resolve polyphase metamorphism^[1]. The method is based on the premise that monazite inherits negligible amounts of common Pb and that radiogenic Pb is retained due to very low diffusion rates at high T^[2]. Monazite (Th, U, Si, LREE, Y, Ca)PO₄ crystallises at greenschist to granulite-facies conditions in Ca-poor aluminous pelites and is also an accessory phase in peraluminous granitoids. The Th-U-Pb and related element compositions may refer to the time of monazite crystallisation and/or re-crystallisation and dissolution/reprecipitation during thermal and fluid-mediated events. Monazite in various microstructures and at grain sizes of 10-50 µm, rarely up to 80 µm, has been detected by automated SEM methods in polished thin sections from phyllites, garnet micaschists and orthogneisses. After detailed BSE imaging of the monazite grains, an electron microprobe Th-U-Pb monazite dating routine was performed with a JEOL-8530F, enclosing analysis of HREE. Garnet micaschists in the Liegendserie of the Münchberg Massif yielded monazite ages between 390±8 Ma and 377±6 Ma, from isochrons defined by single populations. There are also garnet micaschists which display a dominant population at 379±5 Ma and a minor one at 312±13 Ma, interpreted as a metamorphic overprint. An exceptional age of 498±19 Ma in a garnet micaschist could be explained by a regional contact metamorphism, as biotite orthogneiss yielded monazite of 503±12 Ma, interpreted as a magmatic crystallisation age. The Devonian monazite ages match K-Ar hornblende data from various metabasites in the Münchberg Massif^[3]. In the basement unit of the Frankenberg Massif, the orthogneiss samples yielded monazite ages between 515± 11 Ma and 507±17 Ma. Data from the Frankenberg phyllites range at 365±8 Ma, thus matching also the ages from the Münchberg Massif. Geothermobarometry with garnet assemblages in the micaschists and phyllites then allows to relate the pressure-temperature evolution to the pattern of monazite Th-U-Pb ages and mineral chemical characteristics.

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Petrology and geochronology of mylonitic high-pressure granulites from the Variscan Schwarzwald (SW Germany)

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Content

Upper crustal rocks with relics of HP mineral assemblages are widespread within the internal zones of the European Variscan Belt. The discovery of diamond and coesite in felsic granulites of the Bohemian Massif documents the subduction of continental crust to mantle depths around 340 Ma, at least in this part of the orogen [1] [2]. HP granulites of the Central Schwarzwald Gneiss Complex (CSGC), which is part of the Moldanubian Zone, were previously reported to document UHT conditions [3]. The common association with small bodies of orogenic peridotite indicates interaction between crust and mantle, possibly during continental subduction. However, unlike the Bohemian Massif, no UHP relics were found in the Schwarzwald. Felsic and metapelitic HP granulites occurring in mylonitic shear zones within the CSGC record the peak assemblage garnet+kyanite+ternary feldspars+rutile+quartz±biotite and an amphibolite facies overprint. Further, the presence of partial melt during both conditions is indicated by recrystallised melt inclusions in garnet and symplectitic matrix textures, respectively. Thermodynamic modelling indicates peak pressures of 1.4–1.8 GPa and temperatures >850 °C, while Zr-in-rutile and ternary feldspar solvus thermometry gives 860 °C and 950–1000 °C, respectively. HP metamorphism was followed by near-isothermal decompression <0.6–0.7 GPa and cooling to temperatures ≤700 °C. Subduction to mantle depths may account for (U)HT conditions. However, these lithologies are strongly overprinted during their exhumation, involving partial melting, recrystallisation and partial diffusional reequilibration of mineral phases. Therefore, peak conditions and especially peak pressures relying on rare characteristic phases (such as diamond) are difficult to constrain. SIMS U–Pb dating of zircon in matrix and as inclusions in the HP phases garnet or kyanite was carried out using the CAMECA ims 1280 at Heidelberg University. Metamorphic zircon (low Th/U of 0.01–0.06) yielded a concordant age of 344±2 Ma, interpreted to date the HP metamorphic event. The obtained age is similar to the age of continental subduction in the Bohemian Massif and HP granulite facies metamorphism in other parts of the orogen.

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Tracking nitrogen transfer through the Earth's crustal reservoirs

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Content

Nitrogen (N) is the sixth most abundant element in the solar system, the main component of the Earth's atmosphere and an essential element for the evolution of life on Earth. The majority of the Earth's N is stored in the solid Earth [1] and N is a useful geochemical tracer for mass exchange between atmosphere, oceans, crust and mantle over time. Knowledge of the distribution of N in the major crust and mantle reservoirs and of the N isotopic compositions of these reservoirs is necessary to fully understand modern and long-term N cycling on Earth and to track any interaction between these reservoirs. In this contribution, we address how subduction of N in oceanic crust and storage of N in deep continental crust are relevant for contemporary N cycling.

The N subduction flux in deeply (50-90 km depth) subducted oceanic crust is constrained by N contents of 2-20 ppm in eclogites [2]. The N isotopic composition of the eclogites varies from $\delta^{15}\text{N}_{\text{air}}$ values of -1 to +8 ‰. The major host mineral of N in metamorphosed oceanic crust is white mica, where N occurs as NH_4^+ and replaces K^+ . Breakdown of white mica during high-pressure fluid-rock interaction can liberate N into fluids [3]. Both N concentration and N isotopic composition of the eclogites overlap with data for altered oceanic crust, suggesting deep retention of N in subducting oceanic crust. Hence, subduction can potentially deliver isotopically heavy N into the mantle and cause a long-term decrease in N in the Earth's atmosphere.

We have analyzed metamorphosed mudstones from the Ivrea Zone (Western Alps, Italy) to constrain the role of the deep continental crust as major N reservoir and to understand how high-grade metamorphism and partial melting affect the N budget and N isotopes. Nitrogen concentrations decrease from up to 200 ppm at medium grades to ~10 ppm at high grades, consistent with decreasing modal amounts of biotite and loss of N in restites via biotite dehydration melting. The positive $\delta^{15}\text{N}_{\text{air}}$ values of these rocks agree well with values observed in modern sedimentary organic matter, but there is a systematic decrease with increasing metamorphic grade. These results highlight that ancient N biogeochemical signatures can be significantly modified by high-grade metamorphism.

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Session 2.7: Rates and timescales of magmatic and metamorphic processes: Poster

Session 2.7: Rates and timescales of magmatic and metamorphic processes: Poster A-429

Age constraints on high-pressure metamorphism and sedimentation in the Central Indonesian Accretion-Collision Complex (Luk Ulo, Java)

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Content

The Central Indonesian Accretionary Collision Complex (CIACC) is characterized by a complex geodynamic history including seafloor spreading, subduction zone processes, clastic sedimentation and the accretion of Gondwana-derived continental fragments onto the SE-Sundaland margin. A key feature of the CIACC are several occurrences of HP/LT rocks on the islands of Java, Sulawesi and Kalimantan. Previous studies have documented the general field relationships as well as the main petrological and geochemical characteristics of the CIACC. However, both protolith ages and the timing of individual P-T stages affecting the HP/LT rocks remain poorly constrained. Published K–Ar ages broadly indicate Cretaceous metamorphism (110–124 Ma), but additional age data are crucial for a detailed understanding of the metamorphic P-T-t-d paths and to unravel spatiotemporal relationships between the widely separated pre-Tertiary accretionary complexes of central Indonesia. In this study, we report new geochronological data (Rb–Sr, U–Pb) for eclogites, blueschists and clastic metasediments from the Luk Ulo (central Java) and Barru Complexes (SW Sulawesi), respectively. In the Luk Ulo region eclogites and blueschists occur as isolated blocks in a chaotic mélange that is exposed along small beds of the Muncar river system. Judging from previous field descriptions, the outcrop conditions have significantly deteriorated in recent years. Compared to other Indonesian accretionary complexes, e.g. Bantimala complex (SW Sulawesi), well-preserved HP/LT rocks are rare. We found little material suitable for geochronological studies. At this point only Rb–Sr data is available. Multipoint internal isochrons of largely preserved eclogites and blueschists (phengite, omphacite, glaucophane, epidote) yielded well-constrained metamorphic ages of 117.5 ± 0.6 Ma, 118.2 ± 0.6 Ma, 118.7 ± 0.6 Ma and 119.1 ± 0.8 Ma, respectively. Work in progress focuses on pseudo-section modelling of the dated samples to better link ages with P-T data. In order to characterize litho- and/or tectonostratigraphic correlations across the larger region, next we will focus on U–Pb geochronology of detrital zircon populations. The overall aim of our study is to establish an improved scenario for the temporal evolution of the central Java-subduction regime and to deepen our understanding of the relationship to other HP/LT occurrences of the CIACC.

Keywords: Eclogite, blueschist, Rb–Sr geochronology, high-pressure metamorphism

Automated mineralogy improving crystal size distribution studies

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Content

Crystal size distribution (CSD) studies require the knowledge of geometric parameters, at the very least the length of crystals. Automated phase identification techniques such as the Mineral Liberation Analyzer (MLA) can provide these data of entire thin sections.

The MLA combines automated data acquisition and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. Based on back scattered electron (BSE) images individual grains are automatically recognized and their mineral phase is identified by subsequent automated EDX analyses. The resulting image of a thin section shows spectrally homogeneous mineral grains in a color scheme of choice and enables direct extraction of geometric data.

The disadvantage of using BSE images for grain analysis is the inability to segment adjacent grains of the same mineral phase. The lack of contrast results in artificially larger grains, distorting the CSD curves. To overcome this problem we used the classified MLA image as an overlay for optical microscopic images. The phase identification of grains only a few μm in size becomes possible and their geometric parameters can be determined. The improved lower boundary of crystal sizes available for CSD studies facilitates the recognition of subsolidus processes (e.g. Ostwald ripening) that potentially affected the rock texture.

We further used the classified image in combination with various optical images of thin sections (plane polarized light, crossed polarized light with different orientations, gypsum plate addition) and electron backscatter diffraction (EBSD) data. On these stacked images, edge detection methods and region-based growing algorithms were applied in order to digitize the grain boundaries. The distinct phase contrast of MLA images significantly enhances the effectivity of image segmentation. The resulting completely digitized and segmented thin section allows the automated extraction of geometric parameters. In addition to crystal length, these include perimeter, area, form factors and the length of shared boundaries between specific minerals.

Characterization of ultramafic, coarse crystalline lenses sheared into poly-metamorphic meta-sedimentary rocks of the Stora Le-Marstrand Formation near Kungälv, SW Sweden

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Content

In sequence of metamorphic events the Stora Le-Marstrand Formation is dominated by meta-sedimentary rocks associated with different suits of metamorphic magmatic rocks. Within these units coarse-crystalline ultramafic rocks often occur as boudinated lenticular bodies.

In the context of a Bachelor thesis a ca. 1 km² large area ca. 15 km NW of Kungälv, near Skåra, SW Sweden has been mapped. In this area an ultramafic complex, segmented in three NE to SW striking lenses appeared which are sheared into the meta-sedimentary rocks of the Stora Le-Marstrand Formation. These lenses are orientated parallel to the penetrative foliation of the meta-sediments. Close to their margins, these ultramafic boudins have been transformed into amphibolite-like rocks due to a retrograde metamorphic overprint. The occurring amphibolites are characterized by smaller crystal sizes. They are orientated parallel to the foliation of the surrounding meta-sediments and contain a higher proportion of garnets which show an oriented growth direction. They can be referred as shear sense indicators that can be used to determine the original direction of deformation. Although the coarse-crystalline inner cores of the ultramafic lenses show strong magnetic characteristics this feature seems to lack at the edge of these bodies.

Furthermore, this study aims to clarify if all three lenses originate from one complex or represent different ultramafic bodies. Therefore, oriented samples have been taken from all three lenses and have been described macroscopically and were later investigated under the optical microscope. First results Show orthopyroxene as well as amphibolite as the main mineral components of the coarse grained ultramafic rocks. They are accompanied by higher contents of chlorite in the marginal amphibolite parts of the lenses. The ultramafic rocks also have high levels of magnetite, which are the source of the strong magnetic features.

Additionally, poikilitic textures indicate a high grade metamorphic overprint of the ultramafic rocks. Oriented growth of garnet and amphiboles in the margins of the ultramafic bodies, furthermore, indicate high metamorphic conditions during the shearing process. Similar mineral content as well as similar structural features imply a similar origin for all three lenses.

Geochronology and Zr-in-rutile thermometry of high-pressure/low temperature metamorphic rocks from the Bantimala Complex, SW Sulawesi, Indonesia

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Content

Across the Indonesian archipelago pre-Tertiary eclogites and/or blueschists only are known from a few widely separated occurrences on Java, Sulawesi and Kalimantan (Luk Ulo, Bantimala, Meratus), including a rare occurrence of ultra-high pressure rocks on Sulawesi. It had been argued that these outcrops represent isolated remnants of a single Cretaceous subduction system, extending over ca. 1500 km, but to this point there is no unambiguous evidence supporting this interpretation. Establishing a precise and accurate timeframe for the P-T-t-d evolution of the Indonesian subduction complexes is a pre-requisite for in-depth understanding of the individual metamorphic histories and for assessment of possible regional litho- and/or tectonostratigraphic correlations. The focus of our study is on the Bantimala complex, SW Sulawesi. The HP rocks occur as rounded tectonic blocks within a mélangé that is exposed along the Bantimala, Pateteang and Cempaga rivers. The block assemblage mostly comprises eclogites and various blueschist-facies rocks (up to ca. 3 m). This material is mainly well-preserved and shows little signs of low pressure overprinting. The general field and petrological framework of the study area has been outlined in previous studies, but the temporal evolution is as yet poorly constrained. Available age data only comprise K–Ar results that range between 132 ± 7 Ma and 113 ± 6 Ma (e.g. [1]). In order to evaluate the relevance of the K–Ar ages (contamination by excess Ar?) and to obtain a more detailed picture of the metamorphic evolution, we use a multimethod geochronological approach. Up to now Rb–Sr dating of one eclogite and three epidote-glaucophane felses has been completed. Well-constrained multipoint internal isochrons (based on different grain size fractions of phengite, omphacite, glaucophane and epidote) indicate ages of 122.3 ± 0.7 Ma, 124.9 ± 0.6 Ma, 124.2 ± 0.6 Ma, 126.7 ± 0.8 Ma, respectively. In order to complement existing petrologic datasets and to clearly characterize samples selected for geochronology we have applied Zr-in-rutile thermometry (8 samples) that yielded temperatures in the 530–555 °C range. Work in progress focuses on U–Pb zircon geochronology of eclogites and on pseudosection modelling to better characterize the metamorphic evolution of the dated samples.

Keywords: Indonesia, blueschist, eclogite, Rb–Sr geochronology, high-pressure metamorphism

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Heritage and residence of olivines based on modelling elemental diffusion profiles from the 2015 eruption at Piton de la Fournaise, La Réunion

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Content

Diffusion profiles in zoned crystals allow obtaining residence times in volcanic systems given precise knowledge of temperature and diffusivities. The 2015 eruption at Piton de la Fournaise provides the unique opportunity to link zonation patterns and residence times to the seismic signals monitored prior to eruption. The shallow magma reservoir at Piton de la Fournaise consists of a flat magma chamber >2.6 km depth underlain by an extended sill and dyke system. The reservoirs are periodically refilled with mafic magmas from deeper levels.

We measured 59 line profiles in olivines from six quenched lava and tephra samples by electron microprobe from samples of the August-November 2015 eruption at Piton de la Fournaise. We identified three types of compositional zoning: normal, reverse, and complex with wide wavy zonation from core to rim. Two compositions (83.5 ± 0.2 % Fo and 87.5 ± 0.2 % Fo) dominate the cores of olivines that erupted during the first active phase on 15th September 2015. Olivine core compositions vary continuously with on-going eruption to an intermediate level (86.5 ± 0.2 % Fo). At the same time, zoning patterns become more subdued and disappear completely. However, relict Fo-rich cores typical of early olivine compositions were found in all samples. On 31st October low-Fo olivines (77.7 ± 0.2 % Fo) that are compositionally identical to olivines in gabbroic cumulate enclaves were also erupted.

Crystal orientations were determined by electron backscatter diffraction (EBSD) to account for the strong anisotropic diffusion in olivine. Core compositions, zonation styles and calculated residence times distinguish different olivine populations. Different olivine types have different residence times and were derived from (1) newly recharged magma, (2) resident olivine-bearing evolved residual basalts from previous activity (2007-2010) and from still older crystals from the cumulate pile. We compare our diffusion modelling of olivines with those from recent eruptions (2007, 2003, 1986 and 1943) and historical activities (1000 BP and 5000 BP). We observe timescales of 50 to hundreds of years for the residence of olivines derived from cumulates (at $T = 1100$ °C). By contrast, olivines from the shallow plumbing system gave diffusion times from only months to a few years (at $T = 1160$ °C).

Uncertainties in temperature cause large variations in the modelled diffusion times. However, the different timescales for different olivine types and origins remain robust.

Magma residence times from diffusion chronometry on zoned alkali feldspar phenocrysts from the Campi Flegrei caldera (Napoli, southern Italy): the case of Agnano-Monte Spina (4.7 ka) and Campanian Ignimbrite eruptions (39 ka)

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Content

Timescales of igneous processes such as crystallization, mingling/mixing and crystal mush rejuvenation are key to understanding the evolution of crustal magmatic systems, and provide important constraints for volcanic hazard of active volcanoes. We apply Ba-diffusion modelling in sanidine to volcanic deposits of the Campi Flegrei caldera (Southern Italy), one of the most dangerous volcanic areas on Earth. The Campanian Ignimbrite (CI; ~39 ka) caldera-forming eruption is recognized as the largest eruption of the Mediterranean area over the past 200 ka, emplacing at least 300 km³ of trachytic to trachy-phonolitic magma. The Agnano Monte Spina eruption (A-MS; 4.7 ka; ~0.9 km³ D.R.E. of magma erupted) fed by magmas varying from more to less evolved trachyte, is the type-event for a large-size eruption in case of renewal of volcanism in short-mid terms at the caldera.

Sanidine crystals were analysed from these two contrasting eruptions by electron microprobe analysis with particular emphasis on compositional discontinuities near the margins of the crystals. Grayscale swath profiles were extracted from accumulated BSE maps where grayscales are proportional to the Ba content of sanidine.

Diffusion times calculated for outermost overgrowth rims that have grown just prior to eruption onto A-MS feldspar (at 930 °C) and on CI sanidines (at 875 °C) show ranges of ≤60 years and ≤500 years, respectively. A difference in temperature of 50 °C affects diffusion time estimates by 1–2 orders of magnitude.

Even though high temperature implies Ba diffusion faster than in other silicic (e.g. rhyolitic) volcanic systems, we still obtain short diffusion times, and if the gradients were not perfectly sharp initially, these short timescales are in fact maximum values.

Since the modeled compositional profiles relate to the last growth event, the calculated diffusion timescales relate only to processes that affected the last part of the sanidines, whereas the total lifetime of each crystal (as estimated by U-series dating) can be significantly older (6 ka for the CI deposit).

Our results are in agreement with studies showing that there is a relationship between the volume of magma and its residence time. Shorter timescales on A-MS compared to CI sanidines are therefore in agreement with the smaller magma volume erupted at A-MS.

Water transport by subduction: clues from Erzgebirge coesite eclogite

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Content

A key question concerning the water budget of the Earth's mantle is how much water is actually recycled into the mantle by the subduction of eclogitized oceanic crust. Typical hydrous phases in quartz eclogite are not stable in coesite eclogite so that water transport to greater depths should mainly be governed by structural water in omphacite and garnet. Previous, literature data on garnet (and omphacite) of coesite eclogite suggest water contents that vary over orders of magnitude, from a few up to 2000 ppm. The resulting maximum bulk-rock water contents are unrealistically high (wt% level). In contrast, garnet and omphacite from Erzgebirge coesite eclogite imply much lower water amounts that are transported by subduction to >100 km depths. The new data indicate the following amounts of structural H₂O: garnet: 43-84 ppm, omphacite: 400-820 ppm), and bulk rock: ca. 280-460 ppm. Extremely high water contents (up to >1000 ppm) were also found in Erzgebirge garnet, but these are not primary features. They are related to molecular water in fluid inclusions that are attributed to influx of secondary fluid, postdating the metamorphic peak. Fluid influx also caused the uptake of additional structural water in garnet domains in the immediate vicinity of the inclusions. Incorporation of secondary H₂O is only possible in the case of primary water-deficiency implying that, at peak metamorphism, garnet hosted less water than it was able to store. This is insofar astonishing as comparably high H₂O amounts are liberated by the breakdown of prograde eclogite-facies hydrous minerals. Using Erzgebirge quartz eclogite as a template, dehydration of 5-10 % hydrous minerals produces 1500 - 3000 ppm bulk rock water. Apparently, the largest part of the liberated water escaped, probably due to kinetic reasons (sluggish lattice diffusion versus fast diffusion + escape along grain boundaries) and hydrated exhuming UHP slices in the hanging-wall. Depending on the physical conditions, water influx in eclogite during exhumation (i) produces fluid inclusions and simultaneously enhances the content of structural water of nominally anhydrous minerals – as in the Erzgebirge – and/or (ii) it may give rise to retrograde hydrous minerals. In conclusion, our results point to moderate quantities of water (several hundred ppm) that are transported by eclogite to mantle depths beyond 100 km, an amount being equivalent to that in ca. 1 % calcic amphibole.

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A multicomponent diffusion model and experimental calibration of diffusive fractionation of Fe and Mg isotopes in olivine

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Content

Diffusion chronometry by modelling Fe-Mg zoning in olivine is increasingly used to determine time scales of magmatic processes. One of the major caveats of this method is that the inferred time scales rely on the assumptions made for the diffusion model, e.g., the initial composition of the olivine crystal and the boundary condition. It was shown that in-situ measurement of the stable isotopes of Fe and Mg provides additional constraints on the model assumptions because they fractionate by Fe-Mg interdiffusion and the respective effect is strongly sensitive to the diffusive flux present in the crystal (e.g., [1]). However, in these studies diffusion modelling of the fractionation effects is simplified since diffusion of Fe and Mg isotopes is modelled independent of each other, which is incorrect due to charge balance constraints (e.g., [2]). In addition, no experiments exist to date that calibrated the diffusive isotope fractionation of Fe and Mg in olivine.

To improve the diffusion model and obtain experimental constraints on the diffusive fractionation by Fe-Mg inter-diffusion in olivine we applied the multi-component diffusion model of [2] to model natural isotope and chemical profiles in olivine, as well as respective profiles from diffusion experiments. For the diffusion experiments we embedded three crystallographically oriented San Carlos olivine single crystals into a powder mix of San Carlos olivine and ⁵⁷Fe and ²⁵Mg enriched oxide mix. These crystals were annealed at 1195 °C for 165 hours and element and isotope profiles along cross sections of the crystals were analysed by the electron microprobe as well as femtosecond laser ablation ICP-MS, respectively.

The measured chemical and isotope profiles were fitted simultaneously by applying the multi-component diffusion model. Our data document in all cases that Fe isotopes diffuse slightly faster than the Mg isotopes by a factor 2-3. In addition we can show that the magnitude of the fractionation depends strongly on the diffusion direction. For the fastest diffusion direction (c-axis) the fractionation effect is less than half of those of the slower diffusion direction (a-axis). The anisotropy of the diffusive fractionation of Fe and Mg should be considered when modelling natural profiles.

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Complex zoning in olivines of the Shiveluch volcano (Kamchatka)

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Content

Complex zonation patterns in olivine from Shiveluch basalts were studied by electron microprobe. Olivine cores (Fo₈₇₋₉₂) show bell-shaped or flat zonation. In the mantle forsterite first decrease, then abruptly falling with a steeper gradient towards the rim. Fo-Ni relations identify distinct core populations that together form a convex trend in Fo-Ni space. From these different cores, irregular Fo-Ni trajectories meet in a common mantle composition. From there, growth follows the common concave trend in the crystal mantle to the rims. We conclude that cores do not fall on a fractional crystallization trend; in mantles the composition became common and mantle with rim follow typical fractionation trend. We recognize four sequential growth and diffusion events: (1) “core” diffusion at an early stage; (2) “deep” diffusion resulting in variably homogenized cores and forming trend of cores; (3) diffusion between core and mantle; and (4) diffusion at the outermost rim.

Diffusion in the cores at an early stage (1) is observed only in most magnesian rich cores and is described by the analytical solution. “Deep” diffusion in cores (2) is described using Newton's law of cooling. Due to mixing with another melt, there are prominent Ni-inflections between the cores and mantles. The width of the diffusion zone (3) at these boundaries is less for Ni than for Fo, reflecting different diffusion coefficients, allowing to estimate the time after mixing both over Ni and Fo.

Zonation within the mantle towards the rims has smoother gradients for Ni and Fo compared to the gradients at the Ni inflections. This means that the rim gradients cannot be result of a diffusion process only, because the time of diffusion within the outer mantle cannot be longer than at the core-mantle boundary. Rim zonation thus is dominated by growth and this is confirmed by element maps that show narrow growth zones where the width of growth zones increase according to relative diffusivities (4) for P→Al→Cr→Ca→Ni→Fo. Minor element profiles can be extracted as cps-equivalent semi-quantitative values from these element maps. Our data show Fo and trace element zonation reveals a complex history with alternate growth, mixing and diffusion prior to eruption. Elemental maps are essential way to document these processes and form the basis for further diffusion modeling.

Constraining the timescales of evolution of Coorg granulites from Southern India

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Content

In order to understand the timescales of Archean deep crustal processes we have studied mafic granulites from the Coorg Block, South India that experienced a multistage thermal evolution. A sequence of events was identified in an initial two pyroxene granulite (orthopyroxene-clinopyroxene-plagioclase-quartz with minor ilmenite and magnetite). Influx of a silica rich melt (or fluid) is currently represented by veins on an outcrop scale containing quartz-plagioclase and large crystals of orthopyroxene. This event heated the rocks to ~900° C and facilitated the growth of large porphyroblastic garnets (Grt1) (Prp29Alm53Spss02And04Grs12) at ~11 kbar. The garnets are localized near the silicic veins, and textural observations indicate formation by a reaction such as $\text{Cpx} + \text{Opx} + \text{Pl} = \text{Grt1} + \text{SiO}_2$. After some cooling and decompression(?), metasomatism by a K-bearing fluid led to the formation of phases like biotite, followed by their breakdown at ~ 750 °C, 8 kbar according to: $\text{Cpx} + \text{Pl} + \text{Bt} + \text{Qz} = \text{Kfs} + \text{Opx} + \text{Grt2} + \text{H}_2\text{O}$. The second generation garnet is richer in grossular (Prp24Alm54Spss02And02Grs18) and can be seen as both - overgrowths on Grt1 as well as, individual crystals. Subsequently, Grt1 locally breaks down according to $\text{Grt1} + \text{SiO}_2 = \text{Opx} + \text{Cpx} + \text{Pl}$. Compositional zoning formed by diffusion of Fe-Mg has been measured at Grt2-Bt and Opx-Cpx contacts. Modelling of these profiles reveal slow cooling of the rock (1°C/myr) after the formation of Grt2, indicating a long residence at mid-crustal (~ 25 km) depths. Compositional profiles at Grt-Opx and Grt-Cpx contacts are complex and require more detailed studies.

Crustal xenoliths in post-collisional Variscan lamprophyres: records of continental collision and orogenic extension

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Content

Crustal xenoliths entrained in post-collisional Variscan lamprophyres from the crystalline Odenwald (Mid-German Crystalline Zone) include felsic granulites and retrogressed eclogites. Due to the post-collisional timing of lamprophyre magmatism, extraction of the xenoliths from the lower crust takes place after the peak of the orogeny. These rock fragments therefore provide a snapshot of the lower orogenic crust during Variscan collision and regional extension. While a felsic granulite xenolith is well equilibrated, the eclogite records strong chemical and textural disequilibria in terms of (i) rapid eclogite-facies metamorphic crystallisation causing sector and oscillatory zonation of garnet, followed by (ii) incipient partial melting resulting in intra- and intercrystalline fracturing. Yet, it is possible to derive P–T information from both lithologies. Classical thermobarometry, Zr-in-rutile thermometry and equilibrium phase diagrams (pseudosections) record peak conditions of 700–800°C and 1.7–1.8 GPa. P–T conditions of melt-mediated overprinting of the eclogite suggest isothermal decompression to 1.2 ± 0.2 GPa. The lower crustal xenoliths document the Variscan collision process, resulting in crustal thickening to at least 60 km, and subsequent regional extension. Preservation of chemical zonation in garnet and homogeneous Zr-in-rutile temperatures for both samples indicate limited diffusional overprinting. Therefore, the melt-mediated partial recrystallisation of the eclogite must have occurred shortly before extraction by the lamprophyre. This is supported by SIMS U-Pb zircon dating, giving a Visean age for the HP metamorphic event, similar to the age of post-collisional granitoid magmatism. Compositional sector zonation in garnet is caused by rapid crystallisation, related to reaction overstepping. Sudden nucleation and crystallisation possibly takes place due to shearing and fluid-inflow during incipient decompression. During continuing extension, the wet solidus is crossed. Small amounts of partial melt cause a drastic reduction in rock strength due to brittle failure. A consequence of rheological weakening may be a localisation of deformation, resulting in crust-scale shear zones. Such shear zones may accommodate orogenic extension, provide pathways and trigger the ascent of mantle-derived lamprophyres.

Development and application of a new *in situ* femtosecond-LA-MC-ICP-MS method for Li isotope measurements

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Content

At magmatic temperatures metal isotope fractionation is mainly caused by diffusion, as shown by previous studies. These processes can be observed as isotopic zonation in magmatic olivines and pyroxenes where the fast-moving element Li is of special interest to give insights into the time-scales of fast-paced volcanic processes. Modeling of chemical and isotopic diffusion profiles may provide valuable information on cooling or degassing processes shortly before a volcanic eruption [1]. So far, *in situ* Li isotope analyses have been performed with SIMS, but these analyses seem to suffer from composition-dependent matrix effects [2]. Furthermore, conventional LA-MC-ICP-MS techniques have been applied which generate relatively large (50-150 μm) and deep laser spots [3]. However, a laser spot size of $\sim 30\ \mu\text{m}$ is required to analyze diffusion profiles of normal-sized magmatic minerals ($< 500\ \mu\text{m}$) with sufficient spatial resolution. A femtosecond laser ablation system coupled to a Neptune Plus MC-ICP-MS allows for this spatial resolution as well as an ablation depth of only a few μm , and furthermore it enables largely matrix-independent metal isotope analyses [4] and increased internal precision, repeatability and accuracy [5]. Here, we analyzed various silicate reference glasses with low Li concentrations (3-20 ppm) by fs-LA-MC-ICP-MS in order to establish an analytical setup for Li isotope analyses of chemically and isotopically zoned olivine and clinopyroxene crystals with $< 10\ \text{ppm}$ Li.

Materials with Li concentrations down to 3 ppm can be measured with a combination of an ion counter (for ^6Li) and a Faraday cup with a $10^{11}\ \Omega$ resistor (for ^7Li) with acceptable precisions of 1.2 ‰ (2 RSE). Lower Li concentrations at intensities of only 5-10 mV for ^7Li can be measured with a $10^{13}\ \Omega$ resistor. The time delay of the $10^{13}\ \Omega$ resistor has to be corrected by a τ -correction which improves the internal precision of a measurement by up to 30 % compared to only blank corrected results. With the latter combination precise *in situ* $\delta^7\text{Li}$ values can be determined, in theory, for minerals and glasses with Li concentrations of a $\sim 1\ \text{ppm}$ level. First olivine and pyroxene samples will be analyzed with our developed technique in the near future.

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Exhumation history of the migmatites from the Greater Himalayan Crystalline complex in Dinggye, Southern Tibet

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Content

Exhumation mechanisms of high-grade metamorphic rocks in collisional settings have attracted a lot of research and there is a long debate whether partial melting can lower the viscosity of lower crust and thus trigger rapid exhumation. The Greater Himalayan Crystalline complex (GHC) in Dinggye, southern Tibet is an excellent natural laboratory for contributing insights into this problem. It exposes abundant granulite-facies rocks comprised of pelitic and psammopelitic migmatitic gneisses and basic granulites, which preserve locally an imprint of hitherto unrecognized early high pressure metamorphism (> 12 kbar at T ~ 800-850°C) accompanying partial melting in the kyanite (±phengite) stability field (metapelite) and in the omphacite stability field (basic rocks). Subsequent evolution of the GHC involved (a) decompression to 8-10 kbar accompanying development of sillimanite and biotite in metapelites and possibly further melting, and breakdown of omphacite to clinopyroxene-plagioclase symplectite in metabasites, (b) nearly isothermal decompression, down to 6-4 kbar, when porphyroblastic garnet broke down to cordierite-spinel (metapelite), and orthopyroxene-plagioclase (psammopelite and basic), and (c) near isobaric cooling to ~550-600°C when a coronal garnet appeared in pelite and psammopelite and biotite-bearing symplectites appeared possibly as a result of melt-solid reaction. By combining results of monazite dating, we find that this evolution occurred over ~10 Myr. Geospeedometry and isotopic dating suggest cooling rates from 800°C to 650°C at 6-4 kbar to be at least 40 °C/my and even faster. Our results suggest that melting, but not necessarily rapid cooling, is related to rapid exhumation.

The U-Pb isotopic system of rutile: a field based study to constrain Pb diffusion in rutile from the Reynolds Range, central Australia

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Content

A detailed study on rutile from the Reynolds Range, central Australia, was carried out to constrain the U-Pb age response and trace element behaviour of rutile during prograde metamorphism and cooling. Of particular importance is the closure temperature for Pb in rutile, which remains debated. The Reynolds Range comprises a series of Palaeoproterozoic metasedimentary and metamagmatic rocks that were affected by two along-strike metamorphic overprints with increasing metamorphic conditions from the NW to the SE. The Mt Thomas Quartzite, a highly mature (meta-)quartz arenite, can be followed along the length of the Reynolds Range and was sampled from greenschist- to granulite-facies metamorphic conditions. Greenschist-facies metasediments in the northwest Reynolds Range preserve well-rounded detrital rutile grains. LA-ICP-MS U-Pb dating of the detrital rutile grains revealed isotopic compositions of the provenance region with ages > 1780 Ma [1]. Rutile grains recovered from amphibolite-facies quartzites from the central Reynolds Range yield a wide range of U-Pb ages between 1800 Ma and 1300 Ma. Recrystallized rutile grains recovered from a granulite-facies quartzite document a major change in trace element composition and a concordant SIMS age of 1543 ± 6 Ma. This age is interpreted to date cooling from the Chewings Orogeny (ca. 1595–1585 Ma) through temperatures of approximately 600 °C based on the previously published cooling path. Rutile from two other granulite-facies quartzites document partial Pb loss during subsequent burial (Centralian Superbasin) prior to the Alice Springs Orogeny (ca. 360 Ma). Quartz recrystallization fabrics of these two samples show subgrain rotation recrystallization indicating temperatures above ca. 450 °C. In contrast, the granulite-facies quartzite with the single concordant age cluster shows bulging recrystallization and thus temperatures of ca. 400 °C. Opening of the U-Pb system might have started as early as 550 Ma as indicated by the lower intercept of the rutile U-Pb discordia. However, U-Pb ages of rutile grains sampling shear zones date the main deformation and basin inversion during the Alice Springs Orogeny at 359 ± 28 Ma.

Pb diffusion modelling in rutile with input parameters approximated for metamorphic conditions in the Reynolds Range verifies the experimentally constrained diffusion parameters by Cherniak (2000) [2].

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Thermal history of early Proterozoic granulites from S. India: Implications for plate tectonic styles on an early hot Earth

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Content

Records of high-Pressure (Granulitic) metamorphism (HPGM) within Precambrian (>2 Ga) orogens are scarce but are considered to suggest plate tectonic initiation during Neoarchean-Paleoproterozoic times [1]. The Southern Granulite Terrain (SGT) within peninsular India holds record of ca. 2.49-2.47 Ga HPGM [3-5]. Here, we deciphered the thermal history of mafic granulites from SGT to understand P-T-t structure of orogens at the Archean-Proterozoic boundary.

We present the observations from petrography, mineral reaction history, conventional major element thermobarometry, pseudosection modeling and trace element thermobarometry. We found that the peak metamorphism (M1) – exemplified by the assemblage garnet (Grt) + aluminous clinopyroxene (Cpx1) + calcic plagioclase + rutile + quartz – was attained at ~750-800 °C and ~12.5-14 kbar. We found excellent consistency among the temperature values obtained using the - i) Fe-Mg exchange between Grt-Cpx1, ii) isopleth thermobarometry, iii) REE-based thermometry between Grt-Cpx1 and, iv) Zr-in-rutile thermometry. The constrained P-T values suggest deep burial of crustal rocks underneath ~35-45 km thickened Archean crust. The cooling-exhumation history of these rocks following the peak stage is marked by the – i) formation of clinopyroxene (CpxS) + plagioclase (Pls) symplectite at ~700-710 °C and ~10.5 kbar via - Grt + Quartz = CpxS + Pls and, ii) stabilization of amphibole at ≥~580-620 °C and >6-8 kbar.

We did diffusion modeling of preserved Fe-Mg-(Ca-Mn) compositional zonations within garnet-clinopyroxene grains which presumably formed during the retrograde stage. We obtained single stage linear cooling rates in the order of 1's-10's °C/Myr from stage-M1 (~750-800 °C) till the closure of Fe-Mg exchange between Grt-Cpx at ~620-660 °C. We suggest that the Archean-Proterozoic boundary possibly witnessed the presence of plate-tectonics as interpreted from the deep burial of crustal rocks. However, this orogenic belts record the prevalence of high-T conditions for a prolonged time-span unlike Phanerozoic orogens, indicating that the early plate-tectonic style was different than the contemporary plate-tectonics.

[1] Brown, M., 2007, International Geology Review, 49, 193–234; [2] Liou, J.G. et al., 2004, International Geology Review, 46, 1–27; [3] Anderson, J. R. et al., 2012, Geology, 40, 431-434; [4] Ghosh, J. G. et al., 2004, Tectonics, 23, TC3006; [5] Brandt, S. et al., 2014, Precambrian Research, 246, 91-122.

Zoning and exsolution in alkali feldspars from Laacher see volcano (Western Germany) as an indicator of time-scales of carbonate-silicate unmixing and magma evolution prior to eruption

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Content

Time-scales extracted from chemically zoned minerals provide insights into crystal ages, magma storage and compositional evolution of magmas and allow better understanding of pre-eruptive history of large and potentially dangerous magma chambers. We studied chemical diffusion across zoning and exsolution patterns of alkali feldspars in carbonatite-bearing cognate syenites from the 6.3 km³ (D.R.E) phonolitic Laacher See Tephra (LST) deposit in western Germany (12.9 ka).

Diffusion chronometry is applied to major and trace element gradients obtained on alkali feldspars analysed by laser ablation inductively coupled plasma mass spectrometry and energy- and wavelength-dispersive electron microprobe analyses. Grey scale values extracted from multiple accumulations of back-scattered electron images represent the K/Na ratio owing to the extremely low concentrations of Ba and Sr (<30 ppm). Numerical grey scale profiles and quantitative compositional profiles across growth zones are anatomized using three different fitting models in MATLAB®, Mathematica® and Origin®. Diffusion gradients are inverted to give the minimum effective average storage temperature using known U-series zircon ages (at the time of eruption) from the same samples ([1] Schmitt et al., 2010). Estimated temperatures range from 550°C to 660°C. For the exsolution boundaries, an uphill diffusion model is used for a maximum temperature of 712°C to 722°C depending on Or-percentage (based on experimental data on phase separation) and relatively shorter diffusion time scales of 105 to 352 days are obtained. The error values are aggregated from propagated error through calculations and the uncertainty in temperature values. Trace element compositional data of distinct feldspar compositions that are assumed to have grown before and after silicate-carbonate unmixing are used to estimate partition coefficients between carbonate and silicate melt. The resulting values correlate well with available experimental data from the literature. We will present a genetic model based on the compositional data on feldspar zonation and exsolution for the process and timing of silicate-carbonate unmixing, storage and cumulate activation prior to eruption of the host phonolite magma.

References:

[1] Schmitt AK, Wetzel F, Cooper KM, Zou HB, Wörner G, (2010), Magmatic longevity of Laacher See Volcano (Eifel, Germany) indicated by U-Th dating of intrusive carbonatites, *Journal of Petrology*, 1053-1085, 51/5

Session 3.1: Stable isotope proxies in space and time: Processes, preservation and potential: Poster

Session 3.1: Stable isotope proxies in space and time: Processes, preservation and potential: Poster A-855

Barium isotope fractionation during the experimental transformation of aragonite to witherite and of gypsum to barite: Proxy potential implications

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Content

In this study, we present the experimental results for stable barium (Ba) isotope fractionation during the transformation aragonite (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in Ba-bearing aqueous solution to witherite (BaCO_3) and barite (BaSO_4), respectively. The process was studied at temperatures between 4° and 60°C, covering the range of typical diagenetic processes. In all cases, the transformation leads to a relative enrichment of the lighter ^{134}Ba isotope in the solid compared to the aqueous solution, with isotope enrichment factors between -0.10 and -0.16‰ for BaCO_3 , and -0.20 and -0.25‰ for BaSO_4 . The magnitude of isotope ($^{137}\text{Ba}/^{134}\text{Ba}$) fractionation is within the range of previous reports for pure witherite and barite formation, as well as trace Ba incorporation into orthorhombic aragonite (Pretet et al., 2016, The Depositional Record). Ion (de)solvation has been suggested to impact both the crystallization process of Ba-bearing solids and associated Ba isotope fractionation. Therefore, the fundamental experiments reported by von Allmen et al. (2010; Chemical Geology) at circum-neutral pH were repeated by using an aqueous methanol-containing (5%) solution. The observed depletion in precipitated BaSO_4 and BaCO_3 at room temperature is not significantly different to results obtained in pure aqueous solution.

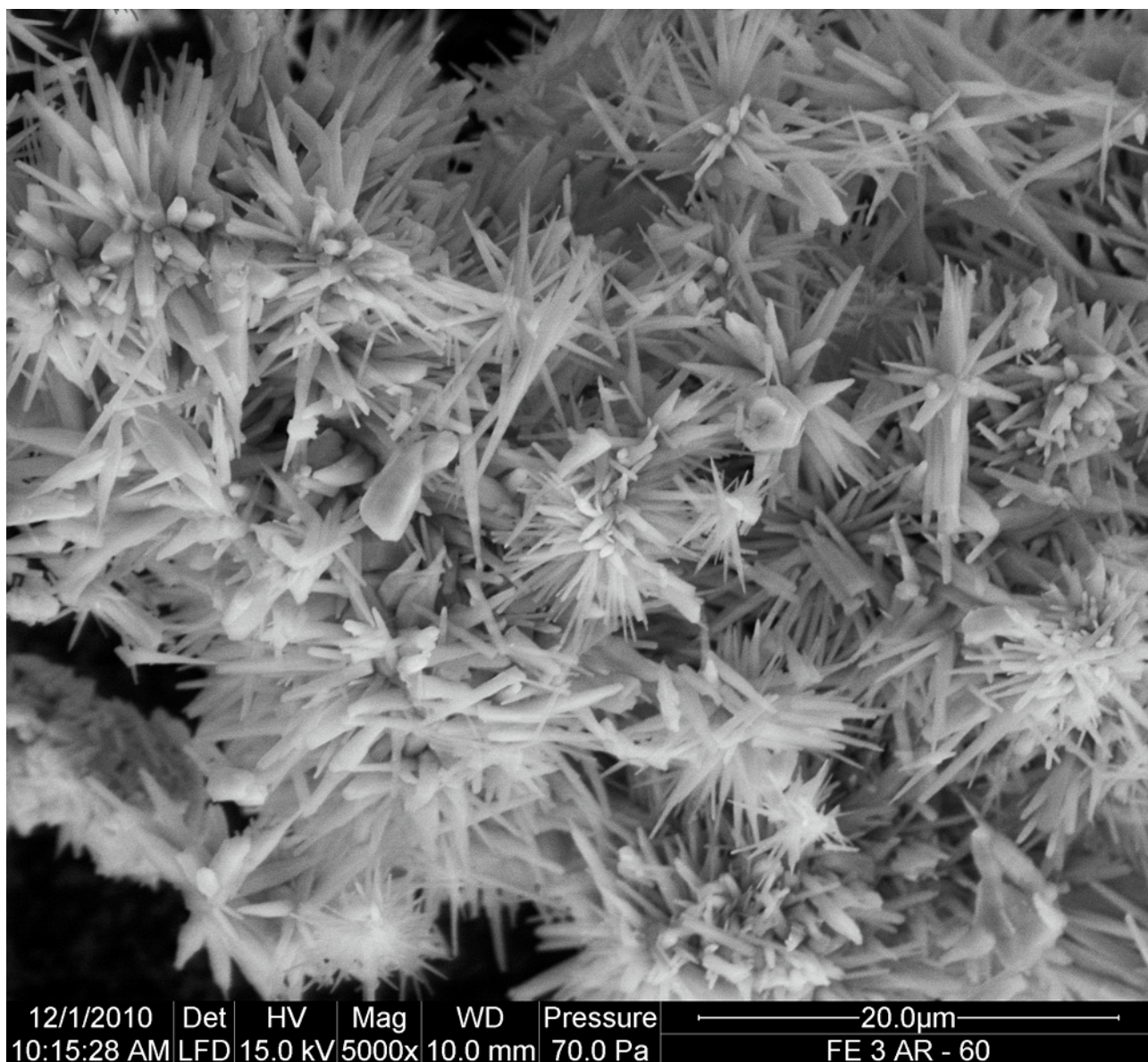


Fig.1 SEM picture of witherite formed via transformation of aragonite in aqueous solution at 60°C

Calcite precipitation from the Novinjak spring (Carinthia, Austria) – Elemental and isotope ratios as proxies for growth dynamics and environmental changes

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Content

The Novinjak-spring in Carinthia, Austria, is an excellent field site, where calcite is precipitating within a kind of natural laboratory. Therefore it has been an object of exploration since more than ten years, documenting its hydrochemical characteristics and stable isotope ratios of hydrogen, oxygen, and carbon of water, DIC and precipitates. From the spring along the stream the fluid shows the typical increase of pH and saturation in respect to calcite, caused by CO₂ transfer from the solution into the atmosphere. Ongoing monitoring in the summer season indicates that the hydrochemistry of the water vary hardly from year to year, while during the winter hydrochemistry is quite constant. Although, the spring itself acts as an ideal opportunity to study the development of supersaturated fluids, the precipitated calcite - often omitted in previous investigations - can be used to investigate the growth dynamics of the present low magnesium calcite. Moreover the biogenic influence, especially locally occurring mosses, show strong tendency to fabric preserving calcification with potential impact of photosynthesis on CO₂-exchange. In order to gain a mechanistic understanding of fluid evolution and calcite precipitation along the stream, we adopt a multi-proxy approach. Complementary to the study of light isotopes of the spring waters and the precipitated calcite, we also present metal-to-calcium ratios (e.g. magnesium, strontium), as well as radiogenic strontium and stable magnesium isotope data. New insights will be particularly gained by the analyses of magnesium-isotopes, as their behaviour in fresh water systems has yet hardly been examined. The above isotopes and elemental ratios are discussed as candidates for their usage as proxies for growth dynamics and environmental changes.

Modern travertine-forming streams on Rügen Island, southern Baltic Sea: A natural laboratory to follow stable isotope and trace element partitioning

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Content

Processes in the carbonate system of near-surface waters of the temperate climate zone are in particular sensitive to climate change. CaCO₃-saturated ground waters that emerge from springs degass carbon dioxide to the atmosphere. This leads to supersaturation of the aqueous solution with respect to calcite. Stable isotope and trace element fractionation are of particular value to link these non-equilibrium processes to the formation mechanisms of calcite and the flow hydrodynamics. Examples linking the past and present terrestrial and marine carbon cycles are found at the cliff coast line of Rügen Island: Carbonates are dissolved in soil solutions and ground water. When these solutions emerge as springs, their dissolved carbonate system is in disequilibrium with respect to the recent earth atmosphere. By following the chemical changes downstream it is found, that two regions of evolution can be differentiated: After an induction period, where only CO₂-degassing takes place, a second stage is observed further downstream (?) where calcite begins to form from the highly supersaturated solutions. At the bottom of the cliff, the carbonate stream water is finally entering the Baltic Sea mixing with brackish coastal waters. In this study, trace element and stable isotope fractionation was followed in several carbonate-precipitating streams. Major, minor and trace element concentrations and d¹³C and d¹⁸O values of carbonate solids and aqueous solutions were analyzed as a function of the flow path. In addition, marine and older travertine carbonate samples were analyzed for a comparison with recent precipitates. Sr/Ca and Mg/Ca ratios were lower in the newly formed calcium carbonate compared to the aqueous solution. The partition coefficients are larger than previous experimental close-to-equilibrium calibrations and indicate relatively fast calcite precipitation rates. The spring carbon isotopic composition indicates ground water evolution under essentially closed conditions with respect to a carbon dioxide gas phase. The d¹³C values of DIC increased along the flow path, due to preferential degassing of ¹²CO₂. Travertine samples displayed a slight enrichment in ¹³C compared to the solution which is consistent with experimental and theoretical studies.



Fig.1: Travertin formation at the Höllgrund (photograph: V. Winde)

Sedimentary authigenesis of iron and manganese sulfides in Holocene sediments of the Landsort Deep: Textural and sulfur isotopic evidence

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Content

The texture and stable sulfur isotope composition of iron and manganese sulfides were investigated in the water column and in up to 5 m long sediment cores from the central Landsort Deep, western Baltic Sea. The sediments were deposited during the Holocene brackish phase of the Baltic Sea. In the modern anoxic part of the water column, very minor abundances of single crystals or proto-framboids of pyrite were observed. These are transported to the surface sediment acting as nuclei for further crystallization. In the sediments, the distribution patterns of framboidal pyrite is consistent, with a dynamic history of the dominating weakly-euxinic conditions with regular oxidation events of the sulfide-bearing part of the water column. When compared to the sulfur isotope composition of dissolved sulfide in the water column, the signatures found in mackinawite and pyrite indicate formation under conditions essentially closed wrt dissolved sulfate below the sediment-water interface. The surface texture together with a strongly zoned sulfur isotope patterns of concretionary authigenic MnS indicates slow growth in a sulfidic pore water gradient that developed towards a system increasingly limited in dissolved sulfate. From a physico-chemical point of view, manganese-calcium solid-solutions should form in the pore waters instead of MnS. We argue, that the inhibitory effect of enhanced phosphate on the carbonate system is responsible for this thermodynamic paradox.

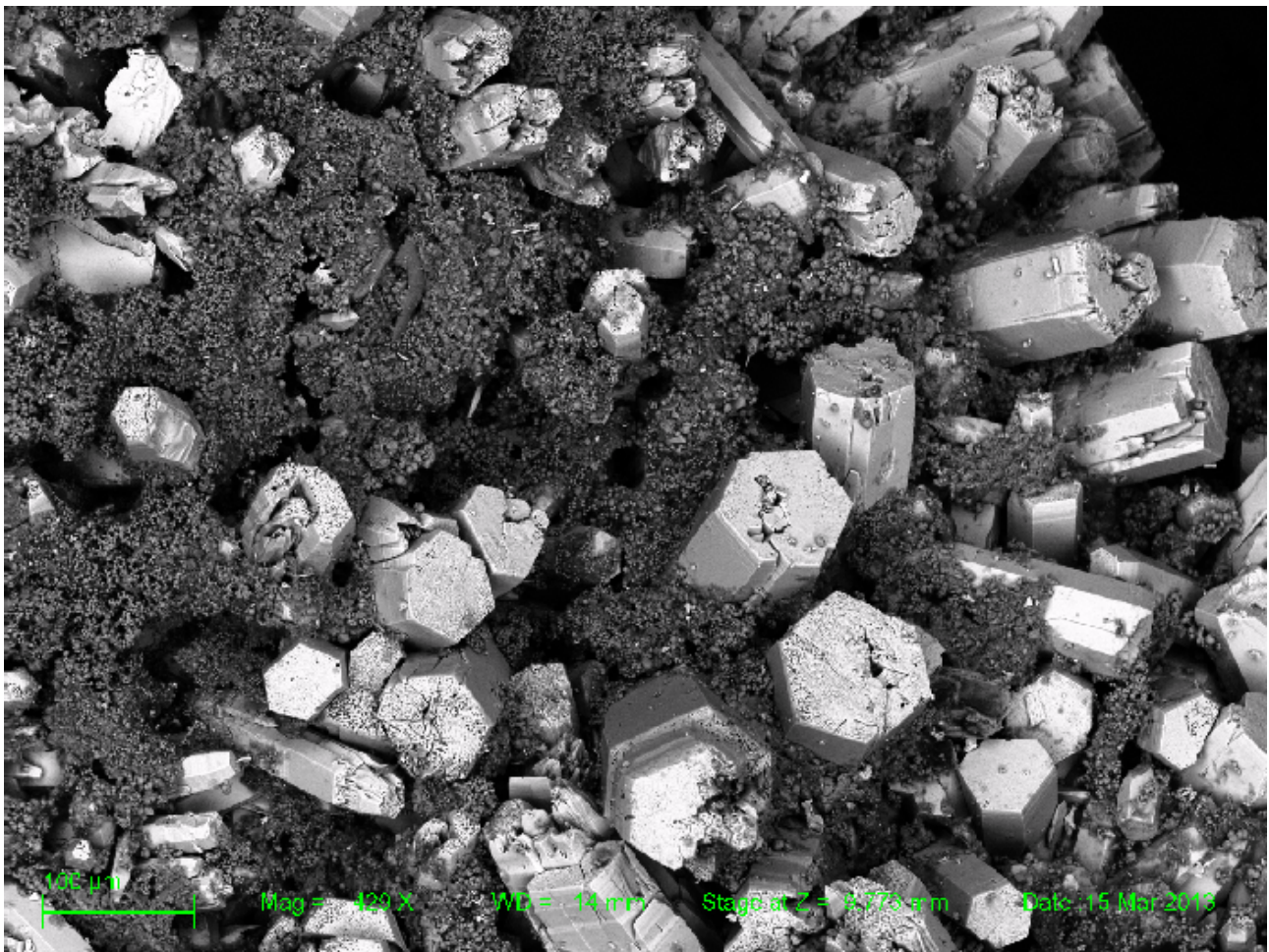


Fig.1: Authigenic MnS found in the sediments of the Landsort Deep

Stable isotope (C, O) and monovalent ion partitioning upon synthesis of carbonate-bearing hydroxyl apatite (CHAP) via calcite transformation: Implications for proxy formation

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Content

Carbonate-bearing hydroxy-apatite ($\text{Ca}_{10-a}(\text{Na,K,NH}_4)_2\text{a}(\text{PO}_4)_6-y[(\text{CO}_3)_2x+(3/2)y(\text{F,OH})_2-2x]$; CHAP) was synthesized by the transformation of synthetic calcite powder in aqueous phosphate- and bicarbonate-bearing solutions between 7° and 90°C using batch-type experiments. Compositional changes of the mother solution and solid phase products are followed by powder XRD (including Rietveld refinement), micro-Raman spectroscopy, SEM-EDX, elemental analysis, and FTIR spectroscopy. It is found that the transformation at pH values between 7.5 and 9.5 takes place via the dissolution of calcite followed by the precipitation of CHAP. A kinetic analysis of the experimental data between 21° and 80°C yields rate constants ($\ln k$) between -13 and -8, and Avrami indices between 0.4 and 0.7. An evaluation of the reaction rates at different temperatures gives an apparent Arrhenius activation energy of 64 KJ/mol, which is higher than previous reports for processes in the pure carbonate system. Via Rietveld refinement a continuous growth of the CHAP crystallite size was observed. After complete transformation, a systematic relation between CHAP crystal grain size and reaction temperature is found, which is due to an enhanced promotion of mineral growth compared to nucleation processes with rising temperature. Whereas low concentrations of dissolved borate or sulfate did not influence the transformation reaction, dissolved fluoride inhibited calcite transformation at 21°C, but enhanced the reaction rate at 60°C with larger CHAP crystals developing. Incorporated carbonate-carbon contents of synthetic CHAP ranged between 0.5 and 1.0 % dwt. similar to naturally occurring abiotic and biogenic apatite phases. An empirical distribution coefficient $\text{DCO}_3\text{-PO}_4$ is obtained, which is not impacted by reaction temperature but by the pH of the solution. Empirical cationic distribution coefficients DNa-K , DNa-NH_4 , and DNa-K were derived experimentally, too. No distinct temperature effect on D values was found between 21° and 80°C. The crystallization of metastable phases (brushite or monetite) was only observed at lower pH values.

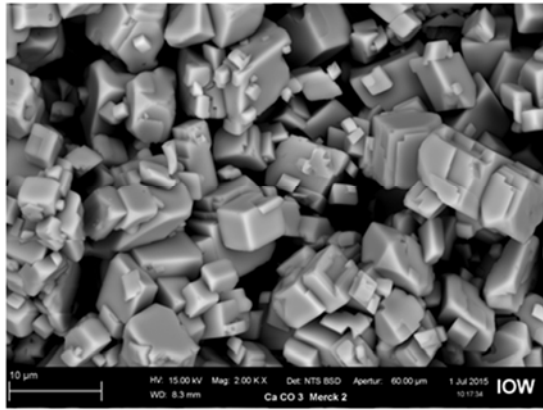
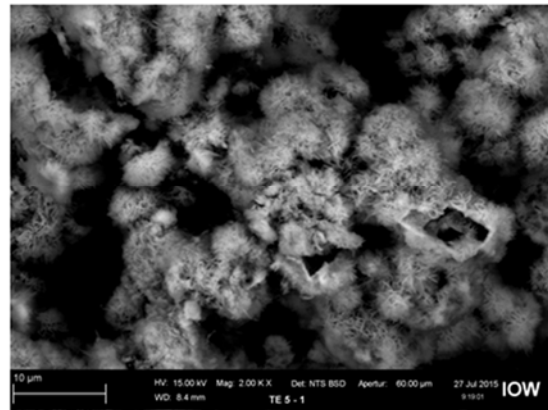


Fig.1 SEM pictures of precursor calcite and CHAP formed at 85°C

Sulfur isotope biogeochemistry of soils from an episodically flooded coastal wetland, southern Baltic Sea: Implications for proxy formation

Fernández-Fernández, L.-E.^{1, 2}, Westphal, J.¹, Schmiedinger, I.¹, Kreuzburg, M.³, Bahlo, R.¹, Koebsch, F.^{4, 5}, Böttcher, M.E.¹

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Content

Coastal wetlands are under dynamic impact both from fresh water and salt water sources, thereby experiencing temporarily sulfur-excess and -limiting conditions. In the present study, nine up to 10 meter long sediment cores from a recently rewetted fen (Hütelmoor, southern Baltic Sea) which has been under impact by episodic

flooding with brackish waters were investigated (isotope) geochemically. The sites are positioned at different distances to the Baltic Sea coastline. The soils were analyzed for the elemental composition (CNS), reactive iron and sedimentary sulfur contents, iron sulfide micro-textures, as well as the stable sulfur isotope composition of inorganic and organic sulfur fractions to understand signal development for the biogeochemical carbon-sulfur cycles in such a dynamic ecosystem.

We found evidence for the activity of dissimilatory sulfate-reducing microorganisms and the associated formation of pyrite with different textures (framboids, single euhedral crystals and clusters) and sulfurization of organic matter. Sedimentary sulfur fractions and their stable isotope signatures are controlled by the availability of dissolved organic matter or methane, reactive iron, and in particular dissolved sulfate and thereby from the relative position to the coast line and the given lithology. $\delta^{34}\text{S}$ values in the pyrite fraction vary in a wide range between -21 and +15 per mil versus VCDT, in agreement with spatial and temporal dynamics in the extend of sulfate-limiting conditions during the oxidation of reduced carbon.

Acknowledgement: This study is supported by the research training group BALTIC TRANSCOAST and the EU ERASMUS program

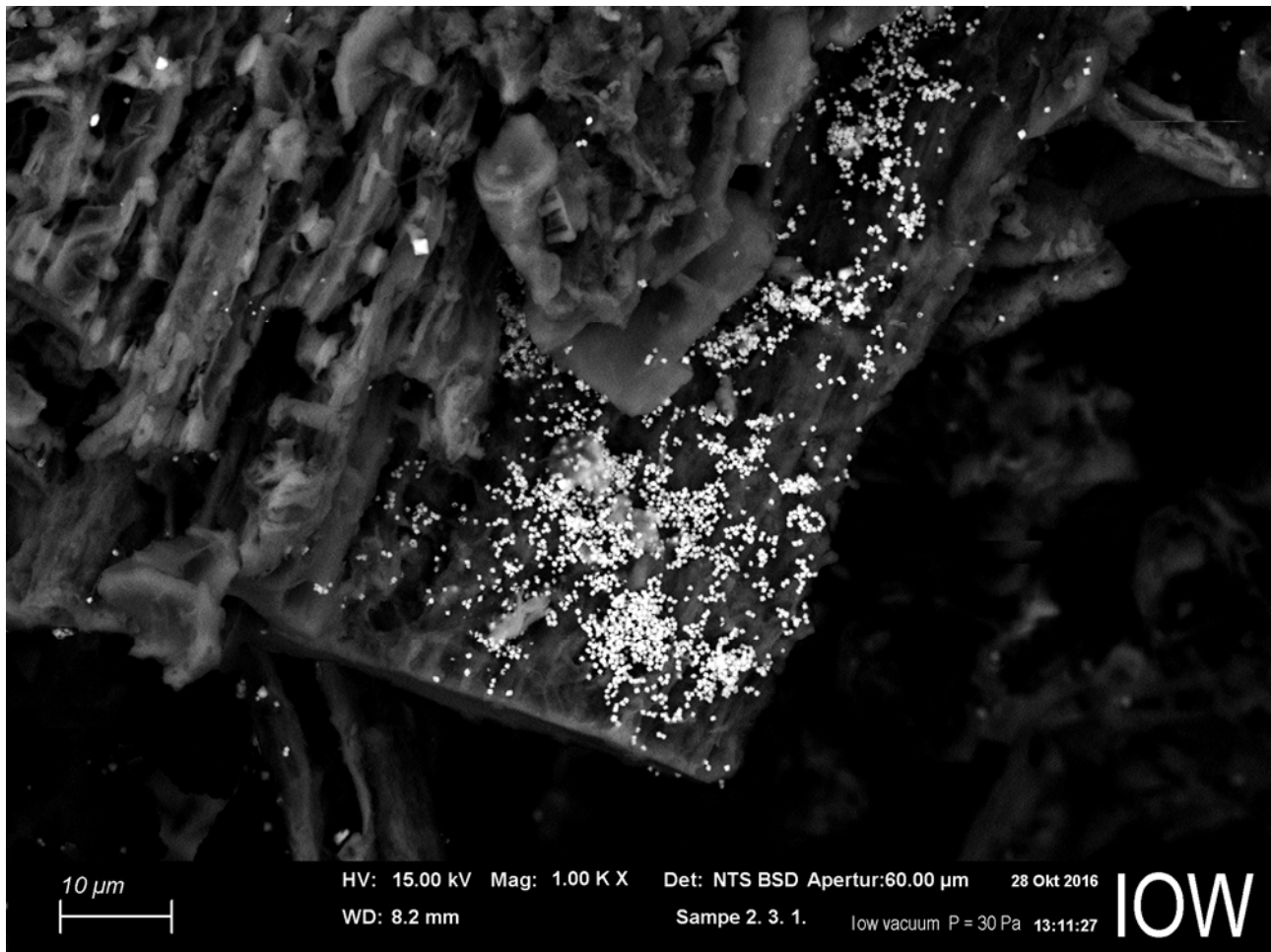


Fig.1 Occurrence of single pyrite crystals formed in peat after flooding with brackish waters

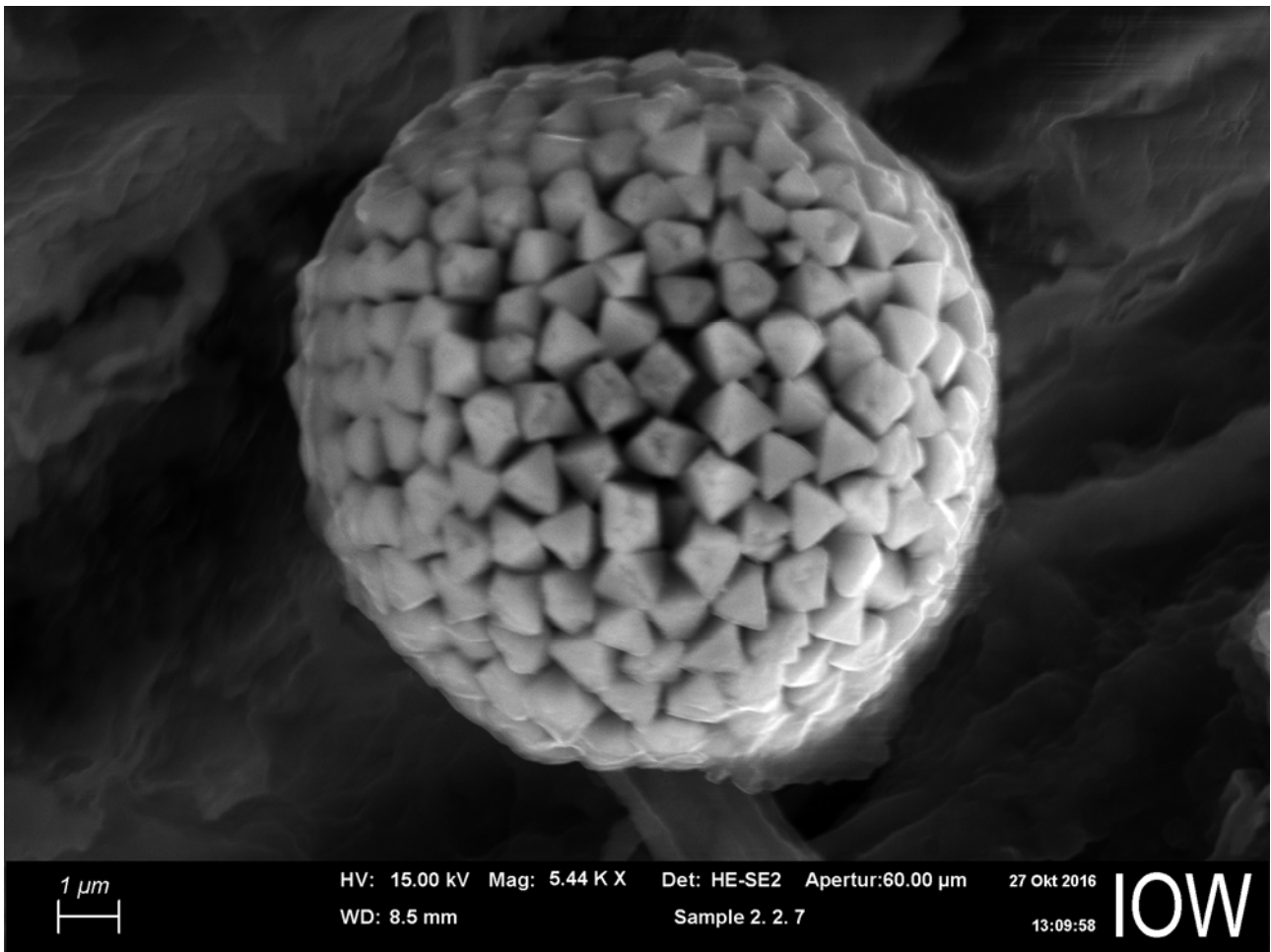


Fig.2 Pyrite framboid formed in the peat after flooding with brackish Baltic Sea water

Tracing organic carbon through an alluvial river system using stable isotope signatures of lipid biomarkers

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Content

Rivers are the primary conduits for organic carbon transfer from vegetation-rich uplands to long-term sinks, and thus are responsible for significant fluxes among different reservoirs of the carbon cycle. Little is known about the behavior of organic carbon during transit (i.e. the source, transport mechanism, preservation, degradation). Lipid biomarkers, primarily n-alkanes derived from terrestrial plants, are a key to tracing organic material through transport pathways in sedimentary systems, because the molecular and isotopic composition of similar compounds found in river sediment can potentially be used for organic sediment provenance.

We adopt this approach in the Rio Bermejo, an alluvial river system in the Andean foreland in northern Argentina. High floodplain erosion rates drive rapid remobilization of floodplain sediment and stored organic carbon. We hypothesize that surface uplift about the Andean forebulge is driving the rapid erosion, and this region is the dominant source of organic carbon transported to the ocean. In this study, we aim to trace lipid biomarkers extracted from suspended sediment back to distinct sources in the catchment to learn where organic material is eroding and how organic carbon is cycled through river systems.

We measured stable isotope values of river water and biomarkers extracted from suspended sediment and floodplain soil samples collected along a 700km reach of the Rio Bermejo. Downstream changes in $\delta^{18}\text{O}$ and δ -excess reflect increased groundwater input from the forebulge reach. Biomarkers extracted from suspended sediment show that the organic material transported by the river is composed primarily of long-chain n-alkanes, including nC29 and nC31 derived from higher terrestrial plants, but also nC15 and nC18 alkanes, as well as mono- and dimethyl-alkanes, which may represent microbial communities in the suspended sediment. Low bulk $\delta^{13}\text{C}$ values and higher concentrations of nC27 and nC31 alkanes in sediment collected from the forebulge reach likely indicate increased contributions from a different higher terrestrial plant community established in this area. Downstream increases in bulk sediment $\delta^{13}\text{C}$ values and microbial lipid biomarker abundance, as well as decreasing total organic carbon content may suggest a loss of terrestrial organic carbon relative to microbial compounds during fluvial transport or during floodplain storage. Compound-specific $\delta^{13}\text{C}$ and δH analyses will refine these preliminary interpretations.

Session 3.1: Stable isotope proxies in space and time: Processes, preservation and potential: Talk

Keynote speaker

A-230

Tsunami sedimentary deposit of Crete records climate during the Minoan Warming Period (≈3,350 years BP)

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Content

Earthquakes or explosive eruptions generate tsunami waves at the origin of thick and chaotic coastal sediments. These commonly fossiliferous deposits are formed instantaneously at the historical or geological timescale and therefore have the potential to provide snapshot records of past climates. In Crete, near the city of Palaikastro, crops out a 1 to 9 m thick sedimentary layer deposited by huge tsunami waves that has been previously estimated of about 9 m high. The presence of volcanic ash, the geometry, the archaeological and faunal contents of the sedimentary deposit along with radiocarbon dating converge altogether for interpreting this tsunamite as coeval with the Minoan Santorini (Thera) eruption ≈3,350 years BP. During its drawback, the tsunami wave deposited rocky blocks and a muddy matrix containing mollusc shells dredged from the seabed as well as cattle skeletal remains and various artefacts belonging to the contemporaneous Minoan civilization. Oxygen isotope measurements of both marine mollusc shells and terrestrial vertebrate teeth and bones revealed that sea surface and air temperatures during MM3 and LM1 periods were about 2°C and 4°C higher than nowadays, respectively. This result compares with the 2.5°C temperature difference already estimated according to both δD and $\delta^{18}O$ values of Greenland ice cores. Incremental sampling of marine gastropods and bovid teeth suggests that the seasonal amplitude was similar to that prevailing during the second half of the XXth century.

A multi-isotope (H - B - C - O - Mg - S - Ca - Ba) study of a brackish-fresh water transition in a Baltic Sea sediment core

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Content

The Holocene Brackish Sea has switched several times between fresh water and brackish water stages. The change in paleo-environmental conditions caused downcore gradients in the concentrations of dissolved species from modern brackish waters downward to fresh paleo-pore waters. These extreme physico-chemical changes caused by, e.g., microbial activity and further physical and chemical water-solid interactions may lead to multiple stable isotope fractionation processes, that in turn have strong implications for isotope and trace element partitioning upon early diagenetic mineral (trans)formations. In the present study, we communicate the results from the first integrated multi-isotope and trace element investigations ever conducted in this type of gradient system.

It is found that concentrations of conservative elements (e.g., Na, Cl) decrease with depth due to diffusion of ions from brackish waters into underlying fresh waters. This is associated with pronounced depletions in H-2 and O-18 of pore water with depth. Co-variations of both stable isotope systems are close to the meteoric water line as defined by modern Baltic Sea surface waters. A downward increase and decrease of Ca and Mg, respectively, is associated with a decrease in the Ca-44 and Mg-26 isotope signals. B-11 isotope signals decrease in the limnic part of the sediments, too. On the other hand, an increase in Ba concentrations with depth is associated with an increase in Ba-137/134 isotope signals. Microbial sulfate reduction and organic matter oxidation lead to an increase in DIC, but a decrease in sulfate concentrations and in C-13 contents of DIC with depth. Suess (1981) was probably the first to suggest, that desorption of Ca and Ba from glacial sediments due to downward diffusing ions may be responsible for a downcore increases in pore water concentrations of earth alkaline ions and the formation of authigenic barites. Coupled S-34 and O-18 isotope signals in authigenic barites suggest O-18 signals near -20 per mil in pre-Yoldia pore waters, which agrees with recent IODP347 measurements (Böttcher, unpubl.).

In the present communication, we will discuss possible impacts of diagenetic processes on multi-isotope signals in pore waters and potential solid phases. A combination of mixing between brackish and fresh water, ion exchange, precipitation/dissolution, and transport reactions is considered to explain most of the observed isotope variations along the vertical pore water profile

Deciphering the relationship between Molybdenum and Uranium isotope signatures in modern anoxic sediments from the Black Sea and the Cariaco Basin

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Content

Molybdenum and Uranium isotopes fractionate characteristically during sedimentation processes under variable redox conditions. Both isotope systems have been widely used to understand recent environmental processes and to reconstruct paleo-redox conditions [1], [2], however, the relationship between them is poorly constrained. In this study, we analyzed the Mo and U isotope compositions of sediment samples from the Black Sea and the Cariaco Basin that were taken at variable water depth below the chemocline along the basin shelves and deeps of both basins. Samples originate (1) from the water-sediment interface (0-1 cm core tops) and (2) from the Black Sea also from 1-2 cm depth below seafloor (bsf). Furthermore, we analyzed core samples (1002B) from the Cariaco Basin from depths of 30 to 595 cm bsf.

Core top samples from both basins show highly variable Mo isotope ratios ($\delta^{98}\text{Mo} = 0.0 - 2.2\text{‰}$, relative to NIST-3134 $+0.25\text{‰}$), but limited variations in $\delta^{238}\text{U}$ ($0.0 - 0.2\text{‰}$, relative to CRM-112A) and no correlation of Mo and U isotopes. The lowest $\delta^{98}\text{Mo}$ are displayed by Black Sea sediments that were deposited just below the chemocline (at $\approx 200\text{ m}$ below sea level). Black Sea sediments from 1-2 cm depth show additional U enrichment and additional U isotope fractionation towards higher $\delta^{238}\text{U}$ (up to $+0.4\text{‰}$), however, little change in Mo concentrations and isotope ratios compared to the samples from 0-1 cm bsf. Furthermore, these latter samples show a negative correlation of $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$. A similar negative correlation of Mo and U isotope compositions (albeit with a slight offset towards lower $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$) was observed for sediments from the Cariaco Basin core 1002B which show $\delta^{238}\text{U} = -0.1 - 0.24\text{‰}$ and $\delta^{98}\text{Mo} = 0.65 - 1.47\text{‰}$.

Although the mechanisms of metal reduction and scavenging in anoxic basins are likely different for Mo and U, our results show related isotope signatures in the sediments of both systems. Hence, the Mo and U isotope fractionation in sediments (at $> 1\text{ cm}$ depth) relative to the water column is apparently coupled. These signatures appear to depend on the redox conditions and H_2S level in the water column, with stronger Mo and U isotope fractionation at anoxic but weakly euxinic conditions. These findings may be of interest for using Mo and U isotopes of sediment archives for paleo-redox reconstructions at local and global scales.

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Extending the boundaries of Isotope Ratio MS - Latest technological improvements

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Content

Stable isotope ratio mass spectrometers usually apply a sector field mass analyzer with a static multicollector array. Typically, these mass analyzers have a low mass resolution allowing the measurement of bulk isotopic compositions of different molecular species, e.g. CO₂, N₂, CO, H₂ and SO₂. The mass resolution of these instruments is in the range of a few hundred which is sufficient to produce flat top peaks for high precision measurements.

The presence of isobaric interferences of molecular species limits the capability of the low resolution magnetic sector instruments. This applies, for instance, when site-specific isotope effects inside a molecule need to be investigated or when very rare clumped isotope species need to be measured in the presence of mass spectral interferences. For these demanding applications high mass resolution is essential as well as ultimate sensitivity and low noise detectors. These requirements lead to the development of the Thermo Scientific™ 253 Ultra™, a new generation high mass resolution stable isotope mass spectrometer. The Thermo Scientific™ 253 Ultra™ allows high precision isotope ratio analysis of gas samples with a mass resolution of up to 40,000. The major features and capabilities of the Thermo Scientific™ 253 Ultra™ for high precision isotope ratio analysis and a discussion on how the high mass resolution extends the boundaries of isotope ratio mass spectrometry and opens new fields of science will be presented. This includes, i) the separation of doubly deuterated methane from other interferences, ii) the analysis of a variety of N₂O isotopologues and iii) site-specific carbon isotope ratio measurements in propane finding applications in the fields of (bio-)geochemistry, atmospheric sciences and oil and gas research.

While the mass resolution of the Thermo Scientific™ 253 Ultra™ is sufficient to mass resolve major interferences on small molecules we also will present first results the Thermo Scientific™ Q Exactive™ GC mass spectrometer and its capability for high precision isotope ratio analysis for larger molecules where a mass resolution of several 100,000 is required to mass resolve interferences. The Thermo Scientific™ Q Exactive™ GC is based on Orbitrap™ technology and delivers mass resolutions sufficiently high to study site-specific isotope clumping effects in intact molecules. Potential applications of these new capabilities will be discussed.

Improving the accuracy of the Δ_{47} -1/T² relationship for (bio)apatites to facilitate temperature reconstruction on teeth from dinosaurs and sharks

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Content

Clumped isotope (Δ_{47}) analysis of carbonates has been proven to be an effective tool to decipher environmental temperatures [1, 2]. Previous studies suggested that this thermometer may also be applied to (bio)apatites to deduce body temperatures of extinct vertebrates, albeit discrepant Δ_{47} -1/T² relationships were ascertained [3, 4].

In order to improve the accuracy of the Δ_{47} -1/T² relationship, we present new Δ_{47} data on (bio)apatites with known precipitation temperatures, eventually enlarging the dataset presented in [4] by four. Data was obtained from chemically untreated modern teeth from an African elephant, Greenland sharks, sand tiger sharks and synthetic apatites.

Our results confirm the preliminary Δ_{47} temperature calibration for (bio)apatite of Wacker *et al.* [4]. The compilation of the datasets leads to a refined calibration that is applied to fossil tooth material from a *T. rex* and a *C. megalodon* shark. Enamel(oid) Δ_{47} data yield a body temperature of 34±4 °C for the *T. rex* and a habitat temperature of 16±6 °C for the *C. megalodon*. The oxygen isotopic composition of the seawater that the *C. megalodon* lived in is additionally derived from the apparent habitat temperature and $\delta^{18}\text{O}_{\text{PO}_4}$ data. The resulting $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ VSMOW values range from -0.6 to -0.3 ‰, which is a plausible range for Miocene to Pleistocene seawater. Taxon specific analyses of enamel(oid) and dentine from the African elephant, Greenland shark and *T. rex* tooth samples reveal that both tissues show identical Δ_{47} values. Varying contents of carbonate and organic matter and the structural differences between enamel(oid) and dentine might thus have a negligible effect on Δ_{47} values of biogenous apatites.

While the slopes of our refined (bio)apatite calibration and the 25°C calcite calibration of Wacker *et al.* [5] are identical, both intercepts differ. The observed difference thereby matches the phosphoric acid fractionation factor Δ_{47}^{25-110} extrapolated from experimental data on calcite and aragonite [6]. This suggests that the bioapatite and calcite phosphoric acid fractionation factors follow a unique temperature dependence.

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Paleotopographic reconstruction from a groundwater-influenced diagenetic system through clumped (Δ_{47}) and oxygen isotope ($\delta^{18}\text{O}$) analyses

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Content

Using light stable isotopes (e.g. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$) for terrestrial paleoclimate or paleotopography reconstructions typically requires unaltered sedimentary records with primary, undisturbed isotopic proxy signals. Combining a wide variety of different proxies can help to assess this requirement by establishing the diagenetic conditions that may lead to proxy resetting.

Here, we present oxygen isotope ($\delta^{18}\text{O}$) and clumped isotope (Δ_{47}) data from carbonate concretions from the Chumstick basin (central Washington, USA) and assess $\delta^{18}\text{O}_{\text{water}}$ values of groundwater from which these concretions formed. Δ_{47} (paleo)thermometry indicates a systematic change in basin burial temperatures from 110°C to 70°C depending on burial depth in the basin. These data are in very good agreement with low-T thermochronological and modeled vitrinite reflectance data, all pointing to preservation of maximum burial temperatures. In concert with field observations, microstructural analysis, and $\delta^{18}\text{O}$ values of the analyzed carbonates, we suggest that the Δ_{47} temperatures and $\delta^{18}\text{O}_{\text{carbonate}}$ values reflect open-system carbonate cement recrystallization in groundwaters of meteoric origin during early burial diagenesis in the Eocene/Oligocene. Calculated mean $\delta^{18}\text{O}_{\text{water}}$ values of ~ -9‰ to -7‰ (based on $T(\Delta_{47})$ and $\delta^{18}\text{O}_{\text{carbonate}}$ data, assuming open-system behavior) reflect a time and area-integrated groundwater fluid signal derived from local recharge and are consistent with low-elevation precipitation supplying the Chumstick basin groundwater system.

We acknowledge that a partially inherited $\delta^{18}\text{O}_{\text{water}}$ signal cannot be excluded currently, and therefore, the reconstructed $\delta^{18}\text{O}_{\text{water}}$ values represent potential upper limits. Quantifying the amount and more precise timing of recrystallization is one of the challenges to evaluate Δ_{47} - $\delta^{18}\text{O}$ systematics in such groundwater-influenced diagenetic systems. However, evaluating our reconstructed $\delta^{18}\text{O}_{\text{water}}$ values in light of the paleogeographic setting of the Chumstick basin, today located in the Cascade rain shadow, now allows a paleotopographic interpretation. Most likely the $\delta^{18}\text{O}_{\text{water}}$ values reflect near-coastal Pacific-derived moisture that did not experience strong rainout and thus preclude an Eocene/Oligocene rain shadow of the ancient Washington Cascades.

The control of the geothermal gradient on $\delta^{18}/^{16}\text{O}$ of chert

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Content

The oxygen isotope ratio $\delta^{18}/^{16}\text{O}$ of chert reveals an increasing trend throughout Earth's history. This trend has been explained by decreasing seawater temperatures [e.g., 1], increasing seawater $\delta^{18}/^{16}\text{O}$ [e.g., 2], or by an overprinting of the rock record [3]. These hypotheses are called into question by recent evidence for constant seawater $\delta^{18}/^{16}\text{O}$ [e.g. 4] and seawater temperatures $<40^\circ\text{C}$ in the Archean [5, 6]. Thus, the use of chert $\delta^{18}/^{16}\text{O}$ as geochemical proxy is still limited. To re-evaluate the utility of chert $\delta^{18}/^{16}\text{O}$ in the framework of detritus-controlled rates of silica diagenesis [7], we have analyzed $\delta^{18}/^{16}\text{O}$ VSMOW at the bulk- and μm - scale of pure cherts and siliceous shales of Precambrian-Cambrian age from SE China. From bulk rock $\delta^{18}/^{16}\text{O}$ we have calculated the $\delta^{18}/^{16}\text{O}$ of the authigenic silica and measured $\delta^{18}/^{16}\text{O}$ of silica in detritus-rich samples by SIMS. Authigenic silica ranges from 12.6 to 24.9 ‰ $\delta^{18}/^{16}\text{O}$ and correlates with detritus concentrations, an attribute of temperature-dependent oxygen isotope fractionation during opal-CT to quartz transformation. Peak diagenetic temperatures of circa 260°C , as determined by Raman spectrometry of carbonaceous material, show that chert reliably records the diagenetic $\delta^{18}/^{16}\text{O}$ signature set during the final diagenetic silica dissolution-reprecipitation step. Our work shows that $\delta^{18}/^{16}\text{O}$ depends on the geothermal gradient, because the rate of silica polymorph transformation is controlled by temperature [e.g., 8] and because temperature exerts the major control over $\delta^{18}/^{16}\text{O}$. We calculate how the geotherm and the burial rate affect $\delta^{18}/^{16}\text{O}$ of authigenic quartz. Our results suggest that at least part of the long-term secular increase in $\delta^{18}/^{16}\text{O}$ of chert is caused by decreasing geothermal gradients due to the cooling of the solid Earth.

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The relation between rock weathering and plant nutrient cycles

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Content

We suggest that in slowly eroding mountaneous landscapes nutrient-bearing mineral grains in the regolith are depleted so that plants are nourished by recycling and by atmospheric inputs. In fast regimes, permanent natural erosion rejuvenates the weathering zone such that nutrient uplift from the weathered rock beneath soil roots and soil takes place by microbes that decrease the rhizospheric pH through respiration of CO₂, or by assimilation through the symbiosis of roots with mycorrhizal fungi.

We have tested these hypotheses in two forested mountain ecosystems using metal isotopes of nutritive elements and geochemical mass balances. In the slowly eroding tropical highlands of Sri Lanka, weathering has run to completion and in the top of the weathering zone the mineral nutrients K, Ca, P, and most of the Mg are fully depleted. Radiogenic ⁸⁷Sr/⁸⁶Sr ratios show that nutrient sources in soil are atmospheric and are decoupled from the weathering zone. We measured ²⁶Mg/²⁴Mg stable isotope ratios. Uptake of Mg by plants is associated with isotopic fractionation relative to the soil and soil pore water. Because we find no isotope ratio shift between trees and soil water, isotope mass balance requires complete uptake of Mg into trees. Given this efficient Mg utilisation the recycling rate is high and loss of Mg from the ecosystem is minimal. In the fast-eroding mountain forest of the Southern Sierra Critical Zone Observatory, California, primary feldspar and biotite have been only partially dissolved. Mg stable isotope mass balances show that Mg is highly bio-utilised: 50-100 % of the Mg released by chemical weathering is taken up by forest trees. The comparison of weathering flux with bio-uptake shows that other bio-utilised elements (K, Ca, P and Si) are also highly bio-utilised, and recycling rates are low. P is enriched towards the surface, hinting at nutrient uplift. Mg stable isotopes further show that Mg can be taken up by Ponderosa Pine at a depth of up to 7m. Mass balances shows that after uptake by forest trees, loss of these nutrients occurs in eroded plant debris and recycling is minimal.

The slow Sri Lanka data confirms the absence of deep nutrient uptake, the importance of atmospheric sources, and the high degree of nutrient recycling. The fast eroding Sierra Nevada data confirms the hypotheses of a rapid nutrient turnover after deep, biogenically stimulated weathering.

$\delta^{34}\text{S}$ COMPOSITION OF ORGANOSULFUR COMPOUNDS AS PALEO PROXY – A CASE STUDY ON THE ISOTOPIC VARIATIONS OF INORGANIC AND ORGANIC SULFUR PHASES ACROSS THE PERMIAN-TRIASSIC TRANSITION

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Content

The Permian/Triassic (P-Tr) extinction was the most severe of the Phanerozoic extinctions, with a disappearance of 95% of marine species over a short time interval. Still, no consensus about the causes exists, with the most popular explanations including i) massive volcanic activity; and ii) global anoxia and euxinia. Either of these processes could have been responsible for the profound impact on the global S-cycle shown by isotopic variations of inorganically bound S-phases (sulfate and pyrite). Here we complement the isotopic analysis of inorganic S with bulk organic S and, for the first time, organosulfur compounds in two Permian-Triassic boundary (PTB) sections from I) the carbonate dominated GSSP at Meishan (South China) and II) a mud-rock sequence at Hovea-3 (Western Australia).

The Meishan PTB section shows an isotopically distinct event horizon beginning ~4 m below the P-Tr extinction and leading up to just below the extinction. In the event horizon total reduced inorganic sulfur (TRIS) shows a profound ^{34}S enrichment (from -30 to -13‰). Compound specific $\delta^{34}\text{S}$ analysis of dibenzothiophene (DBT) reveals a simultaneous ^{34}S depletion (from -17 to -24‰). Following the extinction $\delta^{34}\text{S}$ of TRIS and DBT return to pre-event levels whereas kerogen S becomes depleted by 12‰. This novel data set suggests that DBT represents a sub-fraction of kerogen S that was isotopically sensitive to the changes in depositional setting (e.g. water column redox conditions) during the extinction event, unlike bulk kerogen which showed constant $\delta^{34}\text{S}$ values. An inverse relationship evident in the $\delta^{34}\text{S}$ profiles of TRIS and DBT suggests the disproportionation of a common reduced S source. This isotopic excursion coincided with an increase in abundance of organic sulfur, reflected by decreasing TRIS/(TRIS+KerogenS) values, which likely favoured OM sulfurisation over pyritisation.

A more moderate ~4‰ ^{34}S depletion of TRIS and ~1.5‰ ^{34}S enrichment of DBT was measured across the condensed PTB section in Hovea-3. The direction and lower magnitude of the $\delta^{34}\text{S}$ variations was in contrast to the Meishan data, and may be due to higher abundances of kerogen S and more so inorganic S deposited at this site. The contrasting $\delta^{34}\text{S}$ behaviour of the different S-phases across these PTB sections implies a greater sensitivity to local basin conditions (e.g. water column redox conditions) or lithology than coincident global events such as volcanic activity (e.g. elevated influx of volcanic S species).

Session 3.2: Going deep: Tracking life processes through time and space: Poster

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Bacterial endospores in the deep biosphere – Advancements in their detection with the biomarker dipicolinic acid (DPA)

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Content

Prolonged nutrient deficiency, desiccation or high temperatures are the main triggers for endospore formation of most bacteria of the phylum Firmicutes. Endospore formation is a survival strategy to endure unfavorable conditions and a potentially important adaptation strategy to deep biosphere environments. While there are still many uncertainties regarding the role of such endospores in the microbial community of the deep biosphere, they are slowly being recognized as a potentially important component of subsurface ecosystems [1].

The biomarker dipicolinic acid (DPA), which is specific to intact bacterial endospores, is used for endospore quantification in sedimentary samples via high performance liquid chromatography coupled to fluorescence detection (HPLC-FLD) [2]. DPA concentrations are hereby transformed to endospore concentrations using an experimentally determined conversion factor [3]. However, adsorption of DPA to the matrix during extraction, especially by the common clay minerals kaolinite and smectite, results in decreased sensitivity of the method, limiting its usability in clay-rich low-biomass settings.

To increase the sensitivity of the current methods we conducted experiments with the aim to reduce DPA adsorption to the matrix. Sand, kaolinite and montmorillonite (smectite) as matrix, amended with endospores from pure cultures, were tested along with the following steps (i) fine tuning and stabilization of the pH conditions during extraction, preventing adsorption of DPA in the first place, (ii) supplying additives which actively desorb DPA from the matrix, (iii) adjusting of the instrument conditions and setup for improved chromatography. Optimized pH conditions alone resulted in at least one order of magnitude higher sensitivity in kaolinite and smectite matrix and recovery of DPA reached ~90% compared to non-matrix extraction blanks. Furthermore, we recommend to upscale the sample volume and increase the DPA concentrations of the final extract via evaporation. Combining all improved steps, this new method enables detection of endospores in clay-rich samples from low-biomass samples of the deep biosphere.

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Deep subsoil tree phosphorous sources in forest ecosystems

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Content

Phosphorous (P) is often a plant-growth limiting nutrient as it fulfils life-sustaining functions in living organisms. Over long-term pedogenesis P is converted from bio-accessible P forms (apatite bound P) into barely bio-accessible P forms (organic bound P and occluded P). On geologic time-scales two endmember weathering regimes can evolve comprising kinetically-limited or supply-limited regimes. In the kinetically-limited regime, short soil residence times keep apatite undissolved. If so, forest trees acquire P directly from mineral bound P [1]. In the supply-limited regime, long soil residence times provide the time-frame over which the conversion of P into barely bio-accessible P forms runs into completion. In this case, forest trees are mainly nourished by P uptake from plant litter (recycling) [1] or by external atmospheric sources [2]. However, during recycling P is continuously lost as solute and as particulate. Here we hypothesize that forest ecosystems that are supply limited and where external atmospheric inputs are negligible, are nourished by P uptake from the deep P rich reservoirs.

To test this hypothesis, we selected two study sites with similar environmental conditions in the Black Forest (CON) and in the Bavarian Forest (MIT). Both study sites are underlain by gneissic bedrock, mantled by Cambisols and covered by a mixed deciduous and coniferous forest. At both study sites we drilled up to 30 m deep through the regolith - comprising soil, saprolite and weathered bedrock - into unweathered bedrock and applied geochemical mass balances and the P Hedley fractionation method to characterize the inventory and bioavailability of P in the regolith. We find that P depletion accounts to $\approx 70\%$ relative to parent bedrock. The remaining $\approx 30\%$ occur in barely bio-accessible forms such as organic bound P and occluded P in the top 3 m at CON and MIT. To trace whether P is utilized below the zone of barely bio-accessible P, we applied isotope geochemical tools such as $^{87}\text{Sr}/^{86}\text{Sr}$ and meteoric $^{10}\text{Be}/^9\text{Be}$ to fingerprint the depth of P uptake by forest trees. We find that P, which is recycled more than ten times from plant litter, is originally utilized by forest trees from surprisingly deep layers at 3-7 m at both study sites. This deep P-uptake challenges the common view that mineral-derived P is taken up from shallow soil, only.

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Exploring microbial sulphate reduction under high temperature and pressure – Results of a pilot study on samples from IODP Exp. 370

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Content

Sulphate reduction is the quantitatively most important process in the anaerobic degradation of organic matter in the sea floor. Due to cryptic sulphur cycling it can proceed even if sulphate concentrations are near or below our detection limits. While the effects of elevated pressure and temperature on microbial sulphate reduction have been studied for decades, almost all studies were carried out in hydrothermal systems like Guaymas Basin, whereas sedimentary non-hydrothermal systems did not receive much attention. IODP Exp. 370 (Temperature Limit of the Deep Biosphere off Muroto) was specifically planned to explore the upper temperature limit of life in a sedimentary system off the coast of Japan.

Due to the high heat flow in the area the geothermal gradient is high enough (ca. 100°C km⁻¹) to sample the putative temperature-dependent biotic–abiotic transition zone at relatively shallow sediment depth but still sufficiently gradual for the establishment of distinct, thick depth horizons (>10 m) with suitable conditions for psychrophilic (optimal growth temperature range: < 20°C) mesophilic (20–45°C), thermophilic (45–80°C) and hyperthermophilic (>80°C) microorganisms. This unique location allows exploring the putative biotic fringe at a relatively shallow depth, but with high resolution of the temperature gradient. Radiotracer measurements of microbial turnover was one of the key aspects of this expedition, and each parameter that can be measured by radiotracer (methanogenesis, anaerobic oxidation of methane, hydrogenase enzyme activity, sulphate reduction) will be measured by a different group that has specialized in this kind of analysis.

Due to several logistical limitations it was decided to carry out those experiments mostly on shore, only for methanogenesis and sulphate reduction a small subset of samples was incubated at their approximate in-situ temperature and atmospheric pressure.

The sulphate reduction rate samples from the on-board incubations were processed at GFZ Potsdam to guide subsequent incubations with radioisotopes. Further experiments under different conditions as well as with additions of electron donors (e.g. volatile fatty acids, methane, hydrogen) will explore the upper temperature limit of this important biogeochemical process. Together with previous data from ODP Leg 190, Site 1174, which was drilled in close proximity to Exp. 370, sulphate reduction could be detected down to over 1000 mbsf.

First insight into subseafloor life in Bengal Fan sediments (IODP 354 Site U1449)

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Content

The deep subseafloor microbial biosphere may play a major role in global biogeochemical cycles. However, the state of investigation of the deep biosphere in different marine subsurface environments is rather limited. During International Ocean Discovery Program Expedition 354 (February – March 2015, Singapore – Colombo, Sri Lanka) we sampled sediments from the Indian Ocean along a 8°N transect. Here we present our first insights into subseafloor life in the Bengal Fan sediments.

At Site U1449, we quantified (i) prokaryotic cells using epifluorescence microscopy after detaching cells from the sediment, (ii) bacterial endospores by analyzing the diagnostic biomarker dipicolinic acid (DPA) through detection of fluorescence from the terbium-DPA complex, and (iii) microbial activity by analyzing hydrogen utilization potential based on the activity of hydrogenase enzymes, which are ubiquitous in subsurface microorganisms.

We measured highest cell concentrations of ca. 10^7 cells cm^{-3} in shallow sediments close to the seafloor; these concentrations are lower than in most marine continental margin settings [1]. Cell concentrations followed the global trend and decreased exponentially with depth. Endospore concentrations scattered between ca. 10^5 and 10^7 cells g^{-1} sediment. We could not observe a clear relationship of endospore concentration and sediment depth; instead, it appears to be linked to lithology and total organic carbon content. Potential hydrogenase enzyme activity scattered in the nmolar to μmolar range of H_2 $\text{g}^{-1}\text{d}^{-1}$. Similar to previous observations [2], per-cell hydrogen utilization depends on vertical biogeochemical zones, which could be due to the differences in hydrogen utilization requirements/efficiency of the respective metabolic processes such as sulfate reduction, methanogenesis, fermentation etc.

One striking feature at Site U1449 is a shift in biogeochemical profiles at around 110 mbsf, right below the hemipelagic sediment layer (0.8-1.3 Ma). Above and below the episode of hemipelagic sedimentation, turbidite deposits and thick sand layers dominated the lithology. Based on our current data, we suggest that the origin of sedimentary material influences microbial activity and the deep biosphere.

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IODP-ICDP Expedition 364: A geobiological archive of the recovery and evolution of life after the End-Cretaceous mass extinction event in the Chicxulub Impact Crater

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Content

The End-Cretaceous Mass Extinction event was one of the five largest mass extinction events in the Phanerozoic and the only one proven to be associated with impact of an extraterrestrial object. The resulting Chicxulub impact crater in Mexico is the largest terrestrial crater with a peak ring and a preserved global ejecta layer. For the first time the peak ring of the crater has been cored by the Integrated Ocean Drilling Program (IODP) and International Continental Scientific Drilling Program (ICDP) Expedition 364 in 2016 to study how the peak ring was formed and how microbial and aquatic life evolved post impact.

While the impact event has been fairly well studied for fossilising taxa, the post impact recovery and evolution of the majority of non-fossilizing organisms will need to be studied using molecular fossils (lipid biomarkers and their isotopic compositions) instead. For this project, we will also explore to what extent genetic signatures can be recovered from the relatively immature Cenozoic marine sediments overlying the Chicxulub impact crater and if the analysis of this environmental DNA could assist in identifying biological sources of lipid biomarkers to refine our understanding of the post-impact recovery and evolution of microbial and macroscopic life including taxa that do not leave behind a fossil record.

Initial results show that the meteorite-impacted breccia and overlying marine Cenozoic sediments contain up to 800 picograms genomic DNA per gram of rock.

The subsequent coupling of microbial metagenomic datasets with organic and isotopic geochemistry proxy data and in the context of geological data through collaboration with Expedition 364 science party members will contribute to a deeper understanding of environmental factors that affect the deep biosphere, and its ability to recover and evolve after major, impact-triggered extinction events.

Expedition 364 Scientists: S. Gulick, J.V. Morgan, E. Chenot, G. Christeson, P. Claeys, C. Cockell, M.J. L. Coolen, L. Ferrière, C. Gebhardt, K. Goto, H. Jones, D.A. Kring, J. Lofi, X. Long, C. Lowery, C. Mellett, R. Ocampo-Torres, L. Perez-Cruz, A. Pickersgill, M. Poelchau, A. Rae, C. Rasmussen, M. Rebolledo-Vieyra, U. Riller, H. Sato, J. Smit, S. Tikoo, N. Tomioka, M. Whalen, A. Wittmann, J. Urrutia-Fucugauchi, K.E. Yamaguchi, W. Zylberman.

Microbial lipids in methane seep sediments along the northern US Atlantic margin

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Content

About 570 gas plumes were recently detected on the northern US Atlantic margin (USAM) resulting in conservative estimate of methane emissions of ca. 15-90 Mg yr⁻¹ [1]. Understanding the biological controls that govern methane cycling and ultimately large scale methane flux from the seabed into the overlying ocean and atmosphere is focus of this study. We use a combined lipid biomarker, microbiological and isotopic approach to investigate the composition of microbial communities involved in methane cycling.

Geochemical analysis indicates a microbial origin for methane and 16S rRNA gene sequencing shows strong community differentiation based on location. For example, archaeal communities at the deep water methane-dominated Chincoteague Seep is dominated by anaerobic methanotroph (ANME-1), while the methane-charged but organic matter influenced Hudson Canyon shows more diverse archaeal community compositions including Thermoplasmatales, Marine Benthic Group-B and Deep Sea Hydrothermal Vent Group.

The identification of intact polar lipids (IPLs) and analyses of head-group specific stable carbon isotope is used to assess the potential of specific IPLs as diagnostic biomarkers for microbial groups. These include the use of the newly identified butanetriol dibiphytanyl glycerol tetraether as a characteristic biomarker for Methanomassiliicoccales [2] and intact archaeols (ARs) and OH-ARs as exclusive markers for archaea involved in methane cycling. At Chincoteague Seep the archaeal IPLs are dominated by diglycosidic glyceroldibiphytanylglyceroltetraethers (2G-GDGTs) with notable contribution of 1G-ARs and 2G-ARs, which is in accordance with the ANME-1 dominance at this site. On the other hand, 1G-GDGTs are dominant at the Hudson Canyon and the total archaeal IPL concentration is 2-5 times higher than at Chincoteague Seep, indicating less dominance of anaerobic methane oxidation processes but higher archaeal biomass. This study also promises insights into source organisms of currently orphan biomarkers such as branched GDGTs, overly branched GDGTs and isoprenoid-branched GDGTs.

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**The Ediacaran microbialites and mat-related structures of the Anti Atlas (Morocco):
Evidence for microbial mats thriving in a volcanic caldera setting**

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Content

Microbial communities are widely adapted to various setting including extreme conditions. Evidence of interaction of microbial communities with sediments is preserved in rock record, since the Archean, as a variety of mat-related structures and deposits in both siliciclastic and carbonate successions. The Ediacaran Amane succession in the Anti-Atlas belt provides an example of microbial communities thriving in a volcanic setting. The Amane deposits, up to 15m thick, are interbedded within an andesitic complex and form part of an isolated lacustrine depression of a wide volcanic caldera. Preliminary investigations led to recognize typical facies and structures related to microbial mats. The first type of structures consists of composite bioherms of coarse-grained microbialites with morphotypes ranging from small-scale isolated structures to columnar and laterally-linked domal forms. Planar microbialites preserve typical upturned and overgrown margins related to repeated shrinkage and growth of microbialites. The microfabrics exhibit typical mm-scale wavy and crinkly lamination, and consist of alternating thick epiclastic-rich laminae and thin filamentous laminae. The epiclastic laminae are dominated by feldspars and volcanic clasts including glass shard and lava clasts. All the grains are embedded in a fine-grained microcrystalline matrix of likely EPS origin. The thin filamentous laminae exhibit typical fabrics of entangled microbial filaments with sparse trapped grains. Micro-scale tufts and domes occur together with vertically oriented grains. All these features indicate together a biosedimentary accretion resulting from trapping and binding processes of reworked volcanic and volcanoclastic material in a shallow lake. Most of the microbialites beds develop during stage of limited clastic input into the lake. They are underlain by coarse-grained stromatoclast-rich or wave-rippled calcarenites indicating high-energy events during lake expansion. The second group of structures, associated with siliciclastic intervals, occurs on bedding surfaces of sandstones and consists mainly of gas domes and cone-shaped tufts linked with polygonal ridges. These structures indicate active mat growth and metabolism in the shoreline part of the lake. The short-lived Amane lake microbial mats constitute another example of microbial communities thriving in a clastic environment and an Ediacaran microbial life adapted to extreme setting.

Ultrasensitive detection of biomarkers extends our view on (early) life signatures in the sedimentary record

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Content

The detection of early life traces using lipid biomarkers in the sedimentary record is challenging due to their thermal decomposition during deep sedimentary burial [1] [2]. As a result, biomarker concentrations are often below the detection limit of regular analytical techniques and intense cracking results in the production of smaller fragments that cannot longer be attributed to a source specific precursor molecule. These factors create a major threat to the unambiguous identification of ancient biological signatures. Specific degradation products of hopanes and steranes might still carry diagnostic value for the reconstruction of past biota when found in mature oils and sediment extracts [3] [4], but their concentrations are often exceedingly low. We here report on the use of gas chromatography–mass spectrometry with laser ionization at atmospheric pressure (GC-APLI-MS) [5] for the determination of aromatic steroids deriving from the aromatization and cracking of regular steroids at elevated maturities [4]. This technique is based on resonance-enhanced multiphoton ionization (REMPI) with (1+1)-photon excitation allowing the selective ionization of aromatic hydrocarbons leading to higher sensitivity compared to regular GC-MS techniques and has been mostly applied for the detection of polycyclic aromatic hydrocarbons (PAHs) in environmental samples [6] [7]. By GC-APLI-MS analysis of a reference oil, aromatic steroids are detected successfully with significantly higher sensitivities compared to commonly used EI ionization GC-MS in selected ion monitoring mode. GC-APLI-MS applied to Paleoproterozoic sedimentary rocks (1.64 Ga) [8] yielded the so far oldest unambiguous aromatic steroids, with their varying abundances following a maturity gradient and revealing the occurrence of triaromatic steroids in even deeper parts of the succession at high thermal maturities exceeding 450°C Tmax. GC-APLI-MS is a highly promising tool that might extend molecular geobiological approaches to basins that were hitherto precluded by their thermal maturity.

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Session 3.2: Going deep: Tracking life processes through time and space: Talk

Keynote speaker

A-251

Tracing ancient life processes by analysing mineral coatings in deep rock fractures

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Content

During the last decades, active and ancient subterranean life processes have been discovered in a wide range of geological settings. With an aim to increase the understanding of when and how microbial life has thrived in the omnipresent fracture systems of the upper continental crystalline crust we have during the recent years applied high spatial resolution analysis of stable isotopes (SIMS and LA-MC-ICP-MS), organic remains (ToF-SIMS), and geochronology (*in situ* Rb-Sr¹ and U-Pb² by LA-ICP-MS) to secondary mineral coatings. Conventional characterisation of biomarkers and fluid inclusions as well as morphological analysis of partly fossilized microorganisms (SRXTM) were also done. Samples were retrieved from an extensive record of deep Scandinavian drill cores and underground facilities.

The isotope composition of authigenic calcite and pyrite was e.g. linked to microbial methanogenesis (¹³C-rich calcite) or anoerobic oxidation of methane (AOM, extremely ¹³C-poor calcite) coupled to bacterial sulfate reduction (BSR, featuring pyrite with diagnostic $\delta^{34}\text{S}$ values and remains of BSR-related biomarkers)^{3,4}. Periods of AOM were tracked by intra-crystal SIMS analysis and coupled *in situ* radiometric dating provided timing constraints for several Mesozoic and Paleozoic periods of widespread AOM (e.g. at 400, 350 and 170 Ma) in the upper 800 m of the rock.

An intriguing feature of this deep biosphere is unprecedented isotope variability, particularly of $\delta^{13}\text{C}_{\text{calcite}}$ (ranging -125 to +37‰ PDB, with >100‰ spans within single crystals)^{3,4} but also of $\delta^{34}\text{S}_{\text{pyrite}}$ (spanning >180‰ CDT), which has been characterised with SIMS-ion imaging, giving insight into isotope distillations during microbial processes. Preserved organic material within the crystals indicates that carbon of surficial origin, at least partly, has fueled the deep microbial processes. In addition, new findings of anaerobic cryptoendolithic fungal hyphae present together with BSR-related pyrite in fractures at >700m depth suggest that even eukaryotes may play an important role in the deep continental biosphere⁵. Taken together, the vast deep oligotrophic biosphere in continental Precambrian rocks has been active over long geological time frames and certainly calls for more extended research.

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An unusual ferruginous-calcitic *Frutexites* microbialite community from the lower Cambrian of the Flinders Ranges, South Australia

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Content

Stromatolitic iron-rich structures have been reported from many ancient environments and are often described as *Frutexites*, a cryptic microfossil. A microbial formation of such structures is likely, and evidenced by new research (Heim et al. 2017). The Flinders Ranges of South Australia are famous for their fossiliferous early Cambrian faunas and most important are the Atdabanian– Botomian Ajax Limestone from the environs of the Mount Scott Range; and the more widespread, coeval Wilkawillina Limestone. The Atdabanian-Botomian boundary within the Flinders Ranges is marked by the “Flinders Unconformity” and this boundary is characterized by a decimeter thick “red crust” commonly bearing small up to decimeter-sized caves and crevices (Reitner et al. 2017). In the outcrop the red crust is a complex set of well-laminated domal and branching Fe-stromatolites. In thin sections digitated, and microlaminated stromatolites dominated by *Frutexites* fabrics. *Frutexites* was first described by Maslov (1960) within a stromatolite body and is mainly formed by oxidized iron minerals (Fe-hydroxides, hematite, magnetite), commonly enriched in calcite and also in Mn oxides. *Frutexites*-type microbialites, both ancient and modern, prefer cryptic and dark habitats and are currently formed by diverse microbial communities including Fe- and Mn-oxidizing bacteria and also Archaea (Heim et al. 2017). Geochemical analyses, e.g. a strong positive Ce anomaly suggest that the early Cambrian microbial *Frutexites* red crust was formed under dys- to anaerobic conditions. The ferruginous crusts are up to 10 cm thick and caused a strong electrochemical corrosion of the underlying archaeocyath-bearing carbonates.

Heim, C., Queric, N.-V., Ionescu, D, Schäfer, N., Reitner, J. (2017): *Frutexites*-like structures formed by iron oxidizing biofilms in the continental subsurface (Äspö Hard Rock Laboratory, Sweden).- PloS One, 12(5)

Reitner, J., Langsford, N., Kruse, P.D. (2017): An unusual ferruginous-calcitic *Frutexites* microbialite community from the lower Cambrian of the Flinders Ranges, South Australia.- PalZ, DOI 10.1007/s12542-017-0342-z

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Characterization of lacustrine microbialites from south-eastern South Australia

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Content

Morphologically diverse microbialites occur in a variety of continental environments across southeast (SE) South Australia between Robe and Mount Gambier. These include towers and chimneys growing from the wall of a fresh water volcanic crater lake, complex curtains accreting on the walls of freshwater cenotes, domical heads on the floor of shallow, brackish, intermittent inter-barrier lagoons, coalescing shelves and 'reefs' around an alkaline saline lake (Lake Fellmongery) and unattached "algal biscuits", which accreted on all sides as they were overturned, dispersed over the surface of a recently-drained ephemeral inter-barrier swampy area. All these depositional environments developed on or within Cenozoic limestones of the Otway Basin and are mostly fed by groundwater and experience seasonal evaporation. Salinities increase with proximity to the coast. Optical microscopy, SEM-EDS, XRD, C and O isotopes, ¹⁴C dating, ICP-MS and synchrotron XFM mapping techniques were employed in order to characterise microstructure, mineralogy, age and geochemistry of the variety of microbialites. Microbialites are Holocene in age (4,190-200 yrs B.P.) with estimated growth rates of 0.01 to 0.16 mm/year. Observed differences in microstructure are explained by differences in depth, light, and geochemistry of their environments. All microbialites, except those of Lake Fellmongery, are composed of low-Mg calcite (LMC). The primary mineralogy of Lake Fellmongery microbialites is monohydrocalcite with an early amorphous Mg-Si phase, which is replaced below the active uppermost deposit by aragonite, LMC and a proto-dolomite phase. Microstructure and $\delta^{13}\text{C}$ indicate precipitation mediated by photosynthetic uptake of ¹²C for all microbialites except for those in Lake Fellmongery. Mg and Sr concentrations in the microbialites increase in higher salinity water bodies. Groundwater-fed microbialites of both the volcanic lake and cenotes inherited rare earth element (REE) patterns largely from the host rocks, while the microbialites from the other environments tend to have more shale-like, contaminated elemental distributions. Our results demonstrate that the morphology, microstructure, mineralogy and geochemistry of each of the diverse microbialites of SE South Australia reflect the local geochemistry and geomorphology of each depositional environment.

Evidence for archaeal methanogenesis within in situ veins at the onshore peridotite-hosted Chimaera seeps, Turkey

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Content

Serpentinite-hosted ecosystems have attracted the interest of the scientific community, as they are considered to be likely environments where life first evolved on Earth. Serpentinization reactions produce strongly reducing and highly alkaline fluids that are typified by high concentrations of molecular hydrogen and methane, which can be used as an energy source by chemotrophic microbial communities. Moreover, carbonate formation is a common late-stage alteration process that is induced by the serpentinization of peridotite at the seafloor and on land. It is well established that low-temperature serpentinization at slow-spreading mid-ocean ridges provides an ideal environment for rich microbial communities, including anaerobic archaea and bacteria. Recent studies of lipid biomarkers and their isotopic compositions have suggested that some Euryarchaeota are able to perform methanogenesis and methanotrophy, depending on the prevailing environmental conditions. However, no evidence for archaeal methanogenesis or methanotrophy has yet been reported for similar environments on land. This study is the first to present lipid biomarker evidence for archaeal methanogenesis at the terrestrial, peridotite-hosted Chimaera seep in Turkey. The analyzed Chimaera rock samples are serpentinites that are cross-cut by veins composed of brucite and hydromagnesite. Pentamethylcosane and squalane with $\delta^{13}\text{C}$ values of +10‰ and +14‰, respectively, were identified within the brucite-carbonate veins. Furthermore, archaeol, sn2-hydroxyarchaeol, squalane and squalenes were found. Archaeol and sn2-hydroxyarchaeol also show high compound-specific $\delta^{13}\text{C}$ values of up to +7‰. These isotope signals combined with the absence of crocetane – a biomarker for methanotrophic archaea – reveals that the microbial communities at the Chimaera Seep performed methanogenesis rather than methanotrophy. Our results suggest that biological methane production may play a role during terrestrial low-temperature serpentinization.

Life in an iron sea: A reconstruction of Paleoproterozoic ecosystems

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Content

The 1.64 Barney Creek Formation (BCF) in northern Australia hosts the oldest clearly syngenetic biomarkers in the world, allowing detailed ecological reconstructions. The molecular fossils indicate that purple sulphur bacteria (Chromatiaceae) were dominant during periods that are characterised by ferruginous water column conditions as determined by our Fe-speciation analyses. This suggests that these anoxygenic phototrophs utilised ferrous iron as an electron source for photosynthesis – the first evidence for this unusual metabolism in the Proterozoic. In addition, our data indicate a dynamic redox environment with intermittent oxic and euxinic periods. The oxic degradation of redox sensitive biomarkers indicates intermittent, possibly seasonal, incursions of oxygenated surface waters. The oxygenation events appear to have been short lived, as unique correlations between biomarker and iron speciation proxies indicate that mixing events were followed by periods of euxinia. Concurrent variations in chemocline depth appear to have influenced the community composition of green and purple sulphur bacteria. The dynamic nature of the marine system can be explained by variations in climatic conditions. Wind driven mixing may have deepened the mixed layer, suppressing growth of purple sulphur bacteria that have high light requirements and therefore usually populate shallow chemoclines (< 20 m depth). Growth of green sulphur bacteria (Chlorobiaceae) was instead favoured during more turbulent periods when run-off increased, as suggested by higher abundances of siliciclastics relative to carbonates. The resulting increased influx of sulphate and/or nutrients is envisaged to have fueled bacterial sulphate reduction, leading to the development of euxinic conditions. In addition to short term fluctuations in water column chemistry and microbial communities, long term trends in different proxies are evocative of an orbital control on the inferred climatic processes that underlie the basin dynamics.

Lipid biomarkers in Pleistocene cherts from Lake Magadi, Kenya – microbial signals and hydrothermal influence

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Content

The alkaline, hypersaline Lake Magadi (East African Rift Valley, Kenya) is located in a restricted basin, exclusively fed by hydrothermal springs and seasonal rain fall. During the younger history of the lake diverse siliceous sediments (Magadi Cherts) precipitated, probably triggered by fluid mixing, evaporation and microbial activity [1]. In this study, we used organic biomarkers to track the past microbial communities associated with the formation of the Magadi Cherts. The analytical approach comprised gas chromatography-mass spectrometry, gas chromatography combustion isotope ratio-mass spectrometry and bulk rock element analysis (C, N, S).

The Magadi Cherts show low C_{org} (<0.1–0.3 wt.%), C_{carbonate} (<0.1–0.5 wt.%), nitrogen (<0.02 wt.%) and sulfur (<0.05 wt.%). Biomarkers indicate that cyanobacteria (methylalkanes), Archaea (e.g. archaeol), and thermophilic microbes, most likely sulfate reducing bacteria (fatty acids, 1-O-alkylglycerols) may have been the dominating organisms in a probably CO₂-limited system (¹³C enrichment in archaeol and 1-O-alkylglycerols). Apart from these lipids that putatively reflect the microbial biota present at the time of chert precipitation, abundant *n*-alkanes (unimodal statistical distribution, maximum at *n*-C₂₁) represent contributions of organic matter from a second source of higher maturity. This assumption is underlined by the presence of 17 α (H),21 β (H)-hopanes, showing a C₃₁ S/(S+R) isomer ratio of 0.6. The observed source mixing could be due to hydrothermal activity, delivering material from a deep hot reservoir [2], [3]. Partial alteration during hydrothermal recycling might also explain the mixed maturity signal. It has recently been shown that life on the early Earth flourished in hydrothermally influenced systems on land [4]. Consequently, the Pleistocene Lake Magadi could serve as a modern analog for these fossil settings on Earth and possibly beyond.

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Organic matter forming glass in basalt from Gia Lai, Vietnam

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Content

In a Cenozoic continental intraplate basalt from the province of Gia Lai, Vietnam, we identified organic matter together with magnesite-siderite, in an otherwise common basaltic mineral assemblage of plagioclase (An₅₅)-clinopyroxene (Mg# ~77)-olivine (Mg# 75-80)-magnetite-ilmenite-apatite. The organic matter occurs as C-rich glass together with the carbonate in vesicles, and textures with the formation of pigeonitic clinopyroxene (Mg# 40-50) clearly exclude introduction of organic matter by processes like late stage hydrothermal alteration or weathering (Fig. 1). Energy dispersive analyses of the organic matter, which has a conspicuous low contrast in back scattered electron images, indicate ~50 atom% C, ~5 atom% N, ~32 atom% O, ~8 atom% Si, ~1.5 atom% Fe, ~1 atom% Mg, with traces of Ca, K, Na, Cl. Stable isotope data of around -10 ‰ δ¹⁸OPDB and -13 ‰ δ¹³CPDB were determined in the carbonate and exclude a carbonatitic origin. Values of around -22 ‰ δ¹³CPDB of the C-rich glass and +5 ‰ δ¹⁵NAir are consistent with a biological origin. Radiogenic isotope data for ¹⁴³Nd/¹⁴⁴Nd and ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb of basalt whole rock and of basalt leachates with HCl and CH₃COOH do not differ significantly (Nd: 0.51285; ²⁰⁶Pb/²⁰⁴Pb 18.3, ²⁰⁷Pb/²⁰⁴Pb 15.5 and ²⁰⁸Pb/²⁰⁴Pb 38.5), but ⁸⁷Sr/⁸⁶Sr (0.7044 in whole rock) is significantly higher in the leachates (≤ 0.7078). When and how the organic matter was incorporated is speculative, but incorporation must have occurred in the magma chamber or early during ascent of the melt through C-rich sediments.

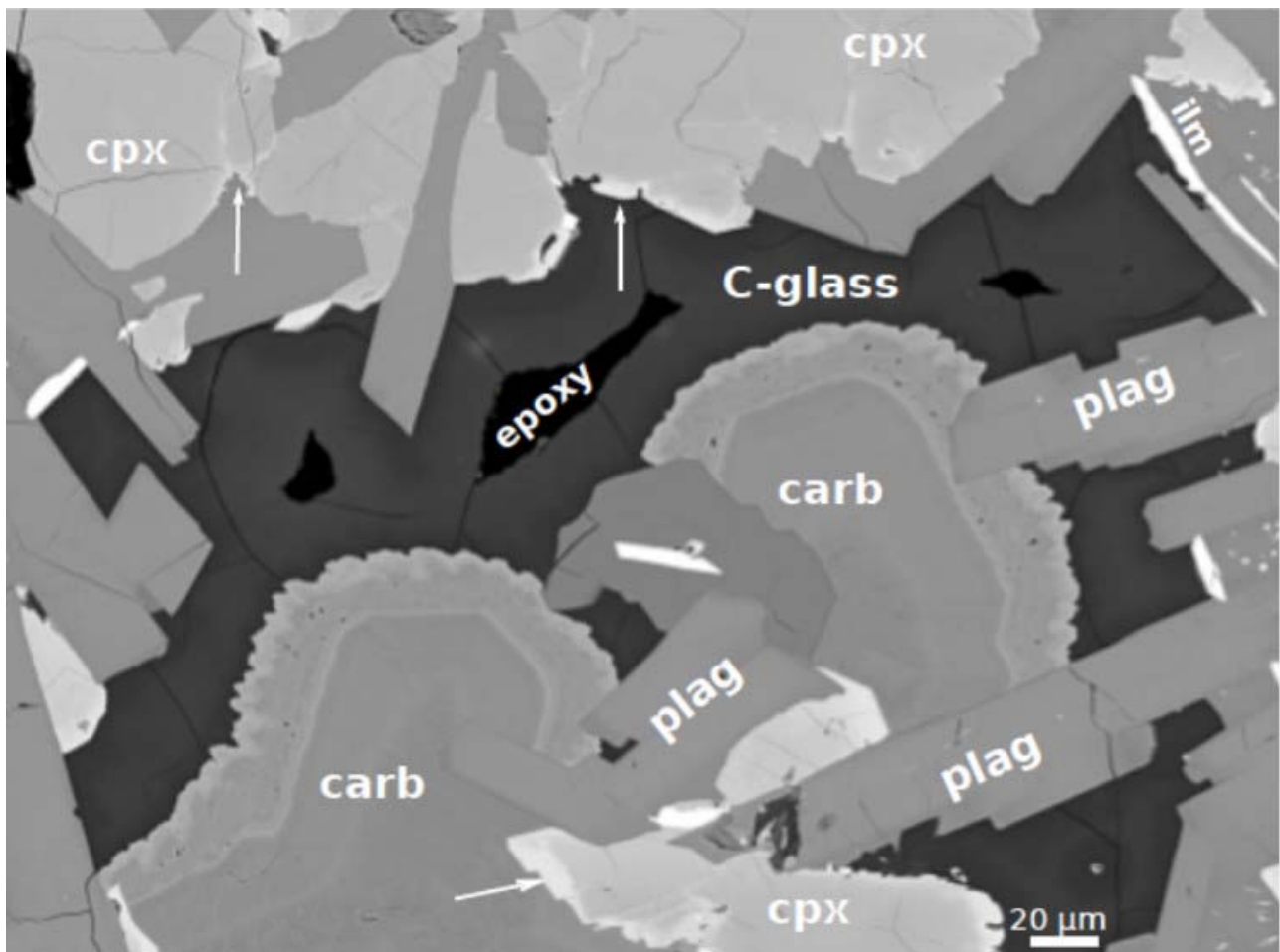


Fig. 1abstract

Fig. 1: BSE image of C-rich glass, together with magnesite-siderite; arrow points to pigeonitic clinopyroxene

Survival of Microbial-Metazoan Reefs in the Early Triassic Greenhouse Climate

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Content

Metazoan reef ecosystems suffered a substantial collapse following the latest Permian mass extinction event. This collapse is hypothesized to have been caused by increased sea surface temperatures, deoxygenation, and ocean acidification. After the mass extinction, impoverished microbial-metazoan reefs filled the ecological niche previously occupied by metazoan-rich reefs. Here we investigated the distribution and composition of sixteen post-extinction reef localities in China, Iran, Turkey, and Hungary. Our results demonstrate that keratose sponges, microconchids, and microbes grew synergistically to form microbial-metazoan reefs in the immediate aftermath of the extinction. The microbial carbonate contains abundant molecular fossils (lipid biomarkers) representing input from cyanobacteria, halophilic archaea, anoxygenic phototrophs, and sulphate-reducing bacteria. Remarkably, up to 50% of the carbonate is represented by sponge fossils (i.e. 'putative keratose sponge fabric'). Abundant fossils of oxygen-dependent metazoans, i.e. microconchids, bivalves, gastropods, ostracods, and foraminifers, are found within the microbial and keratose sponge microfabrics.

Molecular oxygen is critical for the survival of microbial-metazoan reefs ecosystems, yet the process by which oxygen is made available for the metazoans to either contribute to reef building or to dwell within the reef is still poorly understood. Our results show that post-extinction microbial-metazoan reefs with a high faunal diversity were limited to wave-aerated settings. Whereas, microbial bioherms and biostromes that formed below the action of waves but still within the photic zone only contain microscopic, low diversity faunas. The action of waves, therefore, maintained atmosphere-seafloor gas exchange in shallow water settings, and transported enough oxygen to the seafloor to support relatively diverse reef communities in an otherwise stagnant, oxygen-deficient ocean. Contrary to previous suggestions that the equatorial oceans were too warm for enough oxygen to be soluble to support diverse marine ecosystems, we demonstrate that this is not the case in the tropical Tethys. Even though metazoan reef ecosystems survived the latest Permian climate warming event, they are taxonomically and ecologically impoverished compared to their pre-extinction and post-recovery counterparts.

Temperature Limit of the Deep Biosphere off Muroto (T-Limit)

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Content

Expedition 370 of the International Ocean Discovery Program (IODP) aimed to explore the limits of life in the deep subseafloor biosphere at a location where temperature increases gradually with sediment depth to the known maximum of microbial life (~120°C). Since heat flow is elevated in the Nankai Trough subduction zone, such conditions are met off Cape Muroto, Japan, at relatively shallow depths of only ~1.2 km below the seafloor. Expedition 370 established Site C0023 in the vicinity of Ocean Drilling Program Sites 808 and 1174 at a water depth of 4776 m using the drilling vessel DV Chikyu. Hole C0023A was cored down to a total depth of 1180 meters below seafloor. Offshore sampling and research was combined with simultaneous shore-based investigations at the Kochi Core Center (KCC), and long-term monitoring of in situ temperature was initiated in a bore-hole observatory (Heuer et al., 2017).

The primary scientific objectives of Expedition 370 are (a) to detect and investigate the presence or absence of life and biological processes at the biotic-abiotic transition of the deep subseafloor with unprecedented analytical sensitivity and precision; (b) to comprehensively study the factors that control biomass, activity, and diversity of microbial communities; and (c) to elucidate if continuous or episodic flow of fluids containing thermogenic and/or geogenic nutrients and energy substrates support subseafloor microbial communities in the Nankai Trough accretionary complex (Hinrichs et al., 2016). This contribution will highlight the scientific approach of our field-work and present preliminary shipboard and shorebased results of Expedition 370.

Hinrichs K-U, Inagaki F, Heuer VB, Kinoshita M, Morono Y, Kubo Y (2016) Expedition 370 Scientific Prospectus: T-Limit of the Deep Biosphere off Muroto (T-Limit). International Ocean Discovery Program. <http://dx.doi.org/10.14379/iodp.sp.370.2016>

Heuer VB, Inagaki F, Morono Y, Kubo Y, Maeda L, the Expedition 370 Scientists (2017) Expedition 370 Preliminary Report: Temperature Limit of the Deep Biosphere off Muroto. International Ocean Discovery Program. <http://dx.doi.org/10.14379/iodp.pr.370.2017>

Where geo- meets astrobiology: Tackling the origin of organic matter on early Earth

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Content

Tracing the earliest life on Earth is one of the most challenging endeavors of current geo- and astrobiological research. Given that all extant life on Earth is based on carbon, organic matter in ancient rocks may provide evidence of its presence in the deep past. However, the origin of organic matter preserved in the oldest rocks on Earth is still enigmatic: Does it represent an unambiguous fingerprint of life or is it, partly at least, derived from abiotic sources (e.g. extra-terrestrial delivery, hydrothermal synthesis)? We tackle this question by analyzing organic matter in a variety of early Archean environments from the Pilbara Craton (Western Australia) and in selected younger analogue systems. These analyses include detailed field- and petrographic observations, Raman spectroscopy, nano secondary ion mass spectrometry (NanoSIMS), as well as catalytic hydrothermal synthesis (HyPy) followed by gas chromatography-mass spectrometry (GC-MS) and compound-specific $\delta^{13}\text{C}$ -measurements. Together, our observations suggest that a large proportion of the early Archean organic matter was indeed biologically produced – a finding that is supported by experimental data obtained via maturation and pyrolysis of extant biomass and the synthesis of abiotic organic matter via Fischer-Tropsch-like processes. The results underline the existence of a complex interplay between biological and abiological processes in Archean environments, and contribute to our understanding on how Earth became a habitable place. Furthermore, our studies have important implications for the identification of organic biosignatures on Earth and, potentially, beyond.

Session 3.3: Geomicrobiology - from understanding processes in ancient and modern environments to industrial applications: Poster

Session 3.3: Geomicrobiology - from understanding processes in ancient and modern environments to industrial applications: Poster

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Flux rates of phosphorous from sediments of two contrasting reservoirs as a result of temperature and oxic state – an experimental approach

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Content

The reduction of external nutrient loading of lakes and reservoirs is an important restoration strategy of eutrophic lakes and reservoirs. Several examples exist where highly eutrophic water bodies turned into an oligotrophic state after rigorous reduction of external loading (e.g. Lake Constance). Nevertheless, new signs of eutrophication have recently been observed in previously restored lakes without any increase of external inputs (e.g. Lake Zürich). It is well known that internal loading of nutrients becomes as more important as external loading is reduced but for the special cases of re-eutrophication of formerly oligotrophic lakes and reservoirs additional drivers have to be identified.

Since global warming increases the average surface temperature of lakes worldwide (0.35°C to 0.7°C per decade) alternative hypotheses to explain the observation of re-eutrophication of lakes and reservoirs could be i) increase of P-release from the sediment solely by an earlier (spring time) and longer lasting (late autumn) higher temperature at littoral sediment surfaces in the year; ii) increase in anoxic hypolimnia earlier and longer lasting in the year as a result of an increase in surface temperature, or iii) a combination of both. In any case the release of P from the sediment is a bacterial process driven by temperature.

To test these hypotheses we designed a two-factorial sediment core incubation experiment by varying either temperature or oxic status of sediment cores from two reservoirs with contrasting nutrient status in Germany: Reservoir Bautzen, located at the border to Poland, which is highly eutrophic and Reservoir Rappbode in the Harz mountains, which is oligotrophic.

From the results of this experiment it is evident that for oligotrophic lakes with low P content in the sediments only the combination of strongly reducing conditions (due to anoxia) and higher temperature leads to a significant increase in P concentrations in the overlying water column. If the sediment has a higher amount of P content, as typically found in eutrophic systems, temperature increase alone already yields a remarkable P flux towards the water body which is strongly enhanced if anoxic conditions occur in addition.

LIPIDOMIC CHARACTERIZATION OF BACTERIAL COMMUNITIES OF THE SHALLOW-WATER HYDROTHERMAL VENT SYSTEM OF KUEISHANTAO (TAIWAN)

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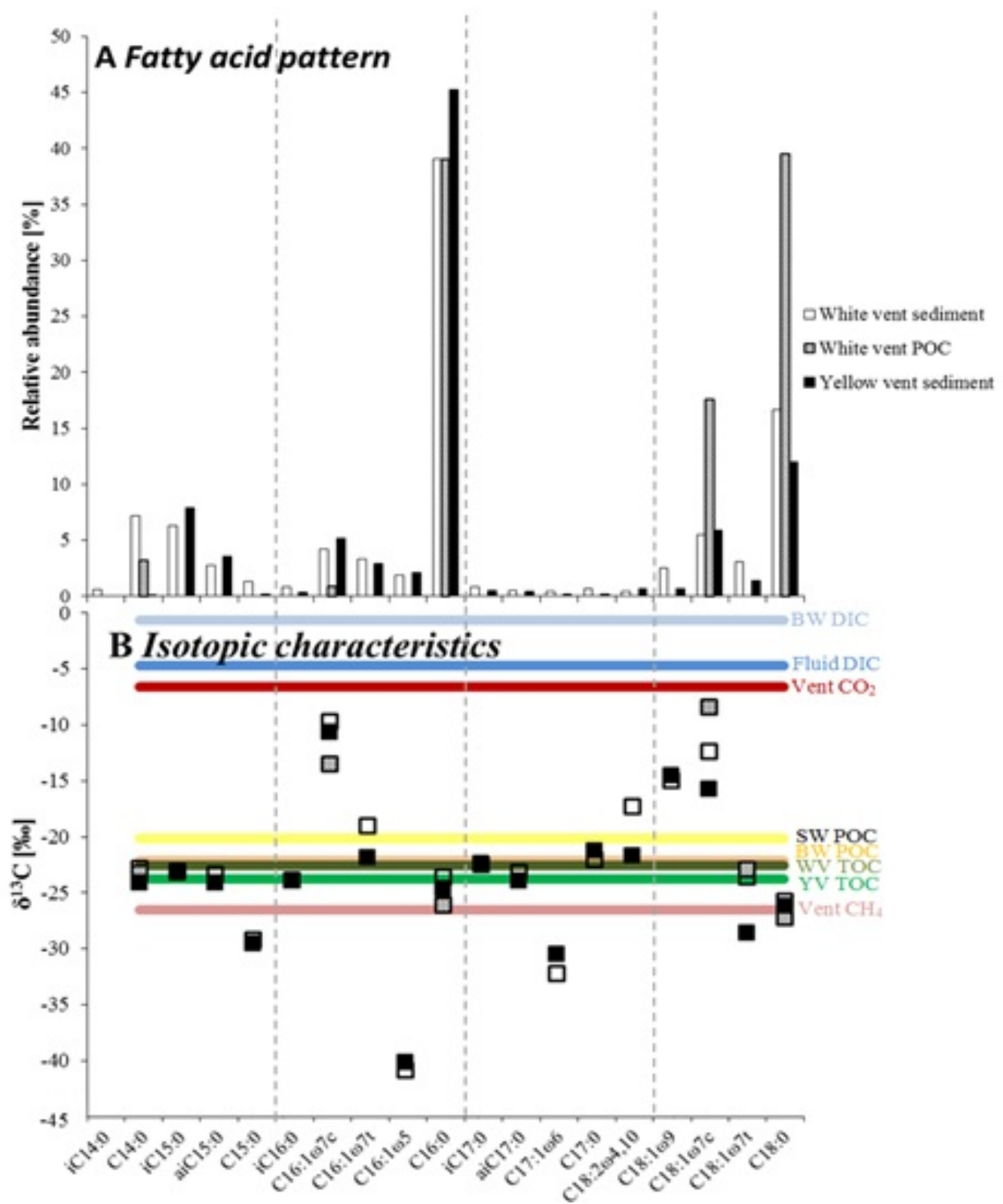
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Content

The Kueishantao shallow-water hydrothermal vent system located off NE Taiwan's coast (121°57' E, 24°50' N) is characterized by world-record low pH conditions (pH < 1) and fluid temperatures of up to 116 °C with gas discharges dominated by CO₂ [1]. In 2015, sediment cores were collected and hydrothermal fluids taken from a hot temperature vent (116 °C, pH = 2.88) and a warm temperature vent (58 °C, pH = 4.51) in order to characterize the difference in the lipidome of the active bacterial communities.

The fatty acid pattern of both vent sediments consists of 19 different fatty acids, ranging in chain length from C₁₄ to C₁₈ (Fig.1A). The fatty acids' stable isotopic ratios (δ¹³C) mostly ranged between -20 to -30 ‰, but with C_{16:1ω7c}, C_{18:1ω9} and C_{18:1ω7c} being most positive with δ¹³C-values of -9 ‰, -14 ‰, and -12 ‰, respectively, in the warm sediments and of -10 ‰, -14 ‰, and -15 ‰, respectively, in the hot sediments (Fig.1B). For both vent sites the positive δ¹³C values of C_{16:1ω7c}, C_{18:1ω9} and C_{18:1ω7c} might be explained by the occurrence of Epsilonproteobacteria, which have been identified metagenomically at the study site [2]. These bacteria possess the reverse tricarboxylic acid cycle (rTCA) for carbon fixation, a metabolic pathway that discriminates less against ¹³C than the Calvin-Benson-Bassham Cycle and is usually conducted in response to carbon dioxide being highly enriched in the environment [2]. Approvingly, the DIC was enriched in ¹³C (δ¹³C = -4.4 ‰; Fig.1B).

The corresponding fatty acid analysis of the warm vent fluid showed the presence of only five fatty acids (Fig.1A) but C_{16:1ω7c} and C_{18:1ω7c} were enriched in ¹³C with δ¹³C values of -13 ‰ and -8 ‰, respectively. Not only may identical Epsilonproteobacteria in the fluid fractionate differently against ¹³C because of diverging small-scale pH values, metagenomic studies revealed that different genera of Epsilonproteobacteria are contained in warm vent sediments vs. fluid [2]. Complementing analyses of intact polar lipids (IPLs) as indicators of bacterial community changes are under progress and will be presented alongside this study.



Pattern (A) and $\delta^{13}\text{C}$ values (B) of fatty acids in fluids and sediments surrounding the vents. $\delta^{13}\text{C}$ values of the major carbon pools are plotted alongside. BW: bottom water; SW: surface water; POC: particulate organic carbon; TOC: total organic carbon

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Tubular carbonate concretions derived from siboglinid tubeworm physiology

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Content

Branched tubular carbonate concretions were sampled on the SE flank of the Athina Mud Volcano (Anaximander Seamounts, eastern Mediterranean Sea) with the ROV MARUM QUEST during the RV METEOR M70/3 cruise. The tubular carbonates were observed in close proximity of several colonies of *Lamellibrachia anaximandri*, siboglinid tubeworms living without any digestive system due to endosymbiotic sulphide-oxidizing bacteria. A multidisciplinary study combining petrography, mineralogy, stable isotopes and lipid biomarkers was carried out in order to assess the geochemical environment of tubular carbonate formation. The results indicate that the precipitation of authigenic ¹³C-depleted aragonite cementing the sediment occurred at the posterior ends of tubeworms within the shallow subsurface. The formation of the tubular carbonates was likely induced by sulphate-dependent anaerobic oxidation of methane, locally enhanced by the tubeworm physiological activity through the release sulphate ions produced by their endosymbionts. Consequently, the tubular concretions represent a specific tubeworm ichnofossil of *L. anaximandri*. We suggest a new name for this ichnofossil, "autichemichnia", based on the in-situ precipitation of aragonite. Comparison of the tubeworm ichnofossil from Athina MV and tubular concretions from various fossil seep-carbonate deposits indicates that the tubeworms can be responsible of the formation of sub-seafloor tubular carbonate concretion.

Session 3.3: Geomicrobiology - from understanding processes in ancient and modern environments to industrial applications: Talk

Keynote speaker

A-486

Green rust in the Precambrian Fe cycle: Iron formation genesis and implications for trace element cycles

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Content

Iron formations provide strong evidence for the mobility of iron in Earth's oceans prior to about 2.3 billion years ago (Ga), which in turn implies that both dissolved oxygen and marine sulfide levels were low. However, despite decades of research, driven by economic interest and the potential of iron formations to constrain marine paleoenvironments, several aspects of their genesis remain incompletely understood. Notably, though recent hypotheses focus on amorphous Fe(III) hydroxides, the precursor to the observed mineral assemblages in iron formations has not been conclusively identified. One heretofore neglected precursor is the Fe(II)-Fe(III) hydroxy-salt green rust (GR). Combining thermodynamic calculations, laboratory experiments and dynamic models of the early Fe cycle, we find that GR likely had a quantitatively important role in iron formation genesis.

In laboratory experiments, carbonate GR readily precipitates from Precambrian-analog seawater solutions of variable composition and transforms upon aging into mineral assemblages observed in iron formations. These assemblages include predominantly Fe(II) or mixed-valence minerals, which form in the absence of organic matter, and may explain the existence of such minerals in some very organic-poor iron formations.

Incorporating these experimental insights into a model of the early Fe cycle, we expect that GR was a quantitatively important shuttle of Fe from the photic zone to the sediments through much of the Precambrian. Spatio-temporal heterogeneity in aqueous silica, inorganic carbon and oxidant concentrations, and in light-driven rates of Fe(II) oxidation would result in heterogeneity in the proportion of GR in the flux of Fe to the sediments.

Well known from environmental remediation studies, GR is highly reactive towards various metals (e.g., U, Cr, Zn, Ni, As), silica and phosphate. Whether this reactivity leads to enrichments or depletions in trace elements (in GR relative to Fe(III) hydroxides) that persist through early diagenesis, is a topic of ongoing experimental work. If the effects survive diagenesis, a Precambrian GR Fe shuttle would affect the cycles of these metals and nutrients, with implications for the construction of proxy records of Earth's surface oxidation state and for early primary production. Thus, our findings require a revision of the current understanding of the Precambrian Fe cycle, and of interpretations of the Fe isotope and trace element records.

***Methanothermococcus okinawensis* and *Methanocaldococcus villosus* respond to changing temperature with modifications of their membrane lipid compositions**

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Content

For the first time, a comprehensive evaluation of the core lipid composition of the hydrogenotrophic, (hyper)thermophilic, methanogenic archaea *Methanothermococcus okinawensis* strain DSM 14208^T and *Methanocaldococcus villosus* strain DSM 22612^T is provided. Both strains exhibit the same lipid biomarker inventory, but grown under varying temperatures they respond to these changing culture conditions differently. Their lipid inventory after acid hydrolysis contains the common diether lipids archaeol (2,3-di-O-phytanyl-*sn*-glycerol), accompanied by the unique macrocyclic archaeol (2,3-di-O-cyclic-biphytanyl-*sn*-glycerol), as well as the tetraether lipids caldarchaeol (2,2',3,3'-dibiphytanyl-*sn*-diglycerol), two tentatively identified isomers of "H-shaped" caldarchaeol and traces of GTGT (glycerol trialkyl glycerol tetraether). Macrocyclic archaeol is for the first time described in the genus *Methanothermococcus*, the occurrence of GTGT and H-shaped caldarchaeol was so far not described in any of these genera. We found two tentatively identified regioisomers of H-shaped caldarchaeol in both organisms, but one is dominant in *M. villosus*, whereas the other is dominant in *M. okinawensis*. Our culture experiments confirm that temperature has an impact on the lipid composition, as described for *M. jannaschii*. *M. villosus* produces less archaeol and more macrocyclic archaeol and tetraether lipids when the temperature rises. *Methanothermococcus okinawensis* shows an even higher flexibility in shaping its membrane lipids than *M. villosus*. The former reveals peak production of macrocyclic archaeol in its optimum temperature range. Furthermore, just *M. okinawensis* adopts the composition of tetraether lipids with changing conditions. The mixture of tetraether lipids of *M. villosus* remains unchanged at varying temperatures. The proportion of both regioisomers of H-shaped caldarchaeol relative to other tetraether lipids is rising at higher temperatures in *M. okinawensis*. In fact, macrocyclic archaeol and H-shaped caldarchaeol behave in a similar way in this strain. All these lipids are typified by a bridge between the alkyl chains in the center of the membrane, allowing the organisms to maintain membrane stability at higher temperatures. The observations made in this study can be a helpful tool in analyzing molecular fossils in environmental samples and thereby to gain information about the temperature at the time of their formation.

An integrated bio-engineering rehabilitation approach for abandoned gold tailings disposal sites.

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Content

In many ways, South Africa's landscape has been dominated by mining, given that, for so many years the sector has been the mainstay of the South African economy. In the South-African rehabilitation industry the establishment of vegetation is a common rehabilitation practice. Poor vegetation cover on South African mine tailings and a lack of biological norms and standards put question marks behind current practices and specifications. Rehabilitation approaches in the past focused mainly on the abiotic factors and plant species selection, instead of a full combination and integration of the soil microbes, plant species with very specific characteristics as well the abiotic factors. The focus of this research is the synergistic use of soil microbes and plants to facilitate the rehabilitation of various abandoned gold tailings disposal sites (TDS). The hypothesis is that the application of various bio-stimulants and use of mother crop species (Brassicaceae members) can affect soil microbial activity and soil function, thereby having a positive effect on the climax grass species (*Eragrostis curvula*) establishment, growth and yield. A combination of chemical, physical and microbiological properties was identified as the major rehabilitation constraints; pH of 1.7, nett acid lime requirement of 300t/ha; low soil dehydrogenase activity (1,4 INF $\mu\text{g/g/2h}$) and compost requirement of >65 t/ha are amongst the worst. Results demonstrated that both bio-stimulants and plant root activity stimulated soil rhizosphere enzyme activities and induced important shifts in the bacterial community structure over time. Various bio-stimulants and mother crop species significantly increased the climax plants germination, survival and biomass. The various bio-stimulants and mother crop species also significantly increased the climax plants germination, survival and biomass. Results indicate that rehabilitation is site-specific i.e. certain bio-stimulants and different mother crop species performed better at different gold mine disposal sites. These results were observed in both nursery and field trials. As such, it is clear that the contribution microbes make to the ecosystems functioning in extreme environments, such as mine waste disposal environments is vastly underrated. Consequently, microbial processes need to be included into mine rehabilitation practices, hypotheses, models, and interpretation of rehabilitation findings.

Carbonate authigenesis at oil seeps from the Campeche Knolls, southern Gulf of Mexico

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Content

The seepage of hydrocarbons from marine sediments produced by persistent upward migration of oil and gas towards the seafloor represents a poorly confined source of fossil organic carbon in the ocean and the atmosphere. Most seeps along continental margins are dominated by the expulsion of biogenic and thermogenic methane. However, an increasing number of hydrocarbon provinces have been discovered that are characterized not only by seepage of methane, but higher hydrocarbons and crude oil. Such seeps are ideally suited to study the impact of oil seepage on the diversity, activity, and distribution of microbial communities, as well as the role of oil degradation in carbonate authigenesis. The Gulf of Mexico (GoM) has served as a natural laboratory for methane and oil seepage over the last decades. In the southern GoM, the Bay of Campeche hosts the “Chapopote Asphalt Volcano”, characterized by extensive eruptions of liquid heavy hydrocarbons, widespread asphalt flows, and seafloor gas hydrate deposits. The most recent visit to this remarkable seafloor site was conducted in 2015 during R/V Meteor Cruise 114, and revealed that oil seepage is more common and widespread in the southern GoM than previously recognized. This study uses thin section petrography and stable isotope geochemistry to characterize newly discovered authigenic carbonate deposits from the southern GoM. Phase-specific trace and rare earth element analyses of aragonite cements confirm that element patterns can be used to constrain the microenvironments in which the carbonate cements had formed; these elemental patterns can also be used to constrain the influence of oil degradation on mineral authigenesis. Additionally, the software code PHREEQC is used to estimate the influence of sulfate-driven hydrocarbon oxidation on carbonate formation. As of today, the relative contribution of the oxidation of various light and heavy molecular weight hydrocarbons to carbonate authigenesis at seeps is not well known. Specifically, the effect of sulfate reduction on alkalinity, pH, and the stability and saturation state of aragonite and calcite is assessed.

Dark inorganic carbon fixation during heterotrophic growth in marine sediment

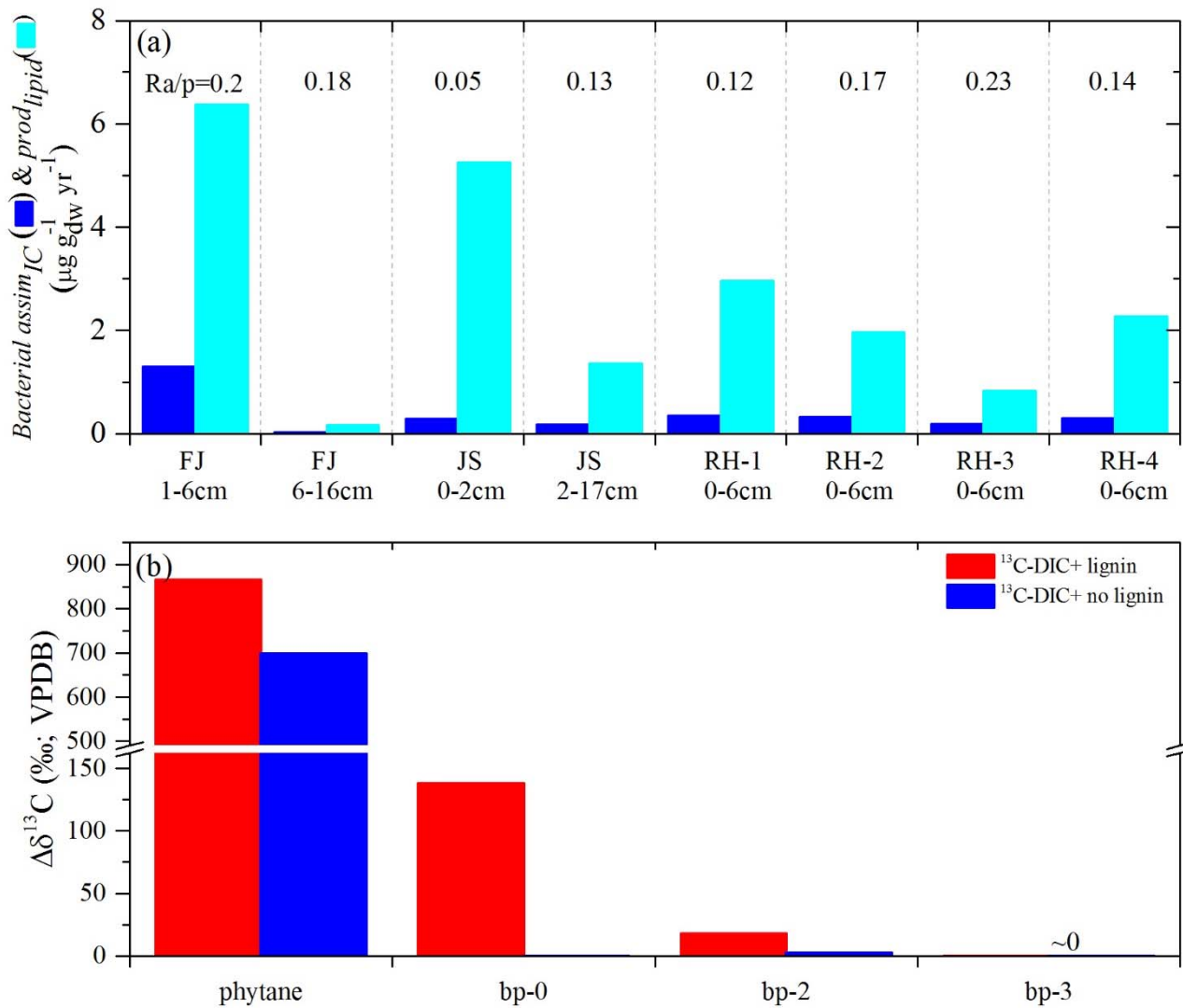
Wu, W.¹, Meador, T.¹, Yu, T.², Wang, F.², Lipp, J.¹, Elvert, M.¹, Heuer, V.¹, Hinrichs, K.-U.¹

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Content

Microbial degradation of organic matter (OM) in marine sediment is the ultimate gateway prior to long-term burial of residual OM and thus an important flux in the global carbon budget; however, quantitative estimates of microbial activity and their metabolism in this realm are limited. To better quantitatively estimate microbial activity and understand their role in the carbon cycle, we incubated coastal marine sediment from intertidal flats and prodelta by using lipid-based dual stable isotope probing with heavy water (D₂O) and ¹³C-bicarbonate [1]. Our results reveal that the turnover time of bacterial fatty acids in surface sediment ranged from 1.9 to 21.3 years with an average of 7.4 years, and was roughly an order of magnitude shorter than that of archaeal lipids (88-136 years with avg. 110 years). In addition, inorganic carbon can be significantly incorporated into bacterial fatty acids during incubation (0.15 to 1.3 µg g_{dw}⁻¹ yr⁻¹ with avg. 0.3 µg g_{dw}⁻¹ yr⁻¹; Fig 1a). We propose that this dark inorganic carbon fixation by bacteria occurs during the heterotrophic growth rather than chemoautotrophic [2] based on the ratio of ¹³C-inorganic carbon to D₂O incorporation into lipids.

In order to test this hypothesis and further explore the potential for inorganic C assimilation among Archaea, we incubated surface marine sediment with refractory organic substrate (i.e., lignin) and ¹³C-bicarbonate (Fig. 1b). Interestingly, the uptake of ¹³C label from bicarbonate into archaeal lipids was stimulated by the presence of lignin. Uptake in archaeol-derived phytane was significantly higher than uptake in GDGT-derived biphytane (bp-0) and bp-2, but the relative enhancement induced by the presence of lignin was much more pronounced for the two biphytanes. The ¹³C-labelling of archaeal lipids thus suggests that both methanogens and other uncultured archaea assimilate inorganic carbon in the surface marine sediment. Our study indicates that dark inorganic carbon fixation may therefore be an important consequence of heterotrophic microbial activity in marine sediments and should be considered for constraining sedimentary C-fluxes.



Summary of ^{13}C and D incorporation rate into microbial lipids in different sediment incubated in sulfate artificial seawater slurry (a) or amended with lignin (b)

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Session 3.3: Geomicrobiology - from understanding processes in ancient and modern environments to industrial applications: Talk
A-679

Diversity-specific iron biomineralization in an Archean ocean analogue

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Content

Microorganisms are important contributors to the reactions driving Fe cycling at redox interfaces in both modern and ancient surface environments on Earth. In particular, iron-reducing, iron-oxidizing and sulfate-reducing bacteria are involved in the formation and alteration of Fe-bearing minerals through their capacity to transfer electrons beyond the cellular surface. Lake Pavin, considered an ancient ocean analogue due to its permanently anoxic, iron-rich bottom waters, hosts a wide diversity of potentially electroactive bacteria involved in Fe cycling. We aimed to investigate this unexplored diversity of electroactive environmental bacteria by enriching microorganisms from several water column depths on iron minerals. Enrichment cultures were amended with the key iron species identified in situ, namely ferric iron phosphate, ferrihydrite, and dissolved Fe²⁺. These different iron phases, the type of electron donor (lactate, acetate, or fumarate), and the presence or absence of added sulfate favored the development of unique Fe-reducing microbial communities. Despite low endogenous sulfate concentrations (< 20 µM), sulfate-reducers were the most competitive organisms in our enrichments containing sulfate and transformed ferric iron into a diversity of ferrous minerals depending on Fe(III) source (e.g. mackinawite, vivianite, magnetite). Additional characterization of the resulting iron minerals with EXAFS and STXM revealed that the proportion of reduced iron varied with the phase of iron supplied as well as with the electron donor and that microbial cells were intimately associated with reduced iron minerals. Our findings reveal an important influence of microbial activity on mineralogical diversity through both direct and indirect biomineralization pathways. Further study of these electroactive communities in microbial fuel cells, with electrodes replacing Fe(III) as the electron acceptor is underway.

Lake level fluctuations and lignite deposition in the Eocene lake “Prinz von Hessen” (Hesse, Germany): orbital versus tectonic control. A palynological study.

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Content

The isolated structure of “Grube Prinz von Hessen”, 5 km NE of Darmstadt (Germany), represents a small pull-apart basin which is filled by lacustrine sediments. They have recently been subject to a high resolution palynological study in a research core. Here we present the results of analyses from 50 samples between 45 and 32 m core depth. This part of the core is lithologically characterized by an alternation of lignitic layers ranging in thickness from 5 to 50 cm and bituminous shales. Each of the lignites is characterized by a particular palynological association dominated by specific fern spores, which shows that the composition of the vegetation at the lake margin frequently changed during the time of deposition. The frequent alternation of lignitic layers and bituminous shales can be related to lake level fluctuations including short time establishment of an open lake. This is confirmed by the regular occurrence of *Ovoidites* sp., a cyst of the freshwater alga *Spirogyra* (Zygnemataceae), in the bituminous shales. The abundance of fern spores in the lignites indicates that ferns were widespread around the margin of the lake. On the other hand, the distribution of Nymphaeaceae (*Monocolpopollenites crassiexinnus*) and Hydrocharitaceae (*Punctilongisulcites microechinatus*) as well as Taxodiaceae (*Inaperturopollenites* spp.) and Nyssaceae (*Nyssapollenites kruschii*) prove that a *Nyssa*/*Taxodium* swamp existed behind shallow water at least in parts of the lake. Ericaceae (*Ericipites* spp.) may also be regarded as swamp elements while the pollen record of the forest vegetation in the surrounding area is dominated by Juglandaceae (*Plicatopollis* spp.) and Fagaceae (*Tricolporopollenites cingulum*). Statistical analyses indicate that a change between humid and less humid phases respectively phases with slightly increasing and decreasing precipitation were responsible for the lake level fluctuations. Since no rooting structures have been observed in association with the lignitic layers and some of them show erosional structures at their base, an allochthonous origin for the organic material in the lignitic layers is suggested. It must have been eroded around the lake and redeposited due to tectonic activity which is a strong argument against orbital control of lake level fluctuations.

Key words: Palynology, Eocene, lacustrine sediments, lake level fluctuation, orbital control.

Stromatolitic Fe-rich biofilms thriving in the subsurface - an analogue to the cryptic microfossil Frutexites?

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Content

In numerous paleo-environmental studies, Fe- and Mn-rich stromatolitic and dendritic structures have often been described as Frutexites. The identification and description of Frutexites is based on two main characteristics: i) dendritic structures mainly composed of iron and/or manganese oxides and ii) heights of several tens to hundreds of micrometres. The formation processes leading to Frutexites structures are as yet unclear. Investigations of stromatolitic Fe-oxide precipitating biofilms growing in the continental subsurface of the Äspö Hard Rock Laboratory, Sweden, exhibit laminar and dendritic patterns that strongly resemble those of ancient Frutexites structures. Combining microscopy, 454 pyrosequencing, Fluorescence in situ hybridization (FISH), Raman spectroscopy, biomarker and trace element analysis allowed a detailed view of the structural components of the mineralized biofilm from Äspö. Side-by-side occurrences of Fe(II) and Fe(III) mineral phases indicate biologically governed microenvironments. Furthermore, the obtained sequencing, FISH and biomarker results make a strong case for the involvement of diverse microorganisms in the formation of Frutexites-like structures. Apart from numerous archaea and bacteria, the presence of eukaryotes i.e. fungi, was observed whose identification and functional role is currently under investigation. The presence of net-like hyphae could serve as a mineralizing template and thereby contribute to the formation of the “typical Frutexites structure”.

Temperature fluctuations in the Precambrian ocean could have caused alternating deposition of Fe-rich and Si-rich layers in Banded Iron Formations

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Content

Banded Iron Formations (BIFs) are marine chemical deposits which were formed between approximately 3.8 and 1.85 Ga. Although it has been suggested that for example changes in upwelling and ocean currents, episodic volcanic activity, evaporation and temperature fluctuations could have caused their characteristic alternating lamination of Fe and Si layers, the exact mechanism leading to the alternating precipitation of Si and Fe minerals is currently unknown. A few years ago, our group proposed that temperature fluctuations in the Precambrian ocean could have coupled the deposition of Fe-rich layers mediated by phototrophic Fe(II)-oxidizing bacteria during warm periods to the deposition of Si-rich layers by abiotic Si precipitation during cold periods. To validate the likelihood of such a process we now conducted laboratory growth experiments simulating Precambrian ocean conditions with the marine phototrophic Fe(II)-oxidizing bacterium *Rhodovulum iodosum*. The temperature was cycled between 26°C (warm period) and 5°C (cold period) to simulate temperature fluctuations. Geochemical parameters (dissolved Fe²⁺ and monomeric silica concentrations as well as pH) were monitored throughout the experiment. Our results showed that the Fe(II) was oxidized by *R. iodosum* during the warm periods resulting in an orange-brown Fe(III) mineral layer, whereas the Si largely stayed in solution. During the cold period, the Si was precipitated, forming a gel-like amorphous silica layer on top of the Fe layer, while no Fe(II) was oxidized. During the next warm period this amorphous silica layer stayed stable while a new Fe(III) mineral layer was precipitated on top. In summary our results show temperature-dependent precipitation of either Fe(III) minerals or amorphous silica forming separate layers. This implies that temperature could have been of significant importance during the deposition of BIFs and could have triggered the alternating deposition of Fe-rich and Si-rich layers. The next steps will be to determine (1) to what extent Fe and Si co-precipitated during the formation of the respective layers and (2) how active *R. iodosum* still was at low temperatures.

The Indian monsoon and chemosynthesis support the growth of deep-water stromatolites in the northern Arabian Sea

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Content

Here we show petrographic and mechanistic evidence that chemosynthesis - not photosynthesis - in concert with monsoonal sedimentation pulses support the growth of stromatolites at ~731 m water depth in the northern Arabian Sea.

The chief controller of particle flux to the northern Arabian Sea seabed is the Indian monsoon. Monsoonal winds and heavy rainfalls deliver nutrients to the surface water, resulting in algal blooms during the summer and winter monsoon seasons and associated peak particle fluxes. Such particles get trapped and bound by benthic microbial mats at methane seeps within the oxygen minimum zone (OMZ) off Pakistan. Methane seeps within the OMZ are colonized by filamentous sulphide-oxidizing bacteria, sustained by local hydrogen-sulphide production from sulphate-driven anaerobic oxidation of methane (AOM: $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$). At the same time, AOM-produced alkalinity induces precipitation of ^{13}C -depleted aragonite cement at the seeps. This effect is amplified when the filamentous sulfur bacteria use nitrate and not oxygen as electron acceptor for sulphide-oxidation ($\text{HS}^- + \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{NH}_4^+$). Microbial fabrics, resembling the filamentous sulphide-oxidizing bacteria in size and shape, preserved in ^{13}C -depleted aragonite suggest that biofilm calcification was induced by the combined effects of nitrate-driven sulfide oxidation and AOM.

Session 3.4: Coastal depositional environments & processes: Poster

Session 3.4: Coastal depositional environments & processes: Poster
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ECOLOG - Environmental change affecting COastal ecosystems of tropical China during the Anthropocene: Landward vs. OCeanic influence

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Content

Tropical coasts are particularly vulnerable to changes in the environment. They contain very productive and diverse ecosystems such as coral reefs, seagrasses and mangroves, but are strongly altered by human modifications. Coastal ecosystems of the Chinese island of Hainan, located in the South China Sea, are affected by a rapid increase in population, industry, aquaculture and tourism. A further expansion of tourism is a priority of the government, and aquaculture as well as fishery production play an important role as income sources of local communities. Therefore, the maintenance of coastal resources and ecosystem services is important for Hainan's further economic development.

The so far unanswered question how humans can simultaneously use and protect natural resources is addressed in the interdisciplinary Sino-German research project ECOLOC. Natural and anthropogenic factors controlling the physicochemical and biogeochemical environment as well as the response of organisms and coastal habitats to environmental change are investigated. The studies are conducted in nine subprojects and cover aquaculture facilities, river estuaries, mangrove forests, seagrass meadows, coral reefs as well as the upwelling system in the South China Sea.

The innovative multidisciplinary research concept includes a module on 'Capacity Building' fostering academic education and exchange and a module on 'Knowledge Exchange' that provides an interface between science and society. The dialogue with stakeholders aims at improving the societal use of research results and refinement of research concepts based on stakeholder perceptions. These modules are provided by add-on project TICAS - 'Tackling environmental change Issues of China's coastal Aquatic Systems: Networking, capacity building and knowledge exchange'. The research results will contribute to globally relevant issues of environmental change and provide locally relevant knowledge for a sustainable management of coastal ecosystems through the dialogue between science, policy and society. The knowledge gained in this project is required to preserve ecosystem functions and services of Hainan's coastal areas on the one hand and to satisfy the demands of a growing population and human uses of coastal resources on the other hand.

Freezing and hungry? Hydrocarbon degrading microbial communities in Barents Sea sediments around Svalbard

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Content

The Polar Regions are characterised by varying temperatures and changing ice coverage, so most of the primary production take place in the warmer season. Consequently, sedimentation rates and nutrient input are low. The diversity and metabolic potentials of the microbial communities inhabiting these sediments in the Northern Barents Sea are largely unknown. Recent reports on natural methane seeps as well as the increase in hydrocarbon exploration activities in the Arctic initiated our studies on the potential of indigenous microbial communities to degrade methane and higher hydrocarbons under in situ pressure and temperature conditions. Furthermore, the subseafloor geochemistry in these areas was studied, together with important microbial groups, like methanotrophs, methanogens, metal and sulfate reducers, which may drive seafloor ecosystems in the Northern Barents Sea.

Sediment samples were collected in several areas around Svalbard in the years 2013-2016 ranging from shallow (200m) areas on the Svalbard shelf to deep sea areas on the eastern Yermak Plateau (3200m water depths). Shelf sediments showed the highest organic carbon content which decreased with increasing depths. Iron and manganese as potential electron acceptors were found in the porewater especially in the top 50 cm of the cores, while sulfate was always present in substantial amounts in porewater samples down to the end of the up to two metre long cores. Concentrations of dissolved methane and carbon dioxide were low.

The potential of the indigenous microorganisms to degrade methane and higher hydrocarbons as well as different oils under in situ temperatures and pressures was widespread in surface sediments. Degradation rates were higher under aerobic than under anaerobic conditions, and decreased with increasing sediment as well as water depths. Similar pattern were found for other metabolic processes, including sulfate, Fe and Mn reduction as well as carbon dioxide and methane production rates. Ongoing molecular biological analyses of original sediments and enrichment cultures indicate the presence of diverse and varying microbial communities.

From soil to ocean: nutrient fluxes through the subterrestrial land-ocean continuum

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Content

Submarine groundwater discharge, the direct discharge of groundwater to the oceans, has long been neglected as nutrient pathway from land to sea. Recently, a number of local studies emerged which highlight the importance of this pathway for the nutrient budget of a specific region based on nutrient concentrations in current submarine groundwater discharge. Particularly in some regions with sensitive ecosystems, submarine groundwater discharge could dominate over river water discharge as nutrient source to the coast (Moosdorf et al., 2015). However, terrestrial groundwater can take decades to reach the coast and thus the situation currently measured in the groundwater discharge does not necessarily reflect the nutrient load which is on its way to the coast. Here, we present a framework to estimate the coastal areas affected by elevated nutrient concentrations in fresh submarine groundwater discharge, i.e. discharging terrestrial groundwater – in contrast to recirculated seawater.

We connect spatial datasets of land cover, rivers, aquifer properties, hydraulic heads and coastal ecosystems in a GIS. Thus, we can estimate the nutrient sources, their transport pathways, travelling time, degradation and finally the sensitivity of the receiving coastal ecosystem. The presented framework can be used to evaluate the effectiveness of the United Nations development goal 14, to “by 2025 prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution”. In addition, the nutrients transported by groundwater strongly change the biogeochemical environment in the coastal sediment and can lead to changes in coastal productivity. Here, we highlight the areas where those effects are particularly likely in the future.

Reference

Moosdorf, N., Stieglitz, T., Waska, H., Durr, H.H., Hartmann, J., 2015. Submarine groundwater discharge from tropical islands: a review. *Grundwasser*, 20(1): 53-67.

Marine sediment archive from the Java Sea reveals soil erosion and coastal eutrophication as consequences of severe deforestation on Borneo

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Content

The island of Borneo has been exposed to severe deforestation since the 1970s. While this land-use change has been documented in recent years, not much is known on the related consequences in the coastal zone. In this study we used stratigraphical, biogeochemical and palynological analyses in a marine sediment core from the Java Sea taken 25 km off the Jelai river mouth, Indonesia, to reconstruct environmental changes in southern Borneo and related impacts on the coastal zone. Significantly lower relative abundances of mangrove and timber pollen and higher relative abundances of pioneer taxa pollen in the upper (~1982-1998 AD) than in deeper layers (~600-1982 AD) of the core reflect severe deforestation of old growth forest in the Jelai River catchment at the end of the 20th century. High amounts of micro charcoal particles in the upper core reveal fires as a significant cause of forest loss. Simultaneous to the changes in land use, sedimentation rates increased enormously from <0.1 to ~1.1 cm yr⁻¹ in the upper layer resulting in much higher accumulation rates of total nitrogen and organic carbon. $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios reflect the organic matter to be a mixture of allochthonous and autochthonous particles throughout the core. Therefore, the strong increase in the sedimentation probably resulted from both: 1) stronger export of terrestrial organic matter as a consequence of enhanced soil erosion and 2) higher primary production in the coastal zone fueled by nutrients leached from the deforested river basin and recycled from exported high organic matter loads. A higher phytoplankton abundance in recent years is inferred from significantly higher biogenic opal content reflecting higher amounts of diatoms. Moreover, higher $\delta^{15}\text{N}$ values in the upper part of the core point to a high degree of nutrient utilization and assimilation. Furthermore, a larger relative abundance of eutrophic dinocysts in the upper core indicates a shift in the phytoplankton composition. Thus, the results point to eutrophication and a shift in phytoplankton communities in the coastal zone as a result of the severe deforestation on Borneo. Here, a sediment core provides valuable information on consequences of land use change for coastal waters in a study area where data from water column are scarce.

Mid-Holocene relative sea-level rise in Northern Java (Indonesia) reconstructed from massive fossil microatolls

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Content

Well-constrained data on the timing and magnitude of mid- to late-Holocene relative sea-level (RSL) fluctuations are required to further improve our understanding of modern and also future RSL changes on local and regional scales. However, published high-precision datasets from central Indonesia, an area that is considered particularly sensitive to future sea-level rise, are rare. This study presents results from a detailed microatoll-survey along the northern coastline of Central Java, Indonesia. The study site is characterized by the presence of numerous fossil microatolls, many of which indicate changes in former RSL positions due to their variable elevations above present-day mean sea level. We provide radiometrically calibrated ages and precise elevation information for the individual fossil microatolls and discuss the implications of these new findings with respect to tectonics, eustasy, isostasy and existing sea-level models for the region.

Monitoring short-term shoreline dynamics using Unmanned Aerial Vehicles: A Case study of Keta, Ghana

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Content

As sea levels continue to rise, coastal erosion is expected to increase along most of the world's shoreline. In Ghana, coastal erosion remains a major challenge to coastal zone management. To effectively manage the situation, coastal managers and engineers often require up to date high resolution information for decision making. However, traditional approaches for monitoring coastal changes have presented challenges due to the limited frequency and resolution of data. Recent advancements in Unmanned Aerial Vehicle (UAVs) technologies have offered the opportunity to collect such data at higher resolutions (temporal and spatial scales). This study focuses on the use of UAV to monitor short-term shoreline changes around the Keta Sea Defence Project site in the Volta delta of Ghana. The approach involves the establishment of reference datum connected to the Ghana National grid system; regular planimetric and volumetric surveys; and critical field observations. Preliminary results reveal that erosion has increased on the down-drift coast of the defense structure which is affecting nearby communities. This has led to another sea defense effort about 4km down-drift. DEM analysis also indicates that sand mining activities are contributing to the vulnerable state of the Keta coast. This project is expected to contribute significantly to Ghana's integrated coastal zone management efforts.

Seasonal controls on groundwater-associated nutrient fluxes in a tropical karstic coastal area (Southern Central Java, Indonesia)

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Content

In tropical karstic regions groundwater and associated nutrient fluxes from land towards the coastal ocean can be fast, due to high aquifer permeability. The low retention capacity of karstic aquifers for nutrients and contaminants in combination with numerous diffuse and point sources (e.g. due to fertilization during certain times in the year or wastewater infiltration) lead to considerable nutrient input to the groundwater. As a consequence, seasonal variability of groundwater nutrient concentrations in the catchment area (e.g. due to fixed fertilization schedules) might significantly influence nutrient input and availability in the coastal ocean due to groundwater discharge. We assessed the seasonal variability of groundwater nutrient fluxes from land to the coastal ocean in the tropical karstic region of Gunung Kidul (Southern Central Java, Indonesia) from November 2015 until December 2016. Major locations of groundwater discharge into the coastal ocean were identified using thermal infrared satellite images. There, measured nutrient concentrations in the groundwater were combined with discharge rates measured at an “underground river dam”, precipitation rates and stable isotopes of water.

Our results show high nutrient fluxes during the rainy season in 2015 and 2016, and low nutrient fluxes during the dry season in 2016. High nutrient fluxes during the rainy season are caused by high aquifer recharge and discharge, counterintuitively combined with high nutrient concentrations in groundwater. High groundwater nutrient concentrations are likely caused by agricultural fertilization practices. Fertilization is mostly carried out in the catchment area during the rainy season. In tropical karstic regions, the anthropogenic activity in the hinterland can thus have a direct effect on the coastal seawater via fast groundwater discharge and may show strong variations over the seasonal cycle.

Shoreline changes in the Keta Municipal District (Ghana): Evidence from multi-decadal records

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Content

In the time of sea-level-rise and global warming, a better understanding of the different processes and factors controlling the beach morphodynamic is essential to prevent and diminish the vulnerability of coastal areas. The densely-populated coastline of the Keta Municipality in southeastern Ghana has experienced severe shoreline recession during the 20th century. The documented shoreline retreat is thought to be related to hard engineering constructions built in the area. The constructions of the Akosombo and Kpong dam in the adjacent Volta River was completed by 1982. Additionally, a number of groins and revetments have been finalized within the frame of the Keta Sea Defense Project in 2005 and the Atokor Sea Defense Project in year 2015, respectively. This study shows, to what extent these hard engineering constructions influence the beach morphodynamic. In order to attain this objective, ancient and recent shorelines from historical maps, satellite images and a shoreline survey in 2015 were analyzed. The multi-decadal shoreline reconstruction from 1913 to 2016 of about 90 km of shoreline provides insights into morphologic changes. The results show local erosion rates in the Keta Municipal District were already high before the construction of the Akosombo dam and consequently the dams are not the main driver for the erosion in this area. Although the groins of the Keta Sea Defence Project and Atokor Sea Defense Project aimed at stopping the erosion, the problem has rather shifted to the east. Therefore, these hard engineering structures appear merely as a local and short-term solution.

The potential of relative heavy mineral abundances in superficial beach sediments for the determination of recent-past shoreline changes: Keta Municipal District, Ghana

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Content

Long lasting coastal erosion has been occurring at the southeastern shoreline of Ghana. As adaption arrangement, the Keta and Atorkor Sea Defence Project (KSDP and ASDP), which included the construction of several groins, a sea wall and revetments, have been implemented in 2005 respectively 2014. The present study tries to determine areas of medium-term erosion and accretion along the Keta Municipal District shoreline based on compositional differences of 42 sediment samples collected along the coast from the beach face in 2015. Primary focus is on the distribution and relative abundances of heavy mineral species within the individual samples to evolve a new indicator for medium-term shoreline displacement. Based on previous studies and the hydraulic equivalence concept concentrations of heavier minerals are expected with erosion. Without evaluating the data the sediment composition give no consistent pattern. Amounts of particular heavy mineral species, especially amphibole and garnet, exhibit an anticorrelation of the particular concentrations, which is used to establish a new indicator. To bring the results into context, a satellite image evaluation of the shoreline from 2009 – 2015 is used. Shoreline movement rates reach up to an accretion of 30 m/a and an erosion of 15 m/a in the period of 2009 to 2015. Comparisons between the heavy mineral assemblages and the shoreline movement exhibit partly correlations. Existing correlations show that concentrations of heavier minerals are corresponding to accretion areas and lighter minerals to erosional areas. The study exhibit, that excepted density sorting is not the crucial factor for sorting in the study area. Factors of grain size and shape have a significant influence and cannot be neglect. Furthermore the study emphasizes, that the energy level of the hydrodynamic system at the shoreline is a deciding factor and selective sorting will be dissolved.

Session 3.4: Coastal depositional environments & processes: Talk

Keynote speaker

A-907

Interpreting the sedimentary record in tropical carbonate systems to reconstruct Holocene paleo-environmental change and landform evolution

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Content

Tropical coral reefs possess distinctive sedimentary systems characterised by the intrabasinal province of carbonate sediments and the prevalence of ecological processes in sediment production. These unique attributes of the sedimentary system, combined with constraints in the application of standard dating techniques, present challenges in the interpretation of paleo-environmental records and the evolution of key sedimentary landforms (e.g. reef islands) on tropical reef systems. Drawing on examples from the tropical Indian and Pacific oceans, approaches to resolve these challenges are explored. First, recent studies to better resolve the Holocene sea level dynamics and reef platform development in the Maldives are examined. Second, the timing and onset of sediment accumulation to form reef islands in the mid-late Holocene are explored in the context of both sea level change and reef platform dynamics. Collectively, these studies of carbonate sediment sequences have improved understanding of the control of environmental processes on coral reef and island evolution and shed new light on global debates related to coral reef system responses to climatic change.

Contrasting effects of land use change, river damming and a mud volcano on carbon, nutrient and sediment inputs into coastal waters of eastern Java, Indonesia.

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Content

Human modifications of the coastal zone and its hinterland are more and more impairing the performance of coastal aquatic systems during the Anthropocene. This is of particular importance in parts of SE Asia situated in the tectonically active "Ring of Fire" where extremes of natural forces and human uses of land and ocean and the respective resources meet. There, naturally high river fluxes of carbon, nutrients and sediments are strongly altered by the demands of a dense population that to a large extent lives in the coastal zone and economically depends on its resources. The Indonesian island of Java, located along an active subduction zone and hosting several active volcanoes, is a prime example in this respect. Its second largest river, the Brantas, empties into the shallow Madura Strait through two major branches, the Wonokromo and the Porong, the latter being responsible for 80 % of the discharge. Major land use in the densely-populated catchment (>1,000 inhabitants km⁻²) is agriculture (61 %) and the hydrology of the river is regulated by eight large dams. The estuarine lowlands are covered by aquaculture ponds. The eruption of a mud volcano near the Porong in 2006 added another factor affecting the river loads.

High concentrations of dissolved inorganic nutrients and particulate organic carbon (POC) related to land use were found with maxima during the rainy season (Nov-April). While high nitrate and POC loads originated from upstream regions dominated by agriculture, high amounts of ammonium were introduced from lowland aquaculture and the city of Surabaya. The high POC load resulted in low oxygen concentrations particularly in the dry season. Oxygen depletion in the Porong was exacerbated by the additional mud volcano input of suspended sediment, POC and ammonium.

Despite the high population density and intensive land use the overall yields of dissolved inorganic nutrients, POC and sediments in the Brantas River are surprisingly low to moderate. This is mainly due to retention in reservoirs behind the eight major dams. However, when adding the mud volcano input and the sediment and POC retained in reservoirs, the sediment and POC yields are among the highest in the world. Our study demonstrates the (i) contrasting effects of hydrological regulations and land use and (ii) how natural controls, human activities and extreme events in a tropical river catchment interact and affect river loads of dissolved and particulate matter.

Drones as low-altitude remote sensing tool in beach environments

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Content

Beaches are among the most rapidly evolving environments on Earth and are subject to continuous changes due to tides, waves, currents and sedimentary inputs. Monitoring morphological changes of beach systems at high resolution is crucial for a better understanding of the factors influencing these systems.

Additionally to traditional techniques (such as satellite imagery, LiDAR and ground surveys), changes in beach topography can be assessed using photographs obtained from small unmanned aerial vehicles (UAVs) processed with photogrammetric software. The typical results of a UAV photographic survey are an ortho-rectified image and a digital elevation model. The advantage of using drones to obtain this kind of data is that beach surveys can be repeated at short time intervals (e.g. before and after a seastorm) with high ground resolution (up to 1cm/pix), at a fraction of the cost of an airborne survey.

In this work, we present the results of multiple drone surveys in the beach of Hörnum, Sylt (DE). We performed several drone flights with varying altitudes, cameras and location of Ground Control Points and we compare the resulting Digital Elevation Models with a dense net of ground-measured DGPS points. We use our data to assess the overall accuracy of drone surveys, and we establish the combination of flight parameters and camera properties that grants the least difference between the UAV data and the independent measurements

Greenhouse gas emissions from shrimp ponds in the northeast of Hainan island

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Content

Since the mid 1970s the production of aquaculture goods is increasing at an annual growth rate of about 8% in response to the increasing demand of an ever-growing population. Consequences are a declining biodiversity and an intensification of eutrophication favoring the spreading of so-called dead zones in which the lack of oxygen hampers the growth of higher organisms. Additionally, it effects the emission of greenhouse gases (GHG) and therewith global efforts to limit global warming to well below 2 °C (Paris Agreement, United Nations, 2015).

Here, we present first results of the joint German/Chinese program ECOLOC where we studied the GHG emission from an aquaculture facility in the north-eastern coast of Hainan. We determined concentrations of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and carbon monoxide (CO) within a head space of equilibrated pond waters by using Fourier Transformation Infrared Spectroscopy (FTIR). Furthermore, fluxes were derived from floating chamber experiments, which in addition to the FTIR data showed that the shrimp ponds acted as a sink for atmospheric CO₂ during the period of our observation. Photosynthesis of the phytoplankton possibly promoted by nutrients released from excreta of the shrimps seems to have caused this. Nevertheless, despite the CO₂ uptake, aquaculture ponds contributed to global warming because the greenhouse effect of the emitted CH₄ overcompensated those caused by the uptake of CO₂. Since the pond was well oxygenated it is assumed that shrimps produced CH₄ in their guts. This topic will be addressed in further detail in future studies.

Numerical modelling of hydraulics and sediment dynamics around a mangrove seedling

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Content

Mangroves grow in the coastal and intertidal zones at tropical and subtropical latitudes. It is widely accepted that the establishment, growth and survival of mangrove seedlings depend on the environmental conditions such as temperature, root length and flow speed. To date we know that, in cohesionless sediment, the higher the flow velocity, the greater the eroded volume and, thus, the stronger the scour around a mangrove seedling that leads to its uprooting or death. But, to which extent a mangrove seedling (cm-scale) may alter the flow pattern and the cohesive sediment transport is, to date, still poorly understood. Investigating the impact on sediment dynamics of a single mangrove seedling would, therefore, lead to a more complete picture of the sediment transport processes such as erosion and sediment trapping. A total of five suits of numerical experiments were setup wherein a natural mangrove seedling (*Avicennia marina* sp.) was subjected to flow speeds ranging from 0 cm.s^{-1} to 20 cm.s^{-1} to reproduce hydraulic conditions occurring in mangrove swamps. The seedling geometry was digitized employing photogrammetry and placed at the center of a computational domain set to $4 \text{ m} \times 0.2 \text{ m} \times 0.5 \text{ m}$. The hydro- and sediment dynamics were simulated using a coupled sediment hydrodynamic continuum approach: the Finite Volume Method. The two phases, silty sediment (median diameter around $20 \mu\text{m}$) and water, constitute a mixture whose motion was estimated with the drift-flux solver. The numerical model was validated against the law of the wall for the hydraulics and the Stokes' law for the sediment settling. This model captures features of the flow and sediment transport around a mangrove seedling similar to the ones observed around submerged cylinders or piles. The results showed that a downward flow associated to a horseshoe vortex enhances scour in front of the mangrove seedling and a vortex shedding keeps the sediment in suspension or re-suspends the sediment in the rear of the mangrove seedling. The numerical simulations showed that a mangrove seedling has a significant influence on the flow pattern and sediment transport: the higher the flow speed is, the less stable the sediment bed is. These findings could ultimately help to better understand how a mangrove seedling and sediment erosion affect mangrove ecology and why the colonization or restoration of tidal flats is successful or not.

Nutrients in fresh submarine groundwater discharge in French Polynesia and an estimation of their provenance using geochemistry

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Content

In many coastal areas, fresh submarine groundwater discharge (FSGD) supplies a substantial amount of land-derived nutrients and other chemical species to coastal marine waters and ecosystems. Consequently FSGD bears the potential to directly influence the health of marine ecosystems and could be particularly relevant on tropical islands where intensive hydrologic cycling on land meets highly permeable rocks and sensitive marine ecosystems. Evaluating the susceptibility of FSGD to anthropogenic activities (e.g. agriculture) requires determining the sources of nutrients in FSGD. Here we combined nutrient concentration measurements with stable isotope analysis on water samples from Tahiti and Mo'orea, French Polynesia. On Tahiti, some clear patterns are visible. While negative $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in FSGD suggest intensive groundwater replenishment at pristine high altitudes, in our water samples high nitrate (and phosphate) concentrations increase for catchments showing urban or agricultural land cover at low elevations. Correlations between nitrate concentrations and $\delta^{15}\text{N}_{\text{nitrate}}$ in groundwater samples also imply an anthropogenic source for high nitrate concentrations. A positive correlation between nitrate and phosphate concentrations might hint at an anthropogenic origin of phosphate. Hence some (small) recharge with very high nutrient load water seems to take place in the anthropogenically used, lower reaches of the island. On Mo'orea our findings are different: nitrate concentrations in groundwater samples are neither correlated with phosphate concentrations nor with anthropogenic activities in their catchment. Instead they are negatively correlated with ammonium concentrations. A possible explanation would be that nitrate ammonification produces NH_4^+ by using up NO_3^- from the system. This might obscure an initial correlation between PO_4^{3-} concentrations and NO_3^- concentrations and explain the systematically lower NO_3^- concentrations on Mo'orea as compared to Tahiti; while PO_4^{3-} concentrations are similar on both islands. On Tahiti and Moorea, significant nutrient input to the Ocean via FSGD can occur due to anthropogenic activities. Hence locally FSGD can threaten the health of abundant but sensitive coastal marine ecosystems. A sensible regulation and management of land use at the coast, on plateaus and in river valleys is thus essential to maintain the health of these ecosystems on which the livelihood of the majority of the local populace depends.

Pleistocene shorelines along the Indian Ocean coastline in Oman (Arabian Peninsula)

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Content

The coastal geomorphology within the study area indicates dynamic landscape evolution during the Quaternary associated with differential crustal movement. The area is characterised by a staircase of raised terraces in elevations of up to 500m. We aim to quantify the vertical crustal movement in order to understand the tectonic geomorphology, neotectonics and related earthquake activity.

Terrace formation took place during the Quaternary. Bioerosion and abrasion produced wave-cut platforms within Upper Cretaceous to Eocene limestone formations during times of global eustatic sea-level highstands. Serpentinised peridotites of the Semail ophiolite underlie the limestone formations.

We mapped the terraces over a distance of 60 km. We identified seven terrace levels aided by terrestrial laserscanning as well as differential GPS measurements and a high resolution digital elevation model. The uppermost terraces are erosional, whereas the lower ones are depositional in style. Mollusc and coral remains as well as beach-rock are encountered on the terrace surfaces. The formations are dissected by NW-SE trending faults. The precise levelling of the shoreline angles revealed a tilting of the terraces towards the north.

Individual terrace levels were sampled for two independent dating approaches. Optically stimulated luminescence dating was performed on delta deposits covering a lower terraces level; surface exposure dating based on cosmogenic nuclide (¹⁰Be and ³⁶Cl) was performed on samples collected on higher levels as well. Our dating results indicate that the terraces formed within the last million years. The highest dated terrace level revealed ages correlated to MIS 17 and the lowest terrace level is correlated to MIS 5. Every warm phase in between is represented by sea-level highstand and expressed as an individual terrace level within the coastal morphology.

Various models have been put forward trying to explain the neotectonic deformation pattern. These include forebulge development in association with subduction processes. Compressional tectonics dominate with continent-continent collision and along-strike transition to ocean-continent conversion forming the Makran Subduction Zone along the Arabian-Eurasian Plate boundary. We conclude that local components associated with the serpentinisation of underlying Cretaceous peridotites have to be taken into account as this process triggers an isostatic response.

Rapid bioerosion in a tropical upwelling setting: implications for coral reef carbonate budgets

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Content

Coral reefs persist in an accretion-erosion balance, which is critical for understanding the natural variability of sediment production, reef accretion, and their effects on the carbonate budget. This study investigates the seasonal pattern of bioerosion and settlement succession by bioeroding as well as calcifying organisms on experimentally deployed coral substrate (*Stylophora pistillata*) in a shallow reef system in the Papagayo Bay (Costa Rica, Eastern Tropical Pacific) during a northern winter upwelling period. This case study within marginal reef conditions in a tropical upwelling region presents a scenario in which prolonged and regular oceanographic anomalies naturally occur.

Time-series analyses show early settlement and bioerosion within the first two months of exposure, proceeded by rapid increase in CaCO₃ loss (>30%) during the third and fourth month with the onset of upwelling. Scanning electron microscopy images indicate that neither secondary cementation nor abiotic chemical erosion contributes to the weight loss observed in the coral fragments. Instead, micro-computed tomography scans (μ CT) of the skeletal fragments reveal that the rapid CaCO₃ loss was primarily due to internal bioerosion by the lithophagine bivalve genus *Leiosolenus*. Although a net weight loss was observed, the coral substrate also provided habitat for encrusting organisms, thus contributing to calcium carbonate production and sediment formation. The net removal of CaCO₃ substrate via intense bioerosion may also directly affect seawater carbon chemistry by elevating the carbonate saturation state. This study emphasizes the plurality of ecosystem functions carbonate bioerosion provides for tropical reefs under temporary environmental stress.

Re-evaluation of phosphorus concentrations in muddy and sandy sediments of a cold temperate lagoon

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Content

Coastal water bodies suffer worldwide from anthropogenic elevated nutrient inputs, which lead to eutrophication. Sediments in eutrophic systems are assumed to be an important internal nutrient source. As a rough standard the total phosphorus (TP) concentration (mg g⁻¹ dry mass) increases with increasing organic content. Sediments with high organic content are mostly found in sinks, where the organic material is transported by water currents. Finally, these findings result in e.g. maps for management plans, where areas of high TP content (mg g⁻¹ dry mass) are drawn in red indicating "Danger". However, with increasing organic content, the sediment density is lowered, which leads to lower TP concentration per g m⁻². Especially area-dependent values are often missing in literature. Therefore, we did a re-evaluation of TP amounts in the model ecosystem of the Darß-Zingst Bodden chain, a typical cold temperate lagoon system of the southern Baltic Sea. Sediment cores were taken at seven stations along transects from shallow to deeper parts of the lagoon. The upper 2 cm were used for water content, loss on ignition and dry bulk density.

We compared our results with results from 40 years ago at the same sampling locations. There was no major change in organic content or TP at the observed stations. As for TP calculated in mg g⁻¹ dry mass the highest concentrations (up to 0.4 mg P g⁻¹ dry mass) were found in the sinks and lowest in the shallow areas of the lagoon (~ 0.1 mg P g⁻¹ dry mass). However, with the inclusion of dry bulk density the results became reversed. Suddenly, the highest concentrations (up to 2 g P m⁻²) were found in the shallow areas and lowest concentrations (down to 0.5 g P m⁻²) in the deeper parts at stations that had a clear gradient in loss on ignition. It was also observed that some stations did not have any differences at all after including the dry bulk density.

These findings suggest two outcomes. First, there seems no improvement in nutrient concentrations or organic content of sediments even after 30 years of reduced nutrient inputs at the observed stations. This result would indicate that nutrient inflows by non-point sources are still too high. Second, the calculation of mg TP m⁻² revealed that there are probably no differences in TP concentrations in the lagoon sediments at all. These findings can have an impact on possible countermeasures for ecosystems rehabilitation.

Residence times of reef-island sediments constrained by post-mortem precipitates

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Content

The precipitation of carbonate cements is a rapid process in tropical marine environments. Distinct from calcification, the onset of cementation coincides with the termination of ¹⁴C uptake within carbonate-sediment forming organisms. Here we show that this relationship presents new opportunities for examining the temporal lag between organism death and deposition in carbonate systems – the prerequisite for reliable depositional chronologies. We dated skeletal constituents collected from discretely stratified reef-island deposits in Indonesia. In each of the strata, internally least cemented segments of the calcifying green alga *Halimeda* yield the youngest ages. Complementary mesocosm experiments on cementation rates reveal that post-mortem cement growth initiates within months after transport commences. Continuous pore-filling cementation promptly stabilizes the initially fragile *Halimeda* skeleton. Furthermore, abrasion experiments show that such cementation significantly increases the durability of segments during transport. Implications of these findings are profound in two respects; first, evaluating residence times of skeletal carbonate constituents based on abrasion features is far from being adequate. Second, the absence of cements within sedimentary *Halimeda* segments signals that post-mortem transport through the intertidal zone occurred quasi-instantaneously. Radiometric ages from such specimens should minimize the temporal lag between organism death and deposition thus making them reliable indicators of sedimentation in supratidal environments.

Shoreline changes interpreted from multi-temporal remote sensing data: Semarang, Indonesia

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Content

Major cities in coastal regions are threatened by present and future environmental changes. The coastal area is a highly dynamic environment where oceanographic processes, such as sea-level rise, interact with natural or human induced land subsidence and other anthropogenic activities. These combined processes play an important role for changes in shoreline positions and land level, and consequently, the recurrence intervals of floods. Especially in low-lying developing countries, flooding is a frequent natural hazard. This study focuses on shoreline changes in Semarang at the northern coast of Java, Indonesia. Semarang is one of the largest cities in Indonesia and residents are suffering from coastal flooding aggravated by anthropogenic activities such as excessive groundwater extraction that leads to increased rates of land subsidence. In this presentation, we will discuss the results from a long-term shoreline and land-level mapping based on multi-temporal remote sensing data and historical topographic maps dating back as far as the year 1908. Shoreline changes for this extensive period of more than one century were evaluated using the software programs ArcGIS, ILWIS and the Digital Shoreline Analysis System. Additionally, land-level changes, which determine the extent of those areas that become frequently inundated, have been reconstructed using the program ENVI.

Session 4.1: Geo-radiochemistry: Poster

Session 4.1: Geo-radiochemistry: Poster A-720

In situ spectroscopic characterization of Np(V) sorption at manganese and iron oxide surfaces

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Content

Neptunium (Np) is one of the most important components of nuclear waste to consider for the long-term safety assessment of nuclear waste repositories, due to the increasing enrichment, the long half-life and the high toxicity of Np-237. Hence, great attention is attracted to its geochemistry [1]. Components of geological materials, such as manganese and iron oxides and hydroxides play an important role in regulating the mobility of actinides in aquifers, due to their wide-spread environmental presence, high sorption capacity and tendency to form coatings on mineral surfaces. In recent years, the sorption behavior of Np(V), the most relevant oxidation state under ambient conditions, onto iron oxides was mainly studied by macroscopic experiments [2]. Manganese oxides were rarely investigated.

In this work, Np(V) sorption on the oxyhydroxides of Fe and Mn is investigated comprehensively by combining in-situ ATR FT-IR [3] and EXAFS spectroscopy under a variety of environmentally relevant sorption conditions with surface complexation modelling of batch sorption data.

A variety of sorption parameters such as Np(V) concentration, pH, ionic strength, and the presence of bicarbonate was considered. Time-resolved IR spectroscopic sorption experiments at the iron oxide–water interface evidenced the formation of a single monomer Np(V) inner-sphere sorption complex. EXAFS provided complementary information on bidentate edge-sharing co-ordination. In the presence of atmospherically derived bicarbonate the formation of the bis-carbonato inner-sphere complex was confirmed supporting previous EXAFS findings [4]. From a comparison of Np(V) surface complexation on different mineral oxides of iron, manganese, silicon and titanium a very similar sorption behavior was elucidated [3]. The obtained molecular structure allows more reliable surface complexation modeling of recent and future macroscopic data. Such confident modeling is mandatory for evaluating water contamination and for predicting the fate and migration of radioactive contaminants in the subsurface environment as it might occur in the vicinity of a radioactive waste repository or a reprocessing plant [5].

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Session 4.1: Geo-radiochemistry: Talk

Session 4.1: Geo-radiochemistry: Talk A-765

Incorporation of Lanthanide(III) into Scheelite-Related Host Matrices ABO_4 ($A = Ca^{2+}$, Sr^{2+} , Ba^{2+} ; $B = W^{6+}$, Mo^{6+}): Role of A- and B- Sites on the Dopant Site-Distribution and Photoluminescence

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Content

Calcium orthotungstates and -molybdates are naturally occurring minerals that have been studied extensively. The minerals are named scheelite ($CaWO_4$) and powellite ($CaMoO_4$), respectively. Scheelite is the most important economic W mineral. Powellite is actively studied in the nuclear waste management field. Powellite is one of the primary Mo crystalline phases expected to form in high-level nuclear waste (HLW) borosilicate glasses during waste processing.

Both scheelite and powellite have a large number of synthetic derivatives that are based on a general formula ABO_4 ($A = Ca^{2+}$, Sr^{2+} , Ba^{2+} ; $B = W^{6+}$, Mo^{6+}). Recently, much of the interest in study of scheelite-type materials arises from their exceptional compositional variability. In the context of nuclear waste disposal, this compositional variability offers a potential pathway for the effective retention of highly radiotoxic actinides like Pu and Am in a powellite secondary phase. However, the thermodynamic stability of these solid solutions will depend on their structural deviation from the stoichiometric phases.

Investigations have shown that the presence of excess positive charge in scheelite-typed ABO_4 materials upon incorporation of each trivalent ion is compensated via coupled substitution with a monovalent alkali cation. Single-crystal X-ray measurements demonstrate that the crystal structure of the resulting solid solutions is disordered, that is, the trivalent dopant and monovalent charge-compensating cation statistically occupy the same divalent A^{2+} site in ABO_4 structure. However, the structural details behind such disordered substitution, such as specific ionic environment around dopants, number of non-equivalent doping species as well as spatial accommodation of doping centers, are difficult parameters to characterize from the crystallographic data, especially when the dopant is present at trace concentration levels.

Polarization-dependent site-selective time resolved laser-induced fluorescence spectroscopy (p-TRLFS) is unique in its capability to characterize the local environment of a fluorescent probe, here Eu^{3+} , in a multi-species system with point-group accuracy at trace concentration levels. This work aims to clarify the impact of site effect on the local symmetry distortion from the bulk crystallographic site symmetry in scheelite-type ABO_4 single crystals. This will improve our understanding of the formation of solid solutions on the molecular scale.

Interaction of Eu(III) with CSH phases probed by time-resolved luminescence spectroscopy

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Content

Cement based materials are discussed as a technical barrier for radionuclides in repository concepts. Hence, understanding the ad- and absorption process of Actinides (An) on a molecular level is indispensable for the development of sound models and ultimately for the risk assessment. Lanthanides (Ln(III)) can be used as analogs for An(III) and offer due to their unique luminescence properties a high potential as optical probes. Among the Ln(III) especially Eu(III) is frequently used as a luminescence probe since its emission shows an outstanding sensitivity towards alterations in the crystal field. Because of its unique electronic configuration among the Ln(III), the Eu(III) luminescence can yield a wealth of information to perform a speciation analysis. The luminescence decay kinetics as well as the spectral intensity distribution of Eu(III) luminescence are sensitively altered by the coordination environment.

In our study Eu(III) was used as a luminescence probe i) to study the ad-/absorption on calcium silicate hydrate (CSH) phases, which are representatives of cement alteration phases and ii) to monitor the alteration of the CSH phase. Different CSH phases with respect to their Ca:Si-ratio are investigated. The Eu(III) ions are added either at the beginning of the CSH formation or in a subsequent step after the CSH phase has been already formed. The latter sorption experiments are performed at different pH (11, 12, and 12.6) and different ionic strength (up to $I = 4$ M). A full characterization of the initial CSH phases and after several month based on XRD, Raman, and ICP-MS data is performed. The backbone of our speciation are time-resolved luminescence data, especially luminescence decay kinetics and time-resolved area normalized emission spectra (TRANES) in combination with site-selective excitation (monitoring the ${}^7F_0 \leftarrow {}^5D_0$ transition). Three different Eu(III) species are identified. The relative amount of the different species is changing with contact time and the pH of the sample. In samples with artificially adjusted pH value the alteration of the CSH phase is corroborated by changes in the observed Eu(III) luminescence parameters. The results are complemented by theoretical calculations for the structure of the CSH phase at different Ca:Si ratios. Based on the structures, one of the Eu(III) species can be attributed to a Ca layer and the other to a Ca/water layer. The third species, which disappeared over time, is identified as surface precipitate.

Study of Np diffusion in Opalinus Clay by synchrotron microbeam techniques

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Content

The diffusion of Np(V) in intact Opalinus Clay (OPA) cylinders was investigated by μ -XRF, μ -XANES and μ -XRD at the μ XAS beamline (Swiss Light Source). The aim was to determine the Np speciation along its diffusion path as a function of time (61 and 83 days) with synthetic OPA pore water (pH = 7.6, I = 0.4 M) as mobile phase. In addition, 1 M NaCl solution at pH 8.1 was used as another mobile phase to investigate the effect of higher salinity on Np diffusion. The diffusion setup has been described in [1].

Np L3-edge μ -XANES measurements showed that inside the clay part of Np(V) was reduced to Np(IV). The average fraction of Np(IV) equalled $36 \pm 13\%$ at randomly chosen spots along the diffusion path. However, in several “hot” spots a nearly complete reduction to Np(IV) was observed that could be attributed to the presence of pyrite. This agrees with our previous study on the sorption of Np(V) on OPA [2]. The diffusion experiment in 1 M NaCl showed a stronger retardation of Np compared to OPA pore water due to differences in pH and alkaline earth metal concentrations. From the measured Np diffusion profiles, the corresponding diffusion parameters were derived that are needed for transport modelling.

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Technetium retention by siderite under anoxic conditions

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Content

⁹⁹Tc is a long-lived ($t_{1/2} = 2.11 \times 10^5$ years) β -emitter formed during the fission of U and is of major concern for radioactive waste disposal. Its environmental mobility is primarily governed by the oxidation states VII and IV, with Tc^{VII} forming the highly mobile TcO_4^- aquo anion, whereas Tc^{IV} is rather immobile due to the low solubility of its hydrolysis products [1]. Redox processes, which are able to convert Tc^{VII} into Tc^{IV} , are hence of paramount importance for the safety of radioactive waste repositories. Fe^{II} -bearing minerals, ubiquitous in nature and also forming as corrosion products of the carbon steel canisters foreseen as a possible first enclosure of radioactive waste, play a vital role in these redox reactions due to their high redox reactivity and high sorption capacity, as has been shown not only for Tc, but also for Se, U, Np and Pu.

Here we focus on the retention of Tc^{VII} by a typical Fe^{II} mineral in carbonate-rich environments, siderite (FeCO_3), which we studied in the relevant pH range (7 – 12.6) under anoxic conditions by means of batch sorption experiments and by X-ray absorption spectroscopy. Sorption experiments showed that Tc retention by siderite is fast (within minutes) and efficient ($\log R_d \sim 5$) across the investigated pH range and independent of ionic strength (0.1 – 1 M NaCl). Tc K-edge X-ray absorption near-edge structure (XANES) data confirmed that the Tc immobilization is due to the surface-mediated reduction of Tc^{VII} to Tc^{IV} . The local structure of Tc^{IV} as probed by extended X-ray absorption fine-structure (EXAFS) spectroscopy revealed two different species: in the pH range 7.8 to 11.5, TcO_2 -dimers form inner-sphere sorption complexes at the surface of siderite or of an $\text{Fe}^{\text{II,III}}$ (hydr)oxide potentially formed during the redox reaction. At pH 11.8 to 12.6, the retention proceeds through the (near-surface) incorporation of Tc^{IV} by siderite.

In conclusion, siderite contributes effectively to the retention of Tc in the near-field of nuclear waste repositories.

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Session 4.2: Fluid-rock interactions: from mechanisms to rates – from atom to plate.: Poster

**Session 4.2: Fluid-rock interactions: from mechanisms to rates – from atom to plate.: Poster
A-539**

Catalytic and redox activity at mineral surfaces: High-pressure pyrolysis of the model compound butyl ethyl ether in the presence of pyrite and illite

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Content

The maturation of sedimentary organic matter (OM) by the influence of elevated heat and pressure eventually leads to the formation of H₂O, CO₂, and a variety of organic compounds. For a better understanding of this process that comprises a multitude of individual reactions, artificial maturation experiments of rock samples are employed for the determination of mechanistic and kinetic data. One alternative approach is the pyrolysis of organic model compounds representing bond types which occur in insoluble OM (kerogen). Ether bonds are important bridging units in kerogen and were described as relatively heat-labile bond types in molecular dynamics simulations [1]. However, pyrolysis of individual model compounds alone does not account for the potential influence of minerals. Minerals may control decomposition pathways of model compounds and OM in general by means of surface catalysis or Eh/pH buffering. Hence, pyrolysis experiments of model compounds should in addition explore the impact of minerals.

Here we present the results of high-pressure pyrolysis experiments (260°C, 200 bar) in sealed gold capsules of the model compound butyl ethyl ether (BEE) alone and together with the minerals pyrite or illite. Gaseous and volatile reaction products were analyzed by headspace-gas chromatography. Experiments with pyrite or illite revealed a strong acceleration of the decomposition rate of BEE and a significant alteration of the product distribution. The formation of branched higher alkanes in experiments with illite indicates a surface catalytic activity leading to the isomerization of alkyl groups and to addition reactions. In experiments with pyrite, a pronounced formation of polar organic molecules (e.g. ketones) and alkenes was observed which can be attributed to the redox activity of the pyrite surface. Gaseous products like CO₂ or H₂ may lead to successive processes at mineral surfaces like redox or dissolution reactions or the precipitation of secondary minerals.

Our findings illustrate how (differently) minerals can control the prevailing decomposition pathways of a model compound. Thus, pyrolysis of model compounds in the presence of individual minerals can provide important insights in the processes that occur at the mineral-organic layer interface. Mineral catalysis may also play an important role for individual thermal decomposition pathways during the maturation of natural OM in the presence of minerals.

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Dissolution kinetics of CO₂ and CO₂-SO₂ mixtures in saline fluids and SO₂ redox reactions at geological storage conditions

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Content

CO₂ captured from industrial processes or power plants contains impurities (e.g. SO_x, NO_x, O₂, N₂, Ar) of variable concentrations. Among these impurities, which will be co-injected with the CO₂ into the geological storage formation (e.g. a saline aquifer), SO₂ is considered to affect chemical reactions and physical processes in the storage formation significantly. For example, it can initiate precipitation of anhydrite and barite, form sulfuric acid in contact with water, and favor the dissolution of storage rock minerals, e.g. calcite, dolomite, pyrite, hematite [1] [2]. Kinetic data of these reactions and processes, as well as the dissolution rates of CO₂ and SO₂ into the formation water at geological storage conditions are scarce, but necessary to precisely predict the impact of SO₂ on the near-well rock integrity, injectivity and the long term storage capacity in modelling approaches [3].

We studied the dissolution kinetics of CO₂, CO₂-SO₂- and CO₂-SO₂-O₂ mixtures into water and saline brine under geological storage conditions (16 MPa, 333 K) using stirred all-titanium autoclaves. The dissolution (or mass transfer) of SO₂ into water under these conditions was significantly higher than that of CO₂, but the CO₂-solubility was not significantly affected by SO₂. Analysis of the different sulfur species (S²⁻, S⁰, S₂O₃²⁻, SO₃²⁻ and SO₄²⁻) in the aqueous phase revealed that hydrated SO₂ was the dominant species when oxygen was absent. The disproportionation of sulfur dioxide to sulfate and sulfide was not observed in the period of the experiments. Either the disproportionation is very slow under the applied conditions or it did not occur at all.

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Distribution of Chlorine between Amphibole and Hydrothermal Fluids: An Experimental Approach

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Content

Amphibole is one of the major chlorine bearing minerals in crustal rocks and can incorporate Cl up to the wt.% level. As such, the composition of amphibole produced during fluid-rock interaction (i.e., alteration, metasomatism, metamorphism) will may reflect the salinity of the reactive fluids. Although the applicability of this approach has been demonstrated for natural amphibole in highly saline metasomatic systems, experimental studies investigating the distribution of Cl between amphibole and fluids are scarce. Here, we present experimentally derived distribution correlations for Cl between NaCl/KCl fluids and Fe-rich amphibole (i.e., Fe-Pargasite, K-Hastingsite). To overcome difficulties during synthesis, namely small grain sizes caused by a high nucleation rate, we seeded the experiments with natural amphibole. In this way, we promoted epitaxial growth of new amphibole that is in equilibrium with the Cl containing fluid and large enough to be analyzed by electron microprobe. To investigate the role of different cations and different salinities on the Cl distribution, hydrothermal experiments were done in cold-seal-pressure vessels at 500-600°C and 0.2GPa using different fluid compositions (i.e., NaCl and KCl at varying concentrations). Epitaxial amphibole from experiments using NaCl fluids shows increasing Cl concentrations with increasing salinities (0.02wt.% $\pm$ 0.01 at 1.7 m(NaCl) to 0.18wt.% $\pm$ 0.06 at 18 m(NaCl)). The observed linear trend follows the empirical formulation: $X_{Cl}^{Amph} = m_{NaCl} * 0.002$. Experiments using KCl fluids produce epitaxial K-rich amphibole that shows up to 10 times higher Cl concentrations than Na-rich amphibole from experiments using comparable NaCl concentrations. This observation suggests that the incorporation of Cl is not only controlled by the Cl concentration of the fluid but also by the cation composition and crystallographic structure of the newly formed amphibole. The results of this study provide a first step to experimentally calibrate an amphibole based fluid probe for constraining salinities in hydrothermal environments.

Dynamics of bimodal, diffusional and ballistic fluid transport in the Earth's crust

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Content

Fluid flow is one transport system that can be regarded as "bimodal". At low hydraulic head gradients, fluid flow through pores is slow and can be termed "diffusional". Structures such as breccias and hydrothermal veins indicate high fluid velocities, which can only be achieved by localized fluid transport via hydrofractures. Hydrofracture propagation and simultaneous fluid transport can be seen as a "ballistic" transport mechanism, which is activated when transport by diffusion alone is insufficient to release local fluid overpressure. The activation of a ballistic system locally reduces the drive, but may cause the escape of most of the fluids. The aim of this study is to investigate the properties of the two transport modes in general and the transition between them in particular.

We developed a numerical model (based on [1] and [2]) in order to study patterns that result from bimodal transport, i.e. coupled diffusional and ballistic transport. Interesting and rich behaviour emerges in the transition between diffusion- and ballistic-dominated behaviour. We quantified this transition from diffusional to ballistic transport using fractal analysis. We compared the spatial and temporal dynamics of the system with fractal analysis data of natural systems, such as hydraulic breccias (Mt Painter, Australia) and hydrothermal veins (Black Forest, Germany). The data show similarities, which is strong evidence for the usefulness of our approach.

We show that the criterion for activation of a ballistic system is mostly scale invariant, thus leading to (multi-)fractal patterns and statistics. The outcome of this study will have implications for a large range of transport related processes in the Earth's crust. Examples of such processes are the formation of hydrothermal ore deposits and the dispersion of contaminants in ground water. The results will also impact the research on tipping points in the crust, as they are often exceeded due to geothermal energy production and well stimulation.

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Generation of fluid pathways by mass transport during hydration of eclogite at the plate interface

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Content

The mechanisms that generate efficient fluid pathways during hydration reactions at depth are still poorly understood. The transformation from eclogite to blueschist during exhumation of the rock occurs at the slab-wedge interface in subduction zones worldwide. This transformation expresses the general problem of how fluids infiltrate into a system that is expected to swell by the fluid uptake of the newly formed hydrous minerals. We found eclogitic pillow lavas that are partly transformed to blueschists along their rims due to the blueschist-facies overprint during retrograde metamorphism. Field observations and petrological data indicate two different fluid flow regimes during retrogression, one major fluid pathway system between the pillows characterized by high fluid fluxes and a second one related to fluid migration into the pillow interiors. The main reaction involves formation of glaucophane which is accompanied by a large volume increase. No significant fractures are observed and mass balance calculations suggest fluid infiltration resulted in shrinkage rather than expansion. Our question focused on how the fluid could migrate into the low porosity pillow interiors and if mass transport could result in overall volume loss.

We simulated this coupled reaction-diffusion process using numerical modelling coupled with local equilibrium thermodynamics for the relevant rock system. Porosity and fluid pressure evolution are coupled to local thermodynamic equilibrium and density changes. As expected the first rim of blueschist that forms around the eclogite pillow increases volume to such a degree that the system is clogged in case of negligible mass transport. However, we found that due to diffusive mass transport of solid compounds dissolved in the fluid at the reaction front, porosity is generated maintaining the fluid pathways and allowing reaction to progress towards the pillow interior.

Geomechanical behaviour changes of a Bunter Sandstone and of a borehole cement due to scCO₂ injection effects

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Content

Cluster (www.bgr.bund.de/CLUSTER) is a research project funded by the German Federal Ministry for Economic Affairs and Energy (BMWi), that investigates the impact of CO₂ streams and mass flow for different scenarios along the carbon capture and storage (CCS) chain. In this work, the geomechanical behaviour changes caused by supercritical (sc) CO₂ in a reservoir rock and in a borehole cement are described. An analogue reservoir formation investigated was the Trendelburger bed, a Bunter Sandstone classified as a subarkose within the Solling formation. This compact silica cemented sandstone ($\rho = 2.3 \text{ g/cm}^3$) is fine to middle grained, has an effective porosity of ca. 9.5 and 12 % and a restricted hydraulic permeability between 3.6×10^{-16} and $2.8 \times 10^{-15} \text{ m}^2$. Conventional triaxial compression tests were conducted on rock and cement specimens saturated either with water or brine, by varying pore- and confining pressures. Core samples (70x140mm) were prepared from rock blocks obtained from a quarry in Bad Karlshafen (Germany) and from the cement sort CEM III/A. In order to analyse directional dependency of geomechanical parameters, rock samples were drilled parallel and perpendicular to bedding. Autoclave experiments were carried out under representative reservoir conditions ($T = 333 \text{ K}$, $p = 16 \text{ MPa}$) by exposing rock and cement specimens to scCO₂ and synthetic formation brine for five weeks. The experimental results show that rock strength, ultrasonic velocities and permeability are higher parallel than transverse bedding planes. Fracture patterns are also direction-dependent. For cement specimens, the hardening process time is significant to develop a pronounced brittle or ductile behaviour, where the modulus of deformation could vary between 2 and 45 GPa. The adsorption of scCO₂ on the intact sandstone could be linearly described as a function of confining and pore pressures, but an influence of scCO₂ could firstly be detected after a long-term reaction in autoclave experiments. The influence of scCO₂ on the deformability of the Trendelburger bed is reflected due to the increase of deformability, a loss of cohesion (20 %), as well as a decrease in tensile and compressive strength (30 % and 20 %). Micrographs made before and after scCO₂ treatment show dissolution effects in mineral phases and development of pore spaces. Additional triaxial compression tests are planned to be conducted with CO₂ in combination with impurities such as NO_x and SO_x.

**Methane migration and gas hydrate occurrence in a 2.5 m sand in the Terrebonne Basin,
Gulf of Mexico**

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Content

At some natural gas hydrate sites, gas hydrate is observed at high concentrations in sand sediment layers and at low concentrations or absent in surrounding marine muds. One example of this case is in the Terrebonne Basin, which was drilled in 2009 by the Gulf of Mexico Gas Hydrate Joint Industry Project. In Hole H of Terrebonne Basin, a 2.5 m sand was observed with a gas hydrate saturation of ~35%. The sand is surrounded on both sides by a hydrate-free interval in marine muds. Additionally, each hydrate-free interval is bounded at the top and bottom by gas hydrate in fractures. In this case, the mechanism which causes high saturations of gas hydrate in the sand layer and hydrate-free intervals surrounding the sand layer is likely related to the difference in solubility of methane between fine-grained marine muds and coarser-grained sediment as well as varying rates of microbial methanogenesis. Low microbial methanogenesis and a low solubility threshold in sand results in different methane concentrations between sand and surrounding mud, causing a diffusive flux of methane from mud intervals into the sand layer.

To investigate this process and the factors that control the evolution of these systems, we develop a 1D numerical model using mass balance equations to predict the volume and distribution of gas hydrate in time. We focus on the 2.5 m sand measured in the Terrebonne Basin, and vary the amount of metabolizable organic carbon, the reaction rate that characterizes the vigor of microbial activity, the methane diffusion coefficient, and the methane hydrate formation rate coefficient. We will present results showing the factors that have the largest control on the occurrence of gas hydrate in and surrounding the sand layer, as well as the range of organic matter and diffusion coefficient anticipated for the 2.5 m sand in the Terrebonne Basin.

Microstructure and Mineralogy of the Trendelburg Sandstone Beds

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Content

Due to its porosity sandstone is considered and investigated as a potential host rock for deep geologic CO₂ storage (BMW project CLUSTER - 03ET7031D). It is critical to know how CO₂, including various by-products (e.g. NO₂, SO₂), interacts with minerals at temperatures and pressures expected at the point of injection (~16 MPa, 333 K). The impact of the chloride rich formation waters have to be taken into account additionally. The experiments were carried out with sandstone samples originating from a quarry near Bad Karlshafen (northern part of the German Basin). The geologic setting of the grey Weser sandstone (Trendelburg beds) represents the lower Solling formation which belongs to the middle Bunter Sandstone [1]. To investigate the CO₂ impact on sandstone alteration the samples were previously characterised by X-ray Diffraction (XRD), X-ray fluorescence (XRF) SEM/EDX (scanning electron microscopy/energy dispersive spectroscopy), optical microscopy (polarized light/digital microscopy), CL (cathode luminescence). The visual inspection showed that the sandstone was light grey and well sorted. The grain diameter was medium to fine grained. The grains were subrounded to subangular. Results of the Rietveld method [2] for currently three samples showed that the grey Weser sandstone consisted quantitatively of ~64 – 72 wt.% quartz, ~11 – 17 wt.% K-feldspar, ~1 – 12 wt.% Na-feldspar, and ~10 – 12 wt.% muscovite. Therefore the sandstone could be described as subarcose. The accessories apatite, biotite, rutile, epidote, chlorite and illite were only detectable by SEM and optical microscopy. XRF data of these three samples revealed a homogenous material with minor variation of the chemical composition. The intergranular porosity was determined by image analysis of blue coloured thin sections. The values (< 10 %) are lower than the porosity which was determined by sample saturation with water and chloride rich solution, respectively. This observation could be ascribed to the porosity of weathered feldspars which could not be detected soundly by analysing blue coloured thin sections. Yet, weathered feldspars could qualitatively observed by means of CL (cf. Fig. 1).

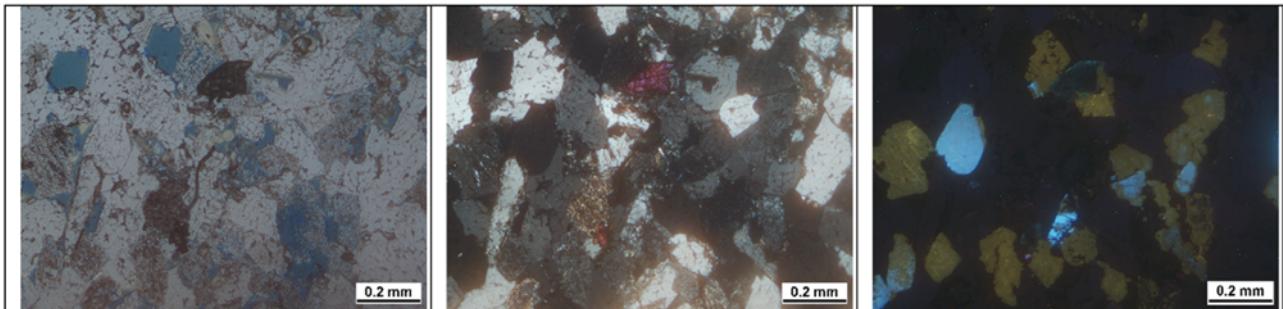


Figure 1: Altered feldspar: Left) Grey Weser sandstone: Pores filled with blue resin, middle) cross polarized light image of left image – also showing epidote (reddish), right) CL image with differently weathered feldspars (light blue to brownish)

[1] [2]

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Mineralogical-geochemical investigations of fractures in Permian z2 potash seam and surrounding salt rocks

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Content

Fractures occur locally in the z2 potash seam (Kaliflöz Staßfurt, Zechstein, Upper Permian) of the Morsleben salt mine, Northern Germany. Most of them extend several centimeter to meter into the surrounding salt rocks. The fractures are distributed on all levels in an extremely deformed area of the salt structure. Samples were taken at two different locations in the mine, which differ distinctly in the tectonic position and thickness of the strata. They belong to the same NW-SE trending synclinal structure, which was reverse folded (1). The composition of the potash seam is heterogeneous and depends on level and tectonic position of the syncline. In some cases the fracture infill changes depending on the type of surrounding rocks.

At the first location, more than 200 fractures were mapped. The opening widths reach max. 2 mm. The potash seam is mainly developed as a sylvite-kieserite rock and shows distinct variations in type of potassium containing minerals and content (max. 35 wt.-%). The composition varies on cm-scale and depends on the position within the potash seam. The fracture infill is dominated by kainite.

At the second sampling location, brittle rock units, like the main anhydrite (z3HA), occur close to the potash seam. The fractures show a huge range of opening widths of only a few millimeters up to 10 cm. The potash seam consists of less potassium containing minerals (max. 5 wt.-%) and is dominated by polyhalite, which originated mostly early diagenetic from anhydrite. In contrast to the first location there is a high diversity of fracture infill minerals.

The bromide accumulates together with the potassium containing minerals in the fractures, which provides a transportation route from the potash seam to the salt rock. The bromide content in halite reaches the highest values (340 µg/g BrHalit) in the surrounding salt rocks.

Different tectonic conditions cause different fluid rock interactions which leads to a different composition of the potash seam including the origin of fractures and their mineral fillings.

Further investigations will focus on microstructural and geochemical analyses of the fracture infill and surrounding salt rocks. Age dating of suitable minerals, e.g. polyhalite (2), could help to reconstruct the formation conditions of the rocks.

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Mineralogy and microstructure of small secondary modified lenses in the grey Weser sandstone

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Content

Due to investigations of different sandstones for their behaviour under the influence of fluid CO₂, a typical grey Wesersandstone is among those rocks tested for their geochemical and geomechanic behaviour. The overall mineralogical composition, microstructure and porosity are very important properties. As a peculiarity of a typically grey Wesersandstone (Solling formation) are some secondary modified lenses with enlowered density within the matrix of the overall grey sandstone. These lenses with higher density do not only show differencies in the overall chemical and mineralogical composition, but do have some interesting compositional specialities. Therefore it seems to be necessary to describe these areas within the sandstone in detail. Mostly, these lenses are oriented parallel to the stratification of the sandstone. In comparison to the silicious sandstone, the mineral content of the lenses is enriched in alkali feldspars and reduced in the total quartz content. A potential potassium-silica transfer process from feldspars is described. Fig. 1 gives an overview of the macroscopical and microscopical structure of the secondary modified lenses.

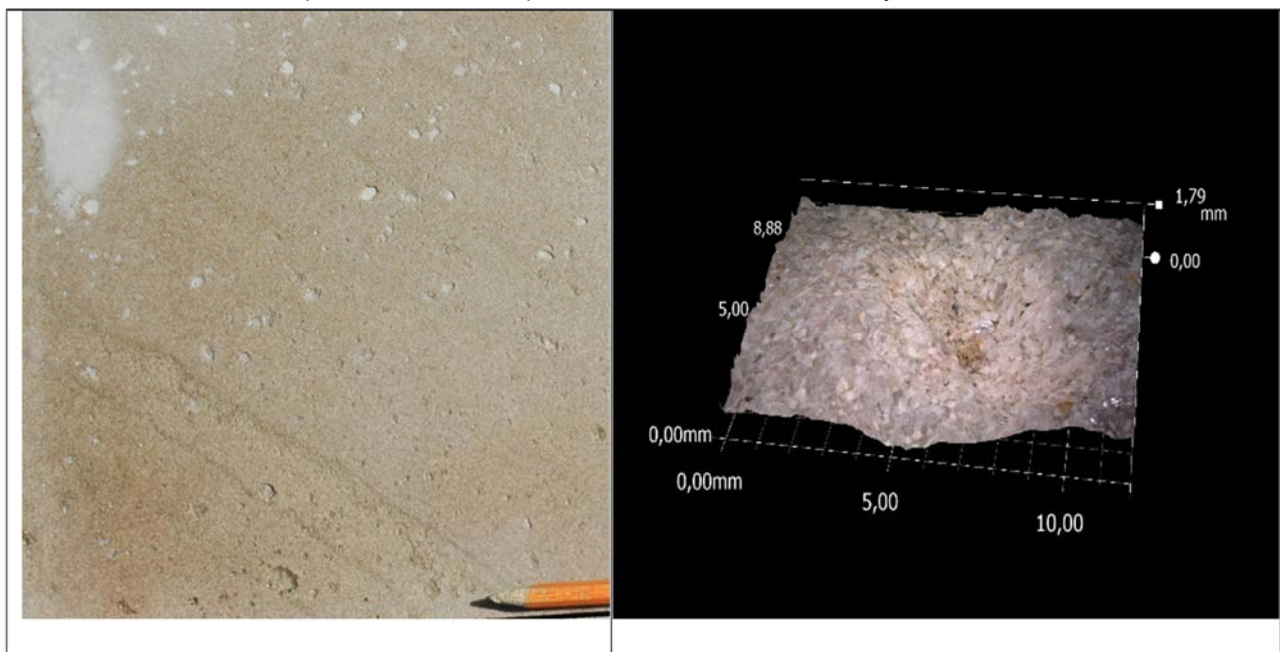


Fig. 1 : Macroscopic view of a typical grey Wesersandstone showing the secondary modified lenses without filling content (left) in the sandstone matrix, - and 3D –digital microscopic image of an empty lense(right)

The genesis of secondary modified lenses is interpreted on the basis of the minerals formed during diagenetic processes including SiO₂ release from alteration of feldspars and newly formed phases (Halite replacement by SiO₂ forming pseudomorphs of quartz after halite, sodium rich feldspars and newly formed clay minerals) (figure 2). This leads to different morphologies of quartz (original grains, newly formed due to alteration, authigenic crystals, replacement forms.

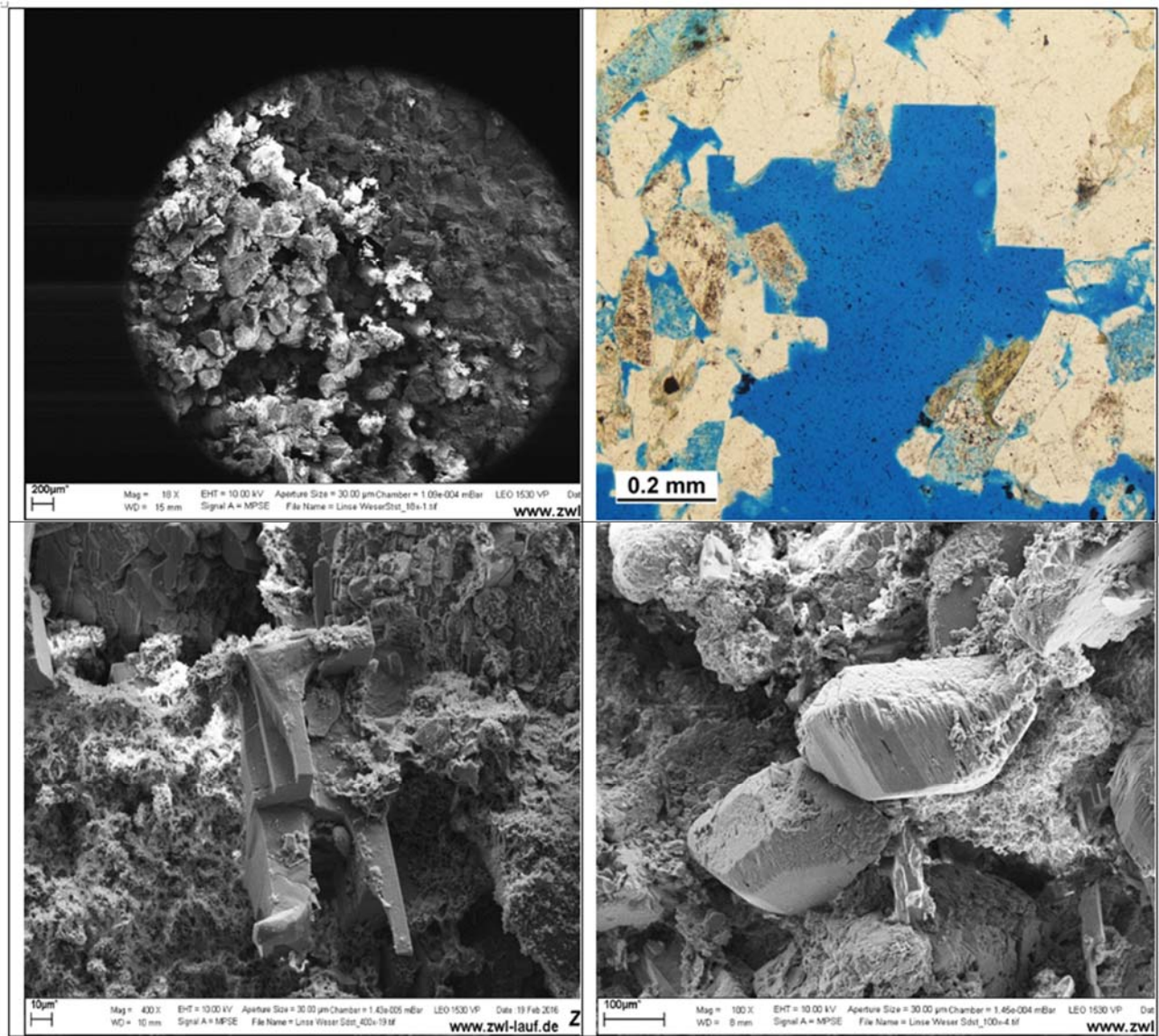


Fig. 2 : SEM image of secondary modified lens in contact to sandstone matrix (upper left), pseudocubic pore space (blue colored) in thin section, SEM of pseudocubic quartz (lower left) albite crystals in secondary modified lens areas, (lower right)

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Nanoscale fluid flow enables crustal-scale metamorphism

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Content

The reaction of fluids with rocks is fundamental for Earth's dynamics as they facilitate heat/mass transfer and induce volume changes, weaknesses and instabilities in rock masses that localize deformation enabling tectonic

responses to plate motion. During these fluid-rock interactions it is the ability of a rock to transmit fluid, its permeability, that controls the rates of metamorphic reactions. However, although some geological environments (e.g., sediments) are open to fluids, the majority of solid rocks (e.g., granites, eclogites, peridotites, etc.) are nearly impermeable. Surprisingly though, even in rocks that are nominally impermeable widespread fluid-rock interactions are observed leading to the question: How can fluids migrate through vast amounts of nominally impermeable rocks? Here we investigate one of the most wide-spread fluid-mediated metamorphic processes in the Earth's crust, the albitization of feldspathic rocks. We show that fluid flow and element mobilization during albitization is controlled by an interaction between grain boundary diffusion and reaction front migration through an interface coupled dissolution-precipitation process. Using a combination of focused ion beam scanning electron microscopy (FIB-SEM)-assisted nanotomography combined with transmission electron microscopy (TEM) we show that the

porosity is dictated by pore channels with a pore diameter ranging between 10 to 100 nm. Three-dimensional visualization of the feldspar pore network reveals that the pore channels must have been connected during the

replacement reaction. Analysis of the pore aspect ratios suggests that a Rayleigh-Taylor-type instability associated

to surface energy minimization caused the disconnection of the pore channels. Fluid transport in nanometer-sized

objects with at least one characteristic dimension below 100 nm enables the occurrence of physical phenomena

that are impossible at bigger length scales. Thus, on the basis of our microstructural investigations we used nonequilibrium molecular dynamics simulations to investigate the influence of nanoscale pore transport phenomena on metamorphic mineral replacement reactions. Our findings suggest that fluid transport through nanoscale transient pore networks may control regional-scale metamorphism and metasomatism.

**Oxidative alteration of partially serpentinized harzburgite in a flow-through reaction cell:
reaction of olivine to Fe-oxyhydroxide phases and serpentine at 120 °C**

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Content

Peridotites at slow and ultraslow spreading ridges interact with seawater under a wide range of P-T-fluid-strain conditions, from higher temperature serpentinization to low-temperature interaction of serpentinites with ambient seawater. The latter alteration type can cause the formation of reaction-induced porosity in the near seafloor environment (Jöns et al., 2017, *Lithos* 268–271, pp. 274–284). This study showed that dissolution of brucite and olivine in the near-seafloor environment results in Fe-oxyhydroxide and carbonate formation in newly generated pore spaces.

To better understand the microstructural changes related to oxidative low-temperature alteration of partially serpentinized harzburgite, we performed a flow-through experiment at 120°C and 42 bars for 43 days. Air-saturated water was percolated through a pre-fractured minicore of a serpentinite sample from Hole 920D (Leg 153 of the Ocean Drilling Program), Mid-Atlantic Ridge south of the Kane Transform Fault (MARK area). The sample is a partially serpentinized harzburgite (90–95% serpentinization) from a subseafloor depth of 140 m; it is completely unaffected by oxidative alteration that prevails near the seafloor.

The core was mounted in an X-ray-transparent flow-through reaction cell (Kahl et al., 2016, *Solid Earth Discuss.*, doi:10.5194/se-2016-25) and was scanned before and after the experiment. Unreacted and reacted materials were inspected by SEM and EDX.

We observe that relict olivine in the serpentinite dissolves much more rapidly than the surrounding serpentinized rock domains. These large differences in dissolution rate created a coarse pitted texture on the cut rock surfaces. The olivine is tarnished with rusty reddish coatings, and macroscopically the rock resembles oxidatively altered serpentinized peridotite from the seafloor. SEM investigations reveal the formation of submicron-sized iron oxyhydroxide globules. In places where coatings are thickest (near the inlet of the reaction cell) serpentine needles are commonly associated with the Fe-oxyhydroxide.

The results show that the iron released from olivine dissolution becomes readily oxidized and precipitates in close proximity to its former host phase. The results also show that the dissolution of olivine proceeds at rates faster than the precipitation of serpentine. These rate differences create permeability, which facilitates the pervasive nature of oxidative alteration typical for abyssal peridotites.

Polyphase alteration of ultramafic clasts from a serpentinite mud volcano (Mariana forearc) unveil shallow subduction zone processes

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Content

Water–rock exchange processes play a major role in the cycling of volatiles and trace elements in subduction zones. In particular for the shallow parts of subduction zones, these processes are poorly understood. Mud volcanoes in the Mariana forearc provide access to natural samples from this zone. Fluids released from the subducting Pacific plate rise buoyantly through conduits in the upper Philippine Sea plate, where they hydrate the mantle wedge. Clasts of serpentinized ultramafic rock are erupted at the seafloor in a matrix of serpentinite mud at several mud volcanoes. The volcanoes occur in varying distance from the deep-sea trench, and hence represent a range of depths and temperatures to the downgoing plate and the subduction channel.

We studied ultramafic rock clasts from the mud volcano closest to the trench (Yinazao Seamount, 55 km) drilled during IODP Expedition 366. The slab interface is situated 13 km beneath the seamount ([1]) and has an estimated temperature of 80°C ([2]). The harzburgite and dunite clasts are strongly altered and exhibit structures, mineral assemblages and compositions indicative of a polyphase alteration history.

Extensive early serpentinization of the clasts was pervasive and is preserved in the form of mesh textures. Bastite after orthopyroxene has elevated Al and Cr compared to serpentine after olivine. The mesh textures are cut by veins of serpentine ± brucite ± magnetite that formed during later alteration stages. Using crosscutting relations, we can distinguish between several distinct vein generations in all samples. These include serpentine-dominated veins with $(\text{Mg}+\text{Fe})/\text{Si} \sim 1.5$ and $\text{Mg}/(\text{Mg}+\text{Fe}) = 0.9\text{--}0.95$ but also (later) veins mainly consisting of brucite with increased Fe contents. The veins show distinct variations in their trace elemental composition, e.g., B or Sr. Remarkable are veins with brucite crystals that apparently grew in equilibrium with a fluid.

The predominance of brucite indicates an environment with low silica activities and alkaline conditions during late alteration stages. This interpretation is corroborated by the presence of late carbonate veins in two of the samples.

Some clasts show a change to orange or brown color towards their outer surfaces, presumably reflecting inward-movement of an oxidative alteration front in the mudflow after eruption at the seafloor.

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Preliminary results from the H2STORE and HyINTEGER projects

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Content

The H2STORE (“hydrogen to store”) and HyINTEGER (“....integrity of wells and technical components”) collaborative research projects were funded by the German Federal Ministries of Education and Research (BMBF) and for Economic Affairs and Energy (BMWi). Both projects investigate potential reactions of hydrogen in depleted gas reservoirs. Thereby the focus in H2STORE was the interaction between reservoir components (minerals, fluids, biocenosis) and H₂, whereas in HyINTEGER additionally the interplay of these components and the technical well equipment is regarded.

Applied well material from six sites in Germany, Austria and Argentina was provided by industrial partners and covered depths from ~ 3.500-800 m. The ages of the samples range from Permian and Triassic to Tertiary.

One major topic of the subproject at University in Jena is the identification of abiotic reactions in the underground and their impact on sandstone porosity, permeability and reservoir quality, respectively.

The presented outcomes emerged from sand- and siltstones which are used in autoclave batch experiments in combination with synthetic formation fluids and 100% pure hydrogen. These experiments are conducted under specific reservoir conditions (pressure, temperature) for up to six weeks.

All samples are analyzed before and after the experimental runs with e.g. DMS, AFM, SEM, Microprobe, ICP-MS/OES and μ -CT. Porosity was determined by helium and permeability by nitrogen measurements. After the six weeks lasting experiments with hydrogen and conditions of ~ 100°C and fluid salinities ≥ 250 g/l (TDS) the microscopic and chemical analyses as well petrophysical data confirmed modifications in the used samples. The interaction between hydrogen and the rock samples at high temperature in such highly saline environments triggered variations in pH and electrical conductivity and forced partial to total dissolution of pore filling cements, like anhydrite, barite and carbonate.

The resulting increase in reservoir quality was substantiated by poro-perm measurements.

These observations are in contrast to experiments at temperatures $\leq 60^\circ\text{C}$ and using low saline fluid compositions. Here no mineral reactions occurred and the petrophysical parameters are unmodified.

These preliminary results suggest that the impact of hydrogen on underground pore space reservoirs is site-specific and detailed investigations are essential in the realization of hydrogen underground storage operations.

The role of CO₂ and SO₂ on cement-brine interactions during geological CO₂ storage and consequences for well integrity

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Content

Well integrity is a key aspect for safe geological storage of CO₂ and its assessment requires sound understanding of the physicochemical processes that take place in the cement-brine-CO₂ system throughout the entire storage life-cycle. This study focusses on the reactivity of a CO₂-resistant cement (D986 EverCRETE, by Schlumberger) that was applied at the Ketzin pilot site for CO₂ storage, Germany. Reference samples of the EverCRETE cement were taken directly from the cementing operation during abandonment of well Ktzi 202 in fall 2013. In addition, after two years - in summer 2015 - a 3 m long core was recovered from this 2013 cement plug representing in-situ well conditions. Static batch experiments were performed with a hydrothermal rocking autoclave system equipped with flexible Titanium cells. Cement samples were mixed with either synthetic 2 M NaCl brine or original in-situ Ketzin formation brine recovered during a back-production experiment plus pure CO₂ or impure CO₂ containing 5 vol% SO₂. In addition, blind experiments without added gas were performed. Run conditions were either 20 MPa/80°C or 8 MPa/40°C (= Ketzin specific conditions). Cement samples were taken and characterized by XRD before and after the experiments. During run duration, fluid samples were taken continuously at isobaric and isothermal conditions. Fluids were analyzed for cations and anions by ICP-AES and ion chromatography. The experiments allow to analyze and characterize individual CO₂-brine-cement reactions and to derive reaction rates for individual mineral reactions. Experiments with impure CO₂ evaluate sulfate reactions during the experiments and addresses the role of sulfate as critical reaction partner for cement during sulfate attack with formation of integrity relevant phases like ettringite. First XRD measurements, however, indicate absence of ettringite in the impure CO₂ and also blind runs at 20 MPa/80°C. Fluid data from runs with synthetic 2 M NaCl brine generally indicate decreasing concentrations of Cl⁻ and Na⁺, except for the pure CO₂ experiment at 8 MPa/40°C that shows no clear trend neither for Cl⁻ nor Na⁺. First data for other cations and anions show no unequivocal trends.

Water-rock interaction in submarine acid-sulfate fluids – a multi-isotope study from the Manus Basin, Papua New Guinea

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Content

Submarine acid-sulfate fluids are thought to form by direct injection of magmatic fluids into unmodified seawater, implying that water-rock interaction is restricted to the discharge zone. To investigate the formation and chemical composition of acid-sulfate fluids especially with regard to the alteration of the oceanic crust, we analysed boron (B), lithium (Li) and magnesium (Mg) isotope ratios of acid-sulfate fluids collected in 2006 and 2011 from DESMOS and North Su, Manus Basin, Papua New Guinea and compared them with black smoker fluids from the same locations.

Mg isotope ratios in acid-sulfate fluids match with the Mg isotopic composition of seawater. These results support the idea, that Mg in acid-sulfate fluids is seawater derived and not added to acid-sulfate fluids by dissolution of Mg-bearing minerals. Mg isotope ratios in “smoker-type” fluids also match with the isotopic composition of seawater, implying that Mg isotopes do not fractionate during formation of Mg hydroxides. B and Li isotope ratios in acid-sulfate fluids are lower than in seawater, indicating water-rock interaction in all fluids. However, their concentrations and isotopic compositions vary between the different locations. For example, B and Li isotope ratios in the DESMOS fluids range from 35.0 to 38.6‰ and from 29.2 to 30.1‰, respectively, whereas the pure acid-sulfate fluids from North Su range from 23.3 to 36.0‰ for $\delta^{11}\text{B}$ and from 17.2 to 24.3‰ for $\delta^7\text{Li}$. These differences can be best explained by water-rock interaction with less altered oceanic crust at North Su relative to DESMOS.

Our results show that all acid-sulfate fluids are influenced by water-rock interaction. However, the isotopic signatures imply a high degree of alteration of the oceanic crust. Furthermore, this multi-proxy approach may help to understand the alteration processes of the oceanic crust at acid-sulfate conditions and appears to be useful to trace the progressive alteration of the oceanic crust in acid-sulfate fluids.

Session 4.2: Fluid-rock interactions: from mechanisms to rates – from atom to plate.: Talk

Keynote speaker

A-848

Reacting porosity waves: a mechanism for fluid flow mediated by metamorphic reactions

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Content

Metamorphic reactions of (de-)volatilization can induce changes in rock density by up to 30%. This has first-order impact on rock deformation as well as on porosity and hydraulic properties. A new fully-coupled model was developed to take into account the couplings between metamorphic reaction, deformation and fluid flow. Thermodynamic calculations with Gibbs energy minimization and a compilation of kinetic data provide the basis for quantitatively considering metamorphic reaction in the model. The calculated changes in density due to reaction are then introduced in the model using a poroviscoelastic rheology and a porosity-dependent permeability. When an initial porosity anomaly is considered, the fluid pressure deviates from the lithostatic pressure in opposite directions at the top and at the bottom of the anomaly. This triggers reaction and the generation of porosity waves with porosity opening on one side of the anomaly and closing on the other side. The study of the porosity waves propagation at high resolution in 3-D indicates that fluid extraction by this mechanism is efficient and can occur from deep to shallow environments. Among the various parameters controlling the impact of reaction on fluid flow, the Clapeyron slope relating the evolution of porosity with fluid pressure is shown to play a key role. The model provides a new mechanism for episodic tremor and slip events migration in subduction zones.

**Archean magmatic-hydrothermal fluid evolution in the Quadrilátero Ferrífero (SE Brazil)
documented by B isotopes (LA MC-ICP-MS) in tourmaline**

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Content

In the Archean Quadrilátero Ferrífero mining district (SE Brazil), tourmaline occurs within leucogranitic intrusions, numerous barren pegmatite and plagioclase- and quartz-veins, as well as disseminated in the nearby greenstone belt. Their chemical and B isotope composition was determined by electron microprobe and LA MC-ICP-MS to constrain the complex hydrothermal evolution of the region.

Tourmaline varies from schorl in the leucogranite to dravite compositions in the metasediments. A net increase in Cr contents from magmatic to hydrothermal tourmalines illustrates that tourmaline major-element composition is mostly controlled by that of the host rock.

$\delta^{11}\text{B}$ values range from -10.7 to -27.1 ‰, with a major cluster around -12 to -18 ‰. There is a general trend of decreasing B isotope compositions from magmatic tourmaline hosted in the leucogranite and plagioclase veins (~ -13.5 ‰) towards those present in the metasediments and quartz veins (~ -18 ‰), which is consistent with a model of tourmaline growth from late-stage exsolved magmatic fluids.

Evidence for a separate fluid component is given by the presence in some metasediments and crosscutting quartz veins of tourmalines with $\delta^{11}\text{B}$ as low as -27 ‰, way beyond the reach of fractionation due to fluid exsolution. Significant chemical and isotope zoning in quartz vein-hosted tourmalines suggest mixing between isotopically heavy magmatic fluids exsolved from coeval crystallizing granites, and an isotopically lighter fluid component released from the host schists during contact metamorphism.

The overall scarcity of tourmaline in the gangue mineral assemblage in the neighboring greenstone-hosted Archean gold deposits contrasts with the absence of gold associated with these widespread B-bearing magmatic fluids, weighing against a magmatic-hydrothermal model for the world-class orogenic gold deposits in the region.

Authigenic barite formation in microenvironments – implications from optical studies and hydrogeochemical modelling

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Content

Nanocrystalline barite is identified in microenvironments of authigenic calcite in sediments above black shales on the Demerara Rise. These sediments are characterized by the presence of black shales in 410 to 490 mbsf and by a diagenetic barite layer above in 300 to 350 mbsf. The controls of authigenic barite formation are identified by combining results from interdisciplinary approaches such as imaging and mineralogical studies (TEM and SEM coupled with EDX) coupled to hydrogeochemical reactive transport modeling (Arning et al., 2015) using the PHREEQC (version 2) computer code.

Microenvironments are a prerequisite for the observed authigenic barite formation and a potential path for different pore fluids to diffuse and react is given by results from hydrogeochemical modeling. Calculations of the authigenic calcite amount in the investigated sediments result in a minimum in the calcite amount just above the observed zone of authigenic barite formation. This minimum relates to calcite dissolution that creates the potential pathways for the pore fluids. Ba²⁺ ions diffuse along a concentration gradient into sulfate-rich solutions within the microenvironments and are almost completely precipitated in authigenic barite.

Our studies reveal three stages of biogeochemical evolution of the investigated sediments until the final barite formation in microenvironments: 1. Ca-carbonate and framboidal pyrite formation in the anaerobic oxidation of methane (AOM) zone. 2. The AOM zone shifted downward in the sediment column. Triggering factors could be decreasing organic matter conversion, decreasing sedimentation rate, increasing sulfate concentration, and reduced methane flux (Arndt et al., 2009; Arning et al., 2015). 3. A second generation of Ca-carbonates crystallizes within the remains of foraminifera and is often closely associated with authigenic quartz and a sheet silicate phase. The coincidence of sulfate flux from above and barium fluxes from below induces barite precipitation within the first generation of carbonates.

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Dissolution kinetics and the initial evolution of porosity of polycrystalline carbonates

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Content

Carbonate minerals are ubiquitous in sedimentary rocks and modern sediments. Their dissolution kinetics plays an important role in many applied problems. Porosity and permeability of reservoir rocks and the process of ocean acidification are important examples. Consequently, there is a need for a fundamental mechanistic understanding of dissolution kinetics in order to provide realistic predictive capabilities with respect to material flux and fluid flow evolution. The mapping of surface reaction rates and the analysis of the resulting rate distribution, i.e., the rate spectra, provides quantitative and mechanistic insight. Such insight is based on the identification of critical rate components that combine to an overall reaction rate. And, the analysis of such concurrently active rate components provides quantitative insight into reaction rate evolution [1] [2] [3].

In this study, we use this concept for the analysis of dissolution kinetics of polycrystalline calcite dissolution as a function of temporal and spatial scales. Two types of calcite marbles [4] are investigated, using a flow-through-cell and reaction periods of 2, 4, 6, 10 and 16 hours. Interferometry microscopy data are used to calculate rate maps that identify the spatial distribution of material flux during dissolution, and, more importantly, the spatial distribution of surface reactivity. A histogram analysis of these maps leads to multimodal rate spectra, and their deconvolution provides mechanistic information concerning the temporal evolution of critical rate components, as well as insight into the reaction kinetics of heterogeneous surfaces. The analysis of material flux maps provides quantitative data about the initial pattern and subsequent evolution of surface pores.

We discuss the quantitative impact of crystal orientation, defect type and distribution, and grain boundary density in order to provide realistic constraints for predictive models.

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Dissolution–precipitation creep in banded iron formations – Interplay between deformation, fluid-rock interaction and mass transfer

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Content

Banded iron formations (BIF) comprise alternating layers of iron oxides and chert, and provide important information about the composition of the Precambrian atmosphere and hydrosphere. They also host the world's major iron ore deposits. In the past, most studies have focussed on the sedimentological origin of BIF, despite the accepted metamorphic origin of BIF mineral assemblages. A second research focus has been on the mechanisms by which the iron content of BIF is upgraded by selective quartz removal to form residual, structurally-controlled iron ore deposits. However, the rocks that make up BIF still remain poorly understood.

Our study aims to determine the processes that occurred between deposition of BIF to their upgrading to iron ore. We combined microfabric analysis, petrography and scanning electron microscopy on BIFs of the Hamersley Province (Western Australia) to improve understanding of physicochemical processes during diagenesis, metamorphism and tectonic deformation. Further, we evaluated the significance of these processes and the role of the associated fluids for the evolution of BIF textures and iron ore.

Our observations indicate that deformation played a fundamental role in the textural development of BIF. Deformation occurred by fluid-assisted dissolution–precipitation creep (i.e., pressure solution) that led to abundant chert dissolution, silica remobilisation and quartz reprecipitation during diagenesis and deformation. Dissolution–precipitation creep is controlled by stress, electrochemical potential differences between different mineral phases (e.g., quartz and hematite) and the fluid chemistry (e.g., temperature, pH, ionic strength). We also show that dissolution–precipitation creep can lead to strong crystallographic preferred orientations of quartz layers. Chert contains abundant iron oxide colloids that are liberated due to quartz dissolution, which accumulate residually and finally transform into new iron oxide bands or hematite ore minerals.

Our microtectonic investigation shows that not all layers in BIF represent primary layers and we challenge solely sedimentary interpretations of BIF textures. Dissolution–precipitation creep can also account for significant quartz removal from BIF and should be considered in iron ore genesis models.

Fast symplectite growth by fluid influx into metastable granulites

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Content

Symplectitic reaction products can reflect a variety of process variables, including low fluid content, low temperature and limited time. When other factors are favourable for fast diffusion, the limited length scales may reflect fast reaction rates. We show the results from two case studies where fluid/melt influx seems to have promoted very fast symplectite formation.

Metapelitic granulite xenoliths from Neogene lavas in the Moroccan Middle Atlas record peak Hercynian P-T conditions of ~900 °C and ~10 kbar, followed by cooling at deep crustal levels. Many garnet (Grt) grains have broken down isochemically to symplectitic intergrowths of orthopyroxene (Opx), spinel (Spl, locally dendritic) and plagioclase. Grt reacted along grain boundaries and randomly oriented cracks triggered by invading melt. Non-equilibrium conditions are inferred from (i) overstepping of the expected reaction involving Grt + sillimanite (Sil); and (ii) the extreme Al₂O₃ content of Opx (up to 17 wt%). We conclude that Grt became metastable during magma upwelling before it broke down rapidly, which is not unexpected in a volcanic setting.

Metapelitic granulites (khondalites) at the Highland-Wanni boundary of central Sri Lanka show a peak assemblage with snowball Grt, prismatic Sil and melt (leucosome) that equilibrated at ~850 °C and ~8-9 kbar, after following a Neoproterozoic clockwise P-T path. Quartz is rimmed by alkali-feldspar (Akfs), which deviates from normal khondalites of the Highland Complex and reflects high-T metasomatism at the tectonic contact with the Wanni Complex, where late-tectonic felsic intrusions abound.

Half the samples show partial replacement of Grt and Sil by Spl-Akfs symplectites. Some samples show more extensive development of Spl-Akfs symplectites, as well as corundum-Akfs symplectites after Sil in domains more remote from Grt. Mass balance calculations and isocon diagrammes reveal influx of Na and K and removal of Fe and, to a lesser extent, Mg and Si. The spatial correlation with a melt-infiltrated tectonic contact and the relative timing of events along the P-T-t-D path strongly suggest that externally derived alkaline fluids promoted the transformation of the already metastable assemblage after decompression. The combination of high-temperature, hydrothermal fluids and symplectites indicates fast process rates, which may have important tectonic implications. Differences and similarities with the xenolith samples (Morocco) are discussed.

Fluid-rock interaction at high temperatures and pressures: thermodynamic models and data

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Content

Aqueous fluids and their solutes play fundamental role in geochemical mass transport over multiple scales, ranging from magmatic and metamorphic devolatilization through focused flow in hydrothermal systems to grain-scale crystallization or reaction mechanisms at atomic level. Understanding of these phenomena requires thermodynamic equations of state and data for relevant species applicable over wide range of sub- and supercritical conditions and solute concentrations. Here we review recent advances in the modeling of solvent properties, functional forms for solute properties and status of their calibration.

Conventional choice of the asymmetric infinite-dilution standard state for aqueous solute requires by virtue of the Gibbs-Duhem theorem that the solute properties scale with those of aqueous solvent. This is treated semi-empirically by the Born electrostatic theory or more explicitly by scaling the solute equation of state to derivatives of the solvent properties. Consequently, accuracy of the solute's Gibbs energy prediction equally depends on the volumetric and electrostatic properties and intrinsic properties of the species. We identify and discuss regions of functional or calibration deficiency in density and electrostatic permittivity that propagate to inaccurate properties of aqueous species. As a consequence, use or recalibration of the Helgeson-Kirkham-Flowers parameters may reproduce experimental solubility and speciation data within a narrow range of conditions, but often not globally.

Critical evaluation of mineral solubilities from ambient conditions to 1100 °C and 20 kbar illustrates superior accuracy of the density models with lower number of parameters over the more empirical electrostatic (Born) formulations. Extensions of infinite-dilution properties to finite concentrations or to supercritical water-silicate systems require internal continuity between infinite-dilution and pure liquid standard state including the solute-solvent mixing properties. This functional consistency is achieved by realizing that limiting slopes of excess properties are dictated by difference between pure and dilute standard states. These approaches illustrate universal constraints, which dictate functional forms of new equations of state for aqueous solutes and their applicability to wide range of crustal and mantle conditions.

RAMAN-coupled Vertical Scanning Interferometry measurements of the dissolution kinetics of zoned feldspar crystals.

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Content

Aluminosilicate minerals play a fundamental role in Earth surface processes. Their dissolution exerts critical feedbacks on ocean and atmosphere composition, and quantitative description of these reactions demands a comprehensive understanding of their dissolution kinetics. Particularly for feldspars, quantitative analysis of dissolution rates is complicated by their extremely slow dissolution rates and their variability of chemical compositions. In addition, significant discrepancies between experimental- and field- derived dissolution rates have long been recognized. However, there is an emerging consensus that dissolution rates are governed by the complex interaction of extrinsic and intrinsic kinetic parameters [1]. Whereas the influence of extrinsic parameters such as pH and temperature are fairly well understood, knowledge of how variabilities in the surficial reactivity distribution relate to minerals' intrinsic properties is poor, and requires thorough and systematic investigation.

Here, we concentrate on variation in surface reactivity as a function of corresponding internal variation in chemical composition of a single zoned crystal. The coupling of vertical scanning interferometry (VSI) and RAMAN spectroscopy in one analytical system allows the quantitative analysis of reactivity variations in solid solutions, by generating spatially-resolved rate maps and corresponding chemical data. Here, we conduct a series of high-precision measurements that provide information on surface reactivity, including chemical signatures that influence reaction kinetics and ultimately generate the overall dissolution rate of the mineral [2].

These experiments utilize a flow-through reactor cell providing far-from-equilibrium, alkaline conditions at elevated temperatures. We demonstrate how spatial patterns of reactivity identified in rate map data are connected to compositional variation. The resulting data will be used as the basis for a quantitative model of solid solution dissolution kinetics.

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Risk of H₂S contamination of natural gas stored in salt caverns

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Content

With increasing demand for storage capacity in salt caverns, the use of less favorable salt formations will increase, and the potential risk of H₂S_(g) generation and release will rise. In consequence, the stored gas will be polluted. H₂S_(g) in salt caverns is generated by bacterial sulfate reduction, a process where the bacteria use aqueous sulfate_(aq) as an electron acceptor to oxidize the dissolved hydrocarbons and generate sulfide. Sulfate_(aq) is available from anhydrite dissolution derived from the rock salt formation surrounding the cavern. The main component of the stored natural gas is methane, which is in solubility equilibrium with the brine and is additionally delivered by diffusion into the brine. The generated H₂S is released into the stored gas by outgassing from the brine.

A hydrogeochemical modelling approach is developed to explain H₂S_(g) generation and release in salt caverns. The one- and three-dimensional hydrogeochemical diffusive mass transport models are based on equilibrium reactions for gas-water-rock interactions and kinetic reactions for sulfate reduction and couple a web of interconnected hydrogeochemical reactions. The modelling codes are PHREEQC and PHAST, both provided by the U.S. Geological Survey. Modelling results show that H₂S_(g) generation in salt caverns by bacterial sulfate reduction mainly occurs on the diffusive path where methane and sulfate meet and react with each other. The parameters that influence the H₂S_(g) generation in salt caverns are determined. Crucial parameters are the amount of available sulfate_(aq), the rate of diffusion (which is coupled with the maximum operating live time of salt caverns) and the chosen kinetic rate constant.

The models help to investigate new technical methods to decrease the H₂S_(g) generation in salt cavern gas storage. The gas and the brine must be analyzed continuously. If H₂S concentration rises, further H₂S generation can be inhibited by addition of dissolved ferrous iron to the brine where the iron reacts with sulfide-sulfur to form mackinawite (FeS_(s)) so that aqueous sulfide is no longer available for H₂S_(g) generation. This method could be alternatively used as a preventative measure, in case the geogenic conditions favor H₂S_(g) generation. Another inhibition method is to add NaOH to the brine to increase the pH. With these conditions, higher fractions of generated sulfide-sulfur are transformed to free S²⁻_(aq) instead of H₂S_(g) and H₂S_(aq).

Spatiotemporal quantitative imaging of leaching processes with positron emission tomography (PET), improving process understanding and modelling performance

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Content

A current application that needs improved understanding of coupled reactive transport processes and fluid-rock interactions is in situ leaching of ore minerals. These processes are largely controlled by the chemical and hydrological heterogeneity of the material and the respective transport process.

We apply GeoPET as method for quantitative spatiotemporal imaging of tracer concentrations, which combines molecular sensitivity (picomolar) with suitable spatial resolution (ca. 1 mm) for elucidating heterogeneous effects on the core scale. This laboratory imaging method is virtually unique for crossing the scale from molecular processes to the macrosphere with its typical heterogeneous geoscientific characteristics. It requires labelling the relevant substance with an appropriate positron-emitting radionuclide, like ¹⁸F or ⁶⁴Cu. PET then makes use of the space-resolved detection of the decay radiation for deriving the tracer concentration.

From the time series of 3D frames of the tracer concentration of conservative flow experiments we compute the distribution of both the process-dependent effective volume and the local velocity distribution of the tracer. These experimental data are the basis of exceptionally efficient finite-element reactive transport models on the millimetre scale with a COMSOL-PhreeqC-coupling.

Our study was conducted within the framework of the French-German project “EcoMetals” which aims at the development of innovative processes for copper (and associated metals) extraction by means of biotechnology. In our showcase experiment we leached copper from pebbles that had been artificially coated with [⁶⁴Cu]covellite. The PET-experiment has two stages. At first we observed the depletion of the ⁶⁴Cu activity concentration in the surface layer during leaching with glutamic acid. From this, we derived local covellite leaching rates. After decay of the radionuclide we conducted a conservative flow experiment with pore water labelled with ¹⁸F. This experiment identifies strongly localized preferential flow zones. From this, we compute porosity and velocity distributions, which serve as input parameters for the numerical simulation. The simulation results are validated in comparison with observed leaching rates.

Tracing mineral replacement using Raman spectroscopy and O-isotopes

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Content

Mineral replacement reactions are an important component of element redistribution within the crust and industrial processes such as building material preservation. Recent experimental work has demonstrated that Raman spectroscopy combined with O-isotope tracers can allow us to probe the mechanism and timescales of such reactions. In this presentation we will review the recent advances in this area and their implications for understanding mineral replacement reactions.

Raman spectroscopy provides information about vibrating groups of atoms within materials and can be used to examine amorphous and crystalline solids, fluids and gases. For solid materials it can also provide information about crystal orientation and crystallinity, therefore Raman spectroscopy is a powerful tool in Geosciences research. Recent experimental work has utilized the sensitivity of Raman spectroscopy to changes in atomic weight, e.g., different isotopes, to examine the uptake of ¹⁸O in aqueous oxyanions and solid material [1]. For example, uptake of ¹⁸O from enriched water has been shown to occur during silicate mineral replacement by amorphous silica [2,3], indicating an interface-coupled dissolution-reprecipitation mechanism governs this reaction. In addition, differences in the extent of ¹⁸O uptake may also be useful to examine how minerals with different silica networks are broken down.

Exchange of O atoms between oxyanions in solution and enriched water is a kinetically controlled process [4], resulting in differently enriched oxyanions becoming incorporated into the solid phases of the replacement rim that have a time dependent signature. Mapping of mineral replacement rims from experiments conducted with ¹⁸O-enriched water can therefore provide information about reaction mechanisms, the reaction speed and the relationship to different fluid penetration pathways. By identifying phases and examining crystal orientation, crystallinity and O-isotope incorporation using Raman spectroscopy a wealth of information can be gained about the processes controlling mineral replacement reactions [e.g., 5].

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Session 4.3: Reactions at mineral-water interfaces in the Earth Sciences: theory and experiment: Poster

**Session 4.3: Reactions at mineral-water interfaces in the Earth Sciences: theory and experiment:
Poster
A-840**

3D numerical investigation of fluid movement and mass transport over a pyrochlore ceramic

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Content

Nuclear waste may be embedded in ceramic materials to shield the environment from the radiation while being deposited in the underground. Dependent on the surrounding host rock the ceramic can be subjected to dissolvent groundwater flows and should therefore be highly resistant against dissolution. Commonly laboratory based experiments are carried out to verify the resistivity of the ceramic material with regard to dissolution. However, it is challenging to directly determine the interaction between fluid movement and mass transport in the interior of the ceramic. In order to overcome this difficulty numerical simulations can be used as a supplementary method. In the present study a hydrodynamic continuum approach is used to simulate the fluid flow and mass transport over a pyrochlore surface.

The finite volume method (OpenFOAM) was used to simulate the fluid flow and mass transport over a pyrochlore surface. The overall size of the rectangular numerical domain is $4 \times 2 \times 2 \mu\text{m}$. The cell size ranges from 0.5 - $0.002 \mu\text{m}$ in dependence to the distance from the surface. In total 13 experiments with changing topographies were conducted to test the influence of changing surface roughness values onto the fluid flow and mass transport. The fluid flows over the pyrochlore surface from the left to the right, with a mean flow rate of $6.25 \times 10^{-10} \text{ m/s}$. The fluid flow was calculated for 20s after which a steady-state was reached. In order to investigate the influence of the flow field onto the mass transport a tracer was injected into the domain at the left and bottom boundaries, for 40000s total runtime.

The results of the hydrodynamic model show the development of a cavity flow in the pore space with velocities of $< 2.5 \times 10^{-12} \text{ m/s}$, dividing the flow into an internal flow and an external flow with velocities of $\sim 6.25 \times 10^{-10} \text{ m/s}$. Likewise the transport simulation shows a preferred transport across the surface. These effects become more pronounced with increasing surface roughness. This limited supply of fresh, unsaturated fluid will lead to the development of a saturated layer covering the pore space and hence slowing further surface dissolution and ultimately might affect the dissolution rate of a ceramic surface. Consequently, by the numerical models it was possible to observe the development of the flow field within the ceramic, allowing for a better understanding of the hydrodynamic processes in the pore space.

Analysis of site specific dissolution rates of sheet silicates using Kinetic Monte Carlo simulations

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Content

The dissolution of sheet silicates plays a key role in many natural processes, such as weathering or diagenesis as well as in their applications in industrial processes, e.g., as additives to paint or cosmetics. Therefore, it is crucial to understand the dissolution kinetics at the atomic scale. Experimental studies of silicate mineral dissolution are difficult to conduct and time consuming. With the increasing speed and decreasing cost of computational resources over the last years, predictive numerical models can allow us to understand dissolution kinetics with a resolution on the atomic scale much faster.

During this project we study dissolution rates of the three different sheet silicate minerals: muscovite, phlogopite and annite. We are able to produce specific dissolution rates for surface atoms with a particular set of next neighbors that enable us to show surface site stability and the evolution of the surface with advancing reaction time. In order to calculate such rates, we use kinetic Monte Carlo (KMC) simulations, starting from an existing successful model for muscovite [1] that is used as a basis for two modified versions, a phlogopite and an annite simulation. Results from these model calculations can be compared to experimental and analytical studies [2] to validate the model, its input parameters and to improve the new code. As a key result from this study the temporal evolution of site specific rates provides insight into differences in dissolution kinetics between minerals of the group of phyllosilicates.

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Calcite dissolution simulation with Weighted Voronoi methods

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Content

Carbonate dissolution is a topic of intense study because of its importance in earth and climate science. To predict surface behavior, morphology development as well as material flux from and to the surface, very good simulation results have been obtained with the Kinetic Monte Carlo (KMC) method. However, such stochastic simulations are computationally limited in terms of system size and reaction time. To study the behavior of larger systems, complementary but faster algorithmical approaches are needed.

The aim of our study was to analyze the suitability of methods from computational geometry, specifically Voronoi diagrams [1] for the simulation of crystal dissolution. This study exemplarily uses Weighted Voronoi [2] calculations of non-euclidean distance functions to simulate the dissolution of the Calcite 104 cleavage surface, a well-known model system that has been successfully modeled by KMC before [3] .

We used a starting model of a fresh (flat) cleavage surface and the position of several screw dislocation outcrops on that surface. Several defect densities were tested and compared to KMC simulation results of the same starting system.

Comparing Weighted Voronoi to KMC simulation results, we were able to show that this new approach is able to reproduce key morphological features of the dissolving surface as well as the distribution of dissolution rate, while only taking up a small fraction of computing time compared to a KMC simulation.

We conclude that the combination of stochastic and geometrical methods is promising for larger-scale simulations of crystal dissolution.

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Calcite interaction with Sr-bearing and Ba-bearing aqueous solutions under diagenetic conditions

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Content

Mineral replacement reactions are common in a large variety of geological environments, where are facilitated by the presence of a fluid phase. In sedimentary basins, these reactions often involve carbonate minerals and lead to mineralogical, compositional and textural changes. In this work we explore the mineral replacement reactions that take place when calcite crystals are in contact with Sr-bearing and Ba-bearing aqueous solutions at temperatures typical of diagenetic environments. We pay especial attention to the influence of the temperature on the kinetics of the mineral replacement reactions and the compositional and textural changes.

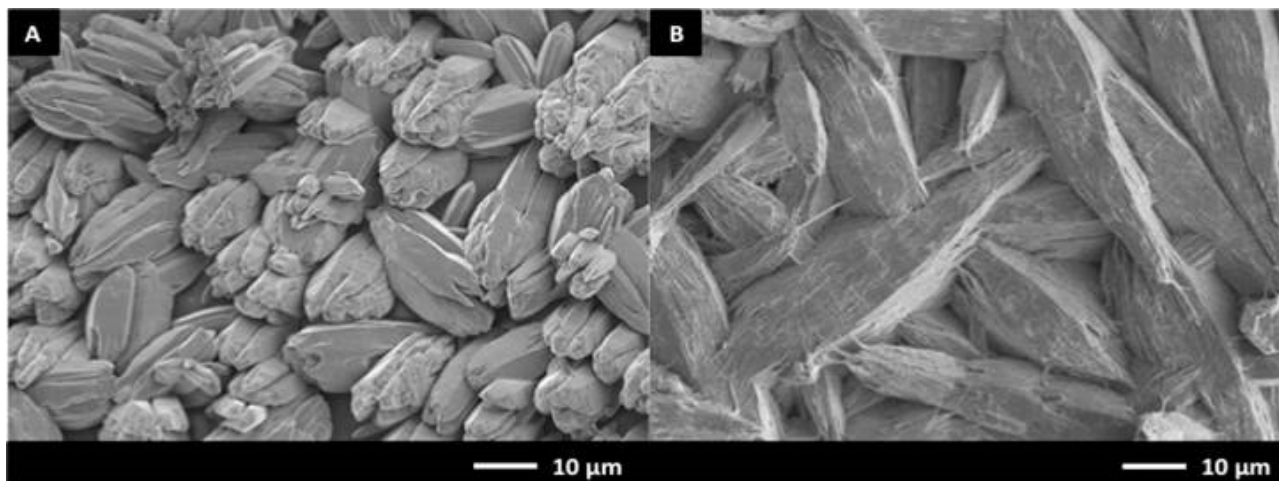


Figure 1. Detail of the surface of calcite crystals after replacement by (Ca,Sr)CO₃ (a) and (Ca,Ba)CO₃ (b) aggregates.

The interaction of calcite with Sr-bearing and Ba-bearing aqueous solutions leads to the development of dissolution-crystallisation coupled reactions and results in the pseudomorphic replacement of calcite by aggregates of crystals of the aragonite-type (Ca,Sr)CO₃ and (Ca,Ba)CO₃ solid solutions, respectively. The secondary phases grow showing epitactic relationships with the primary calcite. Their composition and habit slightly differ depending on the system and change as a function of both, the temperature and the time elapsed since the beginning of the experiment. Thus, the (Ca,Sr)CO₃ solid solution has a final CaCO₃ molar % content of 20, while the final CaCO₃ molar % content of the (Ca,Ba)CO₃ solid solution is 9. Both (Ca,Sr)CO₃ and (Ca,Ba)CO₃ crystals show the typical aragonite type twin. Their habit is prismatic, showing tapering and vicinal surfaces in the case of (Ca,Sr)CO₃ crystals and evolving to sheaf-like morphologies as a result of split growth phenomena in the case of (Ca,Ba)CO₃ crystals (Figure 1). In both systems, the dissolution-crystallization reaction starts immediately upon contact between calcite crystals and the fluid phase. Regardless the system, the kinetics of the reaction is very sluggish and strongly temperature-dependent, though the replacement progresses at a faster rate in the case of the interaction between calcite and the Sr-bearing aqueous solution.

Carbonation of Gypsum and Anhydrite: Reaction Pathways, Porosity and Epitactic Relationships

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Content

The carbonation of anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a common replacement reaction which have led to the formation of diagenetic limestones from Precambrian to Tertiary. Here we compare the characteristics of the carbonation of anhydrite and gypsum in contact with carbonated solutions (0.5, 0.25 and 0.05M Na_2CO_3) at 25 °C. We pay attention to the differences between both processes regarding (1) reaction pathways, (2) volume, distribution and evolution of generated porosity, and (3) existence/absence of structural relationships between primary and secondary phases. Changes in reaction pathways were detected by combining scanning electron microscopy (SEM), glancing X-ray diffraction and Raman and Fourier transform infrared spectroscopy (FTIR) analyses. The generation and evolution of porosity was quantified over time using computed tomography (CT). Electron backscatter diffraction (EBSD) analyses provided information on crystallographic relationships between primary and secondary phases. The interaction of both sulfates with carbonated solutions leads to their pseudomorphic replacement by CaCO_3 phases. Although calcite was predominant regardless the primary sulfate and the concentration of the carbonated solution, the reaction pathway through the carbonation reaction was strongly influenced by both factors. Thus, while amorphous calcium carbonate was detected during gypsum carbonation in contact with highly concentrated carbonated solutions, this phase never formed during anhydrite carbonation. Significant amounts of aragonite formed during the carbonation of both sulfates when it occurred in contact with low concentrated carbonate-bearing solutions. The nature of the primary phase also determined differences in textural features of the CaCO_3 pseudomorphs. These were characterized by containing large volumes of intergranular porosity and a large gap between the primary and the secondary phases when the former was gypsum. When it was anhydrite pseudomorphs contained much less porosity, arranged in small intergranular pores and large channels, and the gap was very thin gap or did not exist. Epitactic relationships were only observed during anhydrite carbonation and involved the matching of anhydrite and calcite through the contact of F planes and parallelism of strong bond chains. The existence of these epitaxies explained the almost complete absence of metastable CaCO_3 phases at any stage along anhydrite carbonation.

Comparison and analysis of phyllosilicate dissolution surface topography – a Kinetic Monte Carlo study

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Content

Natural- or man-made systems such as oil and gas reservoir rocks, e.g., shales and nuclear waste disposal sites and their dissolution or corrosion kinetics are often difficult to analyze numerically. However, the importance of quantifying those systems is significant, because they are important for modern societies. Kinetic Monte Carlo (KMC) simulations are an efficient approach of studying the mineral and material reaction kinetics as a complementary method to experimental strategies. Our modelling approach enables us to resolve relationships of size, structure, and composition that are unique to these materials and significantly increase the range of independent physicochemical variables one must explore. In order to analyze the impact of different types of crystal defects on clay mineral reactivity, we modified an existing KMC sheet silicate model [1] to incorporate various lattice defects. With this extended model we gain an improved insight into the reaction kinetics of several phyllosilicates. It is now possible to analyze the geometric and surface related parameters of minerals, especially the roughness [2] and the shape of developed etch pits, at far-from-equilibrium conditions. Due to the differences in the dissolution behavior (with- and without screw dislocations and point defects) between all minerals, it makes good sense to compare the dissolution stepwave morphology. Results and a discussion about differences and similarities in geometry and surface evolution provide critical insight into the dissolution kinetics of sheet silicates.

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Nanoscale Colloidal Inhibition of Calcite Dissolution Kinetics: An in-situ AFM study

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Content

Calcite (CaCO_3) is a ubiquitous mineral found not only in sedimentary rocks but also in the biosphere. The study of surface reactions on calcite gives us an insight into important geochemical and biological systems, as well as possible applications in carbon sequestration, nuclear waste disposal and colloidal retention. Hence, calcite dissolution kinetics in the presence of impurities, studied from a bottom-up approach, i.e. from a mechanistic level to an overall rate that is made possible by atomic force microscopy (AFM) and coupled with the rate spectra concept. This approach provides significant insight into the details of surface processes. AFM allows nanoscale-resolution in-situ scanning of the dissolving calcite surface, while the rate spectra method generates a quantitative analysis of the elementary processes. [1] [2] [3]

In our study, we use this concept for analysis of the dissolution kinetics of a cleaved calcite crystal (1014) surface in the presence of nanoscale carboxyl-functionalized polystyrene-latex colloids which is of similar dimension to proteins and cell walls [4]. Experiments are carried out on nanoscale-flat surfaces where individual steps (0.3nm height) are clearly discernible and trackable during continuous scanning whilst the calcite is dissolving. AFM measured height data are used to calculate the material rate maps that identify the varying material flux during dissolution. The elementary contributors to overall dissolution kinetics are on step edges of different crystallographic direction and/or roughness index. We are taking into account their interaction with the colloidal particles. Histogram analyses of these rate maps for the different rate contributors and subsequent deconvolution to separate the background noise provides rate spectra of quantitative values. This approach provides a theoretical basis for describing the overall dissolution rate of calcite in real systems on a macroscopic scale. Important examples are the lab verses field conundrum as well as biological phenomena such as shell formation.

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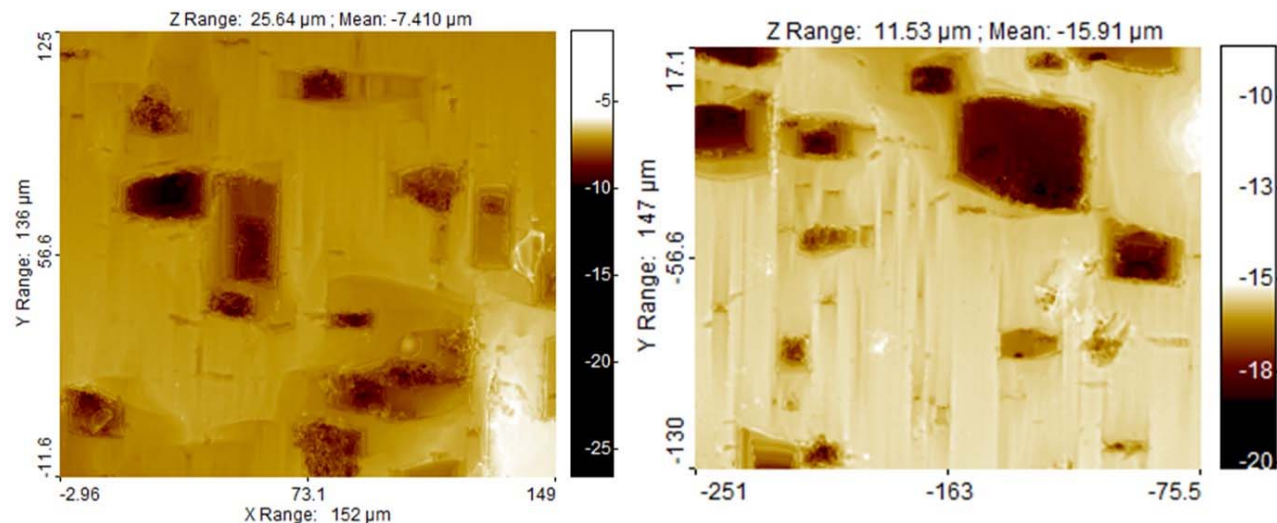
Observations on etch pit development and reaction mechanism on different crystallographic orientated surfaces of olivine

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Content

Naturally weathered olivine crystals from Kohistan District, Pakistan, which were grown in basalt, were studied by using vertical scanning interferometry (VSI) and atomic force microscopy (AFM). Three well terminated faces, namely (010), (110) and (021) faces, were studied by VSI. Different shapes of etch pits on the different surfaces were observed. At the same time, the root mean square average roughness (Rq) for the same field of instrument view is in the order of (021) > (110) > (010). The etch pits, both, on the (010) and (110) surfaces show a general rectangular shape. However, the measured edge growth rates of the pits along different directions are significantly different and cause different shapes and sizes of pits. End-to-end array of pairs of conical etch pits¹ are observed on the (021) surface with random crystallographic orientations, which forms the roughest surface compared with the other surfaces. Surface energies from energy minimization calculations² are in the order of (021) > (110) > (010), which corresponds with the sequence of Rq values. Overall, etch pit development dynamics in combination with atomistic computer simulations are an interesting approach that helps us to understand the nesosilicates mineral dissolution mechanism.



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Surface alteration of alloyed and unalloyed steel constructions in natural sedimentary habitats.

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Content

Corrosion is an important strength degradation phenomenon widely affecting offshore constructions due to harsh environmental conditions such as fluctuation in salinity, oxygen, and temperature. While the corrosion of steel constructions exposed to the water column has been widely studied, corrosion processes on steel foundations buried in marine sediments are not sufficiently explored. It is not known yet how the different geochemical conditions within the sediment may promote corrosion processes and the release of metals into the pore water of the sediments and the overlying water column. We hypothesize that the particular sedimentary geochemical environment resulting from different stages of biogeochemical organic matter degradation determine the intensity and type of corrosion. Whereas sulfidic conditions might lead to precipitation of iron sulfides on steel surfaces, iron reducing conditions might have a strengthening effect on corrosion and the mobility of metals. This study aims to investigate the in-situ corrosion of steel constructions in North Sea sediments as a function of different redox conditions using plastic lances equipped with two different types of steel plates in different sediment depth intervals (Fig.1). Inserted into the uppermost sediment layers of the northern German tidal flat area of Sylt (Königshafen), measurements of topography changes at the steel plate surfaces combined with geochemical pore water analysis, shall reveal the influence of the different redox zones on the rate of corrosion. While topography measurements will be performed with a Mireau vertical scanning interferometer (VSI), Electron microscopy (Jeol JSM-6510) will help to characterize the mineralogy and elemental composition of potentially newly formed precipitates on the steel surfaces.

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Thermodynamics meets kinetics at atomic scale: surface speciation and mechanistic modelling of surface dissolution

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Content

Reaction kinetics at the mineral-water interface is challenging to understand and predict due to the large degree of the system's complexity. This complexity stems from the three primary sources: (1) the internal mineral structure containing local chemical and structural heterogeneities, e.g. order-disorder of constituting compounds, impurities, lattice defects; (2) the structure of the interface fluid containing adsorbed species; (3) the speciation and distribution of the surface sites that are subject to the surface reactions, e.g. dissolution, precipitation, diffusion and adsorption.

Reported reaction rates obtained with different experimental techniques vary orders of magnitude [1]. These variations are a clear indicator of the internal complexity and non-linearity of the studied processes that are hard to understand from the standpoint of a macroscopic experiment. These data are often rationalized in terms of simplistic models of solids and surfaces, where only a few reactive groups of interest are present. The traditional semi-empirical approach describes the reaction kinetics as an analytical function of the activities of either ionic or surface species. This approach does not incorporate the entire system's complexity and possible reaction networks.

We present an advanced methodological approach where relevant molecular scale processes are explicitly described. The reactive system is modeled by using Kinetic Monte Carlo (KMC) method [2], where the surface sites speciation and site-ion interaction are obtained by Grand Canonical Monte Carlo (GCMC) calculations [3]. While KMC models can predict system dynamics in great details, they still require the information about surface complexation reaction. The GCMC models thus provide the necessary input information about the statistics of charged sites and adsorbed ions at the interface in equilibrium with the solvent with respect to the adsorption and (de)protonation reactions. The major power of this approach is its ability to capture the kinetic effects of the solvent composition and surface group acidity onto the kinetics of mineral dissolution and growth. As a result, the mechanisms of the pH and ionic strength/solvent composition dependence can be understood and predicted in details.

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Session 4.3: Reactions at mineral-water interfaces in the Earth Sciences: theory and experiment: Talk

Keynote speaker

A-744

Ion adsorption at mineral-water interfaces under extreme pH conditions

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Content

Pyrite oxidation in the Rio Tinto area is responsible for the release of a high amount of acidity and contaminant ions (As, Se) to the waters of the region. These ions are subsequently mobilized on iron and aluminum sulfate oxyhydroxides that precipitate upon partial neutralization of the acid waters. These poorly crystalline mineral phases are strong adsorbents, which impact the biogeochemistry of the basin. A study of the mineralogy and sorption reactions involved in these processes will be presented, with a special emphasis on new technical developments that allow exploring in detail the atomistic details of the mineral-water interfaces.

Sorption of radionuclides (RNs) is a critical process for a nuclear waste disposal repository safety assessment. Sorption of RNs may occur on cement hydration products under very alkaline pHs, and often involve surface adsorption, ion exchange, or co-precipitations processes. Here, a combined spectroscopic, scattering and wet chemistry study will be presented where molybdate (MoO_4^{2-}) is used as a molecular probe to unravel adsorption sites and mechanisms present in hydrotalcite-like minerals (AFm) present in cement.

: Dolomite surface rate variability under acidic-aqueous conditions

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Content

Microscopic surface rate measurements of mineral-water interface reactions has demonstrated fundamental variability of mineral surface and the heterogeneous distribution of the reaction over the mineral surface (Fischer et al., 2014). These astounding revelations of the recent past have raised concerns over the use of a conventional approach of using 'mean rate' and 'rate constant' for predicting the long term stability of minerals in natural and engineered settings. For instance, there has been substantial amount of literature reporting calcite (CaCO₃) surface variability and the associated heterogeneity of dissolution rates under a wide range of aqueous conditions (Arvidson et al., 2003; Fischer et al., 2012). However, the existence of surface heterogeneity and its effects on surface rates of dolomite (CaMg(CO₃)₂) on interaction with aqueous solutions of variable strength, remains unexplored.

Here, we investigate the effects of aqueous solutions of NaCl of variable concentrations (0.05 M-0.2 M), at acidic pH (pH 3.0), on dolomite dissolution in flow-through reaction cells. The aim of these experiments is to unravel the intrinsic rate variability of dolomite single crystal in contact with variable strength aqueous solutions, under ambient temperature conditions.

Direct surface measurement data obtained from VSI was analysed by material flux maps and rate spectra, permitting identification and quantification of dissolution rate contributors. To our knowledge, this is the first instance of the combined use of advanced surface analytical techniques (e.g. VSI) and rate spectral analyses to unravel the effects of aqueous solution concentration on dolomite surface rate heterogeneity and quantification of rate contributors. These results have implications for a variety of aqueous environments, where carbonate mineral stability is governed by the aqueous solution concentration.

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A mechanistic model of carbonate dissolution in the presence of electrolytes

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Content

The dissolution kinetics of carbonates has been studied over the decades. As a result, the geochemical community shares a large database of dissolution rates studied as functions of pH, electrolyte ions concentration and chemistry, saturation state, crystal chemistry, impurities, inhibitor and catalyst concentrations. Despite these data, the number of mechanistic models explaining observed dependencies is still quite limited. A major obstacle is the complexity of the reacting system, involving a great number of reactions taking place at the a-priori unknown site reactivity[1]. Experimentally measured step velocities and material flux-based rates as functions of environmental parameters can provide insight about the overall mechanisms. However, it is often difficult to test the hypotheses experimentally. Here, we use Kinetic Monte Carlo (KMC) simulations as a tool that allows us to study the validity and applicability of our work hypotheses and deduce the rate controlling mechanism[2]. Our KMC model enables the study of the reacting surface topography evolution. A direct comparison between experimental data and the simulations allow us to validate the model. The reactive system, however, cannot be just reduced to the surface as it is traditionally done in KMC: it also involves adsorbed interface ions that may influence the atomic detachment/attachment probabilities and the surface charge distribution. The structure of the ionic double layer can be a complex function of pH, electrolyte concentration and chemistry. The commonly used theoretical models assuming one or two types of sites with different acidity do not explain the observed data for surface potentials and are quite contradictory for carbonates. As a result, a tapestry of surface sites and complexes is assumed to date[3]. In our approach we aim to understand the chemistry and charges of the interface complexes by employing Grand Canonical Monte Carlo models of surfaces in electrolytes[4]. The data about surface site titration and adsorbed ions are used to parameterize the KMC models. Here, we discuss how this approach can be used to treat complex carbonate systems in realistic environments.

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Atomistic Simulations of Water Confined in Hydroxyapatite Nanopores

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Content

Hydroxyapatite, the main mineral phase of mammalian tooth enamel and bone, grows within nanoconfined environments and in contact with aqueous solutions that are rich in ions. Hydroxyapatite nanopores of different pore sizes ($20 \text{ \AA} \leq H \leq 110 \text{ \AA}$, where H is the size of the nanopore) in contact with liquid water and aqueous electrolyte solutions (CaCl_2 (aq) and CaF_2 (aq)) were investigated using molecular dynamics simulations to quantify the effect of nanoconfinement and solvated ions on the surface reactivity and the structural and dynamical properties of water. The combined effect of solution composition and nanoconfinement significantly slows the self-diffusion coefficient of water molecules compared with bulk liquid. Analysis of the pair and angular distribution functions, distribution of hydrogen bonds, velocity autocorrelation functions, and power spectra of water shows that solution composition and nanoconfinement in particular enhance the rigidity of the water hydrogen bonding network. Calculation of the water exchange events in the coordination of calcium ions reveals that the dynamics of water molecules at the HAP–solution interface decreases substantially with the degree of confinement. Ions in solution also reduce the water dynamics at the surface calcium sites. Together, these changes in the properties of water impart an overall rigidifying effect on the solvent network and reduce the reactivity at the hydroxyapatite-solution interface. Since the process of surface-cation-dehydration governs the kinetics of the reactions occurring at mineral surfaces, such as adsorption and crystal growth, this work shows how nanoconfinement and solvation environment influence the molecular-level events surrounding the crystallization of hydroxyapatite.

Crystals and Equilibrium – New Insight on an “Old” Topic

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Content

A traditional goal of earth sciences, encapsulated by Lyell's Principles of Geology, has been to understand the past through the study of modern processes. A corollary of this concept is that our current observations, gathered both in the field and the laboratory, allow us to predict future behavior as well. In the field of mineral kinetics, this opportunity has become a necessity, as earth scientists are increasingly tasked with using measurements of reaction rates of critical processes to predict the future behavior of complex systems [1-3]. Consequently, we now need to develop a new approach with the necessary tools to predict future system behavior.

At the core of such a fundamental approach is the correct thermodynamic and kinetic description and treatment of heterogeneous solid-fluid system behavior at and near the equilibrium state. "An obvious extension of the correlation between the equilibrium constant and the ratio of forward and reverse rate constants applies to heterogeneous reactions"[4]. Subsequently, many geochemists have built their work on this assumption. But is it really true? For example, theories of the transition state (and its associated activated complex) have been successful in illuminating details of reactions confined to gas and liquid phases, but have largely failed to predict reactions involving the crystalline, solid state. In a larger view, our understanding of the very nature of the kinetic "rate constant" and its relationship to observed reaction rates may also be fundamentally flawed.

Here, we revisit some critical aspects and assumptions made in our macro- and microscopical treatment of such systems, whose examination sheds both new light and raises significant new questions [5].

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Face-specific replacement of calcite by amorphous silica creates natural photonic crystals

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Content

Natural nanoparticles are fundamental building blocks of Earth's bio- and geosphere. Amorphous silica nanoparticles are ubiquitous in nature, but fundamental knowledge of their interaction mechanisms and role in mineral replacement reactions is limited. We here present a natural system that highlights the replacive interaction between two materials ubiquitous in nanotechnology and the Earth system - calcium carbonate and amorphous silica. We show how silica nanoparticles replace Cretaceous calcite bivalve shells in a volume- and texture-preserving process. Using electron microscopy and focused ion beam (FIB)-SEM nanotomography we identify that mineral replacement transfers calcite crystallographic orientations to twinned photonic crystals composed of face-centered cubic (fcc) silica sphere stacks. These sphere arrays perfectly replicate calcite twin lamellae in periodically changing orientations and the intersection angle of calcite {018} twin and {104} cleavage planes. During the face-specific replacement process, silica nanoparticles continuously nucleate, aggregate, and form a lattice of uniform spheres parallel to calcite low-energy facets. We explain the replacement process with a new model that unifies recently proposed, probably universal mechanisms of interface-coupled dissolution-precipitation and crystallization by particle attachment; both are key mechanisms in geological processes and nanomaterials design and synthesis.

Fractionation of Fe and Cu isotopes in acidic mine tailings: modification and application of a sequential extraction method

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Content

As sulfidic mine tailings have a high potential for contamination of the environment by releasing acid mine drainage, it is crucial to understand metal mobilization processes and to develop monitoring tools. For Fe, a six steps sequential extraction method was applied, in order to separate potential Fe-bearing minerals (step 1-6: MQ-extractable, NH₄-acetate-extractable, a dithionite-leach, NH₄-oxalate-extractable, KClO₃/HCl-extractable and residuals). For Cu, this method was modified to a four steps method (step 1, 2, 4 & 6 of above). Metal isotope fingerprinting as a potential monitoring tool for metal sulfide oxidation processes was in the focus of this study. To verify the precision of sequential extraction for metal isotope analysis, isotope fractionation during the extraction was investigated using minerals for which the mineral composition and the isotopic composition was known. The procedure led to a small loss in the elemental budget, but the isotope compositions were identical within uncertainties.

Investigating samples from the upper meter of two sites of a porphyry copper mine tailing in the Atacama Desert in Chile (Chañaral Bay) revealed homogeneous Fe contents and Fe isotope compositions with depth ($\delta^{56}\text{Fe} \approx 0.2\text{-}0.3\text{ ‰}$) and only the deepest samples at ~60 cm exhibited lighter $\delta^{56}\text{Fe}$ values ($\sim 0\text{ ‰}$). The Cu isotope compositions of all bulk samples and individual fractions (except the Cu sulfides) of one site (Ch1) exhibited a decrease of the $\delta^{65}\text{Cu}$ values from the depth towards the surface (the direction of water flow in the arid climate). These data in combination with the pH indicate preferential adsorption of ^{65}Cu on Fe(oxy)hydroxides at site Ch1, associated with Cu isotope fractionation. At another site (Ch12), where the pH at depths was likely not high enough for the formation of such Fe-minerals, only minor Cu isotope fractionation was observed.

Our results show that sequential extraction in combination with stable isotope analyses may provide important information on metal mobilization processes and the distribution of Fe and Cu between different mineral phases like sulfates, oxides and sulfides and thus improve our understanding of metal migration in mine tailings.

Maps of rate, rate acceleration, and rate jerk reveal the dynamics of crystal dissolution

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Content

The interaction of crystals with fluids results in material flux from or to the crystal surface. Such interactions are of relevance for multiple natural and technical processes.

Rate maps that are calculated from sequences of measured surface topography maps identify the spatial distribution of surface reaction rates and surface reactivity [1-3]. Additional information about the dynamics of surface reactions is now derived from maps that quantify the rate acceleration and the change of acceleration, i.e., the rate jerk. Such maps provide insight into the dynamics of surface reactivity over reaction time. They furthermore illustrate the pattern formation on surfaces that are responsible for the evolution of surface pores, thus providing insight into quantitative constraints of initial conditions of the reactive flow.

We discuss results from experimental approaches and from simulation calculations towards the evolution of predictive concepts and as the starting point to upscale microscopic rates.

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Modelling approaches to identify sources of dissolution rate variability on multiple scales

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Content

Dissolution rate variability is a critical phenomenon, recognized during the last decade [1]. Two major parameters are important: the variability induced by the local variations of the fluid chemistry [2] and the variability intrinsic to the material itself [1]. The rate spectra concept approach addresses this problem directly [3,4]. According to this concept, the overall material flux from a reacting surface is the result of multiple rate components. The variability of these components is responsible for the observed spatio-temporal rate variability.

We suggest identification of the rate components by the use of two complementary problem-solving concepts: (1) the inverse problem of finding sources based on the analysis of rate spectra obtained from Atomic Force Microscopy and Vertical Scanning Interferometry measurements, and (2) the direct problem of obtaining rate spectra from the simulation results where the sources of variability are introduced via modifications of reaction parameters. Here, we focus on the second approach. Kinetic Monte Carlo simulations are used as a computational method allowing us to study reactive systems with the desired parameter variability [5]. We systematically explore the sources of variability, from the atomic to the microscopic scales. As a first step, we examine how distribution and density of the different reactive sites, e.g., step and kink sites, affect the rate spectra on a simple Kossel crystal surface. Subsequently, we study the combined impact of the steps and etch pits on the rate spectra evolution on the nano-scale. On the sub-micron scale, we explore the effects of the lattice defects, their density and spatial distribution on the temporal changes of the overall rates and their components. The structures of the real minerals introduce even more complexity because of the greater variance of the surface groups. We further demonstrate how the study of simple Kossel crystals is applied to systems of reacting calcite and quartz, representing carbonate and silicate minerals. We demonstrate how the synthetic rate spectra are directly compared to spectra obtained from experiments on corresponding scales.

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On the easiness of growth of the dolomite-analogue mineral norsethite

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Content

The easy precipitation of norsethite $[\text{BaMg}(\text{CO}_3)_2]$ at ambient conditions is in vast contrast to the growth problems of other anhydrous Mg-containing carbonate minerals such as magnesite $[\text{MgCO}_3]$ and dolomite $[\text{CaMg}(\text{CO}_3)_2]$. The striking structural similarity of dolomite and norsethite makes the different growth behavior even more noteworthy. In order to investigate this remarkable discrepancy further, this study focuses on a comparison of the fate and behavior of aqueous barium and calcium during the growth of magnesite as magnesium endmember in both the $\text{BaCO}_3\text{-MgCO}_3$ and the $\text{CaCO}_3\text{-MgCO}_3$ system.

Results on the effect of aqueous calcium were previously reported by Berninger et al. [1]. Results on the effect of aqueous barium were obtained from growth experiments, which have been conducted on magnesite seeds in hydrothermal mixed-flow reactors ($T = 100\text{ }^\circ\text{C}$, $\text{pH} \approx 7.8$, $0\text{-}100\text{ }\mu\text{M Ba}^{2+}$, supersaturations Ω with respect to magnesite: $\approx 100\text{-}200$) and by hydrothermal atomic force microscopy ($T = 100\text{ }^\circ\text{C}$, $\text{pH} \approx 8.2$, $0\text{-}50\text{ }\mu\text{M Ba}^{2+}$, $\Omega \approx 60\text{-}90$). The presence of aqueous barium left magnesite growth rates unaffected but led to norsethite precipitation. At the conditions of the experiments, norsethite growth rates were found to be controlled by the aqueous Ba^{2+} concentration. The logarithm of the solubility product of norsethite was found to be lower than -18.2 at $100\text{ }^\circ\text{C}$. Microscopic investigations of the growth on the (104) surface of magnesite did not reveal any signs of Ba^{2+} incorporation yielding a partitioning coefficient of barium between magnesite and solution in the range of 10^{-2} or smaller.

The preferential formation of the ordered Ba-Mg double carbonate over a Ba-Mg-carbonate solid solution is presumably facilitated by the large difference in Ba^{2+} and Mg^{2+} ionic radii. Due to the likely very high free energy of formation of the solid solution, ordering into distinct Ba- and Mg-layers is the only way to combine both cations within one phase. Therefore, the lack of a solid solution is one important requirement for the direct and unimpeded growth of an ordered double carbonate from additive free solution at ambient conditions. This behavior is in great contrast to the $\text{CaCO}_3\text{-MgCO}_3$ system where solid solution occurrence is common and growth of the ordered double carbonate (i.e. dolomite) is not observed over a wide range of conditions.

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Radiotracer exchange studies for gaining direct insight into the equilibrium characteristics of elementary processes determining humic-bound metal transport

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Content

The mobility of toxic or radioactive contaminant metals in the subsurface hydrosphere can be essentially governed by their interaction with humic colloids. Predictions on migration processes need thorough consideration of kinetic aspects in the ternary system metal / humic substance / mineral surface. In reactive transport models, reversibility is commonly presumed. However, for adsorption of humic matter, strong hysteresis is observed (hardly any desorption upon dilution), and recoveries in column experiments are far from complete. Complexation of higher-valent metals with humic substances is accompanied by slow processes leading to an increase in complex inertness, i.e., a growing resistance to dissociation.

In view of these uncertainties, the aim of our studies was to elucidate the reversible / irreversible character of interactions controlling humic-bound transport. For this purpose, the principle of tracer exchange was employed to gain insight into the dynamics of equilibria within the ternary system. A radioactive probe, introduced as a reactant into pre-equilibrated systems, will represent the overall equilibrium if there is a dynamic exchange. In case of a static equilibrium, the tracer will not get involved. The chosen model system for these experiments consisted of terbium(III) (as an analogue of trivalent actinides), humic acid and kaolinite. ^{160}Tb as a radioisotope was produced by neutron activation of ^{159}Tb . Humic acid was radiolabelled by azo coupling with [^{14}C]aniline.

After introducing trace amounts of [^{14}C]humic acid into pre-equilibrated adsorption systems of kaolinite and non-labelled humic acid in the state of surface saturation, quantitative exchange was found to take place. Evidently, adsorption equilibria of humic colloids are not static, notwithstanding their size and multiple bonding, albeit an exchange time of more than 4 weeks was required. Isotope exchange of ^{159}Tb / ^{160}Tb on saturated humic acid was completed within a very short time frame, independently of the time of pre-equilibration ^{159}Tb / humic acid. However, if the tracer ^{160}Tb was introduced prior to saturation with ^{159}Tb , the expected partial desorption of ^{160}Tb occurred at much lower rates, decreasing with time of pre-equilibration. Inertisation phenomena are thus confined to the strongest sites of humic molecules. Analysing the time-dependent course of isotope exchange according to first-order kinetics indicated that up to 3 years are needed to attain equilibrium.

Reactive transport modeling to quantify anhydrite dissolution and gypsum precipitation in clay-sulfate rocks

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Content

Quantifying the kinetics of chemical reactions is crucial for many geoscientific applications, such as reservoir engineering, polluted site remediation, nuclear waste storage and many others. However, several studies have shown that reaction rates may differ between scales. For example, the reaction rate of a chemical reaction observed in the laboratory may be different from the rate of the same reaction observed in the field. Also in laboratory experiments, the determination of reaction rates may lead to different results depending on the observation scale (e.g., nm and cm scale). Determining reaction rates at different scales may be very useful for upscaling laboratory results to the scale of application. The present study investigates the chemical reaction anhydrite to gypsum at the field scale. This reaction is accompanied by a volume increase of 61 %, leading to rock swelling. The process is typically initiated by a change in hydraulic conditions in anhydrite-bearing formations, followed by water inflow and a change in geochemistry. We developed a numerical reactive transport model for a site in SW-Germany, where geothermal drillings led to significant swelling in clay-sulfate rocks, heave at the land surface and damage to houses. A dual-domain reactive transport model was employed to quantify chemical reactions within the swelling zone. The model includes (i) a mobile domain that accounts for advective water flow and solute transport; and (ii) an immobile 'reactive' domain considering the rate-limited transformation of anhydrite into gypsum. The model was calibrated by matching calculated volume changes due to the transformation of anhydrite into gypsum with geodetic heave measurements. We compared the rate constants of the calibrated model (representing the field scale) with values from the literature (representing the laboratory scale). We found that the reaction rate constant for gypsum precipitation determined by model calibration is one order of magnitude lower than rate constants reported in the literature from laboratory experiments, whereas the rate constant for anhydrite dissolution of our model matches laboratory results quite well.

Simulations of Reactive Transport in Porous Media: Dealing with Heterogeneities and Examples From Geo-Science

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Content

Introduction

Reactive flows in porous media are an important process in many industrial and environmental applications. The reactive transport in porous media is influenced by the interplay between convection, diffusion and reaction, coupled with the heterogeneity of the pore space and chemical heterogeneity. Understanding these processes and their dependence on chemical and morphological parameters poses a number of research challenges. In this talk we will shortly present a recently developed software tool for simulation of reactive transport, PoreChem, and will show results of simulations for recent applications of reactive flow in porous media, ranging from geoscience to catalytic filters.

Pore-Scale Simulation

To perform the simulations Fraunhofer ITWM has developed PoreChem [1], a software package dedicated to the simulation of reactive flow on the pore-scale. It enables the simulation of reactive flows in resolved porous media in a reasonable time. The software can compute the flow of a fluid in the pore space, as well as the diffusive and advective transport of a solute species. Reactions can then be simulated occurring not only in the fluid volume but also on the surface of the porous medium and on interfaces between two fluid phase regions.

The flow is computed by solving the Navier-Stokes-Brinkman system of equations with a finite volume discretization on a regular voxel grid. Transport and reactions are simulated by solving the reaction-diffusion-advection equation with the same discretization coupled to the surface concentration by Robin boundary conditions. For the reactions, different reaction kinetics, parametrized by reaction isotherms can be taken into account. The fast voxel based solver enables calculations directly on μ CT-Images.

Results

As a geophysical application we consider adsorption of 2-methyl-4-chlorophenoxyacetic acid (MCPA) in Geothite. The starting point for the study is a 3D μ CT-Image of a soil sample, containing reactive and non reactive surfaces. Detailed chemical computations are made using the software PHREEQC. Then, a simplified Henry-Isotherm-Model is fitted to the results, which is then used to compute reactive flow on the μ CT-Images. Computational studies are carried out for different pH-Values and local results are shown together with break through curves. Upscaling for this problem is discussed, as well as comparison with some measurement results.

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Slow reaction of mackinawite in aqueous solutions: A Mössbauer study

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Content

Mackinawite, FeS, is an important iron sulphide that occurs in many anoxic environments. It plays a pivotal role in the cycling of iron and sulphur in aqueous systems through its reactivity and the numerous pathways to stable species. Mackinawite can be preserved over extended periods in reduced sulphur solutions, but it rapidly oxidises at ambient atmospheric conditions. To investigate pathways of mackinawite reaction under controlled oxidation, we undertook a Mössbauer study of mackinawite ageing in different aqueous solutions.

All reactions were carried out in a glove box under anoxic conditions ($O_2 < 1$ ppm). A solution containing freshly precipitated mackinawite was prepared by adding a solution of ^{57}Fe -enriched Fe(II) to a Na_2S solution and then the resulting solution was exposed to different oxidants. Four series were investigated: (1) addition of oxygen as air; (2) addition of synthetic lepidocrocite, $\gamma\text{-FeOOH}$; (3) addition of polysulphide solution; and (4) no exposure to oxidants (reference run). The entire experiment ran over slightly more than five months. Samples for Mössbauer spectroscopy were harvested periodically from the solutions in the glove box and transported in an inert atmosphere to a continuous flow liquid helium cryostat operating at 4 K.

Results show that mackinawite reaction proceeds slowly after exposure to small amounts of oxygen and lepidocrocite as monitored by changes in the single line Mössbauer spectrum, with only around 50% conversion to an intermediate FeS_x phase after 154 days. In contrast, addition of polysulphide promoted more rapid reaction, with complete disappearance of single line mackinawite by the end of the experiment. No reaction was observed in the reference run. While reaction of mackinawite proceeded slowly in aqueous solutions, it took place more rapidly under dry conditions in samples that were stored at room temperature and protected from light in the anoxic glove box. The presentation will provide a summary of all results and discuss implications for mackinawite reactions in different environments.

Surface alteration in the transition zone between soil and bedrock

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Content

Surface alteration processes occur at the nano- to micrometer scale and control solid-water interaction in the weathering zone. Mineral dissolution, transformation, and neoformation, as well as the appearance of organic coatings play an important role for the evolution of a rock's surface reactivity. All of these processes may be strongly influenced by microbial activity.

Our study combines the investigation of natural bedrock to soil profiles (outcrop analogue) with the simulation of the natural conditions by column experiments in the laboratory. For the analysis of alteration features, SEM, microprobe, FTIR, light microscopy and geochemical techniques are utilized. The investigated soil profile is a Terra fusca type located in the Hainich area in Thuringia (Central Germany). The bedrock consists of limestones, marlstones and dolomite of the Trochitenkalk (Upper Muschelkalk, mmTK) and the underlying Upper Dolomite (Middle Muschelkalk, mmDO). Sampling was undertaken in steps of 10 cm including 5 replicates each starting at terrain surface and covering the Ah and T soil horizon as well as several decimeter of the weathered bedrock (Cv horizon) encountered by vertical drilling. For purpose of comparison, fresh bedrock material of the same stratigraphy was sampled from well core material of greater depth.

Column experiments will be conducted using fresh, unaltered material from the Trochitenkalk, crushed into coarse gravel fraction size. In order to compare the influence of organic-free and organic-rich liquids on rock surface alteration, the gravel will be percolated by either artificial rain water or soil litter extract over a runtime of 6 month. In order to mimic natural conditions percolation periods will change with periods of drying. Sampling of the gravel material will be undertaken in monthly time steps.

We will report about the surface alteration features of solid-liquid interfaces investigated in the bedrock material and in soil aggregates of the outcrop as well as in the gravel samples of the experiment. Special focus will be laid on the successive alteration of surface area, surface roughness, chemical and mineralogical composition, presence of organic coatings and the resulting reactivity. The spatial distribution of microbes and the possible presence of biofilms will warrant special consideration.

Temperature Effect on Arsenate Sorption at Goethite

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Content

Research activities within the ANGUS+ project revealed several temperature induced geochemical effects may have a significant impact on ground water composition in case of near surface heat storage will raise an aquifer temperature of up to 70°C, i.e. redox reactions, dissolution or precipitation, ion exchange, and sorption or desorption are effected. Column experiments using aquifer materials and ground water, performed at temperature of up to 70°C, indicate a mostly temporary increase in trace element concentration at increasing temperature. Arsenic concentration is thereby one of the most interesting, because eluted concentration were regularly higher than insignificant threshold levels. Therefore sorption behavior of arsenate at goethite was investigated in more detail in order to understand the temperature effect on the sorption process.

Column experiments using sand/goethite mixtures performed at multiple temperature cycling between 10° and 70°C showed that arsenate sorption is strongly effected by temperature. Increasing temperature leads to an approx. 75% increase in arsenate concentration in the outflow while a temperature decrease leads to an approx. 75% decrease, indicating a strong but reversible temperature effect on arsenate sorption at goethite. Batch and titration experiments between 20° and 70°C indicate a decrease in the PZC of the goethite surface at increasing temperature is probably responsible for the decreasing arsenate sorption observed at low concentration levels (approx. <1 mg/L). At higher dissolved arsenate concentration increasing arsenate sorption at increasing temperature was observed. Surface complexation modelling suggests a change of surface complexation constants and of the capacitance of the electric double layer may explain the dependency of the temperature effect on dissolved arsenate concentration. Langmuir type sorption isotherms derived from batch experiments and surface complexation modelling were combined to a sorption heterotherme for modelling the results of the column experiments. The results suggest that decreasing sorption affinity and concurrently increasing sorption capacity describe the arsenate sorption at goethite surface at increasing temperature. This implies, at small dissolved arsenate background concentration, increasing temperature may lead to increasing dissolved arsenate concentration while at high background concentration decreasing arsenate concentration might be expected.

The Herbicide MCPA is Enhancing Mobility of Copper in Soil

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Content

Crops designed and genetically modified to be tolerant to smart herbicides have led to a boost in soil agrochemicals application. Carboxylic acid herbicides such as 4-chloro-2-methylphenoxyacetic acid (MCPA) are worldwide the 2nd most widely applied herbicide class after glyphosate because of claimed favorable toxicological properties. In MCPA, one methyl group of the phenoxy moiety is replaced by a chlorine atom, increasing its polarity and hence solubility in pure water. Therefore, pure MCPA is relatively weakly retarded by soil at ambient pH values [1]. However, a fact yet neglected is that the residual carboxylate group of MCPA has strong chelating capacity with Cu and other trace metals to form dissolved bidentate complexes. This is of major concern, since the application of Cu-containing fertilizers and of Cu-bearing fungicides in the past have steadily increased soil Cu content. Copper is less mobile in soil at ambient pH values, but its mobility could be enhanced drastically if applied together or in sequence with the herbicide. On the other hand, Cu-MCPA interactions may also facilitate immobilization via co-adsorption processes by ternary surface complex formation as has been shown already for the case of glyphosate. Our batch equilibrium experiments and CD-MUSIC adsorption modeling, however, have shown that the latter is not retarding Cu-MCPA. An overall good match with experimental data on Cu adsorption in presence of MCPA was found when the Cu adsorption model is combined with the dissolved Cu-MCPA₂ complex formation constant. The Cu-MCPA₂ complex becomes highly insoluble (rather than adsorbed) and hence immobile at pH values above 6. In the pH range 4 – 6, i.e. in acidic soils, there is a mobility window where Cu may become mobilized in presence of the herbicide. We used this mobility window for soil column tests at pH values of 5-6, where the high mobility of Cu in presence of the herbicide could be visualized by radioisotope labeling with Cu-64 and positron emission tomography. Movies will be shown of the rapid Cu migration in the soil column as output of the sophisticated PET molecular imaging experiments.

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Session 4.4: Applied materials: Reactions at interfaces: Poster

Session 4.4: Applied materials: Reactions at interfaces: Poster A-328

Arsenite and arsenate sorption to nanoparticulate mackinawite (FeS) in the presence of phosphate

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Content

Arsenic contamination of soil, sediment and groundwater is a global environmental and public health issue due to its highly toxic nature. In sulfidic, subsurface arsenic-rich environments, nanoparticulate mackinawite (FeS) can be an important host-phase for arsenic. Considerably, the presence of competing anions, mainly phosphate (PO₄³⁻), can affect the sorption of oxyanionic arsenic species to mineral surfaces (e.g., iron oxides). While previously unexplored, PO₄³⁻ may compete with arsenic for available sorption sites on nanoparticulate FeS, thereby increasing arsenic mobilization in FeS-bearing soils, sediments and groundwater systems. To our knowledge, no previous studies have examined potential suppression of arsenic sorption to nanoparticulate FeS due to competition by co-existing PO₄³⁻. In the current study, we delineated the influence of PO₄³⁻ on sorption of arsenate (As(V)) and arsenite (As(III)) to nano-FeS at pH 6, 7 and 9. Results revealed that PO₄³⁻ (at 0.01 to 1.0 mM) did not significantly affect sorption of either As(V) or As(III) to nanoparticulate FeS at initial arsenic concentrations ranging from 0.01–1.0 mM. At pH 9 and 7, sorption of both As(III) and As(V) to nanoparticulate FeS was similar, with distribution coefficient (K_d) values ranging from 0.76 to 15 L g⁻¹ (that corresponds to removal of 87–98% of initial As(III) and As(V) concentrations). In contrast, at pH 6, sorption of As(III) was characterized by markedly higher K_d values (6.3–93.4 L g⁻¹) than those for As(V) (K_d = 0.21–0.96 L g⁻¹). Arsenic K-edge X-ray absorption near edge structure (XANES) spectroscopy showed that up to 52% of the added As(V) was reduced to As(III) in the As(V) sorption experiments, as well as the formation of minor amounts of an As₂S₃-like species. In As(III) sorption experiments, XANES spectroscopy also demonstrated the formation of an As₂S₃-like species and the partial oxidation of As(III) to As(V) (despite the strictly O₂-free experimental conditions). XANES data highlight that arsenic sorption to nanoparticulate FeS involves several redox transformations and various sorbed species, which display a complex dependency on pH and arsenic loading but that are not influenced by the co-occurrence of PO₄³⁻. This study demonstrates that nanoparticulate FeS can immobilize both As(III) and As(V) in sulfidic subsurface environments where arsenic co-exists with PO₄³⁻.

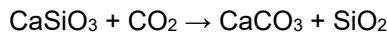
Carbonatisation of Wollastonite

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Content

The sealing of deep geologic formations being considered for carbon capture and storage (CCS) must be sustainable. Therefore the choice of a durable cement, used for sealing, is critical. The material has to resist the extreme conditions at the point of injection considering pressure, temperature, pH, and the composition of aggressive fluids (chloride rich brines, supercritical (sc) CO₂ associated with NO₂ and SO₂). The high amount of CO₂ will have a considerable impact on cement properties. Therefore the use of a cement, based on calcium silicate curing in the presence of CO₂, seems very promising. The interaction of wollastonite (CS) and CO₂ ($\bar{c}$) were investigated within the joint BMWi (German Federal Ministry for Economic Affairs and Energy) research project CLUSTER [1]. The reaction which describes the formation of wollastonite during metamorphism is reversed [2]. Wollastonite reacts in the presence of CO₂ to calcite and amorphous silicon oxide:



At 333 K and ambient pressure the $\bar{c}$ CS reaction is fast (several hours up to one day) [3]. The used raw material (CaSiO₃, calcium silicate, meta, reagent grade) was obtained from the company Alfa Aesar. The reaction of wollastonite, treated with hydrochloric acid 10 % (HCl) and untreated (raw material), with pure CO₂ in the presence of aqueous solutions (H₂O) and varied temperature conditions (296 K, 323 K and 333 K) were investigated. The material was analyzed by REM/EDX (Figure 1) and 3D microscopy, powder XRD and DSC-TG/IR/MS.

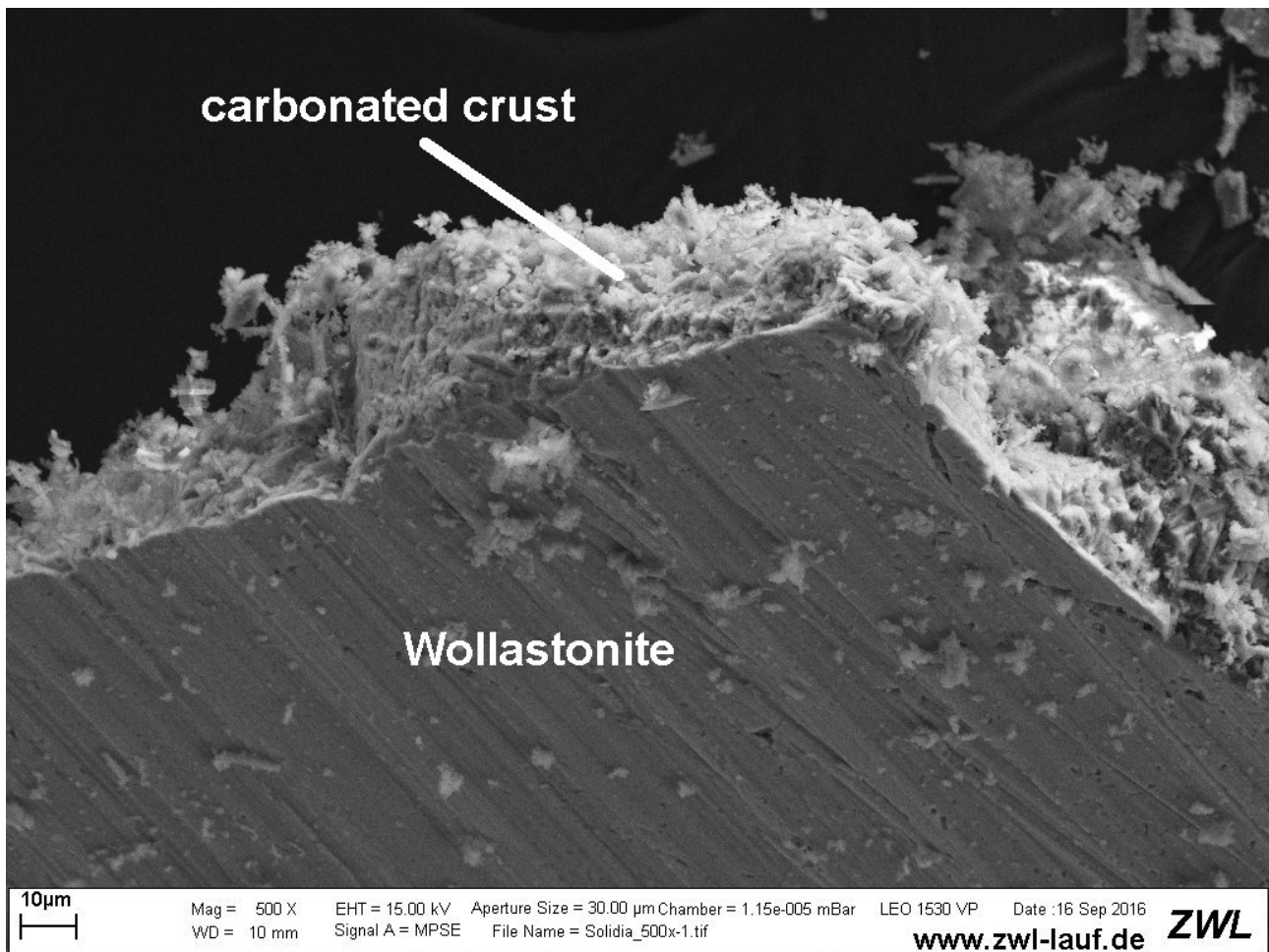


Figure 1: SE micrograph of a carbonated wollastonite grain.

The reaction rate increased significantly at higher temperatures (296 K: >144 hours; 323 K: 48 hours; 333 K: 24 hours). In addition the reaction rate showed a dependency to the pressure applied. The carbonation of treated wollastonite (with HCl 10 %) produced only calcite as carbonated crystalline phase. The experiments with untreated wollastonite produced calcite and aragonite both as carbonation products.

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Studies on the influence of different fluorine minerals portions on the mineral composition and hydration behavior of belite-fluoroaluminate cement

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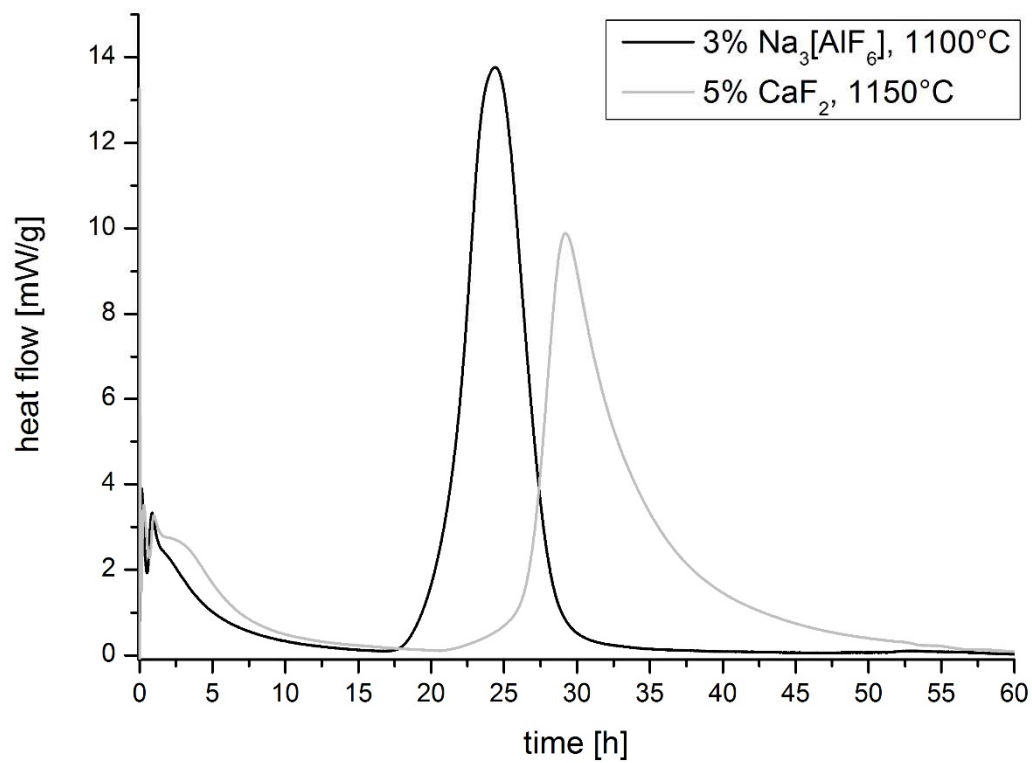
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Content

Belite-fluoroaluminate cement is composed of the main mineral phases belite ($2\text{CaO}\cdot\text{SiO}_2$) and fluor-mayenite ($11\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot\text{CaF}_2$). It is usually produced at $1270\text{--}1330^\circ\text{C}$ and characterized by a short setting time and high early strength [1]. Compared to portland cement, belite-fluoroaluminate cement needs a lower sintering temperature (OPC: $1350\text{--}1450^\circ\text{C}$) and has lower CO_2 -emissions due to the formation of fluor-mayenite which releases 0.34g CO_2 per g formed phase, whereas alite, the main clinker phase of OPC, releases 0.58g CO_2 per formed phase.

A belite-fluoroaluminate cement with a molar ratio of belite : fluor-mayenite of 1 : 1 was synthesized by solid-state synthesis. The influence of different portions of fluorspar (CaF_2) and cryolite ($\text{Na}_3[\text{AlF}_6]$) on this cement system was investigated by using 1.5%, 3%, 4% and 5% fluorspar or cryolite in the raw meal at different temperatures (1100°C , 1150°C) for a sintering time of two hours. The formed cement phases were quantified by the Rietveld method.

With increasing used portion of CaF_2 , an increasing reaction of the starting materials occurs at a constant temperature of 1150°C and the content of the main phases belite (max. 36%) and fluor-mayenite (max. 38%) increase as well. If the portion of 4% CaF_2 is exceeded, the hydraulically inactive γ -modification of belite is formed and the content of fluor-mayenite decreases under the given conditions. When CaF_2 is used at 1100°C , 5% CaF_2 is required for the complete reaction of the starting materials. When cryolite is used, a sintering temperature of 1100°C and a portion of 3% is sufficient (42% belite, 38% fluor-mayenite). At higher portions of cryolite (4-5%), the gehlenite ($\text{Ca}_2\text{Al}[\text{AlSiO}_7]$) content increases and the content of belite decreases. Image 1 shows heat flow diagrams of belite-fluoroaluminate cement using cryolite or fluorspar. Using cryolite, less portion (3%) and a lower sintering temperature (1100°C) is necessary for a faster hydration of belite-fluoroaluminate cement than when using fluorspar (5%, 1150°C).



Isoperibolic heat flow calorimetry of belite-fluoroaluminate cement using 3% cryolite or 5% fluorspar in the raw meal at a sintering temperature of 1100°C or 1150°C (w/c=1).

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The dependence of freeze resistance on the porosity and moisture expansion of silicate ceramic by additives of alkaline and alkaline earth compounds

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Content

Items of the research are roof tiles, which are produced of clay raw materials. The demand for roof tiles increases due to extreme weather and their permanent exposure to environmental conditions, especially precipitations and relative air humidity. The moisture reaches into the roof tile through the porosity and possibly leads to damage. The higher the porosity of the roof tile, the better the path for the moisture. At low temperatures during the winter season, the moisture inside the tile can freeze and the expansion of the ice can lead to frost bursting. There is a direct correlation between the porosity and the moisture expansion (Fig. 1) and the interaction of both determines the freeze resistance. A lower porosity and moisture expansion is resulting in a better resistance to the freezing of roof tiles.

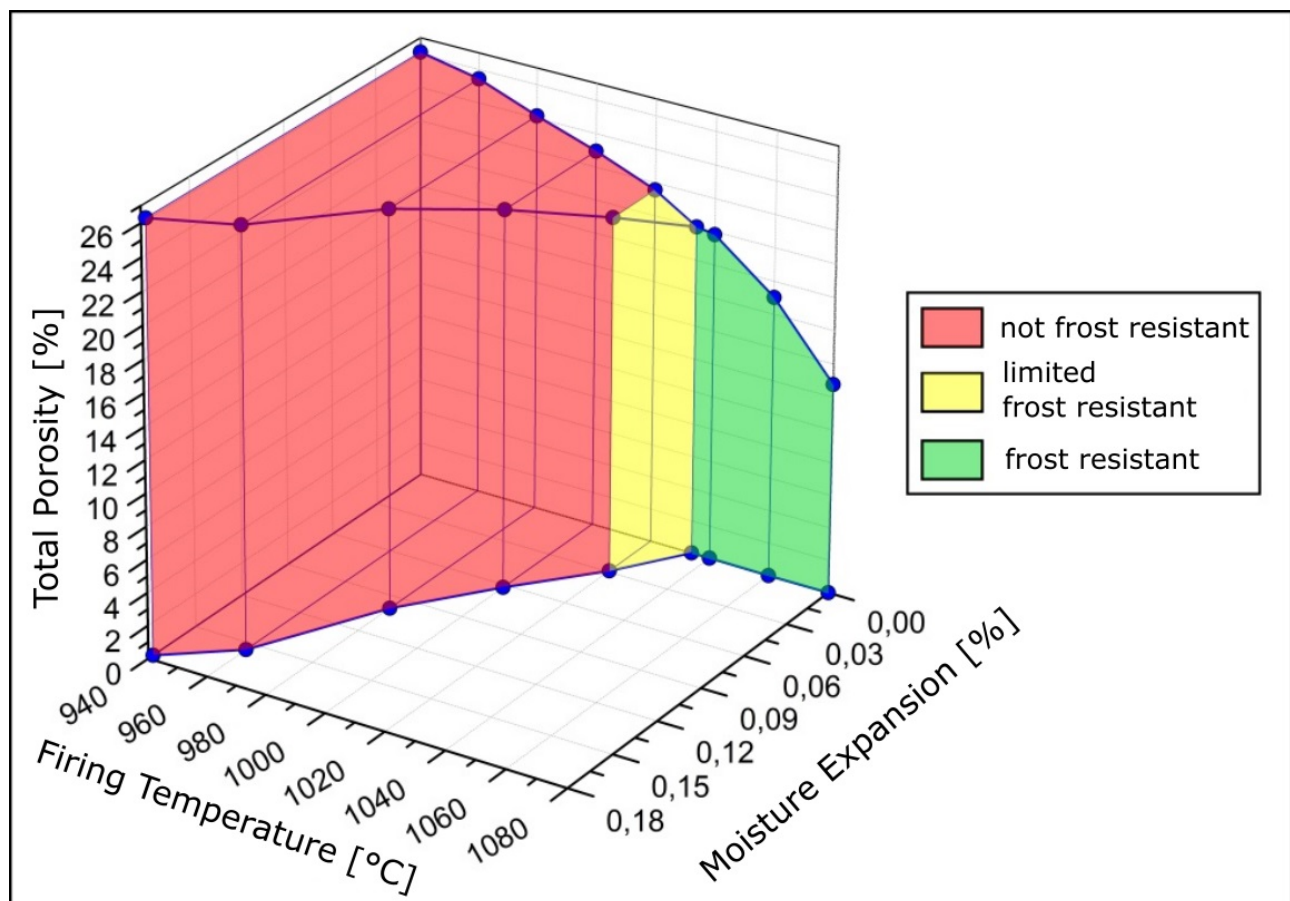


Fig. 1: 3D model of freeze resistance based on total porosity, firing temperature and moisture expansion.

The aim of investigation is to permanently decrease the moisture expansion and porosity in the roof tiles and therefore to increase the freeze resistance. This will be achieved by adding selected alkaline and alkaline earth compounds, in different percentages for definite tendencies (Fig. 2), to the raw materials, which have different influence to the named parameters of ceramic bodies (Ref. [1], [2], [3]).

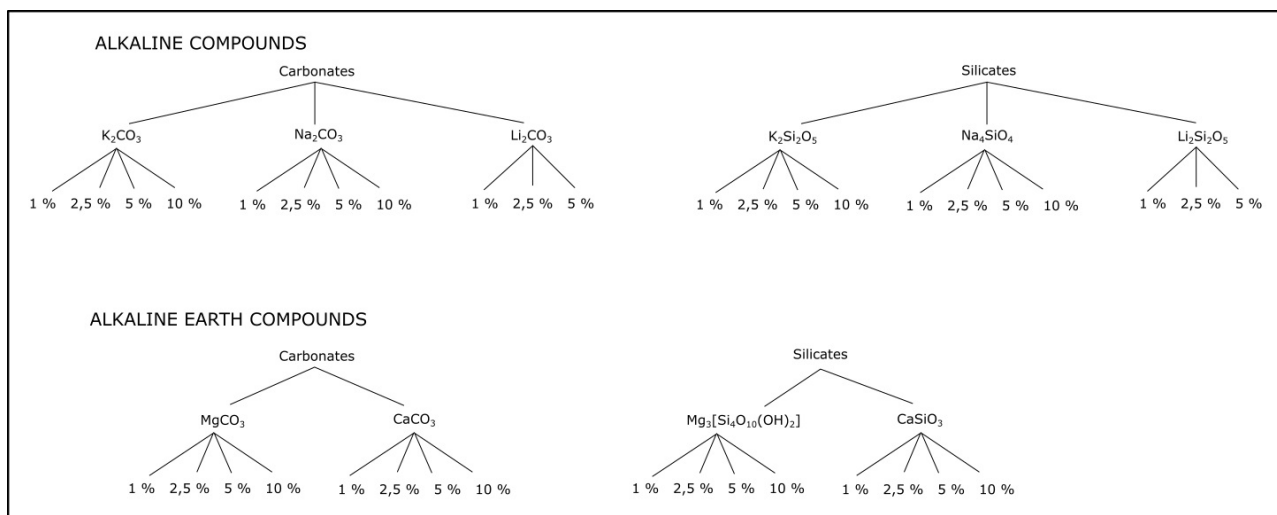


Fig. 2: The additives of alkaline and alkaline earth compounds are added in different percentage relations.

If the results are satisfactorily and the definite tendencies are apparent, then further tests are followed which means, that the firing temperatures are to be lowered. Furthermore, ideal mixtures are to be produced by combining suitable compounds.

The used investigation methods are XRD, RFA and ICP-OES for mineralogical and chemical determination. The physical determination of total porosity, the bulk density and effective porosity is conducted according to DIN EN ISO 10545-3. The true density must be determined by a pycnometer. Optically, the porosity can be determined with the image processing program ImageJ or with a 3D digital microscope and the moisture expansion can be measured with a dilatometer.

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Session 4.4: Applied materials: Reactions at interfaces: Talk

Session 4.4: Applied materials: Reactions at interfaces: Talk
A-548

Calcite formation: mechanistic and empirical rate equations for cement carbonation

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Content

Over the last decade, a range of independent experiments has shown that the rate at which calcite crystals grow depends not only on the degree of supersaturation, but also on the ion activity ratio of calcium to carbonate, i.e. the solution stoichiometry [1,2]. The range of models recently proposed to understand the mechanism behind these experimental observations illustrates its significance for the science of calcite formation [3,4]. Many of these kinetic models describe calcite growth through a spiral growth mechanism and the attachment frequencies of calcium and carbonate ions. We will present an overview of these developments, discuss mechanistic insights and the potential application of rate equations on cement carbonation.

We will then focus on an empirical and a mechanistic ion-by-ion growth rate equation [3]. The latter combines kinetic descriptions of the incorporation of calcium, carbonate and bicarbonate ions at kink sites along step edges, with equilibrium calculations of the surface chemical structure under variable aqueous chemical conditions. Key model parameters have been constrained using edge work and step velocities obtained by Atomic Force Microscopy [2,5] and Molecular Dynamics simulations of the calcite-water interface [3]. The empirical parabolic rate equations have been developed for practical applications, and have been fitted to bulk growth rates of calcite in common background electrolytes and in magnesium-rich saline solutions. Both the mechanistic and empirical growth rate equations agree with measured calcite growth rates over broad ranges of ionic strength, solution stoichiometry, degree of supersaturation and from circum-neutral pH up to alkaline conditions.

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Do crystal defects control early cement hydration rates?

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Content

Over the past several decades, mineral reactions have been revealed in breathtaking detail using high resolution surface microscopies (VSI, AFM). Concurrently, a theoretical framework adapted from the landmark work of Burton, Cabrera, Frank, and others [1] has identified the relationship between *screw dislocations*, saturation state, and the overall dissolution rate of naturally occurring silicate and carbonates [2]. Combining this theory with direct surface observations and stochastic modeling has in turn led to significant increases in our understanding of crystal dissolution kinetics [3]. This success has generated interest in applying similar methods to basic problems in related material sciences [4]. In cement hydration reactions, an anhydrous, highly reactive mineral (Ca_3SiO_5) undergoes rapid dissolution (Fig. 1), triggering a cascade of coupled hydration, nucleation and growth reactions that ultimately produce a complex, composite material. A key question involves the relationship between the initial dissolution rate, the chemical evolution of the dissolving surface and coexisting solution, and the subsequent development of hydrate products. However, despite similarities to natural systems in which a daughter phase develops at the expense of an unstable parent, the velocity of the initial dissolution is significantly greater.

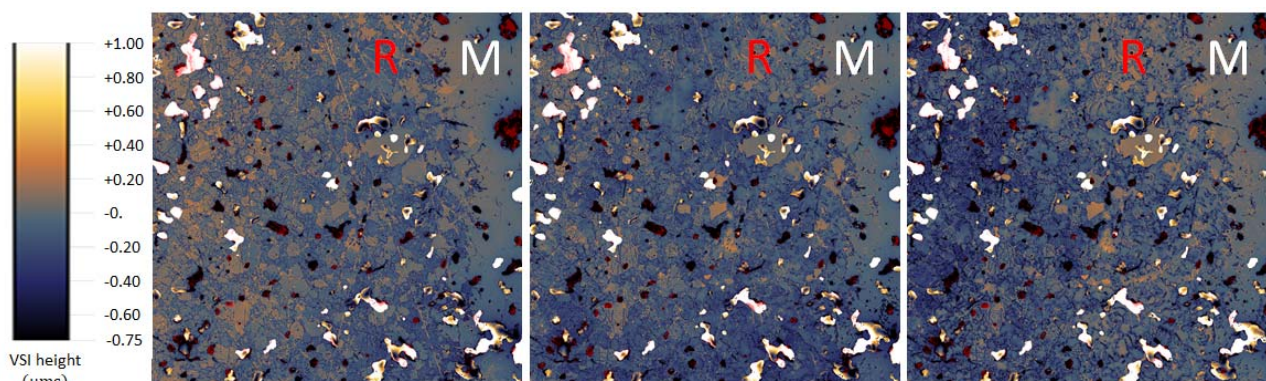


Fig. 1. Dissolution of primary Ca_3SiO_5 , 480 micron field of view at 70, 100, 130 s after DIW contact (M = masked area, R = reacted surface).

Here we present experimental data to address the basic question: can the dynamics of this complex system be understood in the same context as natural minerals, whose reactivities and reaction rates differ by many orders of magnitude? Are key crystallographic and surface properties of cement clinker sufficiently similar to natural silicates to safely permit such a treatment? Conversely, if putative reaction mechanisms are different, how can these models and the thinking that supports them be modified or extended appropriately.

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The influence of external stress on the corrosion of steel

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Content

The impact of external stress onto the surface reactivity is of large interest for fluid-solid interactions. We investigate the influence of external stress onto a steel sample undergoing corrosion. The surface topography in combination with its composition is examined by Raman coupled vertical scanning interferometry (fig. 1). A precision vise applies uniaxial compressive force to the corroding sample. As a metal is exposed to an acidic environment atoms dissolve from reactive sites such as kink sites while corrosion products such as magnetite and lepidocrocite [1] are formed. How these processes take shape on the surface of a stressed material is of key importance. An external stress field can lead to localized microstructures such as the emergence of slip lines [2], resulting in higher surface area. Steel Corrosion is prone to begin at grain boundaries [3] the rise of more grain boundaries due to a rise in surface area may increase the corrosion process.

The spatial heterogeneity of surface reactivity can be accessed via rate maps [4] and linked to the distribution of strain energy. The development and changes of key reactive sites may significantly influence the corrosion rate in comparison to undeformed materials.

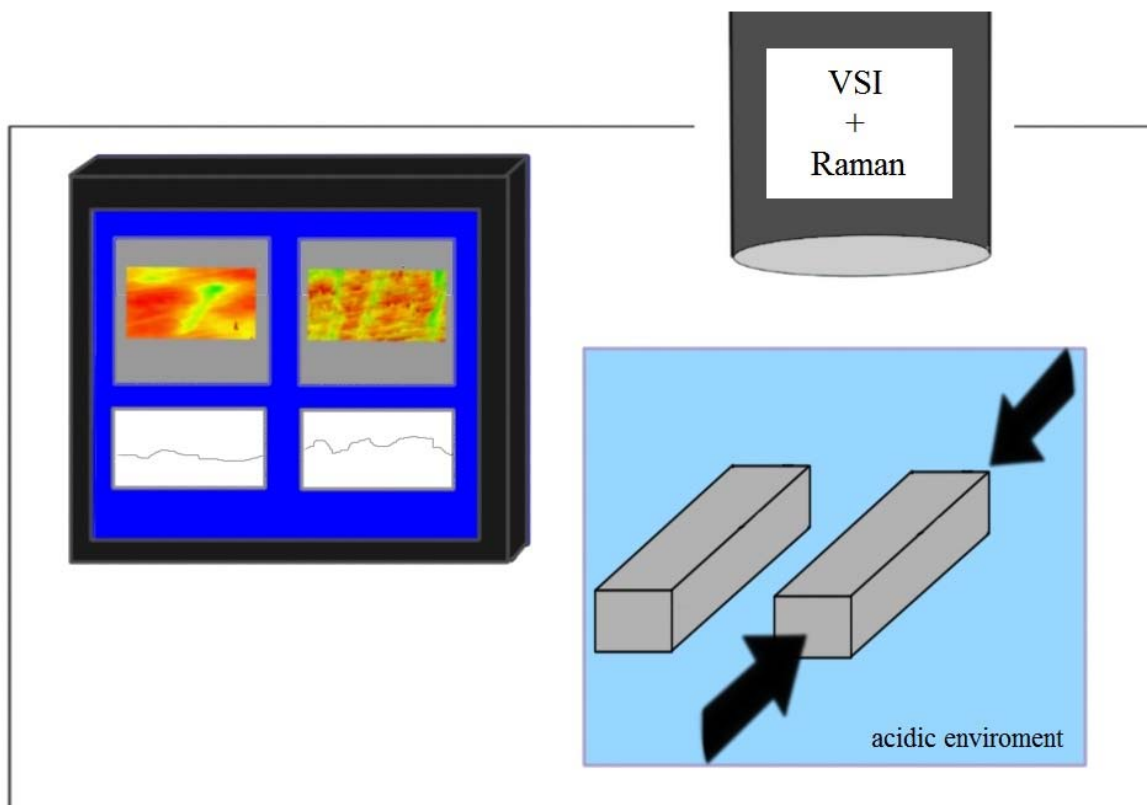


Figure 1 Experimental setup: The topography and elemental composition of an undeformed reference and a deformed sample are compared using vertical scanning interferometry coupled with Raman spectroscopy.

References:

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Session 4.5: Applied materials: Reactions at interfaces: Talk

Session 4.5: Applied materials: Reactions at interfaces: Talk
A-724

Investigation of Granular Materials by Ultrasonic Velocities

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Content

In this study, measurements of sound velocity of selected granular materials was measured. For this purpose, five different lithologic rocks (granite, andesite, tuff, limestone and sandstone) were studied. Compressional wave velocities (V_p) were measured for both core specimens prepared from selected rocks and also in aggregates of different sizes produced from the same rocks.

V_p measurements were easily to made for the core samples while V_p measurements for aggregates were only read by the ultrasonic instrument when compressed. Measurements of V_p , both in rock and in aggregates, were compared with their physical and mechanical properties. It has been found that V_p increases with the increase in size of aggregates.

Keywords: Ultrasonic velocity, compressional wave velocity (V_p), aggregates, bulk density, unit weight and porosity.

Session 5.1: The Last Deglaciation: Poster

Session 5.1: The Last Deglaciation: Poster A-168

Abrupt climate change, sea surface salinity and paleoproductivity in the western Mediterranean Sea (Gulf of Lion) during the last 28 kyr

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Content

The planktonic foraminiferal record of core MD99-2346 (Gulf of Lion) shows a decrease of sea surface temperature (SST) at the time of Heinrich event H2 (24–23.5 cal kyr BP), Younger Dryas and during the early to middle Holocene. These events were associated with a decrease of surface water salinity. The salinity lowering events were similar and synchronous to those recorded in the North Atlantic Ocean during H1, H2 and the Younger Dryas. They can be explained by a decrease in the salinity of the Atlantic surface water entering the Mediterranean through the Strait of Gibraltar. This result indicates that the Mediterranean Sea remained a concentration basin and that its freshwater budget was not significantly different from the modern conditions at the time of these low salinity events.

Deglacial planktonic reservoir ages in the southwest Pacific

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Content

Previous studies suggest that glacial-to-interglacial changes in atmospheric pCO₂ have largely been controlled by processes in the Southern Ocean. The upwelling systems in this region are considered as major pathway of old CO₂ from the deep ocean up to the sea surface and atmosphere and play an important role in regulating the CO₂ exchange between ocean and atmosphere. That means, deglacial changes in ocean overturning circulation in the South Pacific and Southern Ocean may have triggered a major portion of the deglacial CO₂ release from a deep-ocean reservoir into the atmosphere. Preliminary 14C reservoir ages, a tracer of the origin of CO₂, were obtained from core SO213/76-2 from the New Zealand margin on the basis of high-resolution planktonic 14C records evaluated by the 14C Plateau Tuning method. Our dates reveal planktonic reservoir ages that have increased up to more than 2000 years over the last deglacial period. This high level has great implications for constraining deep-water ages at 4500 m water depth and elsewhere nearby in the southwest Pacific and Southern Ocean.

Heinrich Stadial 1 in the tropical West Atlantic: Three-step sea surface temperature development indicative for short-term AMOC resumption?

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Content

The Heinrich Stadial 1 (HS1) event during the last deglaciation evidences a massive release of icebergs into the North Atlantic. The accompanying meltwater discharge is considered to have caused a temporary but complete shut-down of the Atlantic Meridional Overturning Circulation (AMOC). Modeling and proxy data imply that the declined northward heat transport caused warming of the tropical Atlantic, while the mid-latitude North Atlantic surface cooled.

We here present a high resolution, foraminiferal Mg/Ca based sea surface temperature (SST) record across HS1 from Tobago Basin (tropical West Atlantic) proposing a much higher AMOC variability with HS1 as previously thought. The SST record reveals a three-phase evolution pointing to rapid and significant reconfigurations of the North Brazil Current and the Subtropical Gyre synchronous to AMOC variations. During the beginning of HS1 (HS1a), for which 231Pa/230Th data imply the collapse of the AMOC, SST in Tobago Basin rose by ~5°C and suggest instantaneous heat accumulation in the West Atlantic warmpool lasting for ~1.800 years. Subsequently during HS1b, the tropical West Atlantic cooled by ~6°C within ~500 years, opposing the sea surface warming observed at high northern latitudes, and claiming for a rapid and hitherto uninterpreted resumption of the AMOC within HS1 for ~500 years. We further speculate that cooling of the tropical West Atlantic surface ocean was possibly fostered by a short-term southward expansion of Subtropical Gyre surface waters. During the last phase of HS1 (HS1c), which commenced similarly rapidly as HS1 and lasted for ~1.100 years, we speculate on a second AMOC collapse within HS1.

In situ B isotope analysis of reference material by femtosecond LA-ICP-MS with application to the paleo carbonate chemistry of the ocean

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Content

Laser ablation coupled to MC-ICP-MS presents a robust tool for in situ analysis of isotope ratios. Here we explore the potential of our customized 193 nm femtosecond laser ablation system coupled to a Nu Plasma II MC-ICP-MS for in situ measurements of B isotope ratios. B isotopes are detected using ion counters at low mass resolution. The instrumental mass bias and drift are corrected by the standard-sample-bracketing method using reference material SRM NIST 610 as bracketing standard. We determined the B isotope composition of various matrixes with different B concentration including the MPI-DING reference glass series of rhyolitic to komatiitic compositions, a clay standard (IAEA-B-8) and carbonate standards (JCT-1 and JCp-1). The results agree well with published data. Furthermore, we employed this technique to investigate the B isotope composition of foraminifera, which are widely used as a paleo pH proxy to reconstruct the evolution of the ocean carbonate chemistry. The low sample consumption provides an opportunity to produce precise B isotope data for low sample amounts, which is essential for some marine archives. However, single shell analysis show small-scale isotope variation indicating a complex relationship between B isotope composition of biogenic carbonates and pH value of seawater, a process which is still not fully understood.

Millennial-Scale variations in monsoonal precipitation over the central Indonesian Archipelago during the last glacial termination

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Content

We present centennial-scale records of sea surface temperature, oxygen isotopes and x-ray fluorescence (XRF) core scanning from the Celebes Sea, Makassar Strait, Flores Sea and western Banda Sea (Fig. 1), which provide new insights into the variability of Indonesian hydroclimate over the past 25 kyr. The age models of the cores are constrained by AMS radiocarbon ages derived from wood and foraminiferal samples. Mg/Ca derived sea surface temperature reconstructions, based on *Globigerinoides ruber* (s. s., white), exhibit a remarkably consistent gradual increase of 3-4 °C over the last glacial termination, except for sheltered, coastal locations (e.g., Mandar Bay, Sulawesi) and regions affected by seasonal upwelling of cooler water masses (e.g., Flores Sea).

In contrast to previous terrestrial precipitation records, our ice-volume corrected $\delta^{18}\text{O}$ of seawater ($\delta^{18}\text{O}_{\text{sw}}$) and XRF-derived terrigenous runoff data do not support widespread aridity in central Indonesia during the last glacial period. While the $\delta^{18}\text{O}_{\text{sw}}$ was substantially enriched during HS1 and the YD, glacial $\delta^{18}\text{O}_{\text{sw}}$ values were only ~0.2 ‰ heavier during the LGM than during the Holocene, suggesting sea surface hydrology and regional rainfall did not differ markedly (Fig 2). The heavier $\delta^{18}\text{O}_{\text{sw}}$ during HS1 and YD either reflects a decline in precipitation amount and/or increased rainfall $\delta^{18}\text{O}$ values in central Indonesia, both likely caused by a southward displacement of the tropical rain belt. The similarity of the Celebes Sea, Makassar Strait and Flores Sea and Banda Sea records suggests that rainfall isotope and/or amount changes were comparable over Borneo and Sulawesi during the last termination, as the western Banda Sea is connected to a different current circulation system than the other sites [2]. The XRF data, however, do not fully support these findings and are most likely overprinted by sea level variation during the termination.

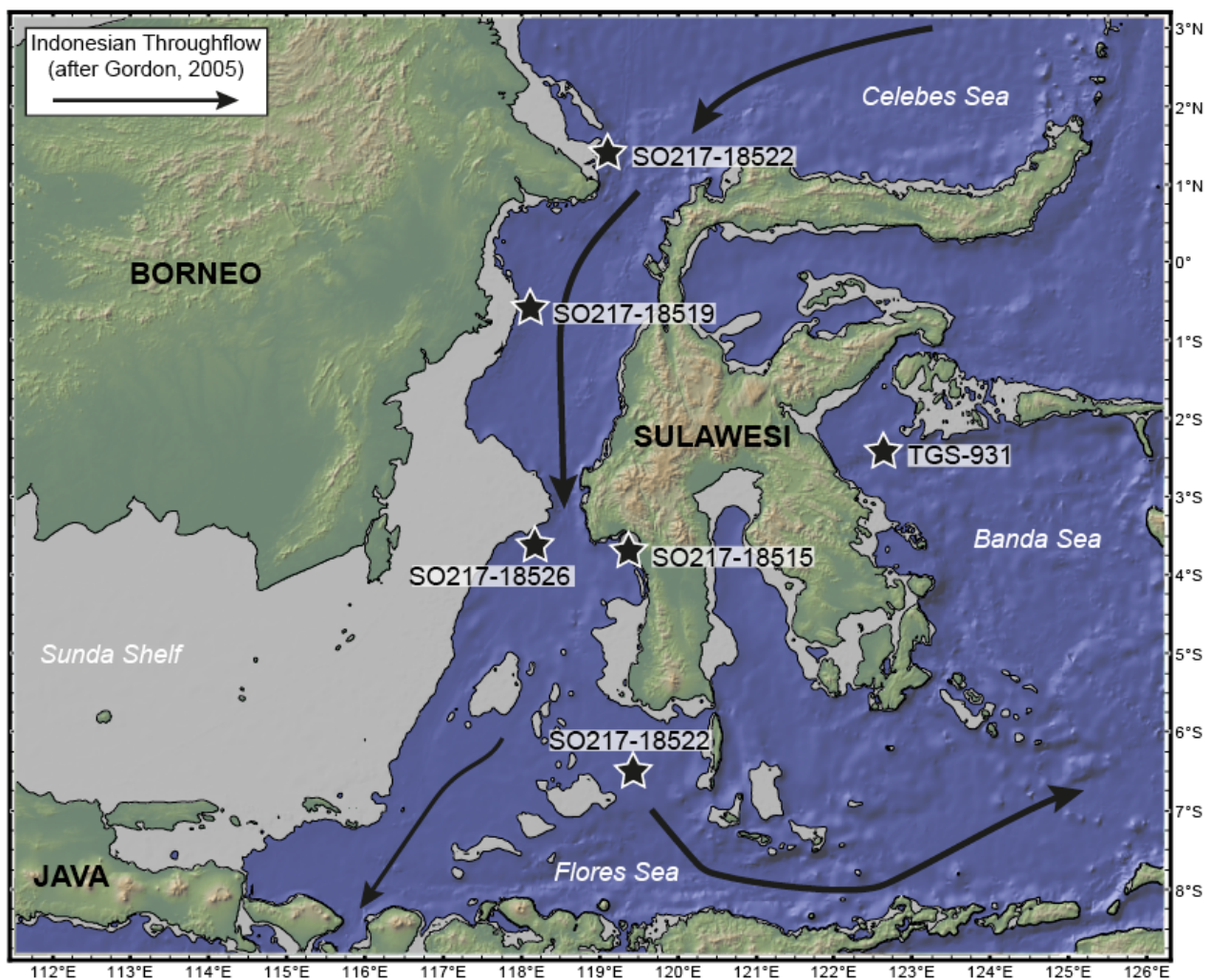


Figure 1. Regional map showing the location of the sediment cores (modified from Ref. 1). Grey shaded areas represent exposed shelf areas during LGM sea level lowstand (~120m isobaths). Black arrows indicate the Indonesian Throughflow (Ref. 2).

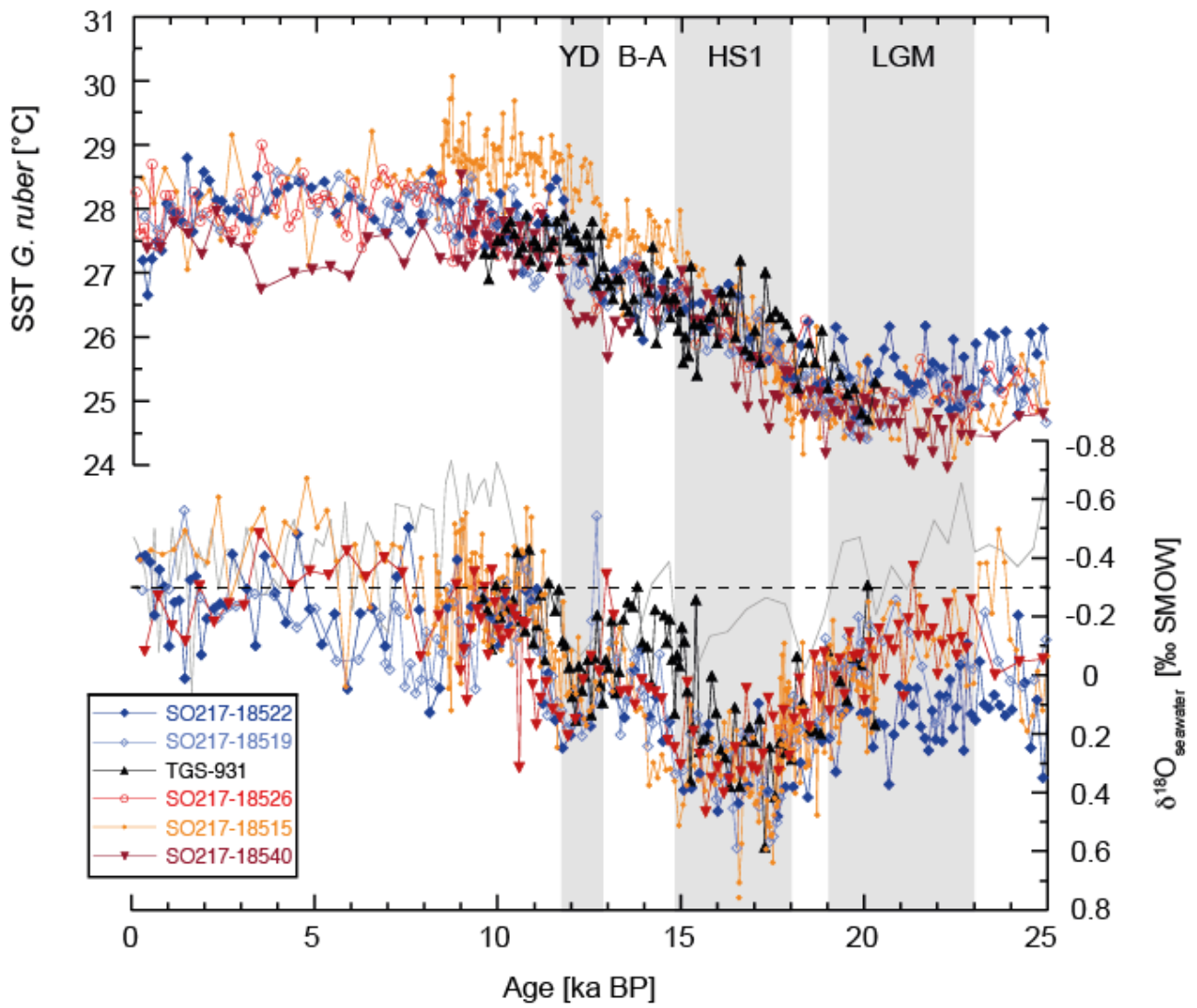


Figure 2. Mg/Ca derived SST and ice-volume corrected $\delta^{18}\text{O}$ seawater. Grey shading corresponds to Northern Hemisphere cooling episodes.

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Rapid changes of the Subtropical Gyre at subsurface in relation to glacial/interglacial perturbations of the Atlantic Meridional Overturning Circulation

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Content

According to coupled ocean-atmosphere models, the partly abrupt climate change in the tropical North Atlantic is directly related to the variability of the Atlantic Meridional Overturning Circulation (AMOC) through both atmospheric and oceanic processes. It has been shown recently that in particular the subsurface tropical Atlantic experienced considerable warming during deglacial AMOC perturbations, initiated by rapid reorganizations of ocean circulation patterns at subsurface water depths.

We here present high-resolution foraminiferal Mg/Ca and $\delta^{18}\text{O}$ -based surface (*G. ruber*) and subsurface (*G. truncatulinoides*) temperature and salinity records across the last glacial/interglacial transition from the Anegada-Jungfern Passage at the southwestern margin of the Subtropical Gyre. In contrast to the rather muted changes at the surface, the changes at subsurface suggest rapid and significant subsurface warming at increasingly high-saline conditions during Dansgaard/Oeschger stadials. We further observe prominent internal (W-shape) subsurface variability within Heinrich Event 2 and the Younger Dryas, synchronous to the North Atlantic Pa/Th proxy data reflecting AMOC change. The tropical West Atlantic changes at subsurface are explained by the rapidly (at centennial timescales) southwestward expanding Salinity Maximum Water of the Subtropical Gyre in concert to the weakened impact of the North Brasil Current in the Caribbean. We conclude that the Subtropical Gyre acts synchronously to deglacial AMOC perturbations at an hitherto undescribed rapidity and amplitude. Its close link to stadial cool periods points to a tight subsurface oceanic teleconnection between the tropical and the high northern latitude Atlantic.

The role of permafrost in safety assessment for high-level nuclear waste disposal in Germany

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Content

For safety assessment of high-level nuclear waste repositories in Germany it is necessary to investigate processes which may influence the safety over a period of one million years into the future. One possible safety-relevant process is the development of permafrost under periglacial conditions. Permafrost can occur up to large depths and changes the thermal, hydraulic and mechanical conditions of the geosphere. In addition, permafrost has a strong influence on groundwater chemistry, groundwater flow and thus a potential radionuclide transport.

An estimation of the future development of permafrost and its maximum depth can be based on model simulations. Relevant input parameters for permafrost simulations depend on controlling factors like climate, topography, characteristics of the underground and the fluids contained therein or the terrestrial heat flux. As the future development of permafrost can be extrapolated from the conditions and trends observed in the past, time series of climate data are necessary. For example the northern hemisphere permafrost extent during the Last Glacial Maximum (Lindgren et al. 2016) can be used as an estimate for a future permafrost extent under similar climate conditions.

In order to use model simulations as a forecast method for the future development of permafrost an evaluation of their accuracy is necessary. Moreover the sensitivity of permafrost simulations to the used parameters and the influence of uncertainties e.g. from past climate reconstructions should be investigated. For this purpose models which are used to simulate future permafrost development should be examined regarding quality and accuracy and if they are applicable in Germany, especially by considering specific local underground conditions.

Lindgren, A., et al. (2016): GIS-based Maps and Area Estimates of Northern Hemisphere Permafrost Extent during the Last Glacial Maximum. –Permafrost and Periglac. Process., 27: 6-16.

Session 5.1: The Last Deglaciation: Talk

Session 5.1: The Last Deglaciation: Talk A-837

A contribution to the understanding of long-term ecology and dynamics of the mangrove forests in Jambi, Sumatra, Indonesia

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Content

Mangroves provide numerous ecosystem services including coastal protection against hurricanes and tsunamis, carbon sequestration and soil erosion prevention, and resources for local communities. The largest area of mangrove forests of the world, corresponding to almost 27% of the total, is found along the coastlines of Indonesia.

Despite their importance, mangrove ecosystems are rapidly declining in Indonesia due to conversion to agriculture and aquaculture. Beside human impacts, the relative sea-level rise could also represent a strong threat to mangroves in the future. However, sea-level have changed markedly in the Holocene, specifically in the Sundaland region. Following the rapid deglacial transgression, estimates indicate that sea-level was 5 m higher about 5000-4500 years ago (Holocene highstand) and then lowered over the following millennia to the current level. Thus palaeoecological reconstructions of mangroves dynamics in the Holocene have a great potential as they can show the dynamics of mangrove ecosystems over long-time scale and under different sea-level scenarios.

We present a palynological result from a sediment core taken from Mendahara Ilir in Jambi Province, Sumatra (Indonesia). The 5 m core was taken from a mangrove secondary forests (0°57'14.6"S 103°40'45.0"E). Radiocarbon dating indicates mangroves developed at the site around 2300 years ago, thus proving a temporal baseline for the establishment of the modern mangroves in the area. We use pollen and spores proxies to reconstruct the ecosystem development since then, with a particular focus on the diversity and rate of ecosystem changes. The diatom analysis was conducted to reconstruct the coastal paleoenvironment. We discuss the results in the light of the past, current and future scenarios of change for the region.

Inter-species planktonic ^{14}C offsets driven by changes in abundance over the last deglaciation

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Content

Proxy data derived from foraminiferal calcite in marine sediment cores have long been used to reconstruct past climate variability. Such reconstructions follow the assumption that the foraminifera retain the stratigraphic order of original sediment deposition. Here we show that radiocarbon dating of two commonly-used planktonic species (*N. pachyderma* (s.) and *G. bulloides*) reveal age offsets of more than 5000 years in a core from the deep South Pacific. We use a numerical model to demonstrate that such offsets can be achieved through changes in species abundance coupled with bioturbation. We emphasise that similar abundance changes can affect other proxy records from the marine sediment archive, leading to significant artificial phase shifts when comparing marine sediment proxy records to other proxy archives. We discuss how to generate age models in the Southern Ocean, where sedimentation rates are low and extreme glacial-interglacial variations in temperature and dust results makes this problem particularly pronounced.

Last deglacial planktic and benthic foraminifera d18O and d13C and D14C records from the Western Pacific Warm Pool

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Content

Despite extensive research, processes related to the last deglaciation (19-10 ka cal BP) are not yet fully understood. For example, the causes and consequences of the observed rise in atmospheric CO₂ during not only the last, but also all glacial-interglacial transitions is one of the long-lasting puzzling questions for palaeoclimatologists and palaeoceanographers. The ocean is the most prominent candidate for storing CO₂ during glacial times. The main current hypotheses to explain how that CO₂ went back to the atmosphere involve: i) storage in the Southern Ocean and ventilation through the Antarctic Intermediate (AAIW) and Equatorial Intermediate Waters (EqIW); ii) storage CO₂ in the deep Pacific and ventilation through other intermediate waters. At the same time, very old 14C dates in several locations in the Pacific Ocean seemed to need the involvement of venting of dead carbon from hydrothermal activity. The search for the most compelling answer is ongoing. One factor that adds uncertainty to the above questions is the timing. A number of studies put forward the need of a better estimate of changing reservoir ages in different periods and ocean basins. We contribute to that question with material from the Western Pacific Warm Pool (WPWP).

We present benthic (mostly *Cibicides wuellerstorfi*) and planktic (*Globigerinoides ruber*, *Pulleniatina obliquiloculata*) d18O, d13C and D14C records covering the last deglaciation from cores retrieved at different water depths off Mindanao (the Philippines) and off Papua New Guinea (PNG). These cores, GeoB17404-3 (404 m water depth, off Mindanao), GeoB17405-3 (848 m water depth, off Mindanao), GeoB17436-5 (845 m water depth, off PNG), GeoB17424-3 (2210 m water depth, off PNG) and GeoB17419-1 (1887 m water depth, off PNG), record the variability of surface and thermocline waters and of North Pacific Intermediate Water, AAIW, EqIW and Pacific Deep Water. Planktic (surface and thermocline) d13C shows the characteristic drop during the Termination of other Pacific records. The D14C values of benthic foraminifera only appear to be extremely old at around 11-14 ka BP at 2210 m water depth. A throughout analysis of these multiple records will enable further constraints on the timing of the last deglaciation and on the processes related to it.

Long-term vegetation, climate and ocean dynamics inferred from a 73,500 years old marine sediment core (GeoB2107-3) off southern Brazil

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Content

Long-term changes in vegetation and climate of southern Brazil, as well as ocean dynamics of the adjacent South Atlantic were studied by analyses of pollen, spores and organic-walled dinoflagellate cysts (dinocysts) in marine sediment core GeoB2107-3 collected offshore southern Brazil covering the last 73.5 cal kyr BP. The pollen record indicates that grasslands were much more frequent in the landscapes of southern Brazil during the last glacial period if compared to the late Holocene, reflecting relatively colder and/or less humid climatic conditions. Patches of forest occurred in the lowlands and probably also on the exposed continental shelf that was mainly covered by salt marshes. Interestingly, drought-susceptible *Araucaria* trees were frequent in the highlands (with a similar abundance as during the late Holocene) until 65 cal kyr BP, but were rare during the following glacial period. Atlantic rainforest was present in the northern lowlands of southern Brazil during the recorded last glacial period, but was strongly reduced from 38.5 until 13.0 cal kyr BP. The reduction was probably controlled by colder and/or less humid climatic conditions. Atlantic rainforest expanded to the south since the Lateglacial period, while *Araucaria* forests advanced in the highlands only during the late Holocene. Dinocysts data indicate that the Brazil Current (BC) with its warm, salty and nutrient poor waters influenced the study area throughout the investigated period. However, variations in the proportion of dinocyst taxa indicating an eutrophic environment reflect the input of nutrients transported mainly by the Brazilian Coastal Current (BCC) and partly discharged by the Rio Itajaí. This was strongly related to changes in sea level. A stronger influence of the BCC with nutrient rich waters occurred during Marine Isotope Stage (MIS) 4 and in particular during the late MIS 3 and MIS 2 under low sea level. Evidence of *Nothofagus* pollen grains from the southern Andes during late MIS 3 and MIS 2 suggests an efficient transport by the southern westerlies and Argentinean rivers, then by the Malvinas Current and finally by the BCC to the study site. Major changes in the pollen/spore and dinocyst assemblages occur with similar pacing, indicating strongly interlinked continental and marine environmental changes. Proxy comparisons suggest that the changes were driven by similar overarching factors, of which the most important was orbital obliquity.

New temporal constraints on MWP-1A from a Hawaiian drowned coral reef terrace

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Content

Investigations of fossil coral reefs yield important records of glacio-eustatic sea-level change and provide temporal constraints on deglacial meltwater pulses (MWPs). This study focuses on samples recovered from the drowned H1d terrace presently at 150 m water depth off Kawaihae, western Hawaii. With the aim of investigating the timing of the initiation of MWP-1A, we present eight new calibrated 14C-AMS ages which support terrace drowning occurring at $14.75 \pm 0.33/-0.42$ ka, consistent with the age of reef drowning from Kealahou Bay, Hawaii (recalibrated U-Th age 14.72 ± 0.10 ka). Using a multi-proxy approach, the chronology is integrated with paleoenvironmental interpretations based on detailed sedimentological analysis and high-resolution mapping data. We conclude from the data that the H1d terrace drowned at the same time along the west coast in response to MWP-1A, within the reported uncertainty of the timing interpreted from the IODP Expedition 310 Tahitian reef record.

Sediment features across the grounding zone and beneath Ekström Ice Shelf, East Antarctica, imaged using on-ice vibroseis

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Content

An extensive grid of seismic reflection data collected on Ekström Ice Shelf, East Antarctica, between 2010 – 2017 are used to constrain palaeo-ice flow and retreat in the region. Sets of elongated bedforms are seen in a topographic trough, indicating a probable former ice-stream under the western part of the ice shelf. A smoother bed and truncated marine sediments under the eastern part of the ice shelf suggest there was slower ice flow in this area. Sediment wedges at the current ice-shelf front show the grounded ice extent likely reached this region; further investigation of these features will allow the style of deglaciation to be better determined.

It is common to map geomorphological sediment features in front of ice shelves and beneath modern-day ice streams using geophysical methods, but there are much less data documenting landforms beneath ice shelves. The data presented here were collected as part of pre-site survey for an envisaged sub-ice shelf geological drilling campaign. These data cover a large portion of the Ekström ice shelf and also extend into the grounded ice areas. Data were collected using an on-ice vibroseis source combined with a snowstreamer. This method of collection is fast and effective allowing for a high volume of data collection. For example, in the 2016/17 season ~280 km of multi- fold seismic reflection data were collected over a 25-day period. In contrast to AUVs with capabilities to measure bathymetry in full spatial coverage, seismic reflection data also allows the vertical structure of sea floor strata and properties to be investigated. The acoustic properties of the sub- surface allow information about the material characteristics, and potentially age and origin of the sediment features to be determined. Moreover, the thickness of the glacial debris, deposited on pre- existing marine sediments, is a first-order indication of where to retrieve short sediment cores. Future integration of these geophysical results with numerical models of ice and sediment dynamics will provide a better understanding of past and present interactions between ice and the solid Earth in East Antarctica; leading to an improved understanding of future contributions of this region to sea-level rise.

The Antarctic Cold Reversal and deglacial onset of the Australian Monsoon

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Content

Austral summer monsoon rainfall over NW Australia during southward shifts of the Intertropical Convergence Zone (ITCZ) increases river discharge, leading to enhanced deposition of terrigenous sediment along the NW Australian continental margin. In contrast, when the ITCZ is locked into a more northerly position, the austral summer monsoon weakens, vast areas of northern Australia dry out and intense trade winds carry increased amounts of dust from the continent into the SE Timor Sea. Sedimentation patterns along the NW Australian Margin are, thus, directly related to latitudinal migrations of the monsoon rain belt, making this area ideally suited to test model predictions of a Southern (Northern) Hemisphere temperature forcing of the Australian Monsoon. Riverine runoff and dust flux patterns in a suite of marine sediment cores along a SW-NE transect across the southern limit of Australian summer monsoon rainfall show that the development of the Australian monsoon closely followed the deglacial warming history of Antarctica. A minimum in riverine runoff documents dry conditions throughout the region during the Antarctic Cold Reversal (15-12.9 ka). Massive intensification of the monsoon coincided with Southern Hemisphere warming and intensified greenhouse forcing over Australia during the deglacial atmospheric CO₂ rise at 12.9-10 ka and a return to dryer conditions occurred between 7.3 and 8.1 ka. Sonne-257 Expedition (May 12th to June 4th, 2017) extended this transect southward across the NW Australian "dust belt" and temperate climate zone with dominant winter rainfall. Reconstructing the history of the Australian Monsoon on centennial timescales during the early deglaciation and last glacial period remains a challenge due to the difficulty in constraining chronologies prior to 15 ka B.P and lack of data from the southern hemisphere. Previously, the substantial regional cooling in the northern hemisphere during Heinrich Stadial 1 was attributed to a southward shift of the ITCZ and tropical rain belt. However, recent work suggests that during the height of this stadial an extreme megadrought also affected the Southern Hemisphere, indicating a severe weakening of the tropical and subtropical monsoonal rainfall systems on a global scale, probably as a response to sea surface cooling. New salinity and runoff records from the Indonesian archipelago and from the NW Australian Margin will provide crucial evidence to test these conflicting hypotheses.

Session 5.2: Tropical coral archives - Reconstructions of climate and environment beyond the instrumental record at society relevant timescales: Poster

Session 5.2: Tropical coral archives - Reconstructions of climate and environment beyond the instrumental record at society relevant timescales: Poster

A-271

Assessing the role of the West Pacific Gradient for global climate teleconnections over the past Millennium

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Content

New research has shown that during both El Niño and La Niña events the global impacts in terms of atmospheric circulation and precipitation were more severe when the SST anomalies in the westernmost Pacific (WP; 0-10°N, 130-150°E) were strongly opposing those in the central Pacific (Niño4 region; 5°S-5°N, 160-210°E) than when the west Pacific SST anomalies were near neutral. This temperature gradient is referred to as the West Pacific Gradient (WPG; Hoell and Funk, 2013; Zinke et al., 2015). A positive WPG is when WP SST anomalies are colder than those in the central Pacific, thus El-Niño-like conditions prevail. Recent changes in the WPG towards a negative phase, combined with strong WP warming after the Indo-Pacific climate regime shift of the late 1990s, are driving significant thermal anomalies from the Indonesian seas to the southern coast of Western Australia and along the southwest Pacific (Zinke et al., 2015). WPG variability over the past millennium is reconstructed using an experimental paleoclimate based reanalysis (PaleoR). PaleoR is analogous to modern reanalysis products, but constrained by paleoclimate data instead of meteorological observations (Goodwin et al., 2014). PaleoR employs an offline assimilation scheme where each year (or decade) is individually reconstructed by using information from a multivariate proxy data array to select best matching analogues from the Last Millennial Ensemble simulations (LME; Otto-Bliesner et al., 2015). The PaleoR approach preserves dynamical relationships between ocean and atmospheric variables and accommodates periods of non-stationary teleconnections.

Our results reveal a sustained positive WPG between AD 1250 to 1650 (a period that Goodwin et al. 2014 identified as being persistent El Niño like) and a mostly negative WPG between AD 1650 and 2000, the latter interrupted by multi-decadal periods with a positive WPG centered around 1760, 1830 and 1900. The periods between AD 1125-1175 and 1185-1250 were characterized by a negative WPG (a period that Goodwin et al. 2014 identified as being persistent La Niña like) with positive WPG excursions in decades around AD 1000-1050, 1100 and 1175.

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Coastal environmental conditions during the 20th century indicated by skeletal parameters of a *Porites lutea* coral from east Hainan, South China Sea

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Content

Anthropogenic sources of CO₂, sediments, and nutrients have been identified as threat to coral reefs worldwide by changing the coastal physical and chemical conditions. Important information about historical environmental changes in a particular reef is recorded in the skeletal material of its massive reef building corals. The reconstruction of anthropogenic influences and natural disturbances, their impacts and interactions may reveal insights into possible future developments of the reef. This work focuses on the northeast coast of Hainan Island in the South China Sea, P.R. China. There, environmental conditions possibly have been modified by an altered land-use and a changing climate since many decades leading to present reef degradation. The skeleton of a massive *Porites lutea* coral colony has been sampled in form of a 'drilling core' of about 1 m length that revealed a data set completely covering the 20th century. Basing on the annual banding pattern, skeletal growth characteristics over 110 years have been analysed along one corallite. Nearly 1000 geochemical subsamples, for each the ratios of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Sr/Ca, have been measured. The results indicate that the cumulative effects of the climate change (e.g. ocean warming and acidification, feed availability) favored the *P. lutea* colony until sampling (2007). The temperature rise calculated from the Sr/Ca ratios seems to have increased linear growth rates, particularly during ENSO events. An enhanced symbionts' photosynthesis can be concluded from the $\delta^{13}\text{C}$ ratios. The salinity reconstruction basing on the $\delta^{18}\text{O}$ ratios argues for a global warming-driven upwelling intensification, potentially supporting coral nutrition and growth, thereby buffering against acidification effects. Thus, the observed decline of the local reef communities seems to be caused mainly by impacts from the land-use change and deforestation (e.g. nutrient and sediment input) and possibly over-fishing. Even though *P. lutea* corals cope with the stressful conditions for now, density and calcification seem to be adversely affected, reducing the resistance capacity of these key reef-builders. If the land-based disturbances continue, they urgently endanger the coral reefs of Hainan before climate change impacts worsen.

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Coral Sr/Ca records from dead coral –quaternary outcrop West Java coast –Indonesia

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Content

Indonesia is an important region for climate studies, as it is located between the Indian and Pacific Ocean. Thus, regional climate in Indonesia is influenced by climate events in the Pacific and Indian Ocean, such as the El Nino-Southern Oscillation (ENSO) and the Indian Ocean Dipole (IOD). The modulation and frequency of those climate events are important to understand for future climate predictions. Thus, Long time series of important climate parameters are required. Coral Sr/Ca from Porites corals is a paleothermometer that can be used to estimate past sea surface temperature variability at seasonal resolution. In this study we present Porites coral Sr/Ca records from dead corals which were collected around west Java coast from the Java sea (Pulau Panjang) to the Sunda strait (Tj. Lesung). Diagenetic screening from the samples show that the Porites samples are well preserved and can be used for paleoclimate studies. First monthly resolved Sr/Ca data from these corals indicate very low seasonal-scale temperature variations.

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High resolution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records from Scleractinian coral (*Porites lutea*) of the Lakshadweep Archipelago

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Content

The $\delta^{18}\text{O}$ variations in seasonal bands of the scleractinian corals (e.g. genus *Porites*) are controlled by the changes in sea surface temperature (SST) and sea surface salinity (SSS). The seasonal changes in $\delta^{18}\text{O}$ of the *Porites* corals growing in the Lakshadweep Archipelago, eastern Arabian Sea are mainly influenced by the monsoon induced vertical mixing (upwelling) that brings colder water to surface. As these islands receive no fresh water fluxes from the riverine sources, the $\delta^{18}\text{O}$ records of *Porites* corals mainly reveal SST variability.

We have generated stable isotope records ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in a drilled coral boulder (*Porites lutea*). Our record is based on oxygen isotope measurements in ~ 1200 samples of 150 cm long coral core. The long term $\delta^{18}\text{O}$ record shows a relationship with the available SST records of this region (ERSST and HadISST). The average skeletal $\delta^{18}\text{O}$ value recorded during the peak of summer months is found to be -5.24‰ vs PDB and the mean $\delta^{18}\text{O}$ value for monsoon months is -4.58‰ vs PDB. The minimum $\delta^{18}\text{O}$ values of each year correspond to low density bands of summer (April-May) and maximum $\delta^{18}\text{O}$ values correspond to high density bands of monsoon months (July-August). The mean $\delta^{18}\text{O}$ difference in seasonal bands (0.66‰) is attributed to the monsoon-induced upwelling in the Lakshadweep Sea. Our $\delta^{18}\text{O}$ record from 1885 to 2003 suggest a gradual decrease in $\delta^{18}\text{O}$ by approximately 0.2‰, which is attributed to an increase in SST in the Lakshadweep Sea.

The skeletal $\delta^{13}\text{C}$ variation in Lakshadweep corals (*Porites lutea*) are also responding to seasonal variations during monsoon and non-monsoon times. Our skeletal $\delta^{13}\text{C}$ record shows mean $\delta^{13}\text{C}$ of -1.005‰ vs PDB. The maximum $\delta^{13}\text{C}$ values are generally observed before or after monsoon months due to increased light penetration and photosynthetic activity. Consequently the coral's carbon pool become enriched in ^{13}C .

High-resolution coral records of South Asian Summer Monsoon variability from the Andaman Sea

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Content

The South Asian Summer Monsoon (SAM) is a dominant feature of the global monsoon circulation that directly affects the socio-economic and agricultural development in the densely populated southern Asian region. In order to understand the mechanisms controlling the variability of the SAM in the past and to provide improved projections of future SAM changes, high-resolution proxy records from this region are required on different time scales. The hydrography of the Bay of Bengal and the Andaman Sea is dominated by river runoff and rainfall during the summer monsoon season, offering a unique prospect for understanding the past variability of the SAM over the land and the ocean. Tropical shallow-water corals record a continuous, well-dated, and high (monthly) resolution geochemical signal of sea surface temperature (SST), sea surface salinity (SSS) and water chemistry in their aragonitic skeletons. The age of a ~70-cm-long core of a dead *Porites* sp. coral head washed onto a beach at Mayabunder, Middle Andaman Island, is established to be ~500 uncalibrated years before present, based on the AMS 14C ages. The coral growth rate is ~1.8 cm/year as estimated from X-radiograph images of the slabbed core, which reveal clear pairs of high-density/low-density bands that likely represent annual growth increments. We have microsampled the upper part of this coral at 1.4 mm resolution, which provides approximately twelve samples per annual growth increment. Using micro-sampling methods combined with high precision measurements of Sr/Ca, Ba/Ca and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in this coral, we present near monthly records of SST and SSS changes in the Andaman Sea. The paired $\delta^{18}\text{O}$ and Sr/Ca signals are used to reconstruct seawater $\delta^{18}\text{O}$ and to infer SSS trends during the approximately twenty years of coral growth. Additionally, coral-derived Ba/Ca ratios are used as direct proxies to infer past river water discharge and estimate SSS changes related to monsoon precipitation on land. The results of this preliminary study demonstrate that the combined use of high-resolution Sr/Ca, Ba/Ca and $\delta^{18}\text{O}$ systematics in corals is a powerful tool for providing a marine perspective and quantitative constraints on seasonal changes of SAM intensity prior to the start of instrumental observations in this understudied region of the Indian Ocean.

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Indian monsoon reconstruction using fossil coral skeletons from Oman

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Content

Monsoon system controls the variations of precipitation in tropics and sub-tropics. Variations of precipitation (e.g. flood and aridification) would have social and economic impacts. Indian summer monsoon is cause of heavy precipitation and used for agriculture in India. To evaluate the Indian monsoon mechanism is important for the future climate prediction and determining the causes of historical incidents in India. Paleoclimate reconstructions using sediment core and speleothem over the last millennium suggested Indian monsoon was intensified in the Medieval Warm Period (MWP) and weakened during the Little Ice Age (LIA). Simulation study suggested Indian monsoon will be strong in response to the global warming in the future. However, it is difficult to predict the influence of Indian monsoon variations on human activities by using low-temporal resolution proxy, and a seasonal-scale variation is required. Here we present new biweekly temporal-resolution coral records in 5 different time-windows for the Indian monsoon reconstructions from 1,166 A.D. to the present, by using 4 fossils and 1 modern coral skeletons collected in the Masirah island, the southern coast of the Arabian Peninsula. In our previous study, coral Sr/Ca ratios in modern specimen reflected low SST corresponding with upwelling occurred in every summer along the southern coast of the Arabian Peninsula and had a correlation with monsoonal precipitation in India. Past Indian monsoon variations from 1,166 to 1,967 A.D. were estimated from coral Sr/Ca ratios in the fossil specimens. Indian monsoons were intensified during the MWP and the early LIA. During the Maunder Minimum in the LIA, the Indian monsoon was weakened, corresponding with the reductions of the solar irradiance. However, Indian monsoon variations based on Sr/Ca ratios in summer during the last 50 years (the global warming-era) were weakened and not coincided with the increase of solar irradiance. Through the last 850 years, the periods of weak Indian monsoon coincided with wars and famines in India. Our results suggested the variations of Indian monsoon had an impact on the historical incidents in India via variations of precipitation.

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Indian monsoon reconstruction using fossil coral skeletons from Oman

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Content

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Indian Ocean corals reveal crucial role of World War II bias for twentieth century warming estimates

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Content

The western Indian Ocean has been warming faster than any other tropical ocean during the 20th century, and is the largest contributor to the global mean sea surface temperature (SST) rise. However, the temporal pattern of Indian Ocean warming is poorly constrained and depends on the historical SST product. As all SST products are derived from the International Comprehensive Ocean-Atmosphere dataset (ICOADS), it is challenging to evaluate which product is superior. Here, we present a new, independent SST reconstruction from a set of Porites coral geochemical records from the western Indian Ocean. Our coral reconstruction shows that the World War II bias in the historical sea surface temperature record is the main reason for the differences between the SST products, and affects western Indian Ocean and global mean temperature trends. The 20th century Indian Ocean warming pattern portrayed by the corals is consistent with the SST product from the Hadley Centre (HadSST3), and suggests that the latter should be used in climate studies that include Indian Ocean SSTs. Our data shows that multi-core coral temperature reconstructions help to evaluate the SST products. Proxy records can provide estimates of 20th century SST that are truly independent from the ICOADS data base.

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Interannual–decadal climate variability over Greenland and linkages to the tropics: Analysis of ice core, corals, and model simulation $\delta^{18}\text{O}$ data

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Content

The nature and causes of Greenland climate variability and its teleconnections are poorly understood beyond interannual time scales due to the paucity of long, reliable meteorological observations. This study analyzes the teleconnections of Greenland climate variability on interannual to decadal time scales using a network of annually resolved ice core $\delta^{18}\text{O}$ records and coral $\delta^{18}\text{O}$ records from the tropics, as well as data from isotope-enabled general circulation model experiments (ECHAM5-wiso).

A correlation analysis reveals significant positive correlations between western, southern and central Greenland ice core $\delta^{18}\text{O}$ records and tropical Atlantic SST anomalies. This link is consistent with the North Atlantic Oscillation anomaly patterns, showing negative (positive) temperature anomalies over both western, southern and central Greenland as well as over the tropical Atlantic during its positive (negative) phase. The $\delta^{18}\text{O}$ ice core records from northeastern Greenland show significant positive correlation with western tropical Pacific SST anomalies. Consistent with this, coral $\delta^{18}\text{O}$ records from western tropical Pacific are positively correlated with northeastern Greenland ice core $\delta^{18}\text{O}$ records. Analysis of model data reveals similar linkages between Greenland $\delta^{18}\text{O}$ variability and tropical Atlantic and tropical Pacific temperature variability. We argue that the Greenland ice core and tropical coral $\delta^{18}\text{O}$ records could be used to reconstruct tropical-arctic teleconnections during past periods.

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Mild and arid climate in the eastern Sahara-Arabian Desert during the late Little Ice Age

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Content

The climate of the Sahara and Arabian deserts during the Little Ice Age is not well known, due to a lack of annually resolved natural and documentary archives. The Little Ice Age (~1450-1850) was characterized by generally cold conditions in many regions of the globe with little similarities regarding the hydroclimate. We present an annual reconstruction of temperature and aridity derived from Sr/Ca and oxygen isotopes in a coral of the desert-surrounded northern Red Sea. Our data indicate that the eastern Sahara and Arabian Desert did not experience pronounced cooling during the late Little Ice Age (~1750-1850), but suggest an even more arid climate than today. The mild temperatures are broadly in line with predominantly negative phases of the North Atlantic Oscillation during the Little Ice Age. The extreme aridity is best explained by meridional advection of dry continental air from Eurasia. We find evidence for an abrupt termination of the extreme aridity after 1850, coincident with a reorganization of the atmospheric circulation over Europe and elsewhere at the end of the Little Ice Age. Climate models fail to reproduce this abrupt change in regional aridity. This study highlights the need for precisely dated high-resolution reconstructions of temperature and aridity from the global deserts to detect the full range of temperature and hydroclimate change over the Common Era, and to improve simulations of future climate change in these vulnerable regions.

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Rare earth element distributions in corals

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Content

The Rare Earth Elements (REEs) form a coherent group, in which seawater speciation varies systematically with ionic radius and elemental fractionation can trace continental input, particle scavenging processes and the oxidation state of seawater. The aragonite skeleton of tropical corals is a promising archive of past water REE chemistry as demonstrated by previous work using REE/Ca ratios. However, the full usefulness of the REEs as a group of elements can only be realised when all, or most, of the group is quantified and the relative concentrations or REE pattern examined. To measure the complete REE series in coral skeletons an online preconcentration ICP-MS method (Hathorne et al. 2012) has been adapted from measurements of seawater samples to remove the large amount of sample matrix and preconcentrate the REEs before measurement. The results demonstrate the very low levels of REEs present in corals and suggest that the considerably higher values obtained in some previous work may not represent REEs present in the aragonite of the coral skeleton.

Hathorne, E.C., B. Haley, T. Stichel, P. Grasse, M. Zieringer, and M. Frank (2012). *Geochem. Geophys. Geosyst.*, 13, Q01020, doi:10.1029/2011GC003907

Reef coral calcification in a globally warm climate (Aquitainian, SW-France)

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Content

Coral reefs are limited by minimum sea surface temperatures and a critically low supersaturation with respect to aragonite, but during the geological past high temperatures and high pCO₂ were an additional critical factor. So far, very few data have been presented on coral calcification from the geological record only. Here we present the first records of reef coral calcification in combination with serial stable isotope data as proxy records of sea surface temperature and coral – algal symbiont relationships from the Early Miocene (Aquitainian, 22 Ma) in SW-France. While skeletal density of the Miocene corals is fully compatible with modern reef corals, annual extension rate and calcification rate were lower or among the lowest recorded in the literature of modern reefs. Causes underlying low extension rates are manifold; the most important seem to be turbid water, water depth (deep water), and SST (low SST). In the Miocene example, no evidence exists for deep or turbid water since the corals were sampled from coarse sediment and do not display ragged outlines being the typical expression of growth under siltation stress. Thus, low SSTs may represent the prime factor since the reefs of SW France were in a rather high latitude position even at that time. It should be noted, however, that all data of extension rates available from Early Miocene and Neogene reef corals worldwide are low compared to modern and suggest an additional environmental factor playing an important role. Coral oxygen isotope data document mean SSTs were 22 - 23 °C and seasonality between 4 - 5 °C, which is substantially above/below that encountered in the Bay of Biscay today (~19/~9 °C). While the estimate of mean annual SSTs depends on assumptions and may represent an overestimation, seasonality can be considered rather robust. Carbon stable isotope data clearly indicate open marine water and active algal photosynthesis; the Aquitainian corals were thus biologically fully compatible with their modern relatives. All in all, this evidence seems to imply that likely neither low nor high SSTs were the essential drivers of low calcification rates of reef corals during the Neogene. We suggest to search the unknown environmental factor for low calcification rates in the saturation state of the ocean with respect to aragonite coupled with high atmospheric pCO₂. This finding would imply rates of coral calcification to decline in the future upon continuing anthropogenic emissions of CO₂.

Reef-scale temperature variability in the tropical Indian Ocean: limits of the coral Sr/Ca thermometer calibrated with in situ and gridded temperature data

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Content

Tropical corals can be used to reconstruct the sea surface temperature (SST) variability by measuring Sr/Ca. This requires a workable calibration of the coral Sr/Ca thermometer with in-situ temperature data. However, for most studies local SST data was not available and larger-scale SST data sets were used. As there may be large differences in SST at different reef sites, it is important to calibrate coral data with SST recorded from the same site to estimate the spatial variability of SST within a reef setting.

Here, we calibrate two modern coral core tops drilled from living massive *Porites* corals from two different settings – open ocean and lagoonal setting – at Chagos (tropical Indian Ocean). We use in-situ logger data and the high resolution satellite temperature AVHRR product to evaluate the coral Sr/Ca thermometer. The in-situ logger data confirms the satellite data, and both settings reveal significant differences in seasonal amplitudes. Furthermore, there are repetitive phases of cooler temperatures recorded at the open ocean setting which are missing in the temperature data recorded in the lagoon.

The two core tops drilled next to the temperature loggers were subsampled at a biweekly resolution for trace element analysis. Sr/Ca ratios were measured using an ICP-OES. For each coral core, correlations of the Sr/Ca measurements with satellite and in-situ logger data were carried out. The magnitude of the coral Sr/Ca variations at both sites reflects the local temperature variability. The correlation of the satellite with the coral data from the open ocean setting is high. The slope of the calibration formula lies within the range of slopes of Sr/Ca vs. SST calibrations listed in Corrége (2006). In contrast, the small seasonal amplitudes of the lagoonal setting prevent a high correlation of the coral temperature with both satellite and in-situ logger data. The Sr/Ca signal is relatively noisy. This shows that the reef setting has a tremendous effect on the temperature variability recorded by the coral Sr/Ca thermometer. Our results suggest that the very high resolution satellite temperature products can be used to evaluate the reef-scale temperature variability and to evaluate the Sr/Ca measurements of modern and fossil corals as an indicator for large-scale SST variability.

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Reproducibility of *Clathromorphum compactum* coralline algal Mg/Ca ratios and comparison to high-resolution sea surface temperature data

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Content

The potential of crustose coralline algae as high-resolution archives of past ocean variability in mid- to high-latitudes has only recently been recognized. Few comparisons of coralline algal proxies, such as temperature-dependent algal Mg/Ca ratios, with in situ-measured surface ocean data exist, even rarer are well replicated records from individual sites. We present magnesium to calcium (Mg/Ca) records from nine coralline algal specimens (*Clathromorphum compactum*) from a northern North Atlantic site. Sections from algal mounds were analyzed using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) yielding individual Mg/Ca records of up to 30 years in length. We first test intra- and intersample signal replication and show that algal Mg/Ca ratios are reproducible along several transects within individual sample specimens and between different samples from the same study site. In addition, LA-ICP-MS-derived Mg/Ca ratios are compared to electron microprobe (EMP) analyzed data on the longest-lived specimens and were found to be statistically commensurable. Second, we evaluate whether relationships between algal Mg/Ca and in situ temperature data can be improved by averaging Mg/Ca records from multiple algal specimens (intersample averages). We found that intersample averages yield stronger relationships to SST data than Mg/Ca records derived from individual samples alone. Thus, Mg/Ca-based paleotemperature reconstructions from coralline algae can benefit from using multiple samples per site, and can expand temperature proxy precision from seasonal to monthly.

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Risk analyses on records of paleoclimate

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Content

Natural archives, such as corals, help to extend the data basis of measured climate variables back in time. Risk analysis is a branch of statistical sciences that deals with the extremes of a variable. Analysis types can be separated into time-stationary and nonstationary models. Stationary analysis types include the fit of a statistical distribution to data. Of particular interest are the tails of a distribution. Nonstationary analysis types include the estimation of the time-dependent rate of occurrence of extremes.

Proxy variables from natural archives, which indicate a climate variable, have certain peculiarities that have to be taken into account for risk analysis: autocorrelation, non-Gaussian distributions, measurement uncertainties, proxy errors and dating errors. We give a short overview of risk analysis methods for proxy variables of paleoclimate. The focus is on heavy-tail estimation and nonparametric occurrence rate estimation. We present novel as well as established statistical tools for paleoclimate data.

Scleractinian corals record increased continental Ca flux to the Great Barrier Reef during the Last Glacial maximum

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Content

Corals play important roles within the System Earth and for unraveling past changes in climate dynamics. Calcium and Sr isotopes of coral skeleton are of interest to constrain the global Ca and Sr budgets and better understand coral biomineralisation.

Experiments on colonies of *Porites* corals cultured under temperature, pH and light controlled environments showed that only temperature significantly affects Ca isotope fractionation during coral biomineralisation [1], consistent with observations for other coral species. The small temperature sensitivity of 0.02‰/°C observed for the temperature range from 21 to 29°C is similar to inorganic aragonite. In contrast to earlier reported data, ⁸⁸Sr/⁸⁶Sr ratios analysed on these samples do not demonstrate a significant dependence on temperature. Changes in seawater pH (7.4 to 8.0) were shown to influence neither the Ca nor the Sr isotopic composition of the coral skeleton.

To test, if the experimentally determined Ca isotope fractionation characteristics also apply to natural corals from downcore records, we determined Ca and Sr isotope ratios of natural *Acropora* (sp.) and *Isopora* (sp.) corals drilled during IODP expedition 325 from the shelf edge seaward of the modern Great Barrier Reef, covering the time between 24 and 11 ka [2]. Calcium and Sr isotope ratios were determined by TIMS doublespike techniques at the University of Münster and MPI Mainz, respectively. Our results show a gradual increasing of $\delta^{44}\text{Ca}$ from the LGM towards the Holocene and no shift in the Sr isotopes. Given the small temperature dependence of Ca isotope fractionation in corals, the temperature rise towards the holocene can account for half the $\delta^{44}\text{Ca}$ rise observed at the Great Barrier Reef. The remaining $\delta^{44}\text{Ca}$ signal can most likely be attributed to $\delta^{44}\text{Ca}$ changes of the local seawater by increased surface or subsurface discharge related to weathering of the exposed carbonate shelf during the LGM. This observation suggests a significant Ca flux to the ocean and points to potential bias in near shore proxy archives.

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Sea surface temperature reconstruction for Europa Island (SW Indian Ocean) from coral geochemistry

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Content

The global climate is strongly influenced by the sea surface temperatures (SST) of the tropical oceans. However, the instrumental observations of SST face several challenges due to limitations on the temporal and spatial coverage of the data, and data quality issues associated with different measurement tools and techniques since measurements began. This holds especially for the tropical oceans where instrumental data is usually sparse. Geochemical proxy archives stored in the skeleton of massive corals can provide natural, precisely-dated, high-resolution reconstructions of SST and therefore can fill an important knowledge gap in our understanding of the tropical oceans.

Here, we investigate *Porites* sp. corals from a 28km² sized atoll named Europa Island (French Eparses Islands; 22°21'S, 40°21'E) located in the southern Mozambique channel in the southwestern Indian Ocean. Europa Island has minor local human impact and therefore is an ideal location to examine natural climate variability from massive corals. Two cores were drilled from two *Porites* sp. colonies in 2013 on the northeastern reef slope of the island at depths between 12 and 15m.

The two cores were analyzed at bimonthly resolution for multiple trace elements including their Sr/Ca ratios, which were used to reconstruct SST between 1970 and 2013. Next to the temperature reconstruction using the Sr/Ca proxy, we also used the new tandem SST proxy Sr-U following DeCarlo et.al. (2016). The Sr/Ca-SST and Sr-U reconstructions were evaluated against several instrumental SST products and in situ measurements (CNRS-INSU's records).

We find a highly significant correlation between Sr/Ca and instrumental SST products, whereas the time series of Sr-U does not correlate with SST. Spatial correlations reveal SST at Europa Island generally reflects local climate variability in the Mozambique Channel. SST over the last 42 years is dominated by interannual variability with a warming trend of $0.61 \pm 0.2^\circ\text{C}$ in close agreement with instrumental data ($0.44 \pm 0.07^\circ\text{C}$). Furthermore, we observe a correlation between the reconstructed SST and regional precipitation, as well as air temperatures over parts of East Africa and South Madagascar.

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Tracking interannual to multidecadal-scale climate variability in the Atlantic Warm Pool using central Caribbean coral data

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Content

Atlantic Warm Pool (AWP) climate variability is subject to multiple influences ranging from internal tropical Atlantic variability to modes of external forcing. However, before the mid-20th century observational data are sparse and the lack of long-term SST and climate records has hampered the detection and investigation of decadal- and longer-scale variability and relationships between climate parameters in the North Atlantic. We present a new seasonally resolved 125-year record of coral $\delta^{18}\text{O}$ and Sr/Ca variations in the Central Caribbean Sea (Little Cayman, Cayman Islands; *Diploria strigosa*). Both geochemical proxies show a decreasing long-term trend, indicating long-term warming. Sr/Ca indicates a much stronger regional warming than large-scale grid-SST data, while coral $\delta^{18}\text{O}$ tracks large-scale sea surface temperature (SST) changes in the AWP. By removing the Sr/Ca derived temperature component from coral $\delta^{18}\text{O}$, sea water $\delta^{18}\text{O}$ variations are reconstructed reflecting past changes in the hydrological cycle, indicating a drying trend over the past century while temperature increases.

High spatial correlation between coral $\delta^{18}\text{O}$ and SST in the region of the Loop Current and Gulf Stream system suggests that Little Cayman is a sensitive location for the detection of past large-scale temperature variability beyond the central Caribbean region. More specifically, our $\delta^{18}\text{O}$ data tracks changes in North Atlantic Oscillation (NAO) variability on both decadal and multidecadal time scales providing new insights into the temporal and spatial nonstationarity of the NAO. A combination of our coral $\delta^{18}\text{O}$ record with two other coral records from different Caribbean sites reveals high spatial correspondence between coral $\delta^{18}\text{O}$ and SST variability in the North Atlantic subtropical gyre, where few instrumental measurements and proxies are available prior to the 20th century. Our results clearly demonstrate the potential of combining proxy data to provide information from these sparsely-sampled areas, helping to reduce uncertainty in model based projections.

Two-dimensional X-ray diffraction as a tool for the rapid, nondestructive detection of low calcite quantities in aragonitic corals

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Content

Paleoclimate reconstructions based on reef corals require precise detection of diagenetic alteration. Secondary calcite can significantly affect paleotemperature reconstructions at very low amounts of 1%. X-ray powder diffraction is routinely used to detect diagenetic calcite in aragonitic corals. This procedure has its limitations as single powder samples might not represent the entire coral heterogeneity. A conventional and a 2-D X-ray diffractometer were calibrated with gravimetric powder standards of high and low magnesium calcite (0.3% to 25% calcite). Calcite contents <1% can be recognized with both diffractometer setups based on the peak area of the calcite [104] reflection. An advantage of 2-D-XRD over convenient 1-D-XRD methods is the nondestructive and rapid detection of calcite with relatively high spatial resolution directly on coral slabs. The calcite detection performance of the 2-D-XRD setup was tested on thin sections from fossil *Porites* sp. samples that, based on powder XRD measurements, showed <1% calcite. Quantification of calcite contents for these thin sections based on 2-D-XRD and digital image analysis showed very similar results. This enables spot measurements with diameters of 4 mm, as well as systematic line scans along potential tracks previous to geochemical proxy sampling. In this way, areas affected by diagenetic calcite can be avoided and alternative sampling tracks can be defined. Alternatively, individual sampling positions that show dubious proxy results can later be checked for the presence of calcite. The presented calibration and quantification method can be transferred to any 2-D X-ray diffractometer.

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A 75-Year Long Absolute SST Reconstruction Reveals Last Interglacial Variability in the Tropical Atlantic Warm Pool: Comparison of Model and Coral-Based Reconstructions

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Content

The Last Interglacial (LIG), when sea level was ~6 m higher than today, serves as an analog for future climate scenarios yet only a few paleoclimatic reconstructions with seasonal to decadal resolution exist from this interval. Hispaniola, in the northern Caribbean Sea, is a desirable site for producing sea surface temperature (SST) reconstructions as it is located in the northern sector of the Atlantic Warm Pool (AWP), a primary moisture source region for precipitation in Central and North America, and this location has significant correlations with SST and precipitation anomalies for much of the region. Here we present an early LIG (128.6 ka) monthly-resolved coral Sr/Ca-SST reconstruction from a well-preserved *Siderastrea siderea* subfossil coral spanning 75 years from the northern coast of Hispaniola (19.913°N, 70.925°W), which is one of the longest subfossil coral reconstructions for any interval and the longest for this region. We compare our LIG SST reconstruction with three modern *S. siderea* microatolls, the longest spanning 84 years (1926–2010 CE), near Port-au Prince, Haiti (18.479070°N, 72.668659°W), as well as the CCSM3 125 ka LIG model simulation spanning 300 years. We find similar SST seasonal cycles in the LIG coral (3.7°C) and LIG simulation (3.8°C) that are greater than those in the modern Haitian corals, observed SST (ERSSTv4.0 and HadISSTv1.1), and CCSM3 20th century simulations. This seasonal variability is consistent with the findings of other LIG coral reconstructions in the tropical Atlantic Ocean suggesting that orbital insolation changes are driving LIG SST seasonality in this region. Furthermore, our LIG reconstruction reveals larger multidecadal (2.8°C, ~20–30 years/cycle) and interannual variability (3.0°C, ~3–8 years/cycle) than the modern coral reconstructions and SST records in the AWP yet similar variability is present in the LIG model simulation but with a reduced magnitude. This interannual and decadal variability may reflect variations in the northern extent of the AWP on these time scales, which may covary with trade wind strength, westward moisture transport to the Americas, and precipitation in the Caribbean.

A Coral Ensemble Approach to Reconstructing Central Pacific Climate Change During the Mid-Holocene

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Content

The processes that control El Niño/Southern Oscillation (ENSO) variability on long timescales are still poorly understood. As a consequence, limited progress has been made in understanding how ENSO will change under greenhouse gas forcing. The mid-Holocene provides a well-defined target to study the fundamental controls of ENSO variability. A large number of paleo-ENSO records spanning the tropical Pacific indicate that 3000-6000 yr BP, a time when Earth's orbital parameters (namely, precession) were substantially different than today, ENSO variability was reduced by as much as 50% relative to modern times. However, while a weak mid-Holocene ENSO appears to be a robust feature in the paleoclimate record, evolution of the mean tropical Pacific climate is poorly constrained. While decades of research have demonstrated the fidelity of tropical Pacific coral $\delta^{18}\text{O}$ records to quantify interannual temperature and precipitation anomalies associated with ENSO, substantial mean offsets exist across overlapping coral sequences that have made it difficult to quantify past changes in mean climate. Here, we test a new approach of reconstructing changes in mean climate from coral records using a large ensemble of bulk $\delta^{18}\text{O}$ measurements on fossil corals from Kiritimati (aka Christmas Island) that span the Holocene. In contrast to the traditional method of high-resolution sampling to reconstruct monthly climate conditions, we implement a bulk approach, which dramatically reduces the analysis time needed to estimate mean coral $\delta^{18}\text{O}$ and enables a large number of corals to be analyzed in the production of an ensemble of mean climate estimates. A pseudo-coral experiment based on simulations with a Linear Inverse Model and a coupled GCM is used to determine the number of bulk coral estimates that are required to resolve a given mean climate perturbation. In addition to these bulk measurements, high resolution records are used to constrain changes in the amplitude of the seasonal cycle. We present preliminary results from this joint bulk/high-resolution sampling approach that provide new constraints on changes in mean climate and seasonality in the central equatorial Pacific over the last 6,000 yr BP.

A high-precision gamma densitometer for quantifying skeletal density in coral skeletons: physical background and first results

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Content

While the focus of coral-based climate studies has been on the use of geochemical proxy data, proxies from skeletal growth patterns (extension rate, density, calcification rate) have been underexploited. Measuring density in coral skeletons with high precision is challenging and forms the dominant source of experimental uncertainty in related studies. To reduce this uncertainty, we developed a precise and easy-to-handle γ -densitometer. This instrument illuminates coral samples with a close-to-monochromatic γ -ray beam and measures the attenuation in the material by means of single photon counting. Knowing the thickness of the sample, the density can be extracted from the attenuation. After calibration, we obtained a precision of 3.7% for absolute and 0.6% for relative density measurements. The spatial resolution is 0.5 mm. The detector system has been tested with the genus *Porites*, typically used in paleoclimate studies in the Indo-Pacific, and with the genus *Orbicella* (formerly *Montastraea*), which has been commonly used in the Atlantic. A record (AD 1965-1999) from an *Orbicella faveolata* from the Belize Barrier Reef exhibits a decrease in skeletal density and in calcification rate; extension rates increase over time. A record from an *Orbicella faveolata* from the offshore Glovers Reef Atoll, Belize, exhibits a density increase during AD 1900-2005 while skeletal extension rate decreased; calcification rate shows a decline over time. Skeletal density in a *Porites lutea* from the Maldives decreases from AD 1917-2007 whereas skeletal extension rate and calcification rate exhibit increasing trends. These first results along with those from other studies suggest that coral density data from numerous corals in a region are needed to establish robust trends in coral calcification over time, and, that susceptibility to ocean acidification apparently might vary among coral taxa.

Change in nitrogen fixation derived from Caribbean coral skeletons

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Content

Oceanic nitrogen fixation is important for providing new nitrogen in oligotrophic oceans and balances with denitrification in the global nitrogen cycle. However, no continuous high-resolution data of past variability in nitrogen fixation is available. In Little Cayman Island, we examined horizontal and vertical distribution of nitrogen isotopes in macro algae and coral skeletons as potential indicator of nitrogen fixation rate in oligotrophic oceans, and we also demonstrate the history of nitrogen fixation change through the 20th century using a long living coral core. The nitrogen isotopes in macro algae alive near the coast of Little Cayman (1 m depth) were +1.2-+1.8‰. The vertical distribution of nitrogen isotopes in macro algae were almost stable in the range from +0.4 to +2.4‰ in the water column (1-60 m depth). These results suggested that nitrogen isotopes of DIN were strongly influenced by nitrogen fixation in Little Cayman. The vertical distribution of nitrogen isotopes in coral skeletons were examined three reef coral genera (*Agaricia* spp., *Orbicella* sp., and *Dipolia* sp.) from shallow (10-20 m depth) and deep (60-70 m depth). Nitrogen isotopes in shallow coral skeletons were ranged from +1.1-+5.1 ‰. Nitrogen isotopes of *Agaricia* in different depth were almost same in shallow corals, however, those of *Orbicella* in depth were +7.0±0.7‰. The variation of nitrogen isotopes in shallow corals reflected seasonal and/or annual variation of surface dissolved inorganic nitrogen (DIN) isotopes. However, corals in deeper depth could switch from autotrophic to heterotrophic nitrogen metabolism depends on genera (or morphology) and ambient environment. The centennial-scale record (94-year) of annual nitrogen isotopes in a coral core revealed changing nitrogen fixation correlating with multi-decadal temperature variability in the North Atlantic Ocean. Reconstructed nitrogen fixation also showed a decreasing trend during the 20th century corresponding to the slowdown of the Atlantic Meridional Overturning Circulation (AMOC) which is led by global warming. Nitrogen isotope variations in coral core suggested that Atlantic Ocean circulation may drive the century scale variation of nitrogen fixation in the Caribbean Sea. Nitrogen isotopes in coral skeletons can be used as a proxy for nitrogen fixation in North Atlantic Ocean.

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Constraining 20th Century Pacific Trade-Wind Variability Using Coral Mn/Ca: The First Wide-Scale Application of a Novel Wind Proxy

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Content

The early-2000s were marked by a pronounced reduction in the rate of global surface warming, despite a steady increase in greenhouse forcing. This slowdown is far from unprecedented, however, as global surface temperatures over the 20th century exhibit similar periods of reduced and accelerated warming that cannot be fully explained by external forcings alone forcings [1]. Recent model and observation studies suggest that decadal climate variability in the tropical Pacific, specifically changes in trade-wind strength, play a profound role in regulating the rate of global surface warming. Yet, Pacific decadal variability remains poorly constrained due to the dearth of instrumental observations from the tropics. Surface corals have dramatically improved our understanding of oceanic variability in the tropical Pacific across recent centuries, however little is known about the associated atmospheric response. Pioneering studies have demonstrated that skeletal Mn/Ca in corals from Tarawa Atoll (1.3°N, 173°E) track El Niño-related westerly wind events on interannual timescales [2], and strength of Pacific trade winds on decadal timescales [3]. Building on this early work, we explore the utility of this novel proxy at other sites in the central tropical Pacific that are hydrographically similar to Tarawa. Preliminary results from Butaritari (3.2°N, 172.8°W) and Kiritimati (2°N, 157.5°W) establish that Mn/Ca in corals growing at these sites also track westerly wind events. By extending this approach to multiple sites in the central tropical Pacific, we aim to develop a more robust and quantitative reconstruction of Pacific trade-wind variability during the 20th century, and more importantly, build a framework for extending coral-based wind reconstructions further into the past.

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Earthquake and tsunami archives in coral growth parameters and geochemical records

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Content

Since the 2004 Sumatra-Andaman earthquake, $M_w \geq 8.0$ earthquake repeatedly occurred with a short-term rate increase. Importantly, it is necessary for developing disaster risk management to understand the earthquake recurrence intervals, the faulting mechanisms, and disaster potential by land- and marine-based approaches. The distribution of earthquake epicenters since 20th century overlaps with that of reef corals along the convergent plate boundaries, especially around the Indian and the Pacific Ocean. Reef coral skeletons have a potential for reconstruction of paleo-earthquake events.

We reconstructed the 2004 Simeulue-Andaman earthquake and the 2005 Nias-Simeulue earthquake by coral growth and geochemical records (stable isotopes ratios and trace elements ratios) using five *Porites* coral cores in Simeulue island, Indonesia. These earthquake events (seismic shaking, coseismic uplift, and tsunami) led the temporal growth disturbance, as a prominent stress band and a significant decrease of annual extension/calcification rates. In addition, annual extension rates of uplifted corals increased, which reflected increasing light availability. Skeletal $\delta^{13}\text{C}$ records showed the significant stepwise increasing which reflected the uplift-related change of light availability. Moreover, there are significant relationships among coral habitat depth, skeletal $\delta^{13}\text{C}$ variation of vertical seafloor displacement (uplift), and uplift-related difference of light availability.

We also applied geochemical analysis on coral skeletons collected in Amami Islands (Kikai island and Amami-Oshima island). Coral growth decreased during tsunami event accompanied with the 1995 Amami-Oshima-kinkai earthquake. The tsunami event could cause sediment resuspension and coastal runoff. Thus, it would be a negative control factor of coral growth. Additionally, skeletal barium-calcium ratios showed a tsunami signal in Amami-Oshima coral. We will also show the latest result of Kikai coral survived the 1911 Kikai Island earthquake and tsunami event.

Coral paleo-earthquake and tsunami archives will support the prediction of earthquake recurrence intervals and disaster risk management in the coastal area where the earthquake occurrence cycles are still unknown or natural/historical archives are rarely available.

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Exploring the influence of climate variability on nitrogen cycling in the Pacific Ocean from coral stable nitrogen isotopes records: preliminary results

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Content

The Pacific Ocean displays a complex nitrogen cycling which dynamic can strongly influences the global nitrogen cycle. For instance, the Eastern Pacific hosts the second largest denitrification zone whereas the nutrient-poor waters of the Western Pacific is one of the largest nitrogen fixation hotspots. Changes in nitrogen cycling within these regions are believed to influence the oceanic carbon pump with potential consequences on the global climate. Climate in turn, can influence the Pacific Ocean's nitrogen cycling through the Pacific Decadal Oscillation (PDO) or the El Nino Southern Oscillation (ENSO). Yet, understanding the complex feedback mechanisms linking oceans'N cycling and climate variability remains challenging due to the lack of long-term nutrient data sets.

We propose to use a recent analytical method developed at Princeton University by Prof. Sigman and Dr. Wang, to obtain stable nitrogen isotopes records from coral skeleton (CS- $\delta^{15}\text{N}$) obtained in the eastern, central and western Pacific regions. This proxy has been proven to reflect changes occurring in ocean's nitrogen sources over geological (10,000s of years) and historical (centuries) time scales, offering the opportunity to understand how the nitrogen cycling of the surface ocean is affected by the PDO and ENSO. Here, we will be presenting preliminary data and discuss the next steps of this study.

Frequency of extreme daily temperatures (HadEX2) over Eurasia documented in a northern Red Sea coral oxygen isotope record during the last century

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Content

The potential of a bimonthly-resolved northern Red Sea coral $\delta^{18}\text{O}$ record as an archive for the occurrence of extreme daily temperature phenomena over Eurasia during Northern Hemisphere winter is investigated for the 1901-1995 period using extreme indices provided by the HadEX2 dataset (e.g., frost days, ice days, cold nights and cold days). The coral $\delta^{18}\text{O}$ record reflects a combined signal of temperature and salinity variations in the surface waters of the northern Red Sea, and has been previously shown to provide a proxy for atmospheric circulation changes over the Northern Hemisphere mid-latitudes at interannual to decadal time scales. Here we show, by applying composite analysis, that cooler/more arid (warmer/less arid) winter conditions in the northern Red Sea region, indicated by positive (negative) coral $\delta^{18}\text{O}$ anomalies (January-February), are related to a strong (weak) Northern Hemisphere polar vortex and, as a consequence, to a decreased (increased) number of days characterized by very cold temperatures and frost over Scandinavia and Central Europe. This situation is associated with an increased (decreased) number of days characterized by very cold temperatures and frost over the Balkan region. The occurrence of these daily temperature extremes is modulated by the frequency of atmospheric blocking over the British Isles and Central Europe, and a shift in the direction of the North Atlantic storm tracks. Importantly, coral records provide a bimonthly to monthly resolution, compared to other high-resolution proxy records which have either an annual resolution (e.g., ice cores, varved sediments) or an annual resolution with a signal that is biased towards a specific season that in most cases is not winter (e.g., tree rings). We argue that bimonthly-resolved northern Red Sea coral $\delta^{18}\text{O}$ records provide an archive of interannual to decadal variations in the occurrence of extreme daily temperature events over wintertime Eurasia prior to the start of instrumental observations.

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Introduction to the session on ‘Tropical coral archives’

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Content

Shallow-water coral archives provide precisely-dated annually to monthly-resolved reconstructions of marine climate and environmental change from across the global tropics to subtropics. They are a key archive to constrain past seasonal, interannual and decadal variability – the time scales most relevant to human societies – beyond the start of systematic reef monitoring programs and instrumental observations of climate. Coral reconstructions extending back for centuries provide a link between the observational period and lower-resolution sediment archives. This is of high relevance for comparisons of proxy data with model simulations of reef ecosystem dynamics and global climate. Well-preserved fossil corals provide high-resolution snapshots for time intervals of the Holocene, the last glacial-interglacial cycles, the Miocene and the Pliocene. Coral paleoclimatology provides an opportunity for collaborations among paleoclimatologists, marine geologists, coral reef ecologists, carbonate geochemists, experts in biomineralization, carbonate diagenesis and U-series dating, climate modellers, climate dynamicists, and climate statisticians, in order to provide robust and innovative paleoclimate and environmental reconstructions and interpretations. The aim of this session is to present and discuss latest research on past marine climate and environmental change at society-relevant timescales (seasonal, interannual, decadal), in order to understand the long-term context and impacts of future changes in the tropical to subtropical oceans, reef ecosystems, and adjacent continents.

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Last interglacial sea levels and regional tectonics from fossil coral reefs at the Gulf of Aqaba

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Content

The tectonic history and sea-level changes at the Gulf of Aqaba (GOA) during the last interglacial are reconstructed by mapping and dating of elevated coral reef terraces. The terraces comprise fringing reefs, some with clear reef structure that includes a reef flat and a shallow back lagoon accurately marking sea-level. Most of the fossil corals in the elevated reef terraces were extensively altered to calcite, indicating extensive interaction of the reefs with freshwater, possibly when the reef-terraces passed through a coastal aquifer that existed along the shores of the GOA, implying a wetter climate during the time of recrystallization from aragonite to calcite. We developed the methodology to apply U-Th isotope data to date the ages of initial formation of the aragonitic corals and the ages of recrystallization to calcite. The latter indicate the times of past wetter conditions in the current hyper-arid area of the GOA. Terrace R3 formed at the earlier stage of MIS5e at ~130-132 ka and recrystallized to calcite at 124±8 ka. Terrace R2, comprising a wide and developed reef flat, formed during the stable sea level of peak MIS5e at ~129-121 ka and recrystallized to calcite at 104±6 ka. Terrace R1 formed during a short still-stand at ~ 117 ka. All terraces formed when sea level was at or slightly above or below its stable MIS5e elevation a few meters above the modern GOA level. The recrystallization age of Terrace R2 implies that at around 104±6 ka (MIS5c) sea level was still close to its MIS5e elevation. The tectonic setting is superimposed by local faulting that caused small vertical displacements within the terraces. The elevation and ages of the reef flats indicate a slow average uplift, 0.12±0.05 m/kyr, similar to rates inferred for other reef terraces along GOA and the Red Sea. This implies an overall long-term slow tectonic uplift of the Arabian lithosphere during the late Quaternary.

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Last interglacial temperature and hydroclimate seasonality reconstructed from tropical Atlantic corals

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Content

Reconstructions of last interglacial (~127-117 ka) climate offer insights into the natural response and variability of the climate system during a warmer climate. However, the seasonal temperature changes of the tropical ocean are not well known for this time interval. Here we present well preserved fossil shallow-water corals from the southern Caribbean Sea (Bonaire) that have been precisely dated by the ²³⁰Th/U-method to between 130 and 118 ka ago. Annual banding of the coral skeleton enabled construction of time windows of monthly resolved Sr/Ca temperature proxy records, providing snapshots of sea surface temperature (SST) seasonality in the tropical North Atlantic during the last interglacial. We detect similar to modern SST seasonality of ~2.9 °C during the early (130 ka) and late last interglacial (120-118 ka), while for the mid-last interglacial a significantly higher than modern SST seasonality of 4.9 °C (at 126 ka) and 4.1 °C (at 124 ka) are indicated. These findings are supported by simulations with a coupled atmosphere-ocean general circulation model, and are consistent with the evolving amplitude of orbitally induced changes in the seasonality of insolation throughout the last interglacial. The climate model simulations suggest that the reconstructed SST seasonality changes are representative of larger regions within the tropical North Atlantic. A 124 ka old coral documents evidence of decadal SST variability in the tropical North Atlantic during the last interglacial, similar to that observed in modern instrumental records. In addition, we will discuss new monthly resolved $\delta^{18}\text{O}$ records generated from the same corals that are combined with water isotope enabled climate model simulations, in order to draw conclusions on tropical Atlantic hydroclimatic change and seasonality during the last interglacial.

Monitoring and assisting coral reefs in the Anthropocene

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Content

With reefs being of paramount societal interest, attempting to correlate subepisodes of the Anthropocene across coral reefs would be a prerequisite for better understanding and assisting the global change of reef patterns. Using an integrated approach of palaeoclimatology, (palaeo)ecology and geosignals helps to evaluate the interconnected subrecent shifts of reef systems, to assess natural and enhanced adaptation strategies of reef, and thus to provide pathways for the future of reefs.

15th Century - 1950: Holocene reefs started to transform since Columbian times, characterising this episode by a first anthropogenic imprint on reefs, increasing thereafter via world trade and industrialisation effects.

1950 - 2017: A great variety of geological signatures is expected at the suggested base of the Anthropocene within coral reefs, allowing to correlate this level globally across reefs and their related environmental settings. Coral reef studies would benefit from additionally focusing on the nuclear fallout signals, on temperature recording, and on heavy metals, plastics etc. in coral skeletons or void and cavity infills. The episode is then characterised by increasing loss of reef biodiversity, accelerating from the 1970s onwards, mostly related to overfishing, nutrient runoff and other pollution, increasing temperature and acidification, being punctuated by diseases, and particularly by correlatable bleaching events and cyclon-induced coastal runoff events.

The **two options for the future of reefs** are:

a) 2017-2100: with **business as usual**, coral reefs continue to face a strong, even more enhanced decline, with a possible near-disappearance of coral reefs;

b) 2017-2200: with **very good management and fulfilling the Paris Agreement** coral reefs could continue to grow, albeit in a completely different form, with the high diversity, stable communities retreating in favour of more „volatile“, new short-lived, types (often with „atavistic“ features, such as adaptations to higher nutrients, sediment runoff, deeper settings, higher SSTs, lower pH). We would have to „assist“ these reefs in various ways, yet they would go through a "vale of tears“ possibly for the next 100, if not 200 years (cf. Hoegh-Guldberg et al. 2008: tinyurl.com/reeftriangle, Leinfelder et al. 2012: tinyurl.com/atavistic-reefs, Hughes et al. 2017: [doi:10.1038/nature22901](https://doi.org/10.1038/nature22901)). After this episode there could be a possible return to robust, resilient and long lasting new set of coral reef ecologies.

Offline Data Assimilation of Pseudo-observations into a Regional Climate Model

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Content

Simulation of climate of the past using high-resolution Regional Climate Models (RCMs) is a challenging approach due to their high computational costs and dependency of such models on their driving General Circulation Model (GCM). Using a very cheap Data Assimilation (DA) approach, we assimilate the pseudo-time-averaged observation into an RCM. The sensitivity of state-of-the-art high resolution RCMs to the initial conditions is highlighted. Pseudo-observations are assimilated within an ensemble of RCM simulations using an “offline” approach, where the ensemble members differ in boundary and initial conditions. We conclude that the “offline” DA is promising for creating high resolution analysis quantities. This method can be applied to improve the climate model simulation estimates constrained by available observations, especially for the time-averaged observations (proxies) and the long-term paleo-climate simulations. Given the computational costs of RCMs, previous studies using the time-slice simulation method, could conduct only a single climate run, which can not provide a sophisticated measure of uncertainty and is only one random draw of infinite possible climate states. In this study, we will introduce the basics of offline DA in an ensemble of RCM simulations and test the performance of this method.

Session 5.2: Tropical coral archives - Reconstructions of climate and environment beyond the instrumental record at society relevant timescales: Talk
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Relict coral reefs in the Mediterranean Sea: a story of adaptation, survival and decline over geological and human timescales

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Content

Shallow coral reefs are restricted to tropical and subtropical marine environments, where they support extensive ecosystems. However, relict coral reefs are to be found also in temperate seas. These reefs offer a great opportunity to study the evolution of coral ecosystems through environmental changes over geological time-scales, thus providing a wider scope to assess and contextualize responses to current climate change.

The Mediterranean endemic coral *Cladocora caespitosa* is a great example of a scleractinian zooxanthellate reef-builder, equivalent to its tropical and subtropical counterparts, thriving in a temperate, high seasonal sea. As the fossil register shows, extensive reefs of *C. caespitosa* occurred in Mediterranean coasts as early as the Pliocene. The occurrence of *C. caespitosa* reefs shows continuity until modern times, it is however linked to great changes in distribution, size and environmental settings.

Cladocora caespitosa is highly adapted to the high seasonality and environmental conditions that characterize the modern Mediterranean Sea. This species shows great ecological plasticity, in terms of the types of biological communities it may thrive among, and in its depth and light requirements, which is a rare trait in long-lived invertebrates with parsimonious dynamics. Despite all this, and the fact that extensive *C. caespitosa* fossil reefs seem to have flourish in warmer periods, *C. caespitosa* is being notably impacted by the rapid warming of surface Mediterranean waters. Its rapid decline over the last decades has led to its inclusion as endangered in the IUCN Red List.

Altogether, the study of adaptation, survival and decline of this species over different timescales may help to understand and contextualize current rapid environmental changes and species' responses, and to better project future consequences in Mediterranean shallow benthic ecosystems submitted to anthropogenic climate change.

Temperature proxies in Holocene corals and their differential susceptibility to early diagenesis: A case study on SST records from French Polynesia

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Content

Coral based reconstructions of sea surface temperatures (SST) using Sr/Ca, U/Ca and $\delta^{18}\text{O}$ ratios are important tools for quantitative analysis of past climate variability. However, post-depositional alteration of coral aragonite due to early diagenesis is restricting the accuracy of calibrated proxies even on young corals. Here we present Mid to Late Holocene SST reconstructions using well dated (U/Th: ~0.07 to 5.4 ka) fossil *Porites* collected from the Society Islands, French Polynesia.

For a few coral samples microscopic observations and electron microprobe mapping reveal the presence of aragonite needles inside coral pores. Coral sections with identified secondary aragonite show on average a 25-30 % higher Sr/Ca ratio than corresponding primary massive parts. Samples with secondary aragonite overgrowth on internal pore surfaces are characterized by Sr/Ca values above 10 mmol/mol, a potential threshold between diagenetically altered and unaltered material. The observed intra-skeletal variability of 5.4 to 9.9 mmol/mol probably reflects the physiological control of the corals on its trace metal uptake and the biological related diurnal cycle of Sr^{2+} uptake variability during CaCO_3 -precipitation. The Sr/Ca, U/Ca and $\delta^{18}\text{O}$ pattern are well correlated. However, we observe a significant systematic offset between Sr/Ca, U/Ca, and $\delta^{18}\text{O}$ based SST reconstructions of up to $\pm 7^\circ\text{C}$ and a trend towards cooler temperatures. Latter shifts mostly reflect trace element specific diagenetic alteration due to partial dissolution and precipitation of secondary aragonite. This process tends to amplify temperature extremes and hence increase the SST-U/Ca and SST-Sr/Ca gradients and consequently their apparent temperature sensitivity.

A relative SST reconstruction is still feasible by normalizing our records to their individual mean value defined as ΔSST . This approach shows that the ΔSST records derived from different proxies are in phase with an amplitudinal variability of up to $\pm 2^\circ\text{C}$ with respect to their Holocene mean value. The ΔSST -values which are higher than the mean SSTs (Holocene warm periods) are observed between ~1.8 ka to ~2.8 ka (Interval I), between ~3.7 and 4.0 ka (Interval III) as well as before ~5 ka. Lower ΔSST s (Holocene cold periods) are observed between ~2.8 to ~3.7 ka (Interval II) and ~4.0 to ~4.9 ka (Interval IV). The corresponding SST periodicity of ~1500 yrs in the Society Island record is in phase with the solar activity reconstructed from ^{10}Be and ^{14}C data.

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Tropical to temperate coral archives around Japan

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Content

Anthropogenic carbon dioxide would accelerate both global warming and ocean acidification, and such climate changes would also dramatically influence on marine ecosystem such as coral reefs with preventing calcification process. However, direct and long term evidences are few to address climate changes with anthropogenic forcing, and it is still unknown the impact of recent climate changes to coral calcification in the past and future.

Cores from long living corals could provide high-resolution and long-term climate changes and coral growth histories during their growth periods up to several hundred years. We demonstrate a century-scale data set of coral records from the mid latitude around Japan. Kuroshio current transporting warm water from tropics to temperate regions sustains “highest latitude” coral reefs and reef corals in Japan. We collected the coral cores with large latitudinal gradient from tropical (Okinotori island), subtropical (Lutao island, Ishigaki island, Kikai island, Amami island, Satsuma Iwo island), and temperate (Koshiki island, Fukue island, Tatsukushi, Kushimoto, Iki island). Marine environments in temperate coastal regions are characterized as lower temperature, higher nutrients, and lower aragonite saturation rate than tropical and subtropical regions relatively.

To address the relationship between coral growth characteristics and environmental changes for coral survival at high latitude area, we reconstructed environmental changes using geochemical proxies ($\delta^{18}\text{O}$ for SST and SSS, $\delta^{13}\text{C}$ for sunlight availability and atmospheric CO_2 , and $\delta^{15}\text{N}$ for Nutrients) and physical parameters (skeletal density, extension rate, and calcification rate) using x-ray densitometry. We discuss the possible linkage of regional and global climate/environmental changes and coral growth in temperate regions and how corals could adapt and survive in marginal and extreme conditions during last 100 years. In the presentation, we would also like to introduce and discuss our recent attempts of establishing Coral Core Center (<http://ccc.kikaireefs.org>) and Kikai institute for coral reef sciences (<http://kikaireefs.org>) to promote and extend coral reef sciences using these coral archives to wider range of researchers with different background and technique.

Session 5.3: Palaeogeography through geologic time: Poster

Session 5.3: Palaeogeography through geologic time: Poster
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A historical account of palaeogeography

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Content

Palaeogeography deals with the reconstruction of physical geographical conditions for the eras of the Earth's history. Palaeogeographic changes profoundly influence ocean circulation patterns and ocean chemistry, palaeoclimate, biological evolution, and the formation and distribution of mineral and hydrocarbon resources. Palaeogeographical research is therefore essential for better understanding the evolution of our planet and for the exploration of raw materials to fulfil the world's need in the future. Palaeogeography focuses on the distribution of land and sea, the spread of mountains and volcanoes, and the expansion of glaciations, among others. The results are presented in geographic depictions called palaeogeographic maps. Today, palaeogeographers use much of the same data as, for example, Alfred Wegener and Alexander du Toit did, i.e. matching up similar rock formations, analyzing the distributions of fossil species, and looking for evidence of ancient climate signals preserved in the rock record. More precise data on the geographic position of continental plates can be obtained by studying remnant magnetism in rocks, among others. Because of the amount of data to be handled and different techniques to be applied palaeogeography may therefore be one of the most complicated disciplines of the Earth sciences. Palaeogeography is tightly connected with plate tectonics, which is largely responsible for shaping the Earth. Today, palaeogeography is an integral part of the Earth sciences curriculum. But commonly, with some exceptions, only the most recent state of research is presented and the historical aspects of how we actually came to the insights which we take for granted is sparsely discussed. It is remarkable how much already had been known about the changing face of the Earth more than three centuries before the plate tectonics paradigm, despite the fact that neither most of our present analytical tools nor our models were available then. Here, we aim to present a brief historical account of palaeogeography. Special emphasis is given to innovative ideas and scientific milestones, which helped to advance the theories of continental drift and plate tectonics, and finally led to establish palaeogeography as a recognized discipline of the Earth sciences.

**Circum-tropical biogeography of the Devonian calcareous alga *Zeapora* Penecke 1894
(Chlorophyta, Bryopsidales)**

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Content

The taxonomy of *Zeapora* Penecke 1894 has a long but inconsistent taxonomic history. Originally identified as cyclostomate bryozoan, it has been later assigned to the trepostomate bryozoans, amphiporid stromatoporoids, thamnoporid tabulate corals and dasycladacean algae before it was finally classified as Halimedaceae or Udoteaceae. Based on newly collected material from the type locality in the Graz Paleozoic (Eastern Alps, Austria) we emend the taxonomic description of the type species *Z. gracilis* and also place the udoteacean genus *Litanaella* Shuysky & Schirschova 1987 in synonymy with *Zeapora*. Following this opinion, *Zeapora* remains no longer endemic in the alpine Noric Terrane but shows a peculiar circum-tropical distribution during the Early to Middle Devonian similar to modern *Halimeda*.

Preliminary results on physical volcanology, paleogeography and ore deposit at the Precambrian-Cambrian boundary in Tassafte area at NE of Saghro inlier, Eastern Anti-Atlas, Morocco

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Content

Tassafte sector at the NE edge of Saghro inlier in the Eastern Anti-Atlas of Morocco contains one of the best exposed Ediacaran and Cambrian successions. It is considered as a key area to highlight the geological events that characterized the Precambrian-Cambrian transition in this region.

The Ediacaran volcano-sedimentary complex includes a series of volcanic rocks from andesitic basalt to porphyritic andesite lava associated with ignimbrite and alternating sandstones and tuffs. The complex is cutted by porphyritic andesite dyke swarms. These sequences were grouped in several lithofacies characterizing a continental evolution. The volcanic styles were recognized such as caldera, scoria cone and minor phreatomagmatic eruptions, punctuated by fluvial systems.

The Lower Cambrian Formations, which are less developed in Eastern Anti-Atlas, rest unconformably on the Ediacaran complex and exhibit thickness varies from 10m to more than 200 m, which range into three major lithofacies: the basal polygenic conglomerates, purplish sandstone "lie de vin" type and an alternated schist and carbonates. These formations record numerous sedimentary environments such as sheet-flat, alluvial fan and deltaic system.

According to [1] this volcanic activity is the last eruption during the Ediacaran time at the North of Saghro inliers. Contrary to the rest of Western and central Anti-Atlas, the North edge of Saghro inlier has not been concerned by Infra-Cambrian sedimentary deposits, which known as "Adoudou formation". Finally, The Evolution of Tassafte area, in the North of Saghro inlier, was controlled by the major E-W trend Sidi Feleh-Imiter faults system, during the Ediacaran-lower Cambrian time [2],[3] and [4].

The Ediacaran volcanic complex and Cambrian series host a N80 to N120-trend ore body showing a dipping varies from 55°E to 90°E. They are centimeter to metric width and appear as continued veins or lenses. Three kinds of ore textures have been recognized in these veins, massive, brecciated and ribboned. The mineralization is represented by chalcocite rarely galena, copper carbonates (malachite and azurite) and barite with quartz as gangue mineral.

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The metamorphic nappes of the Frankenberg Massif, Southern Saxony, Germany, within the Cadomian–Variscan evolution: New geochemical data and relationship to the Münchberg Massif

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Content

Formation and origin of the metamorphic nappe complexes of Münchberg and Frankenberg have been a long-lasting matter of debate (e.g. [1]). Recently, new geochemical and U-Pb age data were obtained for the Münchberg Massif (MM; Koglin et al. submitted). It consists of four different nappe units that represent different stages in the Cadomian–Variscan evolution: the Hangend-Serie (Cadomian arc; 550 Ma), the Liegend-Serie (rift stage at the northern Gondwana margin; 505-480 Ma), the Randamphibolit-Serie (Rheic oceanic crust; 400 Ma), and the Prasinit-Phyllit-Serie (Rheic intra-oceanic island-arc; 407-371 Ma).

As a probable NE continuation, the Frankenberg Massif (FM) was investigated and compared with the MM by using new geochemical data. Comparable to the MM units, the FM comprises a hm-Serie (hornblende-mica gneiss), the Frankenberger Gneis (ortho- and paragneiss) and a Prasinit-Serie (greenschist, minor phyllite) (e.g. [1]). An equivalent to the Randamphibolit-Serie of the MM is missing.

Amphibolitic rocks of the hm-Serie differ petrographically from those of the Hangend-Serie by high contents in biotite and a massive appearance. Geochemically, however, they strongly resemble the Hangend-Serie rocks, except of a MORB tendency of some samples, which possibly represent obducted oceanic crust.

The Frankenberger Gneis comprises a medium-grained gneiss with large feldspar augen and a fine-grained, foliated gneiss, geochemically resembling orthogneiss and paragneiss of the Liegend-Serie in the MM, respectively. Intrusion ages of orthogneiss from both regions are identical (505-480 Ma MM and 484 Ma FM; Koglin et al. submitted, [2]). Therefore, the Frankenberger Gneis is interpreted as NE continuation of the northern Gondwana margin.

The phyllite samples of both, the Prasinit-Serie and the Prasinit-Phyllit-Serie, are sublitharenites with oceanic arc setting. In contrast, the greenschists of the Prasinit-Serie with geochemical back-arc basin signature differ from those of the Prasinit-Phyllit-Serie with clear ocean island arc character. Most probably, however, they belong to the same island-arc/back-arc basin system within the Rheic Ocean.

The equivalent to the Randamphibolit-Serie might be missing due to lack of obduction. Further age determinations are necessary to support the geochemical interpretation.

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Session 5.3: Palaeogeography through geologic time: Talk

Session 5.3: Palaeogeography through geologic time: Talk A-603

Biomarkers and their stable isotopes in Cenozoic sediments (reflecting major changes in biogeochemical cycling of C, H, S) above the Chicxulub impact crater from IODP-ICDP Expedition 364

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Content

The most widely accepted hypothesis for the cause of the End-Cretaceous mass extinction (K/Pg event) ~65.5 Ma ago is the impact of an extraterrestrial body, which produced the ~200 km wide Chicxulub impact structure. The massive extinction in the terrestrial realm is partly attributed to the intense heat pulse and the following widespread wild fires caused by the impact plus rising CO₂ levels within the Cenozoic. The marine realm experienced ocean acidification and therefore a suspected decrease in ocean productivity.

Extractable hydrocarbons in samples from the Cenozoic black shales, the Paleocene-Eocene Thermal Maximum (PETM) and a large number of ash layers have been obtained and analysed to investigate the molecular and isotopic organic record of biotic and environmental change after the K/Pg boundary event. High concentrations of polycyclic aromatic hydrocarbons (e.g. Coronene) relate to combustion rather than hydrothermally processes and are generally abundant with fossil charcoal, supporting the role of fire in terrestrial extinctions. In the post K/Pg early Cenozoic, gymnosperms are likely to have produced a relative high amount of resins due to increased heat stress. We are conducting innovative Laser Raman spectroscopy and HydroPyrolysis (HyPy) of the Cenozoic ash layers. HyPy is useful for characterising geo-macromolecules and their indigenous biomarkers due to its feature of breaking down organic macromolecules into smaller fragments. This supports complete product resolution essential for compound-specific isotopic analyses. U-Pb dating on zircon minerals extracted from the Cenozoic ash layers will help us to identify the timing of suspected wild fires.

Several of Cenozoic sediments (including the PETM) contain biomarkers of green sulfur bacteria and intact organo sulfur compounds indicative of persistent photic zone euxinia. The long term biogeochemical cycling of C, H and S after the K/Pg extinction including the PETM will be presented from a biomarker and stable C, H, and S perspective.

Expedition 364 Scientists: S. Gulick, J.V. Morgan, E. Chenot, G. Christeson, P. Claeys, C. Cockell, M.J. L. Coolen, L. Ferrière, C. Gebhardt, K. Goto, H. Jones, D.A. Kring, J. Lofi, X. Long, C. Lowery, C. Mellett, R. Ocampo-Torres, L. Perez-Cruz, A. Pickersgill, M. Poelchau, A. Rae, C. Rasmussen, M. Rebolledo-Vieyra, U. Riller, H. Sato, J. Smit, S. Tikoo, N. Tomioka, M. Whalen, A. Wittmann, J. Urrutia-Fucugauchi, K.E. Yamaguchi, W. Zylberman.

Carboniferous and Permian system boundaries in continental deposits – multidisciplinary approaches

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Content

The Late Carboniferous (C) and the Permian (P) are exceptional in the Phanerozoic by a degree of continentality, only matched by the last 5 million years of Earth's history. Of the two largest components of the supercontinent Pangea, Gondwana was only about 15% covered by epi-continental seas, while Laurasia was only about 25% covered by epi-continental seas. This extensive continentality causes numerous problems of Pennsylvanian to Late Permian/Early Triassic stratigraphy that range from local biostratigraphic intra- and inter-basinal correlations to global correlations of the continental deposits with the marine Standard Global Chronostratigraphic Scale (SGCS). Solutions to these problems are strongly needed, because the C and P were the time of enhanced terrestrialization and rapid diversification of plants and animals on land, and the time when at the end of the middle and the late P the most severe mass extinctions occurred in both the marine and terrestrial ecosystems. Unfortunately, the understanding of the interactions of abiotic and biotic processes on land and the teleconnections to the marine realm is still hampered by the largely missing correlation between continental deposits of marine and non-marine stratigraphic scales.

Unconventional biostratigraphic tools combined with interdisciplinary multistratigraphic approaches have led to the first promising results of non-marine – marine correlations of the Carboniferous/Permian/Triassic system boundaries. The base of the P (= base of Asselian Stage) is defined by the International Commission on Stratigraphy at the level of the first appearance of the conodont *Streptognathodus isolatus* and is isotopically dated as 298.9 Ma. Based on the co-occurrence of conodonts with insect-biozone species in mixed marine-continental deposits in New Mexico, the *Sysciophobia ilfeldensis*-insect zone straddles the C/P boundary. This is well supported by a 299 +/- 3.2 Ma Pb/U age of the foregoing insect-zone in the Mansfeld Subgroup of Germany. As a result, the C/P boundary should be situated in the lowermost Rotliegend. Continuous transitions of the Zechstein and Buntsandstein groups of Germany were studied for isotope-chemostratigraphy ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$), major and trace element geochemistry, magnetostratigraphy, palynology, and conchostracan biostratigraphy. As a result, it is proposed to place the P/T boundary in the lower part of Zechstein cycle 7 (lower Fulda Formation).

Distribution and sediment composition of two Gondwana glaciations in Ethiopia

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Content

With the amalgamation of Gondwana in the Neoproterozoic the East African Orogen came into existence. Erosion products of this huge mountain range are mature sandstones that blanketed large parts of Gondwana during the Palaeozoic. In Ethiopia, Palaeozoic sedimentary successions can be assigned to the two major Gondwana glaciations during Late Ordovician and Carboniferous–Permian times. The distribution of ice sheets and continent-wide glacier dynamics during these glacial periods are still under discussion. Apart from the Arabian-Nubian Shield as a probable local source region, far-distance transport from central Gondwana (e.g., East Africa) needs to be considered. Ethiopia is a key region between potential far-distant sediment sources and the northern margin of Gondwana.

We compare sediments of both glaciations regarding their petrography, geochemistry and heavy minerals to assess differences in provenance, weathering and transport conditions and the implications for the respective glacial system.

For the Late Ordovician sediments, petrography and geochemistry and the enrichment of ultra-stable heavy minerals (mainly zircon, rutile, and tourmaline) show high maturity pointing to intense weathering and reworking prior to deposition – yet no evidence for sediment recycling was found. In contrast, the Carboniferous–Permian sediments are less mature and show indications for a higher input of juvenile material, most probably from proximal sources. The presence of garnet points to little influence of acidic weathering. No evidence for recycling of the Ordovician sediments were found. Zircon ages of both formations are mainly Pan-African with minor Paleoproterozoic ages. Ordovician samples contain an additional group of Tonian–Stenian detrital zircons.

Comparison with stratigraphically corresponding formations in Saudi Arabia shows similar geochemical patterns in the Late Ordovician samples, whereas in the Carboniferous–Permian major differences can be identified. This supports previous assumptions of a large, uniform sediment system during the Early Palaeozoic, in which a combination of long transport paths and exceptionally strong weathering prior to deposition produced mature sandstones. During the Late Palaeozoic the glacial systems on Gondwana seem to have been more localised and glacial abrasion liberated fresh basement material.

Hiatus maps – a new tool for paleogeographic analysis of interregional unconformities on geological maps

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Content

Unconformities are intrinsic features of geological maps. Yet most studies focus on the rock record, not the hiatal surfaces at the base of geological systems or series. Here, we visualize hiatal surfaces on interregional geological maps as a recorder of missing time in the geological record. We assume that the plate- and plume-modes of mantle convection produce lithospheric responses over on interregional, albeit not global, scales. Consequently, we developed a methodology to visualize the information contained within standard, published continent-scale geological maps by analyzing their shapefiles. We designed a work-flow to automatically depict the duration of hiatal surfaces at the basis of Phanerozoic system- and series boundaries. We then contoured the hiatal surface values by standard techniques. The results are displayed as hiatus maps per time, which we display in their paleogeographic position using the GPlates software (Bowden et al. 2011) in the reference frame of Seton et al. (2012). To examine the significance of the hiatal surfaces, and to identify interregional-scale hiatuses, we mapped their spatial and temporal patterns in a plate-and plume stratigraphic framework. The resultant spatio-temporal hiatus patterns are distinct on continent-scale geological maps. As one example, a more or less radial, long-wavelength hiatus-intensity is visible in the western United States at the base of the Eocene to Miocene series, respectively, while hiatal surfaces at the base of the Paleocene to the base of the Cretaceous are subparallel to the plate margin. We attribute the former signal to the plume-mode (Columbia River flood basalt), while the latter signal mimics plate-mode processes (subducting slabs). Hiatus maps are proxies for paleo-dynamic topography due to mantle convection. We suggest that interregional-scale geological maps are an excellent, albeit currently underutilized, tool to visualize the plate- and plume-related records in continental regions. Given that most interregional geological maps display systems or series, not stages, the current shortcomings of hiatus maps are their limited temporal resolution. Future improvements require integration of subcrop data into the shapefiles, and a temporal resolution of stages.

Paleogeography and styles of rifting of the northern Gondwana shelf during Early Paleozoic: new insights from integrated detrital and magmatic zircon geochronology and structural analysis

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Content

A number of continental fragments that now constitute the Variscan lithosphere in Europe were derived from the Cadomian–Avalonian active margin of northern Gondwana at the end of Precambrian. These fragments were variably extended during Late Cambrian to Early Ordovician opening of the Rheic Ocean, yet their provenance and the style and amount of extension and thus separation from Gondwana mainland remain debated. We combine LA-ICP-MS geochronology and structural analysis to argue that various Cadomian units in the Bohemian Massif, the easternmost inlier of the Variscan orogenic belt, show a bimodal detrital zircon age distribution, with significant peaks at around 2.1–1.9 Ga and 650–520 Ma, suggesting West African provenance. We interpret the source area as an active margin comprising a cratonic (Eburnean) hinterland rimmed by Cadomian volcanic arcs and we demonstrate that this source was available at all times during deposition until Early- to Mid-Devonian. Structural analysis in shallow-crustal basins and associated volcanic complexes demonstrates that the subsequent rifting along the northern Gondwanan margin was a two-stage process involving incipient extension in the mid- to late-Cambrian and a major pulse of extension in the Early Ordovician. The latter process resulted in development of graben-type marine basins and both mafic and felsic magmatism. New U–Pb zircon ages from a number of metagranitic felsic plutons constrain the high-magnitude extension of the northern Gondwana margin to around 490–480 Ma. We conclude that the available geochronologic and structural information from the Early Paleozoic rocks of the Bohemian Massif is at variance with the still popular concept of the Cadomian basement units as far-travelled terranes. Instead, it supports the notion that the Early Paleozoic basins, developed upon the Cadomian active margin, were always part of a wide Gondwana shelf and drifted northwards together before involvement in the Variscan collisional belt. This wide shelf, however, may have been hyperextended in some parts, as indicated by numerous and maybe partly detritic mantle boudins enclosed within Ordovician metasedimentary complexes. This 'broad shelf' hypothesis may also provide an elegant explanation for biogeographic differences among these basins during early Palaeozoic, used as an argument for the large-scale terrane displacement.

Reconstruction of Early Palaeozoic Peri-Gondwana: insights from statistical analysis of the detrital zircon record

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Content

Zircon U-Pb dating of detrital minerals has become the most applied approach in provenance analyses and has produced the largest database of provenance and, thus, palaeogeographic indicators. However, the subjective comparison of individual zircon age spectra with each other or with likely source areas is in many cases inadequate, as pattern may be changed during erosion of the source and the transport to the sink and, therefore, the similarity of pattern alone is not always conclusive. Some of these problems may be accounted for by filtering and by quantitative evaluation of large, compiled data sets. The latter becomes possible because of the increasing number of high-quality data sets on the ages distribution of detrital zircons.

Here, we present a simple yet powerful statistical approach of quantitatively evaluating detrital age spectra that allows to identify provenance endmember populations for a composite crust. We compiled 54808 U-Pb ages from 787 Precambrian to Lower Palaeozoic samples out of 152 publications, filtered the dataset to reduce the age spectra to the provenance signal, and compared the provenance signal with age patterns of potential source regions. We test zircon provenance analysis for the Peri-Gondwana crust of the Variscan orogen because it hosts (i) a huge available data set that is as required for statistical treatment; (ii) detailed geological background information; and (iii) a wide range of tectonic fragments of potentially contrasting provenance that have been juxtaposed during the orogeny.

Multi-dimensional scaling coupled with density-based clustering of the detrital record reveals the temporal and spatial distributions of three principal provenance domains for the Peri-Gondwana crust: Amazonia, West African and Northeast African and Arabian. Our palaeogeographic reconstruction of pre-Variscan Peri-Gondwana is supported by palaeomagnetic, palaeoclimatic and palaeobiographic proxies. Interestingly, the distribution of tin mineralisations correlates with a specific provenance domain, namely the West African domain. Thus, economic deposits represent additional palaeogeographic indications. The resulting provenance map for the Variscan orogen provides fundamental constraints that are tested on published tectonic models, litho-bio-stratigraphic correlations among different terrains and palaeogeographic reconstructions of Peri-Gondwana.

Session 5.4: Lacustrine and marine sediments as environmental archives.: Poster

Session 5.4: Lacustrine and marine sediments as environmental archives.: Poster A-492

Between wet, dry and super dry: Climatic changes during the last 550,000 years in the Chew Bahir basin, an HSPDP key site in southern Ethiopia.

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Content

As a contribution towards an enhanced understanding of human-climate interactions, the Hominin Sites and Paleolakes Drilling Project (HSPDP) has cored five predominantly lacustrine archives of climate change spanning much of the last ~3.5 Ma in East Africa. All five sites in Ethiopia and Kenya are adjacent to paleoanthropological key sites encompassing diverse milestones in human evolution, dispersal, and technological innovation. The 280 m-long Chew Bahir sediment records, recovered from a tectonically-bound basin in the southern Ethiopian rift in late 2014, cover the past 550 kyr of environmental history, a time period that is marked by intense climatic changes and includes the transition to the Middle Stone Age, and the origin and dispersal of modern *Homo sapiens*.

We will present the outcome of lithologic and stratigraphic investigation of the composite core, first interpretations of high resolution MSCL and XRF scanning data, as well as initial results of detailed multi-proxy analysis of the Chew Bahir cores. These analyses are based on more than 14,000 discrete subsamples, including grain size analyses and X-ray diffraction. An initial chronology, based on Ar/Ar and OSL dating, allows the first reconstructions of dry-wet cycles during the last 550 ka. Both geochemical and sedimentological results show that the Chew Bahir deposits are sensitive recorders of changes in climate in the area. First statistical analyses point towards phases that are marked by abrupt climatic changes, whereas several long-term wet-dry oscillations reveal variations mostly in the precession (~15-25 kyr), but also in the obliquity (~40 kyr) and eccentricity frequency bands (~90-120 kyr).

The Chew Bahir record will help us to decipher climate variations on different time scales as a consequence of orbitally-driven high-latitude glacial-interglacial shifts and variations in greenhouse gases, variations in Indian and Atlantic Ocean sea-surface temperatures, as well as local variations in solar radiation. The ~550 kyr record of environmental change in East Africa will ultimately help us to test current hypotheses regarding the impact of climate variability on human evolution, dispersal and technological innovation.

Holocene paleoenvironmental change in the Winter Rainfall Zone of South Africa derived from sediments of coastal lake Verlorenvlei

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Content

Coastal lake Verlorenvlei, located in southern Africa's Winter Rainfall Zone, represents one of South Africa's scarce terrestrial Quaternary climate archives, from which a 15 m sediment core was recovered within the RAIN (Regional Archives for Integrated iNvestigations) project. A total of 24 ¹⁴C AMS ages covering 9.4 ka, indicate continuous sedimentation during the Holocene. Optical luminescence ages suggest that the base of the core dates back to the Last Glacial Maximum (24 ka BP). The oldest part of the record (24 to 9.4 ka) is almost entirely composed of sand, likely indicating sediment reworking. This suggests drier conditions with low sea and lake levels during the LGM and the Late Glacial. During the early Holocene (9.4 to 7.1 ka), elevated carbonate contents, the occurrence of marine gastropods as well as brackish water ostracods and foraminifers suggest marginal marine conditions at Verlorenvlei. Reduced terrestrial minerogenic inputs, highly variable granulometric parameters and slightly elevated amounts of organic matter at the same time point to a dynamic lagoon system. Higher concentrations of long-chain plant waxes indicate enhanced input of terrestrial organic matter into the system. During the early to mid Holocene (7.1 to 4.1 ka) distinctly reduced carbonate contents and enhanced terrestrial minerogenic and organic input, indicate a decoupling of Verlorenvlei from the ocean possibly due to barrier formation. Isotopic δD and $\delta^{13}C$ signatures of plant waxes indicate either drier environmental conditions or a distinctly changed precipitation source signal during that time. A short interval during the mid Holocene (4.1 to 3 ka) is characterized by very fine (4 μm), well sorted particles, very low total organic matter, higher δD and lower $\delta^{13}C$ signals of plant waxes. This might indicate moister conditions with both a very stable catchment vegetation and a stable coastal lacustrine system. Terrestrial input increases during the late Holocene (after 3 ka), suggesting increasingly humid conditions. Low levels of marine indicators, steady increasing concentrations of total organic matter, a distinct shift to mid-chain plant waxes and coarser minerogenic particles suggest a lacustrine phase of Verlorenvlei, being mainly influenced by fluvial input and characterized by aquatic biogenic production. Strong anthropogenic impact becomes apparent during the most recent part of the record (past ca. 300 yrs).

Provenance shift of suspended particulate matter in the Río de la Plata drainage basin over time

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Content

Strontium (Sr), neodymium (Nd) and lead (Pb) isotopic signatures of suspended particulate matter (SPM) in rivers and estuaries are powerful provenance tracers. Differences in composition and age of the continental crust can lead to characteristic radiogenic isotopic signatures in individual drainage basins. These signatures are transported and preserved in the SPM through weathering and depositional cycles and can be used to distinguish between material from different tributaries feeding into a larger river that finally drains into the ocean.

To characterize the modern Río de la Plata system and its drainage network across Brazil, Uruguay, Argentina and Bolivia, we analysed the Sr, Nd and Pb isotopic signatures in river SPM. Each main tributary (i.e. Upper Paraná, Uruguay, Salado, Pilcomayo and Bermejo) is characterized by a specific isotopic signature inherited from the lithological units in the respective drainage area (e.g. the Andes in the western sector of the basin or the Río de la Plata Craton in the south eastern sector of the basin). The SPM gets transported into the Río de la Plata and eventually reaches the shelf and slope off south eastern South America. Marine sediment core GeoB6212-1 was collected from the slope off South Brazil and records the last 30,000 years of the Río de la Plata discharge history. To study the potential impact of environmental changes and changes in the weathering/transport conditions in the different principal drainage areas, we report the same isotopic systems for the terrigenous fraction of GeoB6212-1. All three isotopic systems show variations with depth/time. The three most distinctive shifts occurred during the Younger Dryas (YD), Heinrich Stadial 1 (HS1) and at the onset of the Holocene. The shifts during the YD and HS1 indicate a higher input of Andean material, suggesting that the western part of the La Plata drainage basin (i.e. the Andes) was wetter and received more precipitation during these time intervals. The cause of the shift recorded at the onset of the Holocene is still under investigation. So far, two possibilities are considered: either an external input from material from southern Argentina along the shelf to the core site or more input (e.g. wetter conditions) from the southeastern sector (i.e. Uruguay River) of the La Plata drainage basin.

Session 5.4: Lacustrine and marine sediments as environmental archives.: Talk

Session 5.4: Lacustrine and marine sediments as environmental archives.: Talk
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Comparing source-to-sink environmental signals on- and offshore eastern South Africa

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Content

A common uncertainty working with marine sedimentary archives is the origin of the terrestrial component and its environmental significance. The proximity to a river mouth is often the only clue for determination of the source. In regions with strong ocean currents, however, such assumptions might lead to considerable misinterpretations. To investigate the sourcing of various signal carriers in a region with strong sediment redistribution we have performed a source-to-sink study comparing pollen, plant lipids, rock fragments and heavy minerals as well as bulk inorganic geochemical composition for southeastern Africa. Riverine samples and marine surface sediments were collected along the South African East coast and as far north as the Limpopo River in southern Mozambique. Onshore the proxy-indicators reflect small-scale diversity in sampling locations and associated environments (riverbank sediments, flood deposits, suspension loads, soils). Nevertheless, their overall trends reflect the environmental gradients along the SW to NE transect. The elemental and mineralogical compositions indicate changes in the catchment geology with a dominance of the sedimentary rocks of the Cape and Karoo Supergroups in the south and metamorphic and igneous rocks of the Kaapvaal Craton in the north. Plant wax $\delta^{13}\text{C}$ composition and pollen assemblages parallel the gradient from Mediterranean and mountain shrubland (C3) vegetation in the Cape and Drakensberg regions towards a mixed C4/C3 signal further north in the subtropical grasslands/savannas. Plant wax δD signatures indicate increasing rainfall amounts towards the north. In offshore samples, the sedimentological, mineralogical, geochemical, and palynological fingerprint from the terrestrial environment remains detectable despite the influence of the strong Agulhas Current. We note a general comparability of the studied parameters between the continent and marine sediments regardless of their specific differences in transport and depositional characteristics. . We propose that the influence of the geostrophic Agulhas Current affects sediment deposition and distribution only outward of the mid-shelf and that pockets of sediment remain preserved in the lee of coastal offsets where they are protected from erosion. This study provides the essential prerequisite to allow the attribution of temporal variations of compositional changes in marine sediment cores to environmental changes in eastern South Africa.

Effects of Holocene Sea-Level Changes in Tropical Southwest Sri Lanka

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Content

Sri Lanka is a tectonically stable platform in the central Indian Ocean, and hence is an ideal location for studying relative sea-level during the Holocene. Southwest of Sri Lanka consists of sinuously braided brackish fluvial system flanked by mangrove swamps. Organic constituents were investigated using sedimentary cores from these coastal aquatic systems. Elemental and molecular compositions of sediments were determined using C,N,S elemental analysis and gas chromatography-mass spectrometry, respectively. Chronology of events was determined using accelerated mass spectrometry (AMS) ¹⁴C data for bulk OM, wood and mollusk shells. The history southwest continental shelf of Sri Lanka can be divided into two major chrono-stratigraphic divisions that are quasi-steady state (from ca. 7.5 ky B.P. to 2.5 ky B.P.) and non-steady state (from ca. 2.5 ky B.P. to the Recent). The lower part of the sediment sequence had moderate productivity, and was mainly deposited under marine-terrestrial influence, in oxygen-poor/anoxic conditions during mid-Holocene sea-level highstands. Major environmental change at ca. 2.5 ky B.P. is characterized by increased total organic carbon contents, with accumulation of reworked terrestrial OM and aquatic plants in a semi-enclosed lake system after the sea-level regression. The mid-Holocene regression changed the geomorphology of the brackish fluvial systems from a bay/river-mouth setting to a semi-enclosed brackish estuary. Increase in higher plant organic matter with higher n-C₂₉/n-C₃₁ and n-C₃₇/n-C₃₉ alkane ratios suggest a climatic transition from wetter to dryer after the middle Holocene. Finally, the Holocene sea-level reconstructions were used to understand development of coastal landforms in southwest Sri Lanka. The lower sedimentary succession (Facies 2) can probably indicate the time of mid-Holocene highstands. It is followed by expansion of beach ridges and headlands since marine transgression. The upper sedimentary succession (Facies 1) can probably suggest semi-closed or closed brackish to terrestrial systems after the mid-Holocene highstands.

Implications of lake level variations at Lake Nam Co, Tibetan Plateau, from the 2016 ICDP pre-site seismic survey

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Content

Nam Co is a 100 m deep and hydrologically closed lake on the central Tibetan Plateau located at the intersection of westerly and monsoonal air masses. This makes the sediments of Nam Co an outstanding high-resolution archive, useful to decipher the timing and the influences of atmospheric circulation changes and past climate variations. Residues of elevated lake terraces imply that the lake already exists for more than 115 kyrs [1]. Potentially, Nam Co was part of an ancient mega-lake [2], which connected several modern lakes and covered huge extents of the Tibetan Plateau.

In order to understand the tectonic and depositional environment of Nam Co during glacial and interglacial periods, multichannel seismic surveys in 2014 and 2016 were jointly realized by the *Institute of Tibetan Plateau Research* and the Universities of *Jena* and *Bremen*. After the 2016 survey, we identified basement reflectors for the first time. They are close to the northern shore of the lake and dip steeply towards the center. Being surrounded by strike-slip suture zones the development of Nam Co as a pull-apart basin appears likely. In the seismic data we detected a narrowly spaced pattern of normal and reverse faults. These faults have been active from MIS 5 to early Holocene times in a transpressional setting.

Today, Nam Co is situated in close proximity to the Nyainquentanglha mountain range in the southeast and a chain of hills towards the northeast. According to this morphology, in a mega-lake scenario with a lake level 150 m higher than today, Nam Co would have expanded mainly towards the flatlands in the south- and northwest.

Therefore, seismic indications of a deep-lake facies deposited throughout the modern western extent of Nam Co would support the mega-lake hypotheses. We propose mega-lake sediments to consist of silt and clay sized material homogeneously deposited at 150 to 250 m water depths. Hence, acoustically transparent layers, depositional symmetries and parallel reflection configurations will indicate the presence of these draped sediments. The detection of mega-lake sediments at the flanks of the current basin will suggest deep waters and hence larger lake extension.

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Provenance of modern sands in the Limpopo River system and Maputo Bay

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Content

Shore-based provenance studies in the Limpopo catchment coupled with a detailed study of the composition of sediments collected in the Maputo Bay during the R/V METEOR expedition M123 are presented to study the route of sediments delivered by different rivers to the Indian Ocean. Different bulk methods and single grain methods were applied coupling classical and innovative methods. A quartered fraction of each sample was prepared as a standard thin section and analysed by counting 400 points under the microscope (Gazzi-Dickinson method). Heavy minerals were separated from the 15-500 micron sieved fraction. A particular emphasis was given on the calculated volume percentage of total (HMC) and transparent heavy minerals (tHMC). An appropriate amount of the heavy fraction was analyzed under a polarizing microscope; 200 to 250 transparent heavy minerals were point-counted at a suitable regular spacing of 100 micron to obtain real volume percentages. During point counting we also studied surface textures on detrital grains under the polarizing microscope to estimate the degree of chemical etching. A second split of heavy minerals were mounted on a slide without bonding resin and was checked and properly identified by Raman point-counting by an inVia Renishaw Raman spectrometer equipped with a green laser 532 nm. The introduction of Raman spectroscopy allow us to confidently identify varieties in the enstatite-hypersthene solid solution and to quantify the amount of augite, diopside, and pigeonite. Sediments carried by the Limpopo River are feldspar-rich feldspatho-quartzose with mafic volcanic and metamorphic rock fragments. Biotite occurs and moderately rich to rich heavy-mineral assemblages include dominant clinopyroxene, amphibole, epidote, and minor garnet and hypersthene. Its right-bank Olifants tributary also carries feldspar-rich feldspatho-quartzose sediments, with a few mafic igneous rock fragments and rich heavy-mineral assemblages dominated by clinopyroxene and hypersthene associated with amphibole and minor epidote. Offshore sediments in Maputo Bay mirror the feldspar-rich feldspatho-quartzose composition of Limpopo sand downstream of the Olifants confluence. Heavy-mineral assemblages, ranging from moderately poor to rich, include amphibole, epidote, clinopyroxene, and hypersthene. The compositional fingerprint of sediments deposited in Maputo Bay indicates the major but by no means exclusive contribution from the Limpopo River system.

Session 6.1: Cosmochemistry/Planetology/Asteroidal processes: Poster

Session 6.1: Cosmochemistry/Planetology/Asteroidal processes: Poster
A-411

Quantification of intergranular quartz films in the thermal aureole of the Sudbury Igneous Complex (Canada) using SAGA GIS image analysis

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Content

The 1.85 Ga Sudbury Igneous Complex is the crystallized relic of the largest impact melt sheet known on Earth. The SIC and its thermal aureole are the only lithological units on Earth allowing one to study the post-impact dynamics between an initially superheated impact melt sheet and its target rocks. The so-called Granite Breccia, an approximately 50 m thick heterolithic breccia, lines the contact with the SIC and is the most conspicuous lithological unit of the aureole. The Breccia consists of target rock fragments enveloped by a felsic igneous matrix. In order to better understand the formation and dynamics of the Granite Breccia, we quantified the area occupied by intergranular quartz in the Breccia. This quartz phase is interpreted to have crystallized from residual melt of partially melted target rock.

Quartz films were analysed in selected thin sections viewed under polarized light using a semi-automatic image segmentation workflow. The workflow is based on an automated seeded region growing algorithm capable of including a variance analysis of five or more RGB images. The workflow is implemented in the open-source Geographic Information System (GIS) software SAGA (System for Automated Geoscientific Analyses) developed by one of us (O.C.). Polygonization of the grain fabric is based on spectral information of individual mineral phases and optically distinguishes quartz from other mineral phases, such as feldspars and mafic mineral phases. This allows us to obtain quantitative information on quartz films regarding its surface area, geometry, connectivity and shared contacts with other mineral phases.

Image analysis indicates that quartz films form highly irregular shapes of single crystals, pointing to a large intercrystalline connectivity. Moreover, quartz fills space between skeletal feldspar and shares about 80% of its boundaries with what appears to be primary, i.e., more globular, quartz. These observations corroborate the interpretation that quartz films formed from a residual melt. The fraction of solidified melt amounts to nearly 25 vol%. Collectively, these microstructural characteristics suggest that upon formation, the Granite Breccia must have experienced a considerable reduction in shear strength. This accounts well for the diapiric character of Granite Breccia bodies found in the Sudbury Igneous Complex.

Target rock mobilization at the contact with the superheated impact melt sheet of the Sudbury impact structure, Canada

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Content

The 1.85 Ga Sudbury Igneous Complex (SIC) is the crystallized relic of the largest impact melt sheet known on Earth. The SIC and its thermal aureole are the only lithological units on Earth allowing one to study the post-impact dynamics between an initially superheated impact melt sheet and its target rocks. The so-called Granite Breccia, an approximately 50 m thick heterolithic breccia, lines the contact with the SIC and is the most conspicuous lithological unit of the aureole. The Breccia consists chiefly of rounded gneissic and mafic (amphibolitic) target rock fragments enveloped by a felsic igneous matrix. At the contact to the Granite Breccia, the SIC is made up of the so-called noritic Sublayer, in turn composed of target rock fragments and abundant sulfide droplets, collectively set in an igneous-textured mafic matrix. The Sublayer is overlain by a somewhat more felsic unit, known as the Felsic Norite, that is devoid of lithic fragments and sulfide inclusions. The formation of the Granite Breccia has been attributed to: (1) impact-induced brecciation, (2) intense contact metamorphism and partial melting of the immediate host rocks and (3) a combination of both.

Based on a detailed field-structural analysis, we examined the contact between the impact melt sheet and its host rock, consisting of Archean mafic and felsic gneiss as well as mafic intrusions. Apart from post-impact displacement of the contact, evident by hydrothermally altered faults, the contact is characterized by undulations on the meter to hundred meter-scale. We also observed a lithological gradation between the Sublayer and Granite Breccia. Most interestingly, however, is the occurrence of felsic melt pods in Granite Breccia that partially entrained impact breccia fragments and protruded into the overlying Sublayer. Mingling between the two melt phases indicates that both were viscous during protrusion. Based on the density contrast between the two, the felsic melt ascended into, and was emplaced as diapirs in, Sublayer. Although some structural characteristics of the Granite Breccia can be explained in terms of crater modification processes, our field observations suggest that much of the dynamics at the impact melt-host rock contact are due to thermal softening of target rocks imparted by the superheated impact melt sheet.

Session 6.1: Cosmochemistry/Planetology/Asteroidal processes: Talk

Session 6.1: Cosmochemistry/Planetology/Asteroidal processes: Talk
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Microstructural analysis of the thermal aureole of the Sudbury impact melt sheet, Canada: Implications for the formation of the Footwall Breccia

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Content

The 1.85 Ga Sudbury Igneous Complex (SIC), a crystallized impact melt sheet, and its thermal aureole are the only accessible rock units on Earth allowing us to study the metamorphic and deformational processes between a large impact melt sheet and adjacent target rocks. The Footwall Breccia, an approximately 50 m wide heterolithic breccia, comprised of target rock fragments within a magmatic, dioritic to granitic matrix lining the contact with the SIC, is the most prominent lithology of the aureole. Although the Breccia has been studied for more than 30 years, there is no consensus regarding its origin. Processes of formation include: (1) impact-induced brecciation, (2) intense contact metamorphism and partial melting of the immediate host rocks and (3) a combination of both. Based on a detailed microstructural analysis of Footwall Breccia and adjacent host rocks, sampled in the eastern part of the SIC, we shed light on this controversial topic. Granitic host rocks exposed within a distance of 800 m from the base of the SIC display quartz grains, the size of which decreases toward the SIC and give rise to foam-structured aggregates close to the melt sheet. A 100 m wide transition zone marks the interface between Footwall Breccia and more distal host rocks. This zone is defined by the pervasive occurrence of equigranular quartz and feldspar aggregates, the latter of which displaying interlobate and amoeboid grain boundaries consistent with static recrystallization at temperatures exceeding 850°C. The contact of the transition zone with the Footwall Breccia is characterized by poikilitic textures of strain-free quartz oikocrysts surrounding euhedral to subhedral feldspar. Similar poikilitic textures surrounding recrystallized quartz and feldspar fragments dominate the matrix of adjacent Footwall Breccia.

Static recrystallization of quartz provides evidence for pervasive contact metamorphism in the host rocks and indicates that the thermal aureole experienced temperatures exceeding 300 °C at a distance of up to 800 m from the base of the impact melt sheet. The poikilitic textures within the transition zone and the Footwall Breccia are interpreted as crystallized melt derived from host rocks close to the SIC supporting a magmatic origin of the Footwall Breccia. Based on microstructural analysis, we advocate an origin for the Footwall Breccia entailing host-rock fragmentation induced by thermal stresses imparted by the impact melt sheet.

Mineralogical Chondrule Zonation in Ordinary Chondrites

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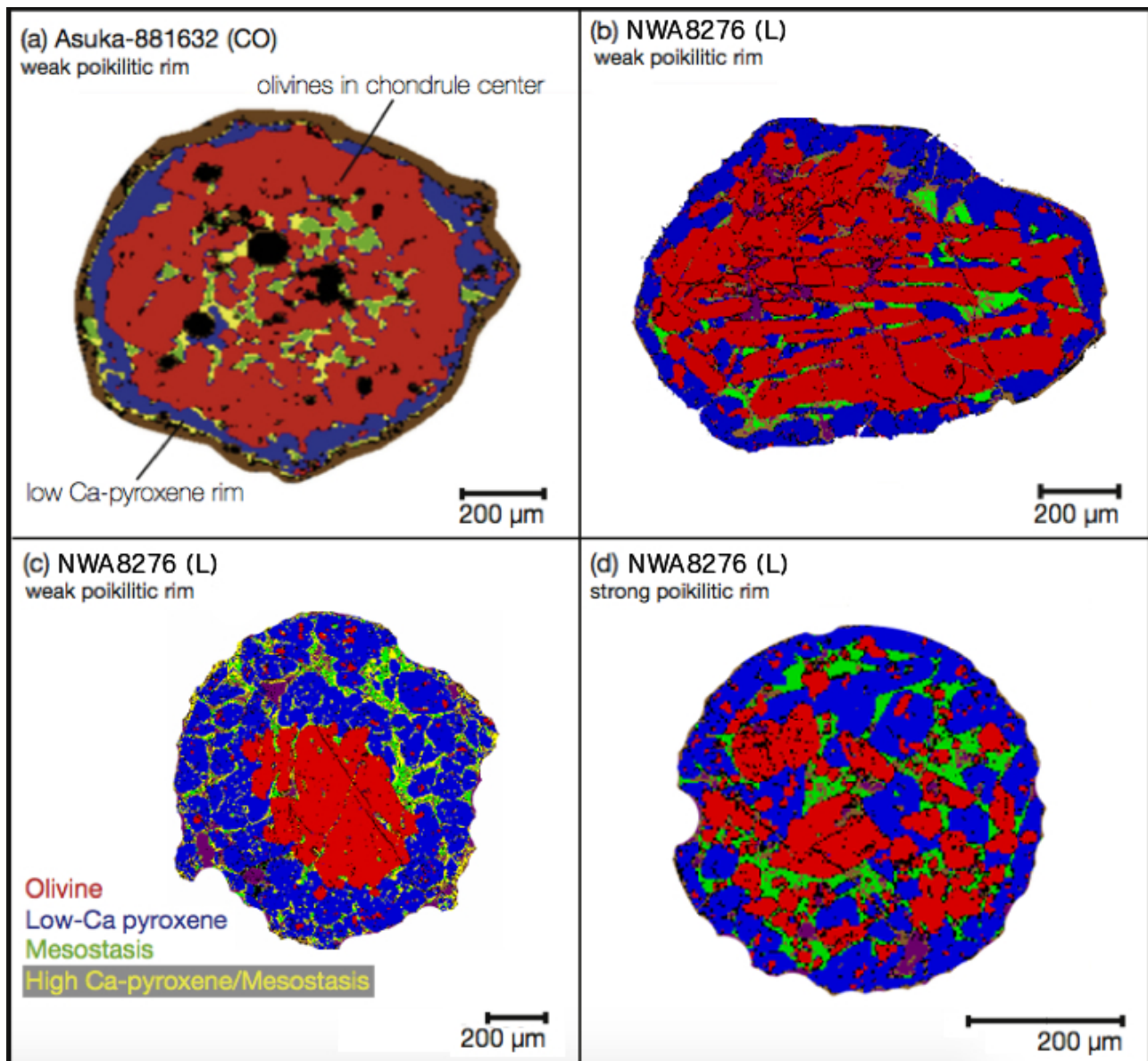
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Content

Introduction: The majority of chondrules in carbonaceous and Rumuruti chondrites is mineralogically zoned [1]. These chondrules consist of an olivine core, surrounded by a low-Ca pyroxene rim. In this study we examine the appearance, abundance and distribution of mineralogically zoned chondrules in several ordinary (H, L, LL) chondrites.

Methods: Chondrule zonation and mineral compositions were investigated with an electron microprobe by spot analyses and element mapping. Phase maps were created from the elemental distribution of Mg and Si. They can be used to identify olivine, pyroxene and mesostasis, as well as structural properties e.g. thickness, abundance and distribution of rims.

Results: In our preliminary survey we studied 230 chondrules in 5 different ordinary chondrites of petrological type 3 (Suwahib, Willard b, Huacachina, Parnallee 38, NWA 8276). Preliminary results show that, in a conservative count, ~35% of the studied chondrules are zoned. They feature weak to strong poikilitic, low-Ca pyroxene rims that surround or enclose the olivine (Fig. 1).



Examples for mineralogically zoned chondrules in (a) CO [1] and (b, c, d) L-chondrites with weak to strong poikilitic, low-Ca pyroxene rims.

Discussion: Zoned chondrules are a typical chondrule type in ordinary chondrites. They are, however, less abundant compared to carbonaceous and Rumuruti chondrites (~75%, [1]). Several chondrules do not show any zonation. Some of these might be rim-sections, in which case they would add to the zoned chondrules count.

Conclusions: Mineralogical zonation introduces fundamental constraints on chondrule formation conditions. The low-Ca pyroxene rim formed by substantial interaction with the surrounding gas when material was exchanged and chondrules acted as an open system [1]. The reaction was SiO rich gas, plus chondrule olivine, forming pyroxene [2]. The remaining gas could then have condensed into the matrix. The open system scenario is in agreement with previous studies on chondrule formation, as well as chondrule matrix complementarity, and suggests a common chemical reservoir of chondrules and matrix (e.g. [1], [3], [4]).

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Mixing and transport of solids in the circumsolar disk as inferred from Ti isotope anomalies in planetary materials

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Content

Nucleosynthetic isotope anomalies found in meteorites and their components are an exciting new tool for tracing genetic relations among planetary materials, and currently are revolutionizing our understanding of the dynamic evolution of our solar system. Here we use Ti isotope variations of individual chondrules of enstatite chondrites, ordinary chondrites, and carbonaceous chondrites together with bulk meteorite and CAI data to investigate mass-transport in the solar nebula and its bearing on the bulk chemistry of planetary bodies [1]. We find that chondrules from ECs and OCs show only small ^{50}Ti variations and scatter closely around the ^{50}Ti composition of their host chondrites while chondrules from CCs have highly variable ^{50}Ti compositions. The ^{50}Ti variations in the CC chondrules can be attributed to the addition of isotopically heterogeneous CAI-like material to EC and OC-like chondrule precursors. Our data demonstrate that isotopic variations among CC chondrules do not require formation over a wide range of orbital distances, but can instead be fully accounted for by the incorporation of isotopically anomalous “nuggets” into chondrule precursors. As such, the data obviate the need for disk-wide transport of chondrules prior to chondrite parent body accretion and are consistent with formation of chondrules from a given chondrite group in localized regions of the disk. The ubiquitous presence of ^{50}Ti -enriched material in carbonaceous chondrites and the lack of this material in the non-carbonaceous chondrites support the idea that these two meteorite groups derive from areas of the disk that remained isolated from each other, probably through the formation of Jupiter [2]. The addition of CAI-like refractory material to the CC reservoir could explain the relative enrichment of refractory elements in CCs relative to OCs, ECs, Earth and Mars. Our study thus questions the assumed primitive composition of CI chondrites and supports models invoking transport of CAI-like material above the disk.

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Structural evidence for long-term crater modification of the Sudbury Impact Structure, Canada

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Content

An outstanding problem of comprehending large-impact cratering concerns long-term crater modification caused by viscous relaxation of crust after cratering. Long-term crater modification occurs on time scales of thousands of years and is most evident by isostatically-driven crater-floor uplift caused by (1) mass removal during excavation, (2) re-equilibration of the Moho, (3) lower crustal flow toward the crater center, or (4) a combination of these processes. To date, information on this process has been obtained only by remote sensing of rocky planets and their satellites, excluding Earth. These observations suggest that long-term crater modification leads to distinct fracture patterns in large craters pointing to horizontal extension.

The Sudbury impact structure hosts an initially horizontal, thick impact melt sheet. Structures associated with cooling and solidification of the sheet, which lasted more than ten thousand years, make the impact structure an ideal target for analysing long-term crater modification. We, therefore, conducted an orientation analysis of granitoid dikes in the solidified melt sheet that are interpreted as back-injections of remobilised target rock. We also analysed mineral shape fabric geometry of the melt sheet to test the hypothesis of horizontal extension during solidification of the melt sheet.

Taking into account back rotation of the melt sheet, required due to post-impact deformation, we found that one population of granite dikes is disposed radially with respect to the center of the melt sheet. Host rocks of these dikes display abundant magmatic fabrics. By contrast, a second population of granite dikes is mostly oriented concordant to the base of the melt sheet. However, host rocks of these dikes display moderately strong metamorphic foliations that are concordant to dike margins, pointing to contact strain. Unlike the first, this population of dikes underwent viscous deformation and, thus, appears to have been rotated, possibly from initial radial orientations, by post-impact deformation. Igneous foliations, although weakly developed, are mostly concordant to the melt sheet contacts. Collectively, the orientations of dikes and planar magmatic fabrics amount to vertical thinning and horizontal extension of the melt sheet. This deformation occurred during cooling and solidification of the sheet and provides the first structural evidence for long-term relaxation of crust underlying the Sudbury impact structure.

Using the ChondriteDB database to determine the number of parental reservoirs for chondrules of individual chondrites.

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Content

Introduction: Chondrules and matrix are the volumetrically most abundant (>95 vol.%) components in chondritic meteorites (chondrites) and considered the most primitive building blocks of the planets. Although many conditions of chondrule formation are known, the actual process producing chondrules remains enigmatic. Chondrule formation is a pivotal process in the early solar system, and understanding would provide deep insights how the protoplanetary disk was structured, formed and evolved. Several models for chondrule formation have been suggested, with a fundamental difference between these: (i) one set of models suggests chondrules from each chondrite formed in only a single parental reservoir (e.g. Bland et al., 2005; Hezel & Palme, 2008,2010; Palme et al., 2015; Ebel et al., 2016). (ii) A second set of models requires multiple reservoirs in which chondrules formed and later mixed into the chondrite (e.g. Shu et al., 1996; Asphaug et al., 2011; van Kooten et al., 2016; Zanda et al., 2017).

A recent compilation of bulk chondrule compositions (Hezel et al., 2017) allows to study the distribution of chondrule compositions within and among individual chondrites. These observed distributions can be compared to modelled distributions. Such model distributions are calculated with the assumption that chondrules either originate from a single, or from multiple reservoirs. The results then allow to decide whether chondrules originate from a single or from multiple reservoirs, and, consequentially which models for chondrule formation can be supported, and which can be dismissed.

Method & Results: Compositional distributions of bulk chondrules in a single chondrite are modelled with a simple Monte Carlo simulation. Parameters were composition of reservoirs, number of parental reservoirs, mixing proportions of the reservoirs, etc. Hundreds of chondrule distributions were modelled covering a large parameter space. Almost none of the resulting models fit with the observed data sets from ChondriteDB.

Conclusions: The results indicate chondrule originated from a single reservoir. This finding supports all and only models not requiring multiple reservoirs for chondrules in a single chondrite.

References

Bland et al., 2005, PNAS; Hezel & Palme, 2008, EPSL; Hezel & Palme, 2010, EPSL; Hezel et al., 2017, CHEMER; Palme et al., 2015, EPSL; Ebel et al., 2016; GCA; Shu et al., 1996, Science; Asphaug et al., 2011, EPSL; van Kooten et al., 2016, PNAS; Zanda et al., 2017, abs.

Session 6.2: Earth interior - mantle and core.: Poster

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Effect of bulk composition and fO_2 on the $Fe^{3+}/\Sigma Fe$ ratio in basaltic and peridotitic majorites

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Content

We conducted Fe-saturated and Re-ReO₂ buffered high-pressure experiments in the multi-anvil apparatus at pressures of 14, 17 and 20 GPa and temperatures of 1600 and 1800 °C to quantify the effect of oxygen fugacity, pressure, temperature and majorite end-member composition on the incorporation of ferric iron in majorite in peridotitic and basaltic systems. $Fe^{3+}/\Sigma Fe$ ratios were analyzed using electron energy-loss spectroscopy (EELS) with an energy resolution of 0.75 to 0.85 eV, enabling us to determine $Fe^{3+}/\Sigma Fe$ ratios in peridotitic majorites with total Fe as low as 6 wt.%. $Fe^{3+}/\Sigma Fe$ varies between 0.09(3) and 0.47(5). Above 14 GPa $Fe^{3+}/\Sigma Fe$ shows little to no variation with pressure but is strongly dependent on bulk composition. Peridotitic majorites, with higher Mg and lower Al compared to basaltic (Na-bearing) majorites, have higher $Fe^{3+}/\Sigma Fe$ ratios. We found that majorite is relatively insensitive to large variations in fO_2 , although the difference between the Fe-saturated and Re-ReO₂ buffered conditions is ~5 log units. The new data will help to deduce the fO_2 structure of the mantle and the prevailing redox conditions of mantle xenoliths. Furthermore, the results are a step towards a comprehensive model for iron partitioning in the upper mantle.

Significance of compositional zoning in pyroxenes from spinel lherzolites and spinel websterites of Banovina ophiolite suite, Croatia

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Content

Spinel lherzolites and websterites of Banovina ophiolite suite (central Croatia) represent the NW end of the Central Dinaridic Ophiolite Belt. This belt is part of the Tethyan ophiolites that exhibit an age progression from Jurassic, in the western Alpine-Apennines to Cretaceous in the Tibetan-Himalayan belts to the east. To better understand the genesis of the ultramafic rocks of the tectonically dismembered Banovina ophiolite suite, we performed detailed petrographic and geochemical analyses of 4 spinel lherzolites and 1 spinel websterite. All samples have granular to porphyroclastic textures. The spinel lherzolites consist of olivine (Mg#core= 86.0-90.8; Mg#rim=87.0-91.0), clinopyroxene (Mg#core= 87.6-91.9; Mg#rim= 88.6-92.5), orthopyroxene (Mg#core= 85.8-90.84; Mg#rim= 85.8-91.2) and Mg-Al chromite to pleonaste. The websterite consists of clinopyroxene (Mg#core= 87.6; Mg#rim= 88.6-89.3), orthopyroxene (Mg#core= 86.6-87.9; Mg#rim= 85.9-88.0) and large pleonaste grains (up to 3.2 mm). Pyroxenes in both rock types occur either as large porphyroclasts (up to 10.4 mm) or as smaller grains in variably sized cataclastic to partially recrystallized matrix (~ 0.1-0.005 mm). The porphyroclasts exhibit different types of deformation textures, including kink banding and undulose extinction. Most contain extensive exsolution lamellae of complementary pyroxene. In orthopyroxene, Al and Ca contents decrease at the grain rims, whereas in clinopyroxene a rimward decrease in Al, but an increase in Ca is observed. Smaller, matrix pyroxenes are characterized by compositions similar to those of the rims of the larger grains. Textures, exsolution lamellae and documented chemical disequilibrium of pyroxenes reveal a sustained cooling of the mantle rocks during uplift. Geothermobarometric calculations [1, 2] suggest that the rocks were derived from < ~ 60 km depth, with pyroxene rim compositions recording temperatures of 800-900°C. These preliminary results are in accordance with data for spinel lherzolites from the neighboring Krivaja-Konjuh ophiolite suite in Bosnia, interpreted as a mantle column that experienced adiabatic ascent in a mid-ocean ridge environment [3].

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Session 6.2: Earth interior - mantle and core.: Talk

Session 6.2: Earth interior - mantle and core.: Talk

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The cause of ^{182}W anomalies in lunar and old terrestrial rocks

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Content

Small ^{182}W excesses have been reported for a number of Eoarchean terranes and some lunar rocks. These isotope anomalies have been explained by two competing models. In the late accretion model [e.g., 1] the excesses are explained by variable additions of late veneer components that exhibit chondritic ^{182}W abundances. In the early differentiation model [e.g., 2] the W isotope excesses are explained by early silicate differentiation within the first 60 Myrs after solar system formation, when the parent nuclide ^{182}Hf was not yet extinct. In support of the late accretion model, the small ^{182}W excesses in some lunar rocks were interpreted as preserving the composition of the silicate Earth prior to late accretion [e.g., 3].

In order to evaluate the validity of both models further, we measured W isotope compositions and the concentrations of W and other highly incompatible elements in distinct rock samples from Isua and lunar samples. Peridotites from the region south of Isua, that were previously identified as mantle rocks [4], exhibit small ^{182}W excesses of ca. +15 ppm [5], although their PGE patterns resemble those of modern peridotites and thus do not show any evidence for a missing late veneer [4]. Based on the element concentration measurements, it can be shown that W is substantially enriched in these rocks. The processes causing this enrichment are either by metasomatic processes or ancient subduction zone recycling. Hence, the ^{182}W excesses found are therefore inherited and cannot be easily combined with PGE patterns to estimate missing amounts of late accretion components.

A new high precision study on the highly incompatible element inventory of lunar rocks [6] reveals that the Hf/W ratio of the lunar mantle must be at least 10-20% higher than that of the present day terrestrial mantle. This new finding is in support of models explaining the ^{182}W excesses in lunar rocks via in situ radiogenic ingrowth at a higher lunar mantle Hf/W. As this must have occurred during when ^{182}Hf was still extant, formation of the Moon is likely to have occurred within <60 Myrs after solar system formation.

References

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An experimental approach to investigation of the partial melting of harzburgite in a reduced, methane-rich fluid environment

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Content

Observed redox heterogeneities, and metasomatism of deep mantle domains and subduction zones are often ascribed to enhanced fluid activity. This is due to the high redox potential and extreme mobility of fluids, which together allow for rapid transport and redistribution of redox-sensitive elements (e.g. C, H, O). Their presence and speciation profoundly influences partial melting processes, magma crystallization and can induce deformation (i.e. uplift). The fluid composition plays a critical role in such processes. At high-pressure conditions, oxidized CO₂-H₂O fluids are likely to be incorporated in wt% quantities by silicate melt, OH-bearing minerals and carbonate phases. In contrast, reduced CH₄-fluids appear to be more incompatible and have higher survival chances, making their existence highly interesting in terms of C-H-O-storage and recycling in the deep mantle environment. However, relatively little is known about the interaction of CH₄-rich fluids with mantle peridotite.

Our aim is to develop a reliable experimental approach that will permit the investigation of harzburgite/peridotite melting in highly reduced, CH₄-H₂-rich environments. A series of high-pressure experiments have been carried out in a belt-apparatus at 3 and 5 GPa in the temperature range of 1150-1300°C. The maintenance of reduced conditions ($f_{O_2} \sim \text{Fe-FeO}$) was achieved by applying a triple-capsule design with a gold outer capsule containing an olivine inner container with sample and an Au-capsule with a solid H₂-buffer assemblage. The fluid in the outer capsule was produced by the in situ breakdown of stearic acid at the onset of the experiment. This arrangement allowed production and maintenance of a high f_{CH_4} and f_{H_2} environment over 48 hours. An Ir-Fe- f_{O_2} sensor was employed to monitor the f_{O_2} in the sample container. In addition to preventing Fe-loss from the sample, the olivine container can serve as a trap for fluids and small-degree partial melts. Raman spectra of fluid inclusions confirm the dominance of CH₄, as well as the presence of other higher order hydrocarbons. Different redox buffers can be employed to vary the f_{H_2} of the fluid at conditions well below the "water maximum". Partial melting experiments on a natural harzburgite are being carried out to determine the composition of initial melts coexisting with methane-rich fluids.

Clinopyroxene as an indicator of mantle oxidation state: the influence of metasomatism on V/Sc ratios

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Content

Oxidation state influences many geochemical processes. For example, partial melting and the resulting magma composition are directly affected by the speciation of volatiles that are controlled by the prevailing the oxygen fugacity (fO_2). Oxidation state can also be modified through metasomatic interactions involving melts or fluids migrating through the mantle. Multi-valence trace elements such as V have been recently proposed as redox proxies, especially when normalised to a geochemically similar monivalent element [e.g. 1] In fact [1] suggested that V/Sc is insensitive to metasomatic interactions, allowing redox conditions during the last partial melting event to be probed. This opens a new avenue for determining oxidation state where, for mantle peridotite clinopyroxene (cpx) is a key player in this type of assessment.

We have studied the V, Sc and Ga concentrations in cpx from a suite of peridotite xenoliths from the French Massif Central for which oxidation states have previously been determined [2]. These xenoliths have experienced metasomatism to various degrees from one or more types of agent [3]. Cpx in weakly metasomatised samples contains 250-300 $\mu\text{g/g}$ V, yielding V/Sc = 4-5 and V/Ga = 60-100. In more strongly overprinted samples, V contents are much less: 180-240 $\mu\text{g/g}$. In some cases this depletion is accompanied by depletions in Sc and Ga so that their ratios are preserved. In other cases, Sc and Ga contents remain constant or may even increase, leading to lower V/Sc and V/Ga. This selective removal of V can be explained in terms of a shift in $DV_{\text{cpx/melt}}$ due to the metasomatic agent being more oxidized, causing V extraction from the host peridotite. The variable behavior of Sc and Ga (and other elements) is related to differing compositions of the metasomatic agents, most of which were significantly oxidising compared to ambient subcontinental lithospheric mantle [3]. Thus, our results indicate that V/Sc and V/Ga can be reset during metasomatism and should be used with caution as a redox proxy when working with strongly metasomatized peridotites.

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Evidence for an Earth-like Mo/W of the bulk-silicate Moon

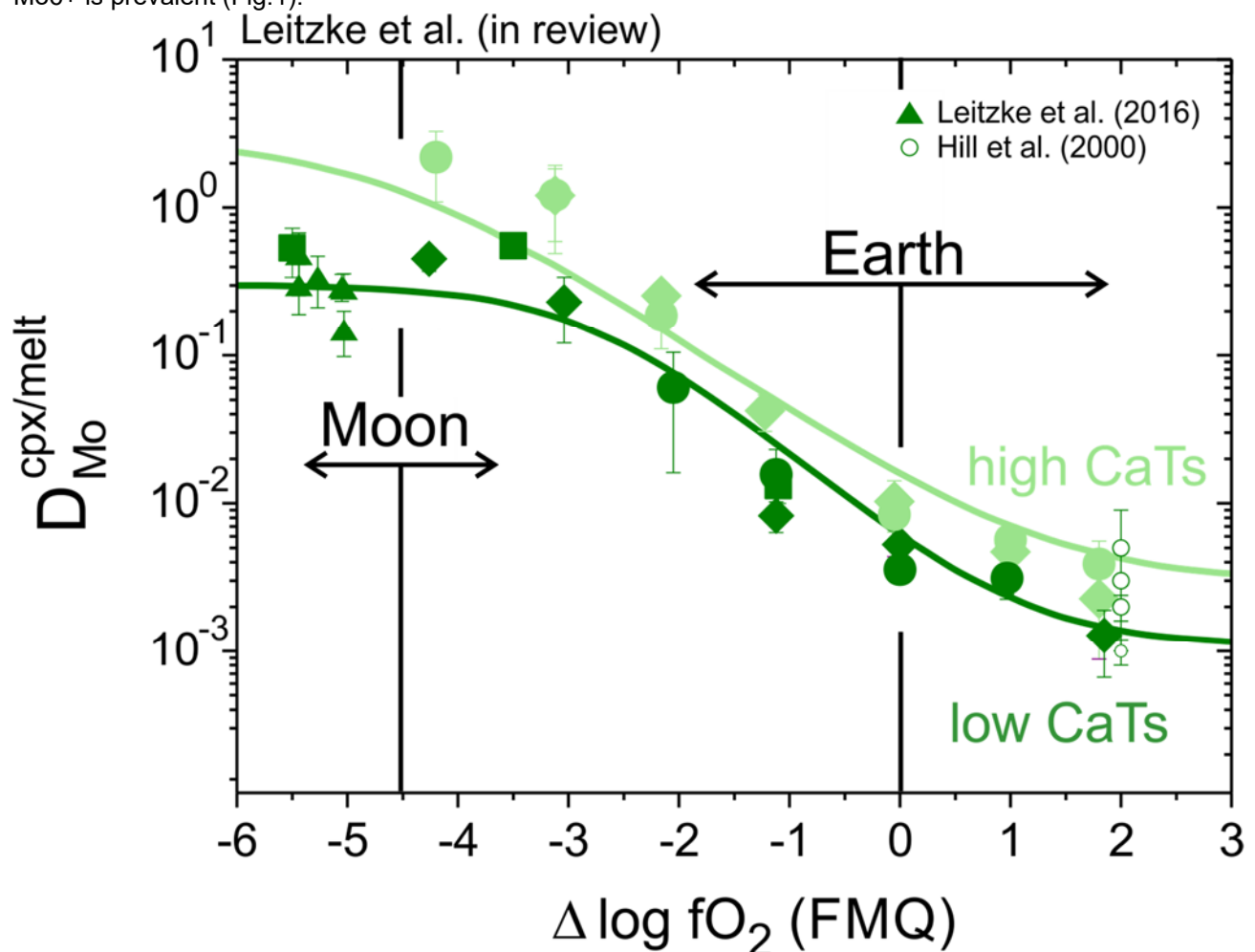
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Content

We have carried out an one-atmosphere experimental campaign that aimed to investigate changes in the partitioning behavior of Mo between silicates (pyroxenes, olivine and plagioclase) and silicate melt as a function of composition and oxygen fugacity. Redox conditions were imposed through the use of CO-CO₂ gas mixtures that cover a broad range of fO₂, ranging from the average expected for terrestrial mantle reservoirs (FMQ-1 to FMQ+2), as well as the extremely reduced conditions expected for the lunar mantle, at IW-0.5 and below.

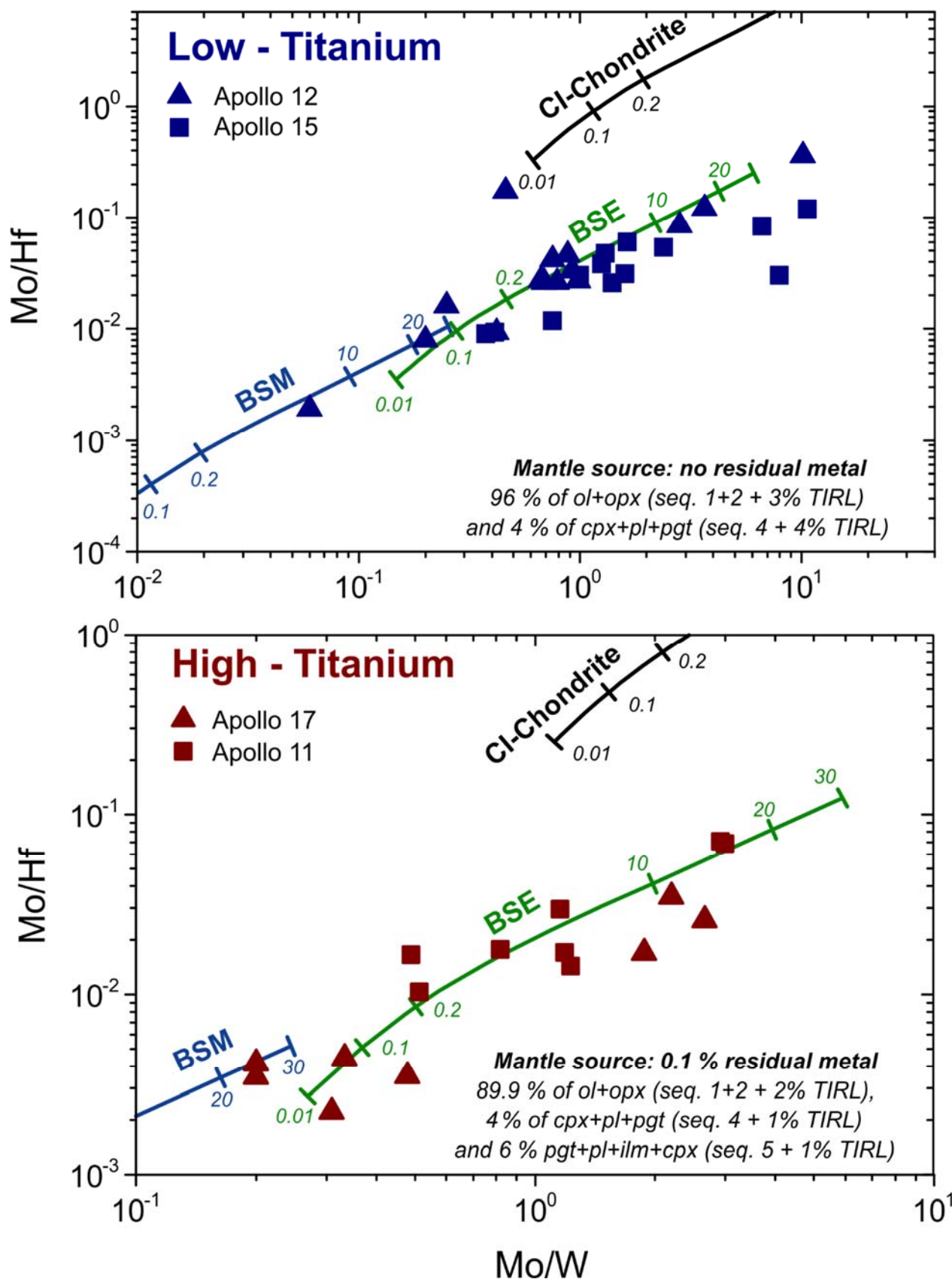
Our results show that Mo is volatile above FMQ and that its compatibility into pyroxene and olivine increases three orders of magnitude within the range of oxygen fugacities covered in this study. At fO₂ below the iron-wüstite reference redox equilibrium, Mo becomes exclusively tetravalent, while at fO₂ values above FMQ, Mo⁶⁺ is prevalent (Fig.1).



Partitioning behavior of Mo between clinopyroxene and lunar basaltic melt shown as a function of oxygen fugacity. The increase in $D_{\text{Mo}}^{\text{cpx/melt}}$ at reducing conditions is suggestive of a two-electron redox exchange from Mo⁶⁺ to Mo⁴⁺.

This indicates that during partial melting in the mantle of the Earth, Mo will be exclusively 6+ and highly incompatible during partial melting of the Earth's upper mantle. For the lunar mantle, however, which is thought to have equilibrated at lower oxygen fugacities, Mo occurs exclusively as 4+ and is less incompatible into olivine and pyroxene, due to its ionic radius being close to the ideal substitution into these crystals octahedral sites (0.65 Å).

Our partitioning data were then used to carry out partial melting models of mixed ultramafic cumulate lunar mantle sources. Our modeled results show evidence that the Mo/W ratio of the bulk silicate Moon may be identical to that of the Earth's bulk silicate reservoirs, in agreement with the hypothesis that the Moon was mainly derived from the Earth's mantle (Fig. 2).



Fractional melting models of a hybrid lunar mantle following the crystallization of the lunar magma ocean (LMO). Curves represent three possible bulk Moon compositions: 1) canonical bulk Moon (BSM), bulk silicate Earth (BSE) and CI-chondrite.

The effect of fO_2 on the crystal/silicate melt partitioning of Mo must be considered in any petrological model that attempts to precisely reproduce natural processes, such as mantle partial melting, mass-dependent Mo isotope fractionation and core formation.

First-principles prediction of element partitioning between melts

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Content

Element partitioning between different phases is an important geochemical process during Earth's accretion and differentiation. Element partition coefficients have been measured experimentally for many systems in a wide range of thermodynamic conditions. Frequently, results of these studies have been interpreted and parametrized using models based on crystal chemistry, e.g. the lattice strain model for mineral-melt partitioning of trace elements. Despite the fact that melts and fluids are present in many geological processes, their role in element partitioning is still poorly understood. A promising approach to quantify element partitioning involving at least one melt or fluid phase is to develop a thermodynamic model based on the local atomic structure of the partitioning element in the melt or fluid. Here, we present results of ab initio and classical molecular dynamics simulations in conjunction with the method of thermodynamic integration and explore the possibility to predict the partitioning of elements between different melts. Examples include studies of trace element partitioning between silicate melts [1] and of Ni partitioning between metal and silicate melts [2]. The predicted partition coefficients are at least in qualitative agreement with experiment. We will discuss the potential and remaining challenges of this new computational approach as well as the relation between partitioning behavior and the corresponding local atomic structure in the melt.

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In situ X-ray diffraction studies on tourmalines at high pressures and temperatures

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Content

Tourmaline is stable over a wide pressure-temperature (P - T) interval. Despite its potential for use as a geothermobarometer, experimental thermodynamic data for tourmaline minerals are very limited. Data describing the volumetric behaviour of tourmalines at elevated temperature and pressure are almost not available.

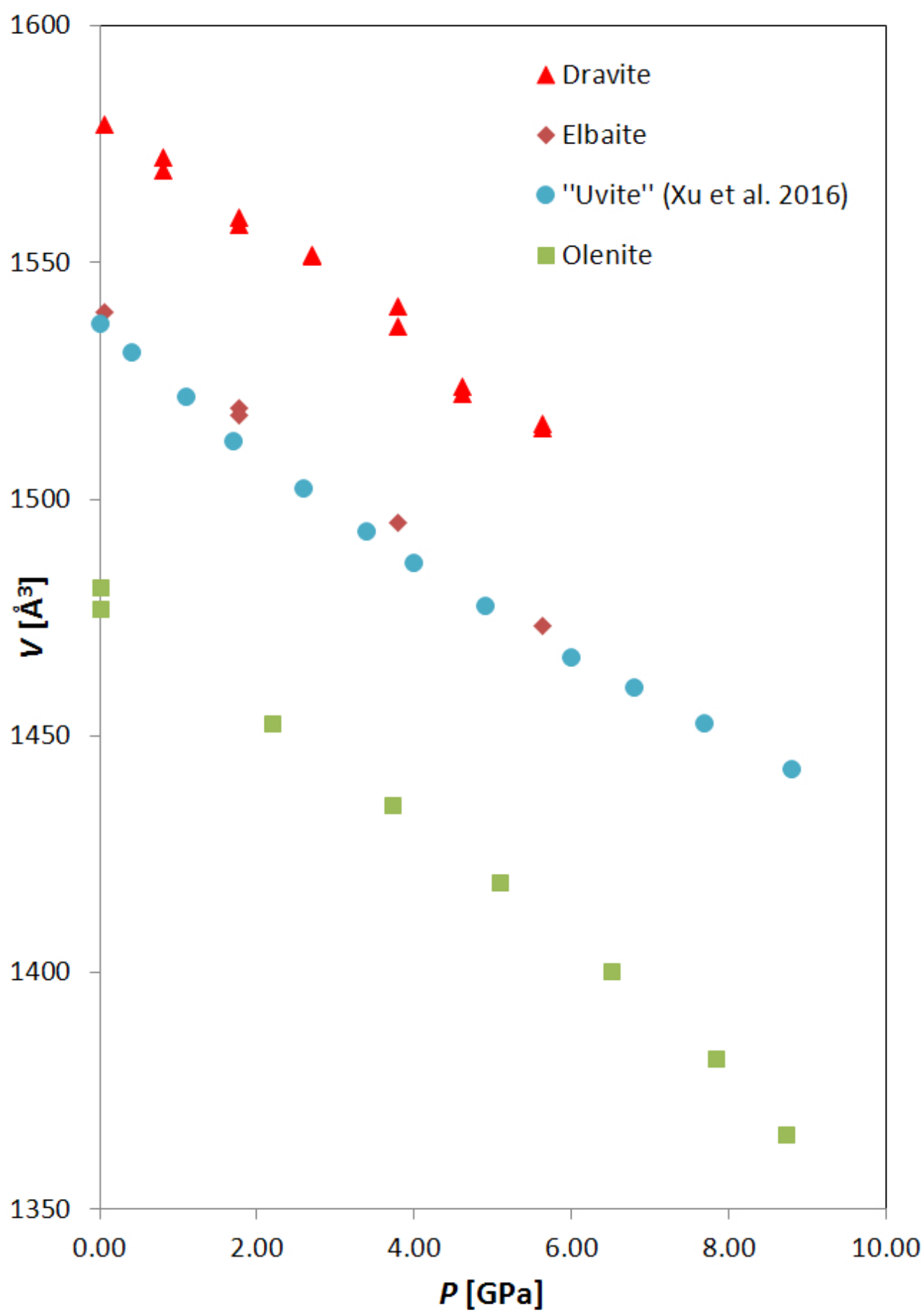
In this study, the P - V - T behaviour of synthetic Al-rich (olenitic) tourmaline was investigated. Additionally, the bulk moduli of two natural samples, a blue dravite from Koksha Valley, Afghanistan and the elbaitic rim of a colour-zoned tourmaline crystal (sample HIM5) from the Himalaya Mine, California are reported.

The volumetric behaviour of all samples has been determined by in situ X-ray diffraction up to 8.5 GPa and 700°C for olenite respectively 5.5 GPa for the natural samples using a MAX 80 cubic anvil high-pressure apparatus (DESY, HASYLAB, Hamburg, Doris III, Beamline F.2.1). The powdered samples were mixed with Vaseline as pressure medium to ensure hydrostatic pressure transmitting conditions. NaCl served as a diffraction standard to define the pressure. Energy dispersive diffraction patterns were collected at a fixed 2θ angle ($\theta \approx 3.67^\circ$).

By fitting a third-order Birch-Murnaghan EOS to the data, the bulk modulus of olenite was determined as 91.18 ± 4.84 GPa, ($K' = 4$), $V_{T,0} = (1484.93 \pm 3.79) \text{ \AA}^3 \exp [J(0.137 \pm 0.090) \times 10^{-4} dT]$, $(\partial K_T / \partial T)_P = 0.023 \pm 0.017 \text{ GPa K}^{-1}$. The fit is improved if K' is taken as a variable, but results in a negative value for K' which suggests the olenite might be heading for a structural phase transition.

The bulk moduli of dravite and elbaite were determined as 119.5 ± 4.8 GPa, respectively 115.7 ± 2.6 GPa, ($K' = 4$).

Recently, Xu et al. (2016) [1] conducted in situ X-ray diffraction experiments on a natural tourmaline sample by using an externally heated diamond anvil cell up to 18 GPa and 450 °C. Based on electron microprobe analyses, they stated this tourmaline sample to be uvite-dominated. In contrast, they indexed their spectra following JCPDS card 71-0716, which belongs to an elbaite-dominated tourmaline with significantly smaller cell parameters. Their reported volumes are very similar to the elbaite volumes obtained in this study.



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New hp-phases of Fe-Mg spinels: Implications for the formation and uplift history of inclusions in diamonds

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Content

Mineral inclusions in diamond provide a unique opportunity to investigate material from the Earth's deep interior and can be indicators for pressure, temperature and redox conditions at time of entrapment. For instance, magnesioferrite (MgFe_2O_4) was reported to occur in (Mg,Fe)O inclusions in diamond [1,2,3]. Based on the experimental study by [4] MgFe_2O_4 can either directly exsolve from (Mg,Fe)O at upper mantle conditions or originate from precursor phases at conditions of the deep upper mantle and transition zone. Since this magnesioferrite [1,2,3] is actually a FeFe_2O_4 - MgFe_2O_4 solid solution, our study was aimed to investigate the phase relations of $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ to place more reliable constraints on the origin of this phase associated with diamond formation. Multi-anvil experiments were conducted between 9-23 GPa and 900-1600 °C using $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Fe}^{3+}_2\text{O}_4$. Run products were analysed by EPMA, XRD and TEM. Our results demonstrate a breakdown of $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ to (Mg,Fe) Fe_2O_5 + Fe_2O_3 at 10-11 GPa and 1000-1600 °C. At 15-16 GPa and <1350 °C this assemblage reconstitutes to hp- $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$. At higher T a new assemblage of (Mg,Fe) $_3\text{Fe}_4\text{O}_9$ + Fe_2O_3 becomes stable.

Thus, this study highlights that the spinel-structured phase is only stable at upper mantle conditions and that no direct transformation from a hp-polymorph is possible. In addition, other novel Mg-Fe oxides that become stable at higher pressures [e.g., (Mg,Fe) $_3\text{Fe}_4\text{O}_9$; (Mg,Fe) $_2\text{Fe}_2\text{O}_5$] need to be considered when interpreting the formation and uplift history of diamonds and their inclusions.

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Rapid decrease in the oxygen-vacancy substitution in aluminous bridgmanite with pressure

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Content

The solubility of the $\text{MgAlO}_{2.5}$ component in bridgmanite was determined at pressures of 27, 35 and 40 GPa and a temperature of 2000 K by means of an ultrahigh-pressure multi-anvil press. Compositional analysis of recovered samples showed that the $\text{MgAlO}_{2.5}$ component decreases with increasing pressure, and becomes virtually zero at 40 GPa. Above this pressure, the oxygen-vacancy substitution becomes negligible, and Al is incorporated in bridgmanite by the charge-coupled substitution mechanism only. The present experimental results are supported by the volume change associated with the change from the oxygen-vacancy substitution to charge-coupled substitution. Although bridgmanite is expected to host water and argon in the lower mantle by trapping them in oxygen vacancies, such capabilities will rapidly decrease with depths and disappear in regions deeper than 1000 km.

The effect of sulfur on the partitioning behaviour of moderately siderophile elements

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Content

Siderophile elements provide important constraints on processes involving metal-silicate equilibration such as the formation of Earth's core. Among these are the moderately siderophile elements (MSEs) which include Co, Ni, W and Mo. Core-mantle partitioning of MSEs depends largely on P - T - fO_2 conditions, but also on the compositions of the phases involved. Sulfur is regarded as one of the light elements in the core and may have a significant effect on the partitioning behaviour of siderophile elements during core formation: The presence of S may change the metal-silicate partitioning behaviour of MSEs and may also lead to the removal of a FeS sulfide melt to the Earth's core, which would affect those MSEs that are also chalcophile (e.g. Co and Ni).

We experimentally studied the effect of S on the metal-silicate partitioning of Co, Ni, W and Mo at 11 GPa and 2350 °C. In addition, the P - T dependence of sulfide-silicate partitioning of these MSEs was investigated at 2000-2400 °C and 7-21 GPa. We equilibrated a molten peridotite with a range of compositions along the Fe-FeS binary (0 - 36 wt. % S), doped with the MSEs at the 1 wt. % level using single crystal MgO-capsules. Quenched silicate and metal or sulfide phases were analysed by electron microprobe for their major element concentrations while trace element abundances were determined by LA-ICPMS.

Overall, the metal-silicate exchange coefficient (K_D) for Ni remains constant with increasing S-content of the metal, whereas those of Co, W and Mo decrease. A continuous trend can be observed for Ni and Co up to ~36 wt.% S (stoichiometric FeS sulfide). In contrast, the linear decrease in K_D with increasing S concentration for Mo and W only continues until the eutectic composition in the Fe-FeS system ($X_S \approx 0.35$ at 11 GPa) and a distinct decrease in K_D is observed for more S-rich compositions. These results underline the importance of verifying whether linear trends can be used for the complete range of compositions along the Fe-FeS binary, or if FeS sulfide-silicate partitioning needs to be determined individually.

Our sulfide-silicate partitioning experiments show that Co and Ni behave as chalcophile elements, while Mo and W do not tend to partition into sulfide liquids. As expected, W shows the strongest S-avoidance of the elements studied. Therefore, segregation of a sulfide melt to the core is expected to influence mantle abundances of Ni, Co and to a lesser extent Mo, whereas W will remain largely unaffected.

The effect of water on the fluorine and chlorine partitioning behavior between olivine and silicate melt

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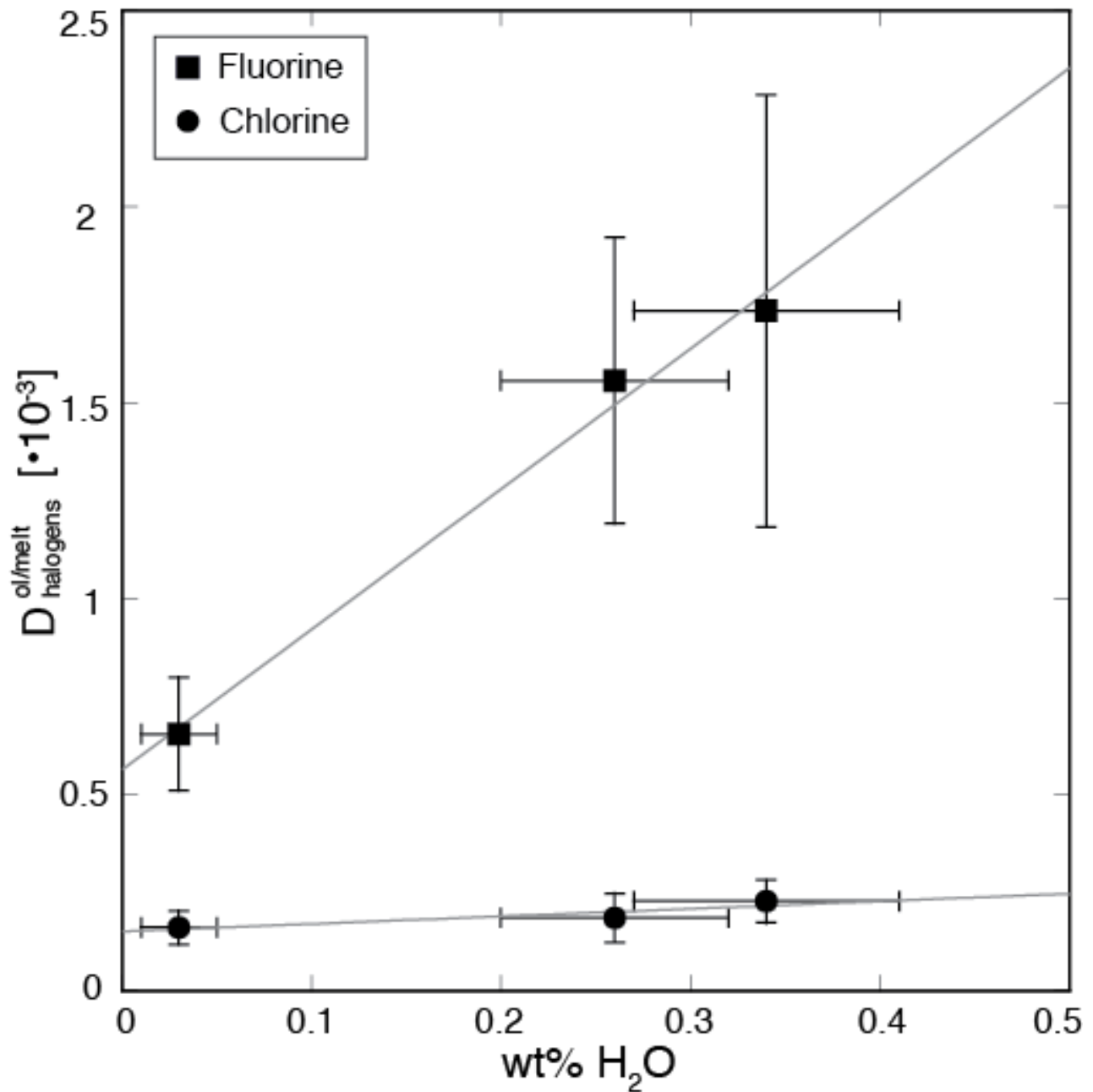
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Content

Owing to their incompatibility and volatility, the distribution of halogens in the Earth's mantle is affected by processes such as fluid mobility, oxygen fugacity, fractionation, degassing and partial melting. This makes halogens an important tracer for volatile transport processes in the Earth's mantle. Knowledge about the abundance and distribution of halogens in the Earth's mantle enables us to better understand the cycling of volatiles from subduction zones to ridge and ocean island settings.

In this study, we investigated experimentally the effect of small amounts of water on the F and Cl partitioning behavior between olivine and melt at 1280°C and 0.3 GPa. Results show that there is, within uncertainty, no effect of water on the chlorine partitioning behavior for bulk water contents ranging from 0.03 to 0.33 wt% H₂O ($D_{Cl}^{ol/melt} = 2.2 (11) \cdot 10^{-4}$). In contrast, fluorine partition coefficients increase linearly in this range and may be described with $DF_{ol/melt} = 3.6(4) \cdot 10^{-3} \cdot X_{H_2O} (wt\%) + 6(4) \cdot 10^{-4}$.



Effect of bulk water content on the fluorine and chlorine partitioning behavior between olivine and silicate melt at 1280°C and 0.3 GPa.

Considering the effect of water on the F partitioning behavior between olivine and silicate melt indicates that OIB source region estimates are about 10% lower than previously expected [1]. This implies that, in contrast to Cl, the effect of water on the F partitioning behavior needs to be considered for a correct estimation of F abundances in OIB source regions.

Recently, it has been suggested that multiple episodes of small degree partial melting are required to generate magmas with a high F/H₂O ratio between 0.1 and 0.9 in the upper mantle [2]. Our results indicate that addition of small amounts of water to a dry peridotitic system may potentially lead to a significantly stronger increase in the F/H₂O ratio of the residue during a single small degree partial melting event. Thus, the effect of water on the F partitioning behavior may explain the generation of high F/H₂O ratios and high F concentrations in the upper mantle without the requirement of multiple partial melting episodes.

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Session 6.3: Early crust.: Poster

Session 6.3: Early crust.: Poster
A-170

Recent disturbance of the Hf and Nd isotope systematics in achondrites – implications for early Earth

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Content

The ^{176}Lu - ^{176}Hf and $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$ radioisotope systems are important tools for constraining the age and differentiation history of silicate reservoirs such as the terrestrial crust and mantle. During crust formation, Lu/Hf and Sm/Nd are fractionated and thus evolve distinct $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ with time. In contrast, resolvable radiogenic variation in $^{142}\text{Nd}/^{144}\text{Nd}$ can have only been produced while the parent isotope ^{146}Sm was still extant, i.e., within the first ~500 Myr of the Solar System.

One way to study silicate differentiation in the early Solar System and thus possible analogs to the evolution of early Earth is by investigating these isotope systems in achondrites, i.e., samples from differentiated planetesimals. However, internal Lu-Hf and Sm-Nd isochrons for eucrites, angrites, and a trachyandesite from the ureilite parent body have often revealed scatter among individual mineral fractions [e.g., 1-3], suggestive of recent open system behavior. These disturbances are probably caused by terrestrial alteration or contamination: Fractionation of Lu/Hf and—to a lesser extent—Sm/Nd may be caused by incongruent dissolution of mineral grains during terrestrial weathering or sample washing in the laboratory [2, 4], whereas recent modifications of $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ may rather be induced by the addition of an isotopically different contaminant [3].

For the trachyandesite sample from the recent Almahata Sitta meteorite fall, we were able to remove such contamination via a thorough mineral separation procedure [3], and the purest, handpicked grains and selectively dissolved phosphate minerals define a 13-point isochron (MSWD = 1.3) with a reasonable age of 4569 ± 24 Ma and an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.279796 ± 0.000011 . This initial $^{176}\text{Hf}/^{177}\text{Hf}$ agrees well with the CHUR-parameters of [5] calculated back to the beginning of the Solar System and the Hf isotope composition measured in eucrite zircon [6]. This agreement implies initial isotopic homogeneity among rocky planetary bodies with respect to Hf. For Nd, $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$ mineral isochrons may be used to further distinguish between recent and ancient (>4 Ga) disturbance mechanisms.

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Session 6.3: Early crust.: Talk

Session 6.3: Early crust.: Talk A-476

Archaean metamorphism and crustal evolution of the Dwalile Supracrustal Suite, Ancient Gneiss Complex, Swaziland

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Content

The Dwalile Supracrustal Suite (DSS) occurs as small remnants of greenstone rocks within the gneisses of the ca. 3.66 to 3.20 Ga Ancient Gneiss Complex in Swaziland. The Palaeo- and Mesoarchaeoan metavolcano-sedimentary rocks are complex and are affected by a polymetamorphic overprint. U-Pb and Lu-Hf isotope analyses were obtained by laser ablation-sector field-inductively coupled plasma-mass spectrometry on both detrital and metamorphic zircon grains. By combining the isotope analyses with cathodoluminescence imaging it is possible to distinguish the detrital zircons with altered domains and newly grown metamorphic grains. In this way accurate information on both the crustal evolution and the metamorphic history of these rocks can be provided.

The oldest Dwalile rocks are represented by a phase of felsic to intermediate volcanism at ca. 3.46 Ga. The zircons of these rocks have superchondritic ϵ_{Hf} values, indicating the formation of juvenile crust. The metasedimentary rocks can be divided in two groups: an older Dwalile Group I that is similar in age to the Hooggenoeg and Kromberg Formations (3.46–3.40 Ga), but with a more juvenile source area. Indicating that crustal recycling or mixing of an older crustal component played a minor role during the early formation and growth of the Ancient Gneiss Complex.

A younger Dwalile Group II is coeval with the Fig Tree and possibly Moodies Groups (<3.23 Ga). The youngest zircon population show near- to sub-chondritic ϵ_{Hf} values suggesting more crustal recycling during the formation of these source rocks.

The DSS was affected by three stages of metamorphic overprint: an event at 3.23 Ga, pervasive amphibolite-facies metamorphism at 3.15 Ga, and low-P granulite-facies metamorphism at 2.99 Ga.

The data support the model of possible amalgamation between the AGC and BGB terranes at ca. 3.23 Ga. In addition the DDS rocks record crustal thickening in the AGC terrane at ca. 3.15 Ga, causing Barrovian-type metamorphism. The ca. 3.15 Ga metamorphic zircon in the amphibolite facies rocks resulted from new growth in aqueous fluids. At ca. 2.99 Ga, in the low pressure granulite-facies rocks, new zircon was formed in the presence of melt. This metamorphic event is most likely related to crustal extension during the onset of Pongola Basin rifting and the emplacement of the ca. 2.99 Ga Usushwana Complex.

Early silicate differentiation of the Isua mantle? Insights from Tungsten isotopes and HSE abundances

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Content

Interpreting the origin of ^{182}W anomalies in mafic Archean rocks and the role of a putative missing late veneer [1,2] hinges on tightly constraining the Archean mantle abundances of highly siderophile elements (HSE). However, most HSE estimates for Archean mantle-derived rocks are based on their mafic derivatives, an approach with large uncertainties. Previous ^{182}W isotope studies did either not include measurements of HSE [2,3] or examined inadequate mafic-ultramafic lithologies [4-6], where the ultramafic rocks could not unambiguously be identified as mantle peridotites.

Here, we present the first high-precision W-isotope measurements for > 3.8 Ga old peridotites from Isua that unambiguously show the geochemical characteristics of depleted mantle harzburgites or associated dunites. These mantle peridotites exhibit resolvable excesses in ^{182}W of +15 ppm (± 2 ppm, 95% conf. limit). The observed absolute abundances and ratios of the PGE (Os, Ir, Ru, Pd, Pt), have previously shown to equal those of modern mantle peridotites [7], arguing against a missing late veneer component in these rocks. Our data are further corroborated by ^{182}W - and ^{176}Lu - ^{176}Hf isotope data for 3720 Ma boninite-like metabasalts from the Isua supracrustal belt and 3.4 Ga Ameralik dikes. Both rock suites exhibit excesses in ^{182}W up to +20 ppm. Positive initial ϵ_{Hf} values point to a derivation from a depleted mantle source. At a first glance, this would tentatively support models, where an early depletion of the Isua mantle might have caused the ^{182}W anomalies. However, up to 100 fold enrichments of W in many samples relative to similarly incompatible elements like Th argue for selective W mobilization. Hence, inheritance of the anomalous W isotope signatures from metasomatic fluids or from subduction zone components in an arc setting can therefore not be ruled out.

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Field geology, petrography, age and geochemistry of the Lomati River Complex: A unique late-phase igneous contribution to the interior of the Archean Barberton Greenstone Belt, South Africa

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Content

The interaction between rising plutons and greenstone belts provides significant information on the dynamics of Archean tectonics and volcano-sedimentary processes because the related rise of plutons, concomitant volcanism and basin development collectively describe the final building stages of greenstone belts and the formation of buoyant, stable continental crust, unique to Earth.

The three-partite Lomati River Complex (LRC) in the central Barberton Greenstone Belt (BGB) is composed of (1) the doleritic - gabbroic Lomati River Sill (LRS), which intruded in strata of the uppermost Fig Tree Group (~3225 Ma) north of the major Inyoka Fault (IF); (2) a basaltoid peperite stockwork > 1 km in vertical extent, cross-cutting and deforming sandstones of the Moodies Group south of the IF; and (3) a stratiform unit of basaltic amygdaloidal lava widespread in Moodies Group strata throughout the BGB (Fig 1). Although mappable contacts between these three LRC elements are only partially exposed, field, petrographic, geochemical, and geochronological relationships suggest their close temporal and genetic relationship. The LRS reaches a maximum thickness of ~500 m. Its primary mineral phases, plagioclase, clino- and minor orthopyroxene, occur as relicts only. Pyroxene is commonly uraltised; plagioclase underwent epidotization, albitization, saussuritization and sericitisation to varying degrees.

Whole-rock main and trace element geochemistry indicate an internal compositional zonation (MgO 5 - 14 wt.%, Cr 15 - 950 ppm, (La/Sm)_N : 1 - 4). Complexly zoned zircons and baddeleyites cluster at 3211 ± 18 Ma, interpreted as time of intrusion, and at 3180 ± 11 Ma, interpreted as time of metamorphic alteration. This intrusion age overlaps within analytical error with the crystallization age of the mafic stockwork in Moodies Group sediments (3208 ± 13 Ma) and with the extrusion age of the amygdaloidal basalt (overlying tuffs $\sim 3220 \pm 3$ Ma). Structural relationships imply intrusion during or shortly after deformation of the sill in an extensional setting, contemporaneous with major deformation of the BGB and the collapse of Moodies basin(s). Lower-greenschist facies metamorphism, judged by the presence of actinolite and minor pumpellyite, occurred at 2870 ± 11 Ma.

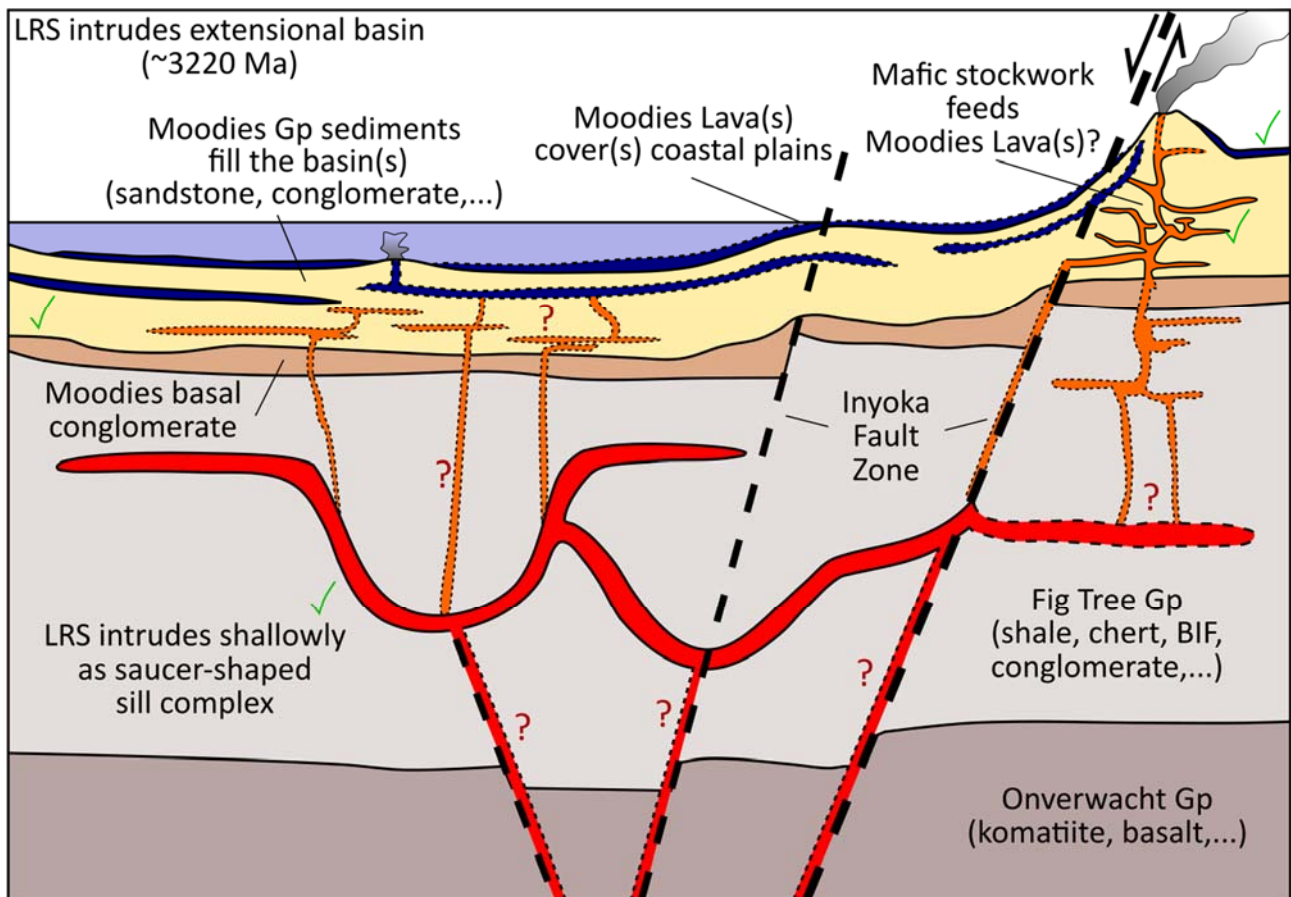


Fig. 1. Relationship of the Lomati River Sill, the subvolcanic stockwork and Moodies Lava(s) to each other and to the extensional setting at ~3230 Ma and the TTG intrusions at 3.2 Ga.

Metamorphic evolution of two granulite facies events (2.62 Ga and 2.0 Ga) in the Central Zone of the Limpopo Belt, South Africa

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Content

Reconstructing the tectono-metamorphic evolution of a polymetamorphic terrane is often a challenging task, as the correlation of the chronological record with the evolution of the mineral assemblages is usually ambiguous in such terranes. The Central Zone of the Limpopo Belt of southern Africa is a classical example for a polymetamorphic terrane with three metamorphic events established at 3.1 Ga (M1), ~2.66-2.61 Ga (M2) and 2.02 ± 0.02 Ga (M3) (e.g., Kramers & Mouri, 2011).

We present new petrological and geochronological data for the two younger events M2 and M3. The Neoarchean M2 event is well preserved in samples from a newly discovered enclave of mainly supracrustal rocks in the 2.61 Ga Bulai Granite Pluton. Consistent with the preservation of an earlier fabric cut by the granite, the enclave rocks record widespread growth of ca. 2.62 Ga metamorphic zircon (Kröner et al, submitted). In contrast, metapelites from outside the pluton record both, 2.62 Ga and 2.0 Ga zircon growth (Kröner et al, submitted). SIMS U-Pb dating of rutile in garnet from a metapelite sample yielded ²⁰⁷Pb/²⁰⁶Pb ages of ca. 2.0 Ga, coeval with matrix rutile. Therefore, high-grade metamorphism in samples from outside the Bulai Pluton can be ascribed to the Paleoproterozoic M3 event.

Based on P-T pseudosection modelling for migmatitic metapelites from outside and inside the Bulai Pluton we reconstructed similar clockwise P-T evolutions for both metamorphic events:

During heating to near-UHT conditions (860-900 °C, ca. 7.5 kbar) the peak-assemblage Grt-Crd-Sil-Kfs-Rt-Pl-Qz formed through biotite-dehydration-melting reactions in the M3-dominated samples from outside the pluton. The preservation of prograde zoning of garnet with rimward increasing XMg and bell-shaped distributed HREE is consistent with the short duration of the 2.02-2.00 Ga event. Cordierite coronas around garnet record subsequent isothermal decompression to ca. 6 kbar. Re-growth of garnet and sillimanite at the expense of cordierite documents late isobaric cooling to <700 °C.

The peak-assemblage Grt-Bt-Sil-Kfs-Rt/Ilm-Pl-Qz formed during heating to ca. 850 °C at ca. 7 kbar through dehydration-melting reactions in M2-dominated metapelites from outside the pluton. Cordierite coronas around garnet document post-peak decompression, and re-growth of biotite records subsequent cooling.

Kramers & Mouri (2011). Geological Society of America Memoirs 207, 85–105.

Kröner et al. (submitted to Precambrian Research)

Tracing crustal reworking processes within the Ancient Gneiss Complex (Swaziland) by ^{176}Hf - ^{142}Nd isotope systematics

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Content

The 3.20 to 3.66 Ga Ancient Gneiss Complex (AGC) (Swaziland) comprises different suites of granitoids that are intercalated with amphibolites. Based on heterogeneous Hf isotope in zircon compositions of these granitoids, it has been proposed that an earlier felsic crustal component was involved in their formation, that interacted with juvenile mantle-derived melts [1;2]. A compilation of Hf isotope data of dated zircons reveals that strongly negative initial $\epsilon\text{Hf}(t)$ values occur in the oldest zircons ($\epsilon\text{Hf}(t) = -6$ to $+1$). The initial ϵHf zircon arrays of the younger Palaeoarchean granitoids progressively increase toward initial ϵHf values of -3 to $+4$ by 3.45 Ga, respectively. The 3.2-3.3 Ga granitoids show strongly variable Hf isotope compositions ($\epsilon\text{Hf} = -10$ to $+4$), suggesting progressive reworking of the Palaeoarchean granitoids. A Hadean protocrust may also be a possible unradiogenic source involved in granitoid formation, if stable throughout the Archean. In order to place constraints on the reworked unradiogenic component in AGC granitoids, we measured the whole-rock ^{142}Nd isotope composition of different AGC lithologies including grey gneisses and amphibolites. The ^{142}Nd isotope compositions are bimodal, showing either a tendency toward slightly negative $\mu^{142}\text{Nd}$ anomalies with an average value of -5.3 ± 2.8 ppm (2s.d.) relative to the JNdi-1 terrestrial standard or are indistinguishable from the standard with $\mu^{142}\text{Nd}$ values of $+0.4 \pm 2.5$ ppm (2s.d.) [3]. Both groups cover samples from different lithologies and ages, suggesting that the negative $\mu^{142}\text{Nd}$ values originate from a Hadean protocrust component. Alternatively, the negative $\mu^{142}\text{Nd}$ signatures may have been incorporated by mantle-derived melts as suggested by negative $\mu^{142}\text{Nd}$ values in the amphibolites. Interestingly, the oldest gneisses with ages of 3.64 Ga have no $\mu^{142}\text{Nd}$ anomaly, indicating that a modern terrestrial reservoir was already present in the early Archean. Interaction of both reservoirs could not be observed. The occurrence of negative ^{142}Nd isotope values in the grey gneisses and their initial zircon ϵHf values, are not linked with each other. Hence, the $\mu^{142}\text{Nd}$ compositions of the granitoids are mantle-controlled as is also suggested by negative ^{142}Nd values of some amphibolites.

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Session 6.3: Early crust.: Keynote speaker

Session 6.3: Early crust.: Keynote speaker
A-651

A few good samples: Reconstructing Earth's early crust

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Content

As Earth cooled after the giant moon-forming impact and magma ocean stage, its crust may have evolved from a thin mafic lid (e.g., [1]), perhaps becoming thicker with Iceland-like plateaus (e.g., [2] [3]- [4] [5]), and eventually transforming to the continental-oceanic crust dichotomy with subducting plates and spreading ridges. These structural and dynamic changes would have been closely interrelated to changing formation mechanisms, bulk chemistry, buoyancy, and residence time of crust, the mode of its recycling back into the mantle, and the emergence of water oceans. Key to studying the differentiation and geodynamic processes behind the paired evolution of crust and mantle is identifying intact chemical and isotopic compositions of differentiation products and accurately linking them to the geologic timescale. This is especially challenging for Archean continental crust, which originated in part by recycling of even older crust and was then subjected to a long geologic history punctuated by metamorphism, deformation, and fluid ingress. Much—but not all—original chemical and isotopic information from Archean whole rocks has thus been disturbed. Despite this difficulty, rapid progress is being made in multiple fronts: The simultaneous measurement of U-Pb ages and Hf isotopes in zircon [5] , [6] will allow a clearer view of the degree of mantle depletion and thus the volume of crust during the Hadean and Archean. The zircon record may be biased, however, underrepresenting depleted mantle sources. The latter may be tracked using low-scatter Sm-Nd isochrons [7] . Most recently, improved analytical techniques have spurred the use of short-lived ¹⁴⁶Sm-¹⁴²Nd systematics and ¹⁸²W anomalies as tracers of early differentiation and to make inferences about mantle convection and mixing dynamics (e.g., [8] [9] [10]).

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Session 6.4: Precambrian biotic and environmental (co-)evolution.: Poster

Session 6.4: Precambrian biotic and environmental (co-)evolution.: Poster A-235

Geochronologically resolved evidence for oxygenic photosynthesis 3.22 Ga ago

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Content

Multiple lines of evidence suggest that the evolution of oxygenic photosynthesis predated atmospheric oxygenation by several hundred million years (Myr) or more (1). However, with few exceptions (2,3), geochemical signals for oxygen production before the Great Oxidation Event (GOE) have been largely restricted to deep-marine sediments (4,5). Their links to photosynthetic activity at Earth's surface is thus inferential; none have been unequivocally demonstrated as syngenetic. Here we present new rare-earth-element (REE) and Sm-Nd isotope data for shallow-water (prodelta)-facies banded-iron formation (BIF) from the ca. 3,224 to 3,219 Myr old Moodies Group, Barberton Greenstone Belt, that carry an unambiguous signal of Ce oxidation in oxygenated surface waters (Ce/Ce*PAAS as low as 0.2). Sm-Nd isotope compositions of these samples are indistinguishable from the overall Sm-Nd dataset of Moodies and Fig Tree Groups and demonstrate closure of the REE system at 3144 ± 200 Myr, thus dating the anomaly. Mixing relationships exclude the possibility of late REE addition and constrain O₂ production as syndeositional. Nearby, regionally mappable, in places abundant tidal-zone microbial mats in the same stratigraphic unit provide a clear link to contemporaneous O₂ production. Our findings provide unambiguous and geochronologically resolved evidence that oxygenic photosynthesizers flourished on shallow coastlines by 3,210 Myr ago.

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Lipids of the Placozoa: A key to early animal evolution?

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Content

Animals (Metazoa) have dwelled on this planet for more than half a billion years, as testified by molecular clock studies [1] and biomarkers that are thought indicative of demosponges [2]. Placozoa are very simple Metazoa of uncertain taxonomic position [3][4] that, based on morphological and behavioural similarities, have been suggested as candidate organisms for the remnants of the Ediacara biota [5]. They consist of only a few cell types and rarely extend over more than 2 mm in diameter [6]. This morphological simplicity suggests a basal placement of these organisms within the animal tree of life and supports the hypothesis of a placozoan origin of animals, the so-called placula-hypothesis [3], based on a wide array of molecular data. Yet, other studies have often placed the Placozoa near [4] or amongst [7] the clade of the Coelenterata.

To shed more light onto the taxonomic relationship of basal animals and their early evolution, we studied the lipid inventory of Placozoa and compared these to the biosynthetically expressed lipids in neighboring clades: Ctenophora, Cnidaria, and Porifera (Demospongia and Calcarea). Additionally, genome databases were searched for gene coding enzymes involved in various processes of steroid biosynthesis. Hierarchical clustering analysis on the basis of chemotaxonomy reveals the relationships between these specimens and indicates a close proximity of Placozoa to demosponges, while a second group is formed by Calcarea, Cnidaria and Ctenophora. To date, demosponges are considered the first animals, as derived from the fossil record [8] and geochemical evidence [2]. Based on the observed lipid profiles and the subsequent hierarchical analysis, Placozoa maintain their ground among the earliest branching Metazoa on Earth. This presentation will discuss the resulting taxonomic relationships in the context of Neoproterozoic environmental conditions that prevailed when complex life first emerged.

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Organic matter preservation in a Mesoproterozoic carbonate concretion

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Content

The timing of the emergence and radiation of Eukaryotes has been a long-standing conundrum in geobiology: The first unambiguous record of Eukaryotes dates back to ~1,600 Ma [1] but the oldest uncontaminated diagnostically eukaryotic lipid biomarkers, steranes, only appear at ~800 Ma [2]. It has been previously shown that ancient sterol biomolecules can be well preserved in carbonate nodules [3]. The aim of this study was to test whether Mesoproterozoic carbonate concretions could similarly serve as taphonomic windows into early eukaryotic evolution.

We analyzed two samples from the 1.1 Ga Nonesuch Formation, a carbonate concretion and an adjacent shale, for hydrocarbon biomarkers, $\delta^{13}\text{C}$ isotopic composition and CSIA, and mineralogy. In contrast to previous studies, these samples did not contain any indigenous acyclic isoprenoids, steranes, or hopanes. We also found higher thermal maturities based on MPI-1 and MAI than previously suggested, but the values were still within the oil window and thermal cracking of polycyclic terpenoids should not have occurred. The identical molecular signatures and $\delta^{13}\text{C}$ of kerogens, along with the gradient in TOC values and mineralogical composition of the samples, indicate solely a dilution of shale matrix during growth of the nodule. Additionally, the isotopically enriched alkyl lipids relative to kerogen might point towards strong heterotrophic reworking during biomass deposition and corresponding preservation bias [4]. Such effect might have been caused by a microbial mat [5], whose metabolic activity would create ambient carbonate supersaturation and fuel the nodule formation. An enhanced preservation potential of the analyzed Mesoproterozoic carbonate concretion over the surrounding shale could thus not be confirmed.

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Redox and community steer Proterozoic carbon isotope systematics

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Content

The stable carbon isotopic composition of organic matter can hold valuable clues towards metabolic processes such as carbon fixation and lipid biosynthesis, as well as environmental information in the form of estimates of atmospheric pCO₂ and its bioaccessibility. In particular the compound-specific determination of $\delta^{13}\text{C}$ values is a promising tool to obtain more specific information on past ecosystems. Stable carbon isotope systematics in modern photoautotrophic biota and systems of sedimentary organic matter are overwhelmingly consistent in that cellular phytol is ¹³C-enriched over fatty acids, and hydrocarbons released from kerogen exhibit a slight relative depletion in ¹³C. But these systematics seem perturbed, particularly in Precambrian rocks: kerogen is frequently significantly lighter than associated bitumens, while alkanes tend to be enriched in comparison to phytol lipids [1][2]. These inverse signatures were hypothesized to have co-varied with the evolution of complex life, which increased the preservation of primary produced biomass via fecal pellets at the turn of the Proterozoic/Cambrian transition. But over the last years a number of studies have reported highly variable isotopic offsets throughout the Proterozoic, with both typical 'Precambrian' and 'Phanerozoic' values [3][4][5]. Using a model Close et al. [6] showed that the depositional redox conditions and community composition may be the primary drivers on the aforementioned carbon isotope systematics. We here provide the first observational support for Close et al. [6]. In five sedimentary sequences deposited throughout the Proterozoic no typical 'Precambrian' offset prevails. Detailed analyses of kerogen–alkanes and alkanes–phytol isotopic offsets, between 33 samples from the Chuar Group, revealed strong systematics with, on one hand molecular indicators of depositional redox conditions and on the other the abundance of eukaryotic steranes. These results debunk the idea of 'typical Precambrian' carbon isotope offsets and highlight the complexity of Proterozoic carbon isotopic systematics. At the same time they offer a potential new tool for an enhanced understanding of past ecosystems.

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Session 6.4: Precambrian biotic and environmental (co-)evolution.: Talk

Keynote speaker

A-485

The evolution of Earth's biogeochemical nitrogen cycle

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Content

Nitrogen is an essential nutrient for all life on Earth and acts as a major control on biological productivity in the modern ocean. Accurate reconstructions of the evolution of life over the course of the last four billion years therefore require a better understanding of nitrogen bioavailability and speciation through time. For most of Earth's history, the biogeochemical nitrogen cycle has evidently been closely tied to the redox state of the ocean and atmosphere. Multiple lines of evidence indicate that surface environments have passed from an anoxic state in the Hadean to an oxic state in the later Phanerozoic. It is therefore likely that the nitrogen cycle has changed markedly over time, with potentially major implications for the productivity and evolution of the biosphere. Here we compile nitrogen isotope data from the literature and review our current understanding of the evolution of the nitrogen cycle, with particular emphasis on the Precambrian. Combined with recent work on redox conditions, trace metal availability, sulfur and iron cycling on the early Earth, we then use the nitrogen isotope record as a tool to test existing and new hypotheses about biogeochemical pathways that may have controlled nitrogen availability through time. Among other things, we conclude that (a) abiotic nitrogen sources were likely insufficient to sustain a large biosphere, thus favoring an early origin of biological N₂ fixation, (b) evidence of nitrate in the Neoarchean and Paleoproterozoic confirm current views of increasing surface oxygen levels at those times, (c) abundant ferrous iron and sulfide in the mid-Proterozoic ocean may have caused an onshore-offshore gradient in the speciation and size of the fixed nitrogen reservoir, and (d) nitrate availability alone was not the main driver of eukaryotic evolution but may have been a control on where and when it occurred.

Archean terrestrial environments in the rock record of the Moodies Group (~3.22 Ga)

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Content

The Moodies Group (~3.22 Ga), uppermost unit of the Archean Barberton Greenstone Belt (BGB), South Africa and Swaziland, is one of the oldest well-preserved shallow-water and terrestrial sequences on Earth. Its quartzose sandstones, siltstones and minor conglomerates reach ca. 3.2 km in thickness and encompass depositional environments ranging from alluvial fan to pro-delta slope. Terrestrial and marine environments interfinger strongly, possibly due to high tidal range and rapid relative sea-level changes along unstable coastlines in a dynamic tectonic setting. Evidence of subaerial exposure is widespread south of the Inyoka Fault, a major fault system trending axially about midway in the BGB, and includes evaporitic paleosols (Nabhan et al., 2016), abundant desiccation cracks, and early diagenetic quartz cements in beach rock sandstones, aside from common braided-fluvial facies elements. The origin of large-scale foresets in some sandstone units, interpreted by Simpson et al. (2012) as representing the world's oldest desert, is debatable. The apparent lack of detrital feldspar south of the Inyoka Fault contrasts with a local arkosic composition north of that fault and argues against its origin by chemical weathering; it may rather reflect a different provenance and/or a different diagenetic history. Photosynthetic (likely early cyanobacterial) microbial mats in associated fluvial-estuarine deposits underline the potential of this unit to record not only terrestrial and atmospheric processes but also aspects of the early colonization of the land surface. Moodies terrestrial environments contribute to our understanding of Martian conditions where aqueous environments were more tenuous.

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Biomarker taphonomy and terrestrial organic matter fluxes in mid-Neoproterozoic rocks

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Content

The Neoproterozoic Era (1000–542 Ma) was marked by drastic environmental turbulence and witnessed not only a pulse of eukaryotic radiation but also the advent of complex life in the form of the first animals [1]. Two global and long-lasting Snowball Earth glaciations [2] during the Cryogenian (720–635 Ma) put life under severe pressure and it has been variably debated how life either survived these events or became reorganized by them. Particularly sessile aerobiotic demosponges, considered to be the most basal metazoa [3], would have been heavily affected by a 'hard snowball' glacial scenario [4]. A novel and only recently described 24-desmethyl-26-methyl sterane, named cryostane, was reported in Tonian sediments and attributed to early demosponges [6]. In this study we set out to obtain a greater understanding of possible environmental, facies or lithological controls on the occurrence and relative abundance of cryostane in a Tonian rock sequence.

Eleven samples from five different outcrops of the Tonian Visingsö Group were studied using conventional organic geochemical techniques. In addition to organic marker molecules, various inorganic redox-sensitive elements were quantified in order to obtain a complementary view of depositional redox conditions. All samples were characterized by an advanced stage of thermal maturity, yet still contained indigenous hopanoid and steroid biomarkers. Apart from the focus on cryostane, we observe an appreciable amount of steranes (up to around 20% compared to the sum of hopanes), suggesting that eukaryotes were abundant in this littoral, shallow-marine environment. The most interesting observation involved an anti-correlation between organic and inorganic parameters susceptible to oxidation, which can only be explained by periodic input of basin-ward fluxes of terrigenous organic matter and oxidized metals. This points towards a mildly oxidizing atmosphere during the Tonian and provides some of the first indicators of terrigenous organic matter fluxes into the marine realm prior to the much later advent of land plants, whose cuticular and molecular remnants strongly facilitate the recognition of terrigenous organic matter in Phanerozoic, marine sediments.

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Declining importance of high-temperature hydrothermal fluid input into shallow Transvaal seawater prior to the GOE

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Content

Pure marine stromatolitic carbonates are excellent geochemical archives of ambient shallow seawater and provide insight into the physico-chemical conditions prevailing in Earth's atmosphere-hydrosphere system during the time of carbonate precipitation. Here we report rare earth element and yttrium (REY) and Nd isotope data for ~2.42 Ga old Rooinekke stromatolitic carbonates, which directly underlie the Makganyene diamictite and, therefore, formed shortly before the Great Oxidation Event (GOE).

Shale normalized REY (subscript SN) patterns of pure, i.e. detritus-free limestones from Rooinekke bioherms are sub-parallel to those of modern seawater with positive La_{SN} and Gd_{SN} anomalies, a depletion of the light relative to the heavy REY_{SN} and super-chondritic Y/Ho ratios. This is in marked contrast to the non-seawater-like REY_{SN} distribution in dolostones from the Rooinekke Formation, which reflect secondary overprint during dolomitization.

The lack of negative Ce_{SN} anomalies in Rooinekke limestones confirms that shortly before the GOE, redox conditions in the atmosphere-hydrosphere system were not yet oxidizing enough to stabilize Ce(IV) compounds and to decouple redox-sensitive Ce from its neighboring REY. In contrast to other Archean chemical sediments, Early Paleoproterozoic Rooinekke limestones do not show positive Eu_{SN} anomalies, suggesting that input of REY from high-temperature (>250°C) hydrothermal fluids into shallow Rooinekke seawater was minor to negligible. This is corroborated by unradiogenic $\epsilon\text{Nd}_{(2.42\text{ Ga})}$ values of pure Rooinekke limestones, which reflect the predominance of continent-derived REY in the dissolved REY inventory of shallow Rooinekke seawater.

However, older marine chemical sediments from the Transvaal Supergroup, such as the Campbellrand carbonates (2.52 Ga) and the Kuruman and Penge iron-formations (2.46 Ga) show significant REY contributions to Transvaal seawater from high-temperature "black smoker-style" hydrothermal fluids, as shown by positive Eu_{SN} anomalies and more radiogenic $\epsilon\text{Nd}_{(t)}$ values [1], [2]. The sedimentary succession from the older Transvaal BIFs and carbonates to the slightly younger Rooinekke limestones, therefore, reveals the declining importance of a high-temperature hydrothermal component in the marine REY budget of Transvaal seawater during the Late Neoproterozoic to the Early Paleoproterozoic, shortly before the GOE.

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Evolution of peptides in the continental crust

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Content

A basic problem in all postulated pathways of prebiotic chemistry is the low concentration which generally is expected for interesting reactants in fluid environments. Even though compounds like nucleobases, sugars or peptides principally may form spontaneously under environmental conditions, they will always be rapidly diluted in an aqueous environment. In addition, any such reaction leads to side products which often exceed the desired compound and generally hamper the first steps of a subsequent molecular evolution. Therefore, a mechanism of selection and accumulation of relevant prebiotic compounds seems to be crucial for molecular evolution. A very efficient environment for selection and accumulation can be found in the fluid continuum circulating in tectonic fault zones. Vesicles which form spontaneously at a depth of approximately 1 km present a selective trap for amphiphilic molecules, especially for peptides composed of hydrophilic and hydrophobic amino acids in a suitable sequence. The accumulation effect is shown in a numeric simulation on a simplified model. Further, possible mechanisms of a molecular evolution in vesicle membranes are discussed. Altogether, the proposed scenario can be seen as an ideal environment for constant, undisturbed molecular evolution in and on cell-like compartments, the latter offering preferential starting conditions for a subsequent RNA world.

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Extreme heterotrophy after the Neoproterozoic Snowball Earth glaciations

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Content

The Neoproterozoic Snowball Earth events (0.72–0.64 Ga) represent the most severe climatic perturbations in all of Earth's history [1]. The termination of these global glaciations is marked in the rock record by several meters of dolomitic carbonates (i.e. cap dolostones) that drape the glacial diamictites and which were deposited as a consequence of strongly elevated pCO₂. Yet their mineralogy remains enigmatic since dolomite precipitation is kinetically inhibited at normal marine temperatures and salinities. The 'dolomite problem' has occupied geologists already well over a century [2] —e.g. despite Mg²⁺ super-saturation, dolomite does not form in the modern ocean. Over the last decades lab and field experiments have revealed that certain microbes, in particular heterotrophs can play a role in nucleating Mg-rich carbonates on their cell walls and induce the precipitation of dolomite [3] [4] [5].

We here report on a newly characterized pentacyclic terpenoid biomarker observed in exceptional abundances in Marinoan cap dolostones, whose concentrations dwindle at the dolostone-limestone boundary. The component occurs throughout the last 800 Myr of Earth history independent of lithology (271 samples), with a prevalence in warm periods and environments. Statistically relevant parallels to compound-specific stable carbon isotope systematics reveal a mechanistic connection to severe heterotrophic reworking of biomass. Our results highlight the role of biology in precipitating Mg-carbonates, and provide a new biological explanation for both the mineralogy and the exceptionally rapid deposition (estimated at ≤10⁴ [6] of post-glacial cap dolostones.

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Local and regional controls on the maturation state of carbonaceous matter in the Barberton Greenstone Belt

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Content

The volcanic-sedimentary fill of the 3.57 - 3.21 Ga Barberton Greenstone Belt (BGB) of southern Africa is affected by hydrothermal, metasomatic, metamorphic and magmatic events. While the BGB's center shows a regional lower-greenschist facies metamorphism, contact metamorphism reaching amphibolite-facies-or-higher equivalent dominates its margins. Geothermometers, determined by Raman spectroscopy of carbonaceous matter (CM) from metasediments, contribute important information to identify the least affected and best preserved regions of the greenstone belt for paleobiological and geochemical studies. Calculated peak temperatures of samples from the Onverwacht, Fig Tree and Moodies Groups range from 320°C to 480°C $\pm$ 50°C. Carbonaceous cherts of the Onverwacht and Fig Tree Groups show, in agreement with former observations [1] and independent of stratigraphic position or sampling locality, a homogeneous thermal overprint of 350°C to 380°C $\pm$ 50°C with little to no variability. The lowest temperature of ca. 320°C is indicated by a paleosol of the lower Moodies Group in the Stolzburg Syncline while microbial mats of similar stratigraphic position in the Saddleback Syncline reach up to 480°C and show an internal variability from 400°C to 480°C.

The homogeneous moderate maturity of Onverwacht and Fig Tree cherts is probably due to their early silicification, reducing the effects of subsequent high-temperature overprints. CM of the Moodies paleosol is exclusively preserved as inclusions in early diagenetic pyrite, resulting in preservation comparable to or better than in the cherts. The high thermal overprint of Moodies microbial mats in parts of the central BGB is likely a result of their proximity to the magmatic Lomati River Complex. Finally, primary differences in recalcitrance of original organic material might account for the small-scale variability in crystallinity of CM observed in Moodies microbial mats.

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Looking for Archean cellular life: natural vs. experimental approaches

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Content

Looking for the earliest communities in the Archean fossil record is crucial in order to understand the nature of biology-driven changes to the early environment. However, the few Archean sedimentary formations that have been preserved are all metamorphosed and often affected by hydrothermal fluids. Microbial remnants from this period are therefore strongly altered chemically and structurally. Furthermore, these remnants have to be distinguished from complex abiotic artefacts such as carbonaceous materials associated with silica-witherite biomorphs (Garcia-Ruiz et al., 2003). This complicates the interpretation of the various micro-textures displayed by organic matter in these rocks (Schopf et al., 2002; Brasier et al., 2002).

In order to better interpret the Archean microfossil record, the influence of diagenetic and metamorphic processes on fossilizing microbiota has to be assessed. Here we present new experiments, in which the chemical and structural changes of an entire microbial community are observed after experimental metamorphic alteration. This is compared to similar experiments conducted on silicified mixtures of silica-witherite biomorphs and organic compounds.

The natural community used for these experiments has been sampled from siliceous sinters of the hypersaline lake in El Tatio, Chile. The silica-witherite biomorphs were synthesized in an alkaline (pH 9-11) silica-rich solution. Subsequent artificial silicification was achieved using TetraOrthoEthoxySilane (TEOS). The experimental alteration mimicked conditions up to lower-greenschist facies conditions (250°C, 2.5 kbars) for time intervals from several days to several weeks.

SEM analyses show a progressive degradation of bacteria with temperature. The cytoplasm is lost at low temperature, while the walls and sheaths can be preserved at higher temperatures. Above 250°C, the formation of large quartz crystals clusters may destroy morphological remains.

The conclusions of these studies will be used to discuss the potential origins of textures and microtextures displayed by organic matter in natural Archean cherts sampled in the Pilbara Craton.

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Reconstruction of the Neoproterozoic Urucum habitat in the fate of severe glaciogenic epochs

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Content

Marine chemical sediments from the Urucum Iron and Manganese Formation (IF/ MnF), Brazil, are reliable archives of Neoproterozoic seawater and provide unique insights into the physico-chemical environmental conditions of the Urucum area at the time of deposition. We here present a study targeting the rare earth and yttrium (REY) and Sm-Nd isotopic compositions of marine chemical sediments, clastic sediments and ambient igneous rocks of the Urucum area to reconstruct the ancient habitats of the Urucum region during the Neoproterozoic in the fate of severe glaciogenic epochs.

Shale-normalised REY patterns (subscript SN) of pure chemical sediments, i.e. marine chemical sediments that are devoid of syn- or post depositional alterations, are subparallel to the REYSN patterns of modern seawater and show super-chondritic Y/Ho, enrichment of heavy relative to light REYSN ratios, positive LaSN and GdSN anomalies and negative CeSN anomalies. These REYSN systematics combined provide information that oxic atmosphere–hydrosphere conditions were prevalent in the Urucum environment and that the marine habitat was dominated by open ocean water masses. Furthermore, the lack of positive EuSN anomalies, indicative of high-temperature, hydrothermal fluid contributions to Precambrian seawater, strongly supports the idea that REY supply via high-temperature hydrothermal fluids into Neoproterozoic seawater had insignificant influence on the global Neoproterozoic REY budget [1]

Pure IF samples yield $\epsilon_{\text{Nd}}^{0.635\text{Ga}}$ values between -4.56 and -4.08 and are more positive than those of the MnF (-5.52 to -4.66), associated siliciclastic rocks (-8.35 to -7.69) and are considerably less negative than the crystalline Rio Apa Basement of the Amazonia Craton (-13.7). The Nd isotope data support former Dantas et al. [2] arguing that clastic sediments in the Urucum basin originated from the Amazonia Craton. In contrast, the dissolved REY budget of Urucum seawater, represented by pure marine chemical sediments, was tapped from terrigenous sources of the nearby Brasília Belt. Furthermore, Mn-rich chemical sediments were deposited in more oxidised, shallow-marine environments and sedimented from oceanic waters whose inventory of dissolved REY was additionally affected by a riverine and/or benthic REY flux.

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The Archean continental crust as a location for the origin of life

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Content

Tectonic fault systems in the continental crust offer huge networks of interconnected channels and cavities. Filled mainly with water, carbon dioxide and nitrogen, containing a wide variety of hydrothermal chemistry and numerous catalytic surfaces, they may offer ideal reaction conditions for prebiotic chemistry. In these systems, an accumulation zone for organic compounds will develop at a depth of approximately 1 km. Here, rising super-critical CO₂ turns to the sub-critical gas state causing dissolved components to precipitate. At this point, periodic pressure changes caused for example by tidal influences or geyser activity may generate a cyclic process involving repeated phase transitions of carbon dioxide. Long living gas-permeable faults are often documented by quartz- and ore mineralization. During the growth of hydrothermal quartz minerals, fluids from the surrounding are enclosed which conserve the chemical composition of the given fluid medium. Archean hydrothermal quartz minerals provide important information about the first organic molecules formed by hydrothermal synthesis. Analyses of quartz veins from the Archaean Yilgarn craton and hydrothermal quartz pebbles from a 2.7 to 3 billion years old conglomerate (Jack Hills, West Australia) were carried out. A wide spectrum of organic compounds has been detected in these pebbles. With comprehensive two-dimensional gas chromatographic analysis a variety of organic compounds was found which unambiguously show that prebiotic organic molecules have been formed by hydrothermal processes. The analytical results of the fluid inclusions allow for a more detailed understanding of the synthetic processes which have occurred in the rising fluids inside the fault zones and which may have led to the formation of early organic molecules. Based on the findings, laboratory experiments have been designed which are meant to reproduce these processes and to yield further understanding on their mechanism. Further, they should yield a collection of possible products which in the early history of earth may have formed the basis for the first biomolecules. We conclude that these organic substances could have made an important contribution to prebiotic chemistry which might eventually have led to the formation of the first living cell.

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Application of electrical resistivity tomography (ERT) and sedimentological study for investigation of Upper Jurassic debris flow deposits from the Kraków Upland (Southern Poland)

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Content

This paper highlight the application of shallow non-invasive geophysical survey (Electrical Resistivity Tomography) supported by traditional sedimentary study to investigate, description and interpretation of the Upper Jurassic debris flow deposits in a site located in the vicinity of Tomaszowice village (Kraków Upland). In this area, gravity flow sediments are very common and are encountered along the boundaries that defines the course of the northern margin of Krzeszowice Graben.

Electrical resistivity tomography study comprising dipole–dipole array has been carried out along 5 parallel 110 m long profiles (separated by each other by 10 m distance) as well as 1 perpendicular 110 m long profile, in an area placed north of quarry wall. Lengths of current and potential dipole 'a' = 1, 2, 3, 4, 5, 6 Δx and separation factors 'n' = 1, 2, 3, 4, 5, 6 a have been used. Electrodes elevation along profiles obtained by geodetic measurements with the use of Jogger 20 leveler of Leica Geosystems, have been conducted simultaneously with the geophysical surveys. The obtained ERT data was inverted using the commercial software RES2DINV of the Geotomo Software with the use of inversion process based on the l1-norm (robust, blocky) and l2-norm (smooth) inversion method. In this paper, we present inverted resistivity sections only for robust inversion method, which tends to produce models with a much sharper and straighter boundary between different regions with different resistivity values.

Microfacies analyses were carried out on samples collected from the exposed section at the quarry wall spanning the entire thickness of the Upper Jurassic limestones. Detailed analyses of the microfacies development were carried out using 18 thin sections and 12 polished slabs.

The use of these geophysical survey in combination with geological data allowed the determination of the lithological features as well as detailed internal architecture (spatial distribution, geometry as well as general structuring). Furthermore, the ERT results have revealed several zones that can be explained as fault zones closely linked to the Krzeszowice Graben. The distribution of the debris flow deposits, in the vicinity of Tomaszowice, reflects the patterns of the complicated fault zones corresponding to the margins of the Krzeszowice Graben, and indicates their Late Jurassic activity.

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Carbonate Facies of Isolated Carbonate Platforms from the Kepulauan Seribu Complex, Indonesia

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Content

Cenozoic shallow-marine tropical carbonates form major hydrocarbon reservoirs in various parts of the world are located in drowned carbonate platforms. Quantitative facies models from modern systems are essential for the interpretation of their fossil counterparts. The aim of this study is to comprehensively and systematically investigate the carbonate facies distribution in Panggang, Pramuka, and Semak Daun Island, Kepulauan Seribu complex, based on texture, composition and mineralogy of modern surface sediment. Kepulauan Seribu is a chain of coral islands. Many of these islands are atoll-like with a nearly continuous reef belt exposed to bidirectional monsoon wind. Four carbonate facies may be delineated based on quantitative statistical analysis; (1) coral packstone to grainstone, (2) coral–mollusk packstone, (3) coral–mollusk wackestone to packstone, and (4) mollusk packstone. Coral packstone to grainstone facies preferentially occurs in the less wind expose part of the sand apron in depth of 0.3-23m. The coral-mollusk packstone facies occurs along the fore reef and reef front in depths of ca. 0.3-21.5m. Coral–mollusk wackestone to packstones occur in the windward parts of the sand apron and the back reef to shallow lagoon (0.3-17m deep). Mollusk packstones occur in the inner lagoon in depths of ca. 3-11.5m. The occurrence of mollusk packstone in the central lagoon is controlled by the water depth, while the reefal environments (fore reef, reefs, and reef flat) do not show significant facies separation with depth. The co-occurrence of these different facies in the same depth window is contrary to the common thought that changes in bathymetry should be reflected in facies changes. The most abundant fragments in the >125 µm fraction are corals (49%) and mollusk (32.8%), while echinoderms (5.9%), foraminifera (5%), red algae (3.2%) and Halimeda (2.2%) occur as minor constituents. The fine sediment fraction is dominated by fragments of skeletal grains such as as Halimeda flakes, foraminifera tests, diatoms, sponge needles and tunicate spicules, aragonite needles, and nanograins (< 1 µm). The sediment distribution is influenced by alternating east-west directed monsoonal current due to the fact that coarser grains are mostly found in the less current exposed sand apron towards the east and west of the platform, while finer grains tends to be found in the northern and southern more wind expose parts of the sand apron and back reef.

Contourite induced turbidity-current activity in the Mar del Plata Canyon (Argentina)

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Content

Submarine canyons are supposed to be direct conduits for sediments exported from the shelf into the deep sea. However, blind canyons, which are strictly confined to the slope, make up the majority of all canyons along the Southeast American margin. Although this canyon type is most common at continental margins, its evolution and the oceanographic factors influencing sedimentary processes are still poorly understood. The Mar del Plata (MdP) Canyon on the Argentine continental margin is incorporated into a major contourite depositional system. The canyon head originates on the Ewing Terrace at about 1000 m water depth and acts as a sink for contouritic material delivered by the Antarctic Intermediate Water (AAIW) nepheloid layer. The canyon-downslope track crosses all intermediate- and deep-water masses shaping the continental slope off Argentina and expires on the Necochea Terrace (3900 m water depth).

Three studied sediment cores provide millennial scale records along the canyon thalweg covering the last 20,000 years. Importantly, turbidity-current activity was limited to the Last Glacial Maximum (LGM) until the late deglacial. During the LGM and early deglacial, turbidity currents reached the proximal and distal canyon sector and are more abundant at the distal northern flank than close to the thalweg. Due to persistent Antarctic Bottom Water flow along the Necochea Terrace, suspended sediment clouds were deflected to the north and resulted in a contour-current controlled distribution pattern. During the late deglacial most turbidity currents thinned out or did not reach the distal canyon area at all. During the Holocene, turbidity-current activity was absent.

Similar grain-size data and mineralogy of all turbidite beds indicate a contouritic source derived from the southern Ewing Terrace. Under glacial conditions, a strengthened and/or shallowed AAIW nepheloid layer probably favored enhanced sedimentation along the Ewing Terrace. In addition, V-shaped patterns in the uppermost canyon area indicate areas of canyon flank instability where retrogressive failures were induced when pore pressure was exceeded. Specific knickpoints along the thalweg are assumed to act as hydraulic jumps to accelerate turbidity currents.

In conclusion, we state that turbidity-current activity in the MdP Canyon is related to strong currents causing high sediment supply. In turn, temporary accumulated sediments became unstable and subsequently transformed into turbidity currents.

Facies analysis and provenance constraints from the Upper Cretaceous (Turonian) Oybin Formation, Zittau Mountains, Germany

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Content

The Zittau Mountains represent the southeasternmost part of the Upper Cretaceous sediments exposed along the Elbe Valley (Saxonian Cretaceous basin). The Turonian Oybin Formation is part of the Elbtal Group and comprises more than 400 m thick coarse grained siliciclastic sediments that are well exposed as steep cliffs. Only minor tectonic overprint is observed near the northwest-southeast-trending Lausitz fault and thermal overprint is restricted to Cenozoic volcanic centers. Current palaeogeographical models indicate that the Oybin Formation was deposited within narrow, shallow-marine strait between the West-Sudetic Island (NE) and the Bohemian Massif (SW) [1]. These sediments thus preserve an important link between the Saxon Cretaceous Basin in the northwest and the Bohemian Cretaceous Basin in the southeast. Thickness and facies changes of the Turonian sediments of the Saxon Cretaceous basin indicates deepening of the basin towards the northwest.

Although the stratigraphic and sedimentological framework of the Saxonian Cretaceous Basin is well defined, the current palaeogeographic model lacks consistency. The major challenge is to define a consistent tectonosedimentary model that explains erosion, transport and deposition of the massive (> 700 m) and coarse grained Turonian-Coniacian shallow-marine siliciclastic sediments exposed in the Zittau. Current provenance models include the West-Sudetic Island and the Bohemian Massif as potential source regions [2]. However, the timing of uplift of these regions and thus the availability of erosional potential in the Late Cretaceous remains debated.

To answer these questions detailed profiles of the Turonian Oybin Formation were mapped. Facies analysis indicates deposition in a shoreface environment with periodic deposition of up to 30 cm thick conglomerates interpreted to be storm deposits. Preliminary palaeocurrent data indicate overall filling from NE to SW, although some cross-bedded layers imply E-W transport. Whether the West-Sudetic Island, its pre-Cretaceous sedimentary cover or a more distal, high-standing region served as source will be validated by U-Pb dating and trace element analyses of detrital rutile grains extracted from the Oybin Formation.

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First data on Serpukhovian foraminiferal assemblage from limestones of carbonate platform bordered the Upper Silesian Block (Southern Poland)

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Content

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Keywords: Serpukhovian, carbonate platform, benthic foraminifera, Upper Silesian Block

The grey, massive and thick bedded limestones outcropping in the Czernka Valley (35 km west of Kraków) represents carbonate platform deposits in the shallow, photic zone, occurred in the environment of lagoon and shallow shelf (Tomaś and Zajac, 1996). Such deposits were widely distributed alongside the southern part of the Kraków-Częstochowa Upland. These Palaeozoic deposits belong to tectonic structure called the Upper Silesian Block, which was a part of southern margins of Laurasia (e.g. Kalvoda, 2001).

The foraminiferal assemblage founded in the youngest outcropped deposits contains species as: *Eostaffella infulaeformis* (Ganelina), *Eostaffella aff. irenae*, *Ganelina*, *Eostaffella subulba*, *Niko*, *Endothyranopsis eocompressa* Skipp, *Globoendothyra globula* (Eichwald). Age of the foraminiferal assemblage has been assigned based on the correlation with local biozonations (Russian horizons) from the Tengiz platform in Kazakhstan, and the Protvinsky horizon (Brenckle and Milikina, 2003) on the Serpukhovian stage (Upper Carboniferous). Some of observed taxa as *Ozawainella cf. Alchevskiensis* Potievskia suggest even Bashkirian age (Akavassky horizon). The studied foraminiferal assemblage is very similar to those one occurring in limestone of the Tengiz carbonate platform, in Kazakhstan, deposited in similar marine conditions during the Famennian through middle Pennsylvanian (Brenckle and Milikina, 2003).

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Grain-size fractionated heavy and magnetic mineral quantification

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Content

Transport of sediment subjects coastal and shallow marine environments to frequent changes. Main driving forces are currents and wave action. Facies and sediment-physical parameters determine how easily a sediment - or parts of it - can be transported. Enrichment of heavy minerals, up to the dimension of placer formation, caused by the entrainment of lighter minerals, is a proxy for erosion in coastal areas [2]. Understanding of the correlation of provenance and sediment physical parameters in relation to the environmental aspects is crucial to define and quantify sediment transport models and interpret real examples. Ordinary sampling and lab methods take a lot of time and are not applicable everywhere. Magnetic minerals like Magnetite can be used as a proxy for heavy minerals in lab- and (non-invasive) field-studies. Through consecutive wet-sieving, density fractionation and magnetic susceptibility measurements (proxy for magnetite content), the contribution of each grain-size and density fraction to the bulk can be determined. This allows the identification of e.g. possible transport processes and heavy and light grain-size classes in settling equivalence. The study compares samples from the episodically mobile Fehmarn Belt Submarine Dunefield (FBSD), comprised mainly of reworked glacial till [3] and the Bay of Plenty (BoP), New Zealand, a volcanic province affected by constant coast-parallel currents and wave-action [1]. Samples from both areas show a clear maximum concentration of (discrete) magnetite in very fine sand to coarse silt fractions. Apart from that the FBSD samples show an elevated susceptibility in the coarse light sand fraction (magnetic intrusions in lithic fragments) and a fine-grained tail of elevated susceptibility towards heavy finer silt. The BoP does not show these features and is instead well sorted concerning the heavy magnetic fraction. These differences show how an energetically constant wave- and current-action (BoP) leaves a different signal in the sediment compared to intermittently active dunes in the FBSD. Sediments in the BoP also have travelled shorter distances. The method works fine for samples with comparatively high concentrations of magnetic minerals (BoP) as well as very minor concentrations (FBSD) and allows a quick comparison of different environments.

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Investigating the deep-time evolution of the Earth's orbit and searching for chaotic transitions and tidal dissipation patterns in geological time series

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Content

Climate changes in Earth's history were caused by cyclic variations of insolation on Earth. These variations were triggered by pseudo-periodic variations in the Earth's orbit. Detected astronomical driven cycles – with well-known periods - recorded in sediments are used to develop age models. Age models are adjusted to astronomical solutions based on numerical integration of the modern gravitational interactions in the Solar System that calculate past changes in the orbital parameters and insolation. Due to the chaotic behaviour of the Solar System, theoretical astronomical models become imprecise prior to 50 Ma, and Earth physics' related aspects like tidal dissipation even more recently. It is thus important to detect the detailed astronomical fingerprint of characteristic patterns, including chaotic transitions occurring between the 2:1 and 1:1 resonance of long-term obliquity and eccentricity patterns as variations of the astronomical frequencies describing the constellation of and interaction between Mars' and Earth's orbit. In addition, it is necessary to extract interference patterns between obliquity and climatic precession which are sensitive to the Earth-related parameters (tidal dissipation and dynamical ellipticity) that affect astronomical frequencies. We provide the deep-time evolution of the Earth's orbit in a long dataset covering the entire Cenozoic plus part of the upper Cretaceous, generated from already published data, by extracting eccentricity, obliquity and climatic precession amplitude modulations to extend and verify existing astronomical solutions.

Particulate organic matter composition and chemostratigraphy during the onset of Oceanic Anoxic Event 2 (Southern Provence Basin, SE France)

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Content

Deposition during the Cenomanian-Turonian Boundary Event (CTBE) was characterized by exceptional climatic conditions and prominent perturbations in major biochemical cycles. Widespread anoxic/euxinic conditions in oceanic deep waters triggered formation and preservation of organic carbon-rich black shales representing a characteristic feature of the so-called oceanic anoxic event (OAE) 2. In this study Cenomanian deposits of the Southern Provence Basin (SPB) cropping out close to the village of Cassis, SE France are investigated. Overlying the Aptian "Marnes Bleues" Formation, a heterolithic succession covering Middle and Upper Cenomanian strata occurs. The shallow-water to hemipelagic deposits cover a thickness of 65 m and include limestones, breccia, marls and sandstones. A total of 125 samples were collected for sedimentological, palynofacies and geochemical investigations. Rock-Eval pyrolysis data combined with palynofacies results provide information on the composition and preservation of the particular organic matter (OM). Despite significant variations with lithology and stratigraphic height, the bulk of the OM is well preserved and of terrestrial origin. Evidence of enhanced marine productivity and/or increased OM preservation during OAE2 is lacking, maybe due to the proximal setting of the studied deposits. Carbon and oxygen isotope analyses of carbonates and OM were used to generate a high-resolution chemostratigraphic record for the Middle to Upper Cenomanian strata of the SPB. Despite diagenetic alteration of stable isotope signatures in certain lithologies (e.g. bioclastic limestone unit; sandstone unit), both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ records show a pronounced positive isotope excursion (CIE) in the uppermost Cenomanian strata (reaching up to 6.0 ‰ and 22.9 ‰, respectively). Based on its characteristic trends the CIE form in the SPB can be correlated with existing global OAE2 records and documents the onset of the global positive CIE characterizing the CTBE. Differences in absolute values and amplitudes of the SPB CIE compared to existing data can be best explained by (1) the overall terrestrial nature of the bulk OM, (2) variable input of marine OM and (3) contribution of isotopically heavy, platform-derived carbonate, all being superimposed on the global CIE trend.

Provenance of sandstones from the Karaburun Peninsula (western Turkey) and implications for the Late Palaeozoic–Early Mesozoic Palaeotethys evolution

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Content

During the Late Palaeozoic–Early Mesozoic the Eastern Mediterranean region was strongly influenced by the evolution of two major oceanic domains, namely the Palaeotethys and Neotethys. Despite considerable effort the closure history of the Palaeotethys ocean and the role of Palaeotethys-related rocks exposed on Karaburun Peninsula are not fully understood. The virtual unmetamorphosed nature of sedimentary rocks of the study area allows to obtain provenance data for well-founded discussions of existing geotectonic models. New data from a multi-method approach, including thin-section petrography, whole-rock geochemistry, single-grain geochemistry of heavy minerals, and U–Pb dating of detrital zircons from Upper Palaeozoic and Lower Mesozoic siliciclastic sediments, were used to unravel maximum depositional ages and decipher possible source areas. Samples yielded zircon ages from Triassic to Archean that record major input from Palaeozoic to Neoproterozoic sources and set the new limit of maximum depositional ages for two formations (Küçükbahçe and Dikendağı) to Late Carboniferous–Early Permian. Compositional data on rutile and garnet indicate sediment supply from low- to medium-grade metamorphic rocks of generally acidic character. However, the presence of detrital Cr-spinel in some of the sedimentary successions also documents input of ultramafic detritus. Idiomorphic grains from Lower Triassic sandstone are consistent with Cr-spinels from podiform chromitites and were probably derived from a proximal source. Based on data from heavy mineral analysis and zircon age spectra of our samples we conclude that the Carboniferous–Triassic successions were deposited along the active Eurasian margin and received their detritus from rock units located in the present-day Balkan region, the Sakarya Zone and/or facies equivalent successions that are not present anymore.

**Sea level change and shallow burial diagenesis on a subtropical carbonate ramp,
Carnarvon Ramp, SW Shelf of Australia**

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Content

The role of aragonite sedimentation with respect to sea-level variations and its postdepositional dissolution is poorly studied in subtropical carbonate systems. IODP Site U1460 on the Carnarvon Ramp (SW Shelf of Australia) recovered a nearly continues Pliocene to Recent record of outer shelf sediments deposited at the transition between cool and warm water environments. The origin and composition of the carbonate sediments were investigated using scanning electron microscopy, X-ray diffraction (XRD) and X-ray florescence-scanning (XRF). The aragonite content of these subtropical sediments reaches up to 39 % and originates mainly from maceration of ascidians spicules with minor amounts from bivalve shells, bryozoans, serpulid worms and pteropoda, while Halimida spp. occurs only sporadically. Inorganic aragonite, such as reported for the Northern Carnarvon Basin, seems to be absent. X-ray diffraction analyses indicate a systematic decrease in aragonite content with depth due to a combination of dissolution and platform progradation. Variable aragonite contents over the first 100 mbsf might be related to sea-level variations, with high aragonite values related to the sea-level low stands during MIS 10, 12 and 14 (pers. Comm. Beth Christensen). The use of XRF-scan derived Sr/Ca ratios as proxy for aragonite content is hampered by the common presence of celestite, which can be recognized through its association with sulfur. Geochemical modelling indicates that celestite is supersaturated below a depth of ~15 m CSF-A due to high pore-water concentrations of sulfate and strontium. Strontium in the interstitial water is derived from aragonite dissolution. A further increase of celestite supersaturation is hampered by a strong increase of salinity with depth. We proposed that the aragonite, from skeletons of ascidians, pteropods, infaunal bivalves, serpulid worms and bryozoans (Cheilostomatida), is dissolved in the shallow subsurface due to bacterial sulfate reduction. A pteropod fragmentation index and the Limacina Dissolution Index (LDX) will be used to disentangle the relative contribution of dissolution vs. input on the aragonite record at the Site U1460.

Session 7.1: Young Sedimentologists.: Talk

Session 7.1: Young Sedimentologists.: Talk
A-140

Current-induced erosional unconformities and calcarenite deposits of the pelagic Tafilalt Platform (Devonian, Morocco)

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Content

Although the facies and facies architecture of current-derived sediments in modern ocean basins have been thoroughly mapped and described, little is known about facies, spatial distribution, temporal occurrence and facies architecture of fossil contourites in ancient marine basins. The ongoing project focuses on fossil calcareous contourites formed during Middle-Late Devonian time with narrowing oceanic passageways between the approaching continents Gondwana and Laurussia, as well as the various micro-continents drifting in between. As a first step, the study aims to record, map and describe the occurrence of current-induced unconformities and contourite facies of the Devonian of the Tafilalt pelagic carbonate platform, Morocco, in order to provide more reliable criteria for identifying contourites.

Detailed sedimentological work backed by lithologic logs, descriptions of microfacies and outcrop scale pictures, are supported by representative thin sections and measurements of paleo-current patterns, plotted and visualized in comprehensive charts. Well-established biostratigraphic conodont zones provide key information on temporal distribution of erosional episodes on the Tafilalt platform. To support the model of a current-driven orientation of *dacryoconarid* conchs, coarse grained *dacryoconarid* beds are being statistically analyzed for paleo-current patterns. The results of these investigations are interpreted in the context of sedimentary traction structures and temporal trends in facies characteristics.

Preliminary results in the study area of the Tafilalt-platform, support platform wide erosional episodes during the Taghanic event of the Upper Middle Givetian, during the Upper Givetian / Lower Frasnian boundary, and the Middle Frasnian Rhinestreet events, followed by periods of coarse-grained, current-aligned styliolinite calcarenite sediment accumulation in an otherwise pelagic environment. The calcarenite facies include cross-laminated grainstones of current oriented *dacryoconarids*, as well as normal and inverse graded grain- and packstones.

Evolution of the Palaeotethys in the Eastern Mediterranean: A multi-method approach to unravel the age, composition and origin of the Late Palaeozoic Konya Complex (south central Turkey)

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Content

The Eastern Mediterranean region experienced a highly geodynamic history and has been shaped by two major oceanic realms, the Palaeozoic to Early Mesozoic Palaeotethys and (mainly) Mesozoic Neotethys. Various tectonic models have been discussed for the evolution of Palaeotethys, but essential provenance data for verification are still scarce. Important exposures of Palaeotethys-related sedimentary successions are known, for example, from Chios (eastern Greece), Karaburun (western Turkey), and the Konya Complex (south central Turkey). They are considered as key areas for understanding the closure history of Palaeotethys. The Konya Complex is generally thought to comprise a Palaeozoic carbonate platform that is overlain by siliciclastic sediments with olistoliths and volcanic-sedimentary rocks. Our main objective is to provide an extensive dataset for the siliciclastic rocks of the Konya Complex to shed light on their age, composition, and origin. Here, we present results from a multi-parameter provenance analysis utilising thin section petrography, bulk-rock geochemistry, U–Pb LA-ICP-MS zircon dating, and single-grain geochemistry. Detrital zircon ages – in particular Silurian–Devonian and Ordovician–Silurian populations – record major sediment supply from units of the southern Eurasian margin but minor input from North Gondwana as well. In contrast to sediments from Chios and Karaburun, detrital garnet and Cr-spinel are virtually absent in the studied rocks from the Konya Complex. Results from Zr-in-rutile thermometry revealed that a majority of grains were derived from amphibolite- to eclogite-facies rocks and the Cr–Nb composition indicates prominent input from acidic sources. Tectonometamorphic and structural studies will contribute for reconstructing the palaeoposition of these rocks within the Tethyan realm.

Facies belt vs. facies mosaic: Architecture and sedimentological heterogeneities of a carbonate ramp reservoir analogue (Middle Triassic, SW Germany)

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Content

Carbonate ramp depositional systems show a much higher degree of complexity than the schematic depositional models with predictable facies patterns and simple “layer-cake” stratal configurations, which are widely used in exploration and reservoir characterisation. This is exemplified with an Upper Muschelkalk outcrop example that represents a bioclast-rich reservoir analogue (Quaderkalk-Formation), deposited along an epicontinental, very gently inclined carbonate ramp in the regressive part of a third-order depositional sequence. In an area of 30 to 80 km south of the city of Würzburg, coquina dominated carbonates build up a complex system of four stratigraphically separated wedges with prominent geometries.

This outcrop investigation focused on the sequence stratigraphic architecture of the Quaderkalk-Formation (Upper Muschelkalk) and the detailed sedimentological and petrophysical characterization of the largest and thickest wedge (wedge 3). In order to improve the understanding of internal reservoir heterogeneities on various scales, 102 quarry outcrops and core samples, including 41 measured sections from previous studies were investigated via facies and sequence stratigraphic analysis and gamma ray measurements. Facies analysis was based on macroscopic field logging and was refined in detail by the analysis of ca. 550 thin sections; poroperm measurements were carried out on 468 plug samples. Outcrop walls were mapped to identify spatial and lateral changes on small-scale. To characterize the architecture and lateral trends, 2D correlations on local and regional-scale were established and facies maps were produced.

The results of this reservoir outcrop study present a heterogeneous ramp setting which is characterized by an overall regressive dominated architecture with a progradational trend towards the basin (NW). The fundamental development of the four wedges is controlled by stratigraphic cycles, which caused expansion (regression) and drowning (transgression). Instead of a continuous facies distribution within a wedge, several separated high-energy facies zones form a carbonate shoal complex “mosaic”. Shoal-internal lithofacies distribution present a heterogeneous pattern which is strongly influenced by a combination of small-scale cyclicity and event-type deposition. In addition, the petrophysical analysis document a complex and vuggy dominated pore system.

Gamma ray und in-situ X-ray fluorescence analysis of the core WW203302 from the Cubango Megafan (Namibia)

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Content

The core WW 203302 was drilled to provide information about the geological structure of the Ohangwena groundwater system in the centre of the Cubango Megafan, which is a part of the Cuvelai-Etoshia Basin in northern Namibia. It reaches a depth of 400 m and intersects the Andoni Formation as well as the Olukonda Formation, which are probably Neogene in age. The aim of this study was to gain continuous information about sediment composition, sequences, depositional environments and paleoclimate using a multi-parameter approach.

The Andoni Formation is composed of well-sorted yellow to green sands or clayey sands and a few clay layers. The Olukonda Formation consists of red sands, silts and clays with frequently intercalated conglomerate layers. Calcretes and dolocretes are irregularly distributed in both formations. Seven subformations were identified on the basis of spectral gamma ray (SGR) measurements of the core material. The subdivision is supported by the results of the X-ray fluorescence analysis, which were carried out by the Federal Institute for Geosciences and Natural Resources (BGR). The subformations can be distinguished by changes in element concentrations in terms of Al, Na, Cr, Mg, Fe, Ti, Zr. The most significant changes occur between the Olukonda and Andoni formations, where the former shows lower Al, Na, Fe Zr and Ti concentrations. Further, overall trends are visible in upward increasing Th/K and upward decreasing K/Al ratios.

Data from spectral gamma ray, X-ray fluorescence and sedimentological criteria are used to reconstruct paleoclimate trends. The depositional dynamics of the Olukonda Formation indicates more arid conditions with frequent (seasonal) flooding, which is supported by the geochemical results such as the weathering index. The overlying Andoni Formation is characterized by increasing humidity and stronger weathering, indicated by upward increasing Th/K ratio, upward decreasing K/Al ratio and more perennial fluvial sedimentation. Other data such as magnetic susceptibility, pXRF and granulometry (provided by BGR) fit well in this framework and allow for enhanced paleoclimatic studies of the Neogene in southwest Africa based on a multi-proxy approach.

Long-term controls of sedimentary basin architecture in the Tres Cruces subbasin, Jujuy, Argentina

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Content

Concepts of reciprocal sedimentation link the vertical alternation of clastics and carbonates and their lateral continuity in shallow-marine environments with relative sea-level changes. Mixed, clastic-carbonate strata of the Maastrichtian to Danian Yacoraite Formation provide an ideal setting to test how the concept of reciprocal sedimentation can be applied in a syn- and post-rift basin with significant lateral and vertical facies heterogeneity. The formation is part of the Salta Group, which comprises Lower Cretaceous to Eocene syn- and postrift deposits of the Salta rift. Focus of this study is the Tres Cruces subbasin. The Tres Cruces subbasin is the northern extent of the triradiate Salta basin (NW Argentina). The elongated trough extends 50 km from north to south and has a width up to 20 km. The sedimentary infill reaches up to 4 km, of which the Yacoraite Formation comprises 160 to 280 m.

A total of 14 stratigraphic sections have been measured along two regional transects. One from north to south from the paleo-swell, connecting the Salta Basin to the Potosi Basin in Bolivia, to its depocenter and a second one from east to west parallel to the paleo-swell.

Sedimentary facies include sandstones deposited as fluvial and reworked eolian dunes, silts and marls from ephemeral water bodies, bioclastic wacke-packstones, ooidal pack- and grainstones, bioclastic rud- and floatstones deposited in a subaqueous relative high-energy setting and stromatolite framestones. The physical correlation of the facies packages, integrated with petrographic, geochemical and biosedimentary analyses, provide a tool to visualize how facies and sedimentary architecture change throughout the Tres Cruces subbasin.

The spatial superposition of lithofacies at basin-scale indicate a longer-term control by relative sea-level changes. However, observations at the outcrop scale suggest that a locally heterogeneous facies distribution is governed by environmental changes. Hence, concepts of reciprocal sedimentation must be applied with care in spatially complex rift basins, because environmental conditions may locally overrun regional stratigraphic patterns.

Soft-sediment deformation structures (SSDS) of Late Pleistocene sediments on the islands Hiddensee and Rügen (NE Germany)

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Content

The topography of NE Germany is the result of glacial processes during the Late Pleistocene. The repeated advance and decay of massive ice sheets led to complex geomorphological and sedimentological features such as moraines and glaciofluvial channels. These Late Pleistocene deposits crop out along cliffed coastlines of the southern Baltic Sea and reveal extensive soft-sediment deformation structures (SSDS). The aim of this study is to carefully document and analyse the latter in regards to their process of formation.

While some of the SSDS can clearly be explained by glacial or glaciotectonic processes, there are other structures which are atypical and have been described as consequences of liquefaction. These include injection structures, pseudonodules and pillow structures which generally occur in relation to earthquake-related seismic shaking with magnitude >5.5. Since there is very limited evidence of earthquakes within the area of NE Germany, the SSDS are controversial geological features that deserve further exploration.

Two horizontal profiles on Hiddensee, 7 m and 5 m long, and one on Rügen, 65 m long, have been surveyed with regard to SSDS within contact zones of sandy and silty sediments. Furthermore, four sedimentological profiles of the deformed layers have been logged. Within the deformed deposits on Hiddensee, small scale faults are the dominant structures. However the sediments on Rügen show two main horizons of concentrated SSDS including pseudonodules and clastic vents, faults are less abundant. All profiles have been displayed digitally very detailed in order to better understand the processes which formed them.

Session 7.2: Chemostratigraphic and biotic events in Earth history.: Poster

Session 7.2: Chemostratigraphic and biotic events in Earth history.: Poster A-771

Association of stromatolites and ooids of the Yacoraite Formation, Jujuy, Argentina

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Content

The spatial association of stromatolites and ooids has been known since the pioneering work of Kalkowsky (1851-1938), but remain rare in the geological record. Both provide archives of environmental, geochemical and evolutionary changes, which makes them of interest for geoscientists and biologists equally. Ooids and stromatolites are exceptionally well exposed in the Tres Cruces subbasin is the northern extend of the triradiate Salta Basin (NW Argentina). Its stratigraphic record includes the post-rift Yacoraite Formation (Maastrichtian-Danian), composed of alternating bioclastic, oolitic and stromatolitic limestones and marls. This study aims to characterise the spatial and temporal distribution of ooids and stromatolites and to perform detailed analysis of the stromatolitic fabrics in order to infer the factors controlling their origin and development.

The stromatolites are continuously exposed and exceptional well preserved in individual beds along kilometer-scale transects alternating with green and purple silts. Each bed forms a succession (0.3-1.5m) consisting of basal oolitic grainstone (0.05-0.5m), overlain by planar stromatolites with marked millimeter-scale laminae and entrapped ooids (0.05-0.4m). The laminae grade upward into the oolitic grainstone, whereas the amount of incorporated ooids decrease. The uppermost interval of the stromatolites show domal morphologies, with oolitic grainstone cores (0.1-1.0m). In general, the stromatolites show an upward increase in size and complexity and are capped by either laminated marly beds or oolitic grainstone levels. The ooids change their microstructure from laminar concentric, partly obscured by micritization at the base of Yacoraite strata to a radial fibrous microstructure towards the top. Systematic geochemical sampling (C-, O-, Sr-isotopes) and elemental mapping of individual ooids under the SEM provide insights into changes in environmental conditions through time. The assessment of the associations of stromatolites and ooids and their geochemical signatures will provide a record of changes in salinity, climate and freshwater input. This data will shed light on the on-going controversy on the marine versus lacustrine origin Yacoraite Formation.

Latest Sinemurian to Earliest Toarcian $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ fluctuations in belemnite rostra from the Aubach section of the Wutach area, South Germany

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Content

In the Early Jurassic (Latest Sinemurian-Earliest Toarcian) siliciclastic and carbonate sediments, now exposed in the Aubach section in SW Germany, were deposited in the Swabo-Franconian Basin at mid-latitudes in a relatively shallow marine epicontinental environment of the Laurasian seaway north of Tethys Ocean. From this succession, a total of 225 subsamples were taken from calcitic belemnite rostra, checked for diagenetic alteration by the common screening techniques, and subsequently analyzed for carbon and oxygen isotopes.

The new $\delta^{13}\text{C}$ data show the negative excursion at the Sinemurian–Pliensbachian boundary and is compatible with an injection of isotopically light carbon into the atmosphere-ocean system. In contrast, relatively heavy values are observed in the margaritatus Zone (Late Pliensbachian Event) supporting the burial of organic carbon and increased black shale deposition combined with a decline in the atmospheric carbon dioxide. Belemnite oxygen isotope ratios fluctuate throughout the Pliensbachian and the earliest Toarcian reaching heaviest values of $> +1.0\text{‰}$ VPDB in the upper margaritatus Zone. These data of carbon- and oxygen isotopes lend further support to the existence of a pronounced Late Pliensbachian ‘cooling’ Event (LPE) in SW Germany and point to its superregional nature.

Organic geochemistry and high-resolution chemostratigraphy across the Toarcian Oceanic Anoxic Event (T-OAE) in the Aubach section, Wutach area, SW Germany

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Content

The Toarcian Oceanic Anoxic Event (T-OAE) is characterized by significant organic matter burial, numerous geochemical anomalies and one of the most significant negative carbon isotope excursions (CIE) in the Mesozoic. Early Jurassic strata covering the T-OAE are exposed in the Aubach section, Wutach area, SW Germany. In the present study, we generated new organic and inorganic carbon isotope data as well as element concentrations (Mn, V, Mo), common organic geochemical data (rock eval, TOC, $\delta^{13}\text{C}_{\text{org}}$) and biomarkers of bulk rock samples. The results are currently utilized to determine fluctuation in the carbon cycle, to evaluate bottom water redox conditions during sediment deposition, and to determine variation in the source of organic matter.

The first results show that the negative inorganic carbon isotope excursion from the semicelatum to exaratum Subzones is well-expressed in the Early Toarcian strata of the Aubach section. Organic geochemical characterization additionally points to the preliminary interpretation that the organic matter source changed during the T-OAE (more marine organic matter in the Unterer Schiefer) in line with observations from multiple other Tethyan successions.

Session 7.2: Chemostratigraphic and biotic events in Earth history.: Talk

Session 7.2: Chemostratigraphic and biotic events in Earth history.: Talk
A-505

Changes in sediment composition at the edge of Baltica during the late Neoproterozoic and Cambrian: Insights from a multi-method approach on the Digermulen Peninsula (Finnmark, Arctic Norway)

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Content

Few localities worldwide contain an almost complete sedimentary record across the Ediacaran–Cambrian transition as well as macrofossils for studying the 'Ediacara biota' and the Cambrian radiation. The Digermulen Peninsula in Arctic Norway is one such exceptional locality. The site was located at the edge of Baltica during the Ediacaran–Cambrian transition, where potentially the dramatic climatic turnover from icehouse to greenhouse conditions can be deduced and tied to large-scale plate tectonics. Since 2011, studies by the Digermulen Early Life Research Group have recorded important new finds, promising to establish the site as a significant Ediacaran biota locality. The Ediacaran succession is about 1000 m thick. Ediacara-type fossils occur in the Indreelva Member of the Stáhpogieddi Formation. Discoidal fossils dominate the Ediacaran assemblage, although a potentially much greater diversity is suggested by the recent discovery of frond-shaped and dickinsonimorph fossil. The Ediacaran–Cambrian boundary is located within the Manndrapselva Member of the Stáhpogieddi Formation, based on biostratigraphic age control (i.e. trace fossils and organic-walled microfossil assemblages), followed by the lower Cambrian Breidvika Formation. The succession consists mainly of quartz-rich sandstones and mudrocks. Deposition took place in various environments including fluvial, shallow marine and deeper marine settings. As shown by previous studies using palaeocurrent data, sediment supply was from the Baltic Shield toward the passive margin of Baltica in pre-Ediacaran time. At one point within the Ediacaran succession, it shifted by 180 degrees due to the newly formed Timanian orogen. This orogen formed in north-eastern Baltica during the late Neoproterozoic. It caused a shift in sediment transport direction and change in source area due to the formation of the Timanian foreland basin to the east of Digermulen Peninsula. In order to track sediment supply and test current palaeotectonic models a multi-method provenance approach on Neoproterozoic and Cambrian sedimentary rocks of the Digermulen Peninsula has been applied. We present and discuss first results to decipher the sediment sources and to track changes of sediment supply through this critical time interval of Earth history.

Diagenetic calcite - an underused resource for high-fidelity studies of macrofossil geochemistry

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Content

The risk of diagenesis erasing palaeoenvironmental information locked in the calcite of fossil shell materials has been recognized in the early days of palaeoclimate research. Particularly the 1980s and 1990s have seen seminal publications on this topic from which most commonly cited geochemical trends of diagenesis are derived.

During the last decades, technological advances have enabled analysis of new isotopic systems and improved sensitivity and precision for measurements of traditional geochemical proxies, but research on geochemical trends of diagenesis has not kept pace. In particular – and perhaps surprisingly – the analysis of clearly diagenetic calcite phases in sedimentary successions is often avoided in palaeoclimate studies. However, these diagenetic phases – cements, slickensides, recrystallized shell material, microbialites, veins and the such – are direct witnesses of the conditions under which fossil materials experienced postdepositional alteration.

While diagenesis often follows a standard set of geochemical and isotopic trends, detailed analysis of geochemical alteration trends adds a wealth of information, enabling palaeoclimatic reconstructions from fossil calcite at much improved levels of robustness. In particular, lithology- and species-specific trends of alteration can be identified and may permit reconstruction of primary geochemical composition of partially overprinted shell material.

Here we present case studies of diagenetic trends in fossil shell materials and diagenetic endmembers which do not reflect the current dogmata but help define regional, local, time- and material-specific trends of alteration. These examples may spark a renewed effort of defining alteration trends locally and specific to the studied materials and feed into a comprehensive and up-to-date database for the geochemistry of diagenetic phases.

Paleo-environmental reconstructions of the Late Cretaceous – Paleogene black shale, Safaga, Egypt

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Content

The Mesozoic era witnessed wide prosperity of life but ended by one of the most disastrous events that led to the extinction of various groups of organisms in the Phanerozoic record. Although numerous studies have been done on this time interval, there are many debates and controversies on the paleo-environmental conditions, e.g., global carbon cycle and paleo-temperature etc., during this period. This contribution will discuss facies-diagnostic criteria for the Late Cretaceous-Paleogene interval, based on three cores from the Safaga area. In Egypt, the sedimentary sequence of that interval has potential economic significance due to the occurrence of phosphorites and including unconventional resources, like black shale.

The Upper Cretaceous – Paleogene black shale is well represented in three cores in the Safaga area, Eastern Desert, Egypt, namely; Um El-Huaitat, Mohamed Rabah and Wassief. This study is based on integrated biostratigraphical, petrographical, mineralogical, and geochemical investigations. XRD, geochemical (major and trace elements), TOC measurements of 368 samples, as well as stable isotopes (both carbon and oxygen) will allow to discuss the paleo-ecologic variation within the studied interval. High resolution chemostratigraphic correlations will be applied to achieve an optimum age model that will allow for the paleo-environmental interpretations.

Upper Cambrian to Upper Ordovician $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ stratigraphy of the western Baltic palaeobasin, Öland, Sweden: A closer look at climate during the onset of the Ordovician Radiation

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Content

The Late Cambrian to Mid-Ordovician of the Baltic palaeobasin is characterised by significant biotic and environmental perturbations. The Great Ordovician Biodiversification Event (GOBE) and the mid-Darriwilian Isotope Carbon Excursion (MDICE) perhaps constitute the most significant expression of these perturbations, and a causal link has been suggested between climate and mid-Ordovician biodiversity changes. In the present study, we used 217 brachiopods and 168 bulk rock carbonate subsamples originating from the western Baltic basin (Öland, Sweden) to construct a continuous, high-resolution $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ record of the Furongian to lowermost Sandbian (Upper Cambrian to Upper Ordovician) period. Common screening methods have been applied for the samples or are still in progress and the first results show that brachiopods, as well as bulk rocks, yield significant palaeoenvironmental information. Our Cambrian brachiopod and bulk rock results show light $\delta^{13}\text{C}$ (up to -5.1 ‰) and $\delta^{18}\text{O}$ (up to -8.9 ‰) values, and values for Ordovician brachiopods and bulk rocks are considerably heavier (up to +1.6 ‰ for $\delta^{13}\text{C}$ and -4.1 ‰ for $\delta^{18}\text{O}$). Our Lower to Middle Ordovician $\delta^{13}\text{C}_{\text{brachiopod}}$ data are ~ 0.5 ‰ heavier than published data for the Baltic basin, and ~ 1.3 ‰ heavier compared to literature results from other regions of the globe. Furthermore, our $\delta^{13}\text{C}_{\text{brachiopod}}$ values are ~ 0.4 ‰ lighter, and our $\delta^{18}\text{O}_{\text{brachiopod}}$ values are between 0.5 ‰ and 2.5 ‰ heavier than corresponding bulk rock values. The study documents a general increasing trend for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from the Furongian to the Sandbian, with some superimposed negative and positive isotope excursions. A short negative excursion in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the upper Floian, and a sudden shift to heavier $\delta^{18}\text{O}$ values after the Dapingian-Darriwilian transition, which coincides with the significant positive $\delta^{13}\text{C}$ excursion in the mid-Darriwilian (MDICE), are recorded. The results of the Baltic palaeobasin confirm the proposed secular isotopic trends for the Cambrian-Ordovician. Our results further suggest a strong connection between lower Darriwilian climatic cooling, the coeval GOBE, and carbon cycle perturbations in the mid-Ordovician indicated by the MDICE.

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3D pore network visualisation and petrophysical analysis of skeletal-oid grainstones: A case study from the Germanic Basin (Middle Triassic, E Germany)

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Content

Porosity in carbonate rocks often show a high variability, which mostly results in complex pore networks. This is due to the susceptibility of carbonates to diagenetic processes, such as dissolution and precipitation. This case study is focused on a detailed three-dimensional pore network analysis of several skeletal-oid grainstone plug samples. The samples originate from the "Schaumkalk Zone" (Lower Muschelkalk), which is exposed in a large quarry outcrop close to the village of Steudnitz (Thuringia, East Germany). The Anisian sediments were deposited along an epicontinental, very gently inclined carbonate ramp within the semi-enclosed Germanic Basin.

Bioclast-rich section investigated has a thickness of approximately two metres, composed of decimetre-thick, cross-bedded pack- to grainstone and grainstone beds, and represents a shallowing-upward sequence. The section was logged according to lithology, Dunham texture, components and sedimentary structures. Hand specimen were collected to illustrate small-scale facies changes. In order to visualise three-dimensional pore networks, ten plug samples (diameter: 25 mm, length: 20 mm) were extracted from representative specimens and measured with a Zeiss Xraidia 520 3D microscope. Measured data were interpreted via VolumeGraphic Software. In addition, thin sections were prepared of every plug sample for microfacies and diagenetic analysis, and detailed pore type classification.

The results of this interdisciplinary investigation document a moldic porosity dominated pore network, which is essentially influenced by (1) initial deposition processes, such as storm events and wind-induced currents, and the (2) stratigraphic position. As expected, porosity increases with the progressing regression. The x-ray scans reveal a relationship between the porosity distribution pattern and smaller sedimentological structures. No relationship between microfacies and porosity trends could be identified.

Acknowledgement

We thank the Central Research Development Fund (CRDF) - University of Bremen for sponsoring this case study via the "impulse grants" program for Postdocs. In addition we gratefully acknowledge the financial support of the German Research Foundation (Deutsche Forschungsgemeinschaft - DFG) within the call for major equipment (X-Ray-microscope) at the University of Bremen.

Detailed seismostratigraphic mapping of the Upper Cretaceous to Early Cenozoic (Cenomanian - Danian) in the southern German North Sea area

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Content

In the southern German North Sea the Upper Cretaceous is generally developed as a uniform cover of mainly crumbly, whitish, micritic limestones commonly known as 'chalk'. These 'chalk' sediments were deposited from Cenomanian to Danian times. In contrast to the adjacent North Sea sectors of the Netherlands or Denmark, no comprehensive and detailed mapping of Chalk sediments exists in the southern German North Sea until now. In order to fill this gap, we performed a detailed seismostratigraphic analysis and mapping of the Late Cretaceous (Cenomanian) to Early Cenozoic (Danian) sedimentary record of the southern German North Sea based on available seismic and well data.

The high quantity and good quality of available seismic data allows us to study the geometry, structural features and seismic facies of sedimentary sequences in considerable detail. Based on seismostratigraphic concepts, we subdivide the sedimentary succession records into more than 10 regional seismic sequences. We also examined the distribution, age, orientation and internal geometry of deep erosional channels within the Chalk.

In contrast to contractional deformed basin areas nearby (i.e. German Central Graben & Lower Saxony Basin), we found little to no evidence of significant shortening or small-scale tectonic segmentation and accompanying thickness variations within the study area. However, local thickness variations of Upper Cretaceous sediments within the study area are related to increased halotectonic activity (rim synclines, crestal anticlines). Although Upper Cretaceous to Lower Paleogene sediments were deposited and are preserved over most of the German North Sea and adjacent areas, our mapping results illustrate distinct variations in structural style, thickness and facies. Especially uplifted Cretaceous strata and thickness variations along salt diapirs, structural features like erosional channels or slumps indicate strong sedimentary re-deposition within an active sedimentary environment. We also investigate the temporal and structural linkage between contraction/inversion history in the adjacent areas and the thickness distribution, timing, intensity and style of halotectonics as well as subsidence and uplift history in the study area. We also will work to understand the coupled basin-scale tectonic processes and resulting dynamics of salt movements in adjacent areas, providing the base for consistent and basin-wide deformation models for the Upper Cretaceous.

Incised channel fills of the Stuttgart Formation (Schilfsandstein) in the Central German North Sea (Horn Graben)

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Content

For the project TUNB ("Subsurface Potentials for Storage and Economic Use in the North German Basin"; www.bgr.bund.de) a new detailed seismic mapping campaign on the deeper subsurface of the Central German North Sea was carried out. For the Triassic formations a consistent seismostratigraphic concept was developed evaluating available well data and seismic surveys. Based on this concept hundreds of 2D seismic lines were interpreted resulting in depth and thickness maps for all Triassic formations.

The interplay of high subsidence in the Early Triassic, mobilisation of Permian salt in the Middle to Late Triassic and uplift and erosion in the Middle to Upper Jurassic resulted in complex spatial relations of Mesozoic strata in the Horn Graben and deep erosion outside the graben. Flattened 2D seismic lines revealed erosional structures of the Stuttgart Formation cutting into the underlying Grabfeld Formation. The reflection pattern within these seismic lines correlates with the succession exposed in an intra graben well. There, the Stuttgart Formation disconformably follows the truncated top of the Upper Grabfeld Formation with at least 150 m of strata missing in comparison to onshore outcrops.

The interpretation of the seismic lines suggests the incision of channels and their subsequent fill with clastics of the Stuttgart Formation. This seems to be in congruence with contemporaneous channel fills described from southern parts of the Central European Basin. In detail, the incision in the Horn Graben seems to be more complex as indicated by terrace-like features. Mapping the depth of base Stuttgart Formation shows three channel-like structures trending NNE-SSW; two inside the Horn Graben and one at its eastern flank. They are oriented along the flanking salt structures suggesting at least some halotectonic control.

In our contribution (poster), we will present the results of the seismic mapping study in greater detail and discuss the genesis of the described features.

Late Permian to Early Triassic sediment provenance at the southeastern margin of the Central European Basin

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Content

The Central European Basin constitutes a widespread epicontinental basin fed by clastic, mainly fluvial and eolian sediments derived from basement highs at its northern and southern margins. Permian to Triassic subsidence was controlled by postorogenic cooling followed or superimposed by extension related to the breakup of Pangea. The basin was generally shallow with low relief, which gently increased towards the southern margins as reflected by coarser-grained clastic material. Provenance changes in such basins are expected to be often rather subtle in contrast to basins controlled by active tectonics such as, e.g., synorogenic basins.

In search of provenance contrasts and related source area evolution at the SE margin of the Central European Basin, we have analysed Late Permian to Early Triassic red beds of the Palatinate Forest and the Black Forest for petrographic characteristics and framework composition, heavy mineral assemblage, tourmaline and rutile chemistry as well as detrital zircon and rutile U-Pb age distributions. The studied stratigraphic range starts with few upper Rotliegend samples but concentrates on Zechstein and the entire Buntsandstein sequence; it thus covers at least 15 Myrs (approx. 258 – 243 Ma), which is expected to reflect the aftermath of progressive post-orogenic planation.

The Zechstein and Upper Rotliegend samples are characterized by low degree of grain rounding along with a relatively high intersample variability of Q/F ratios as well as heavy mineral and zircon U-Pb age distributions. This is interpreted to reflect more proximal depositional settings, which record small to medium scale variations in source area characteristics. In the lower Buntsandstein, grain rounding increases significantly while compositional variability decreases. Likewise zircon U-Pb age distributions have become rather uniform. This is interpreted to reflect a more distal depositional setting, where the provenance signal is largely homogenized due to increased drainage area and possibly sediment recycling. This trend culminates in the Middle Buntsandstein where the mineralogical maturity (i.e. quartz content, Q/F and Q/L ratios) is highest. A major break is detected at around the Middle/Upper Buntsandstein transition where compositional changes are accompanied by a partial shift towards older zircon U-Pb ages. This break is roughly contemporaneous to a major erosional unconformity in the Buntsandstein of the Central European Basin.

Modeling oil migration pathways in the Central Adriatic Sea

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Content

An integrated and calibrated 2D petroleum systems model was setup using the PetroMod software for the Central Adriatic Basin region to test different oil migration pathways in the carbonate platforms developed from late Triassic throughout the Mesozoic until the onset of the Apennine orogeny in late Cenozoic.

Heavy, immature, isotopically light oil impregnates the karstified paleotopographic high of the Apulian Platform and margin, but the source of this oil and its migration path have been debated for long time.

It is in general assumed that the source rock is the oil prone Upper Triassic Burano Formation and migration should be relatively recent and subvertical, along faults. Alternative hypothesis are a Middle Triassic Besano-Meride Formation equivalent, and migration would be also subvertical along faults or the Lower Jurassic Emma Limestones from the Ugento Formation. The latter migration being lateral up dip from the Adriatic Basin margin.

The model is fully calibrated with wells and downhole measurements. Model simulation runs not only visualize the different migration paths with unprecedented clarity, but also open new perspectives on the co-existence of multiple sources and their interconnection. Indeed the model identifies several phases of top losses which might have played a crucial role as ocean fertilizer and hence high productivity along the carbonate margins during Lower Jurassic.

Mudstones of the Lower Muschelkalk from Thuringia

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Content

Mudstone deposits are the prevailing lithology of the Lower Muschelkalk (Jena Formation) and were studied in outcrop and subsurface sections from Thuringia. The succession reflects a shallow ramp environment of deposition, formed in a restricted, marginal-marine epicontinental setting with starved basin conditions.

Mudstones of the Jena Formation are deposited in protected shallow marine environments, interrupted by episodic high-energy intervals (storms layers, slumping and mass-flow beds).

Various carbonate and siliciclastic mudstone facies were analysed microscopically (including μ XRF-scanning) and demonstrate textural, biogenic, and mineralogical heterogeneity. Textural analyses reveal that some mudstones are deposited by suspension settling and commonly dispersed by a combination of waves, gravity-driven processes, and unidirectional currents driven variously by storms and tides. Others were formed by microbial processes as indicated by bacterial structures. The lateral and vertical changes of both carbonate mudstone types argue for a predominant stratified water column and may reflect changing levels of oxygenation, as indicated by varying contents of TOC and pyrite framboids.

The carbonate mudstones often exhibit microspar fabrics, due to late diagenetic processes and may have overprinted the original depositional interrelationships and textures. Early diagenetic processes resulted in occasional highly cemented zones, especially at stratal surfaces, as demonstrated by firmgrounds and hardgrounds with characteristic burrowing and boring successions.

OH-defects in quartz as monitor for provenance

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Content

OH-defects of more than 500 quartz grains from siliciclastic sediments and their potential source rocks were studied by FTIR-spectroscopy. Sediment samples were derived from the Rhine River at Rhöndorf and from the Baltic Sea coast at Darß. As potential source rocks Hercynian granites from the Black Forest and Proterozoic granites from Sweden were investigated, respectively. Prior to analysis, all quartz grains were manually aligned parallel to the crystallographic c-axis, and polarised measurements were performed in two perpendicular directions in order to erase the IR-signal of fluid and melt inclusions and to minimize the contribution of mica inclusions. IR-absorptions of the hydrous defects were converted into concentrations for water equivalents.

Results show that quartz grains from Darß and Rhöndorf exhibit fundamentally different defect water contents, where quartz grains from Darß are generally low in defect water (in average 4 wt ppm, most grains below 2 wt ppm) compared to grains from Rhöndorf (in average 20 wt ppm with significant populations at 10, 20 and 50 wt ppm). Most granites from Sweden have defect water concentrations around 2 wt ppm water, no grains >20 wt ppm water were observed, and the average value of all analysed grains (N=120) is around 4 wt ppm. Quartz grains from the Black Forest granites cluster around 24 wt ppm water. In addition to the defect water content, IR spectra bear information concerning the OH-speciation of the hydrous defects that occur as characteristic absorption band at 3378 cm⁻¹, 3470 cm⁻¹, and 3595 cm⁻¹, depending on the charge balancing cation (Al, Li, or B, respectively) during H-incorporation. If spectral characteristics are parametrised with respect to absorption band ratios, IR spectra can be used to identify grain cluster from distinct source rocks in their siliciclastic counterparts.

Based on the current data set it can be concluded that detrital quartz derived from the Proterozoic Scandinavian Shield is in average by far less rich in OH-defects than detrital quartz derived from the Hercynian orogeny and may thus be used as tool for provenance analysis in sedimentary basins, where both sources are mixed.

Rift systems at continental margins: A case study of facies and provenance of the sedimentary-volcanic Mitu Group (Permotriassic; Central Andes, Peru)

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Content

The transition from the Late Paleozoic magmatic arc regime of western South America to the Andean accretionary orogen initiated in the Early Jurassic is marked in Peru and northern Chile by the development of a system of extensional basins in the course of the Permian and Triassic. It is still undecided whether extensional tectonics occurred in a back-arc or a rift setting. The basin fills consist of stratigraphically poorly controlled volcanosedimentary successions commonly known as the Mitu Group and equivalents. We present first results of our analysis of the facies evolution and provenance of the late Permian and Triassic basin fills in southern and central Peru. Our study aims at constraining the sedimentology, chronology, spatial development and tectonic setting of evolving depocenters. Our fieldwork showed that deposition of the Mitu Group was initiated by a transition from the carbonates of the Copacabana Group via a mixed carbonate-siliciclastic transition of c. 30 m thickness to the siliciclastic and volcanic Mitu Group. The beginning of Mitu sedimentation in the Cusco Province is characterized by short-lived alkaline and calc-alkaline volcanism interbedded with fluvial deposits, followed by an extended development of floodplain facies and a lack of volcanism. This transits to a coarsening-upward evolution of fluvial facies associated with increasingly voluminous alkaline volcanic rocks. Increased rates of deposition and volcanism took place in semi-grabens accommodating alluvial fans at the top of the Mitu Group. We constrain the provenance and geochronology of the depositional record by single-grain studies of heavy minerals and LA-ICP-MS dating of detrital zircon and rutile. Here we present first detrital zircon age dates of key strata at the transition to and the base of the Mitu succession. A sandstone from the top of Copacabana Group, within 1 m of the basal contact of the Mitu succession, gave a maximum depositional age of 258.9 ± 5.3 Ma. The stratigraphically oldest sample of the Mitu Group from 2 m above its base yielded a maximum depositional age of 254.3 ± 8.7 Ma. These preliminary ages are similar within error and pertain to the late Permian indicating the absence of a significant hiatus in this region between the Copacabana Formation and the Mitu deposits. The beginning of the Mitu sedimentation appears to be characterized by variable initiation of basin filling and subsequent asynchronous development of the semi-graben depocenters.

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3D geocellular Facies Modeling of epicontinental carbonates: Muschelkalk Basin (S Germany)

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Content

The study, an excerpt of a larger project of the Sedimentary Geology Research Group of Tübingen and Shell Global Solutions provides two nested reservoir analog models of an epicontinental basin, the Upper Muschelkalk in Southern Germany. Detailed sedimentological logs from 14 boreholes and 29 surface outcrop sections form the database used, together with a well-established litho- and biostratigraphic framework. All sections were studied using facies analysis, as well as 1-D and 2-D sequence stratigraphic analysis, leading to regional correlations, that integrate the sequence architecture and marker beds. Using subsurface 3D modelling tools, two nested geocellular models were generated:

1) For a basin-scale model (201 km x 325 km) covering the complete southwestern part of the Germanic Basin, TGS (Truncated Gaussian Simulation) was used to model the lithofacies associations, in order to represent the large-scale lateral facies successions.

2) For a field-scale model (50 km x 50 km) covering the area around the Kocher and Jagst valley (Hohenlohe), SIS (Sequential Indicator Simulation) was used in order to model the more detailed distribution of lithofacies types.

In the basin-scale model, the overall paleo-landscape changes per cycle as well as facies tract shifts were reconstructed.

In the field-scale model the overall transgressive hemicycle shows retrograding, isolated and rather small shoal bodies while the overall regressive hemicycle displays prograding and larger, well-connected shoal bodies.

These general patterns might have relevance for better understanding the reservoir distribution in hydrocarbon-bearing epicontinental basins, e.g. on the Arabian plate.

Late Jurassic to Cretaceous Epi-Continental Basins of the Eastern Arabian Plate – Interplay between Tectonism, Global Anoxic Events and Carbonate Platform Dynamics

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Content

The deposition of Mesozoic source-rock sequences of the eastern Arabian plate is directly tied to the generation of epi-continental basins. Using a combination of regional stratigraphic correlations, age dating, geochemical indicators and global climatic/tectonic events this paper investigates the driving forces behind the formation of the intra-shelf basins and related source-rock/seal sequences. Results impact topics such as hydrocarbon exploration, reservoir distribution, regional tectonics and climate modelling.

In eastern Arabia intra-shelf basins existed during three time periods in the Mesozoic: in the Jurassic during the Oxfordian/Tithonian, and in the Cretaceous during the Aptian and the Cenomanian.

The late Jurassic basin is predominantly generated by tectonism. Uplift at the eastern plate margin caused exposure at the eastern plate margin towards the Neo-Tethys, which in combination with sea level fluctuations resulted in the deposition of several large scale sedimentary cycles. In central Abu Dhabi westward progradation of the Tuwaiq Mountain, Hanifa and Jubaila Sequences into an intrashelf basin with source rock deposition are key evidence for the eastern uplift as are collapse features reported from the eastern margin itself. The widespread regional deposition of the Arab and Hith anhydrites (the seals) are taken as further evidence for tectonically driven basin isolation leading to restricted evaporitic conditions. In contrast, the Cretaceous Aptian and Cenomanian intra-shelf basins formed as a consequence of environmental/climatic disturbances. During times of global climate stress carbonate sedimentation was unable to keep up in areas with higher subsidence rates. This provided the impulse for a switch from flat-topped platforms to a nascent basin topography (Hawar & Lower Shuaiba, latest Bar/Early Aptian; Maaddud FM, latest Albian). Subsequent differential aggradation in combination with continued subsidence led to the full development of the basin topography in the early Aptian (AP Apt2-4; Bab Basin) and early Cenomanian (Shilaif Basin). Significantly, detailed carbon isotopic data indicate that climatic disturbances and the onset of global oceanic anoxic events correspond to the generation of the initial topography and not to the onset of organic rich basin fill sedimentation. Subsequently Cretaceous intra-shelf basins were covered by argillaceous limestones and siliciclastics which form excellent seals.

Sedimentary facies and genetic stratigraphy of Coniacian deposits in the northwestern part of the Bohemian Cretaceous Basin: state-of-the-art.

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Content

Data provided by recently drilled boreholes, combined with archival subsurface and outcrop data, allowed the interpretation of lithofacies and regional-scale depositional architectures in Coniacian sandstones in the NW part of the Bohemian Cretaceous Basin.

Presented depositional model interprets the depositional system as dominated by coarse-grained deltas that prograded from the faulted northern basin margin. Coarse clastics were transported downslope by gravity currents, while most of fine-grained material was delivered offshore by overflow hypopycnal plumes. High- and low-angle geometric types of foreset packages are distinguished, representing two end-members of the deltaic environment.

Delta bodies of both foreset types were intensely reworked by tidal currents. However, L-type foreset packages were sensitive to tidal reworking as a result of progradation into shallow water where tidal currents proved to be more effective. In the most proximal part of the depositional space, poorly sorted, burrowed argillaceous sandstones arranged into obscured coarsening-upward cycles, were deposited. They are interpreted as deposits of nearshore shoals or lagoons, protected from tidal action. Presence of red claystone bed may indicate subaerial exposure. Such sequence may be present in other parts of the study area adjacent to the basin margin, as indicated by similar well-log signature. Based on drill core section, heterolithic ("flyschoid") facies is interpreted as bottomsets deposited by underflow hyperpycnites. Laterally extensive turbidites (Žandov and Okrouhlá sandstones) not directly attached to the prograding deltaic bodies indicate existence of distal turbidite distributary systems.

Nearshore sandstones were correlated to their fine-grained time-equivalents in the offshore realm and the depositional record was subdivided into genetic sequences (TUR 7 to CON 5), bounded by maximum flooding surfaces. Within individual sequences, stacking pattern of delta bodies was controlled by interplay of tectonic subsidence and sediment supply, although minor influence of eustatic sea-level fluctuations is expected. Increased tectonic activity between the latest Turonian and middle Coniacian is assumed to be precursor to the inversion of northern Alpine foreland. In addition, geochemical and mineralogical data were employed for assessment of clastic input, intensity of weathering and erosion, as a key to decipher sequence of tectonic processes in the uplifted source area.

The sandstone complex of the Valanginian in the Lower Saxony Basin (North Germany) – a geothermal perspective

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Content

Numerous clastic aquifer complexes with a potential for geothermal applications are expected in the North German Basin. This study focusses on sandstone units of Valanginian age in the Lower Saxony Basin (LSB). These sandstone complex are one of the Lower Cretaceous sandstone units in the LSB which form the shallowest Mesozoic aquifer complex. Deposits of the Valanginian are widely present in the LSB and can be found at depths up to about 1700 m. The aim of this study is to determine the facies units, their regional distribution and associated hydraulic properties.

Facies changes were analyzed on well sections using Gamma Ray and Spontaneous Potential logs, core descriptions and thin section analysis. For each well a Volume of shale (VSH) model was established to differentiate between sand and clay, and to determine the sandstone thickness. Aquifer properties like porosity was calculated from logs and permeability was derived from calculated porosities in the wells. Existing porosity and permeability measurements from conventional core plugs analyses were used to quality-control the log derived values. A lithostratigraphic correlation was established to map the major sandstone units.

The Valanginian comprises a sandstone belt ("Valendis-Sandstone") along the northern margin of the basin, deposited in a shallow marine environment. This relatively narrow belt pinches out to the basin centre, where clay-rich deposits dominate. The "Valendis-Sandstone" is a homogenous, structureless, fine- to medium-grained sandstone and reaches a maximum thickness of around 70 m. Large sections of this sandstone consist of poorly consolidated sand with high porosities, and only a few well-cemented zones were recorded. The eastern part of the basin includes a fluvial to deltaic dominated sandstone complex and an overlying sand unit deposited as a shallow marine shore face sand. The fluvial dominated sandstone consists of cross-bedded, fine to medium grained sandstones with intercalated clay layers. The shallow marine shore face sand is characterized by flaser-bedding and bioturbation.

The "Valendis-Sandstone" is a well-known oil reservoir in the LSB. According to the transmissivities determined in the present study, this sandstone unit could be a primary target for geothermal use. In comparison, the sandstone complex in the eastern part of the LSB is characterized by moderate to poor aquifer properties and could meet the requirements for geothermal use on a regional scale.

Session 7.4: Carbonate mounds: Poster

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***Lophelia pertusa* morphotype differentiation in computed tomography data – a first approach**

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Content

Lophelia pertusa is well-known for its high morphological plasticity with morphotypes ranging from very large, elongated and heavily calcified (*brachycephala*) to small, fragile (*gracilis*) corallites. Thereby it seems that the variability is mainly caused by two factors: (i) the degree of calcification resulting in considerable thickness variations of the outer theca ranging from thin (<1mm) to thick (~1 cm), and (ii) the corallite length (the calices opening seems to be rather constant). So far, observations of the various morphotypes in *Lophelia pertusa* are exclusively qualitative, which prohibits an in-depth comparison of these morphotypes, such as the identification of morphological endmembers and subsequently their potential preferential occurrences within and between regions or through time.

Computed tomography (in this case medical CT) can be used to produce virtual three-dimensional models of various specimens from seabed surface as well as sediment core samples. These virtual models can be used for further analysis. We explored the capability of a calice segmentation and parameterisation to separate morphotypes by their basic calice characteristics (e.g., length, width, volume). The presented methodology forms the potential basis for a quantitative, observer-independent characterisation of morphotypes of *Lophelia pertusa* and their subsequent automatic classification in the future.

Early Holocene cold-water coral mounds on the Namibian margin

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Content

A new large province of mounds build up by cold-water corals (CWC) has been discovered by a hydroacoustic survey on the northern Namibian margin. During RV Meteor cruise M122 in 2016, first video observations with the ROV SQUID and geological sampling clearly proofed these seafloor structures to be coral mounds formed by the ubiquitous species *Lophelia pertusa*. The newly discovered Namibian CWC mounds are spatially limited to an area geomorphologically characterized by a long NW-SE-trending straight escarpment (63 km long, 45 m high). In general, the coral mounds exhibit a rather circular shape and their heights increase from the south to the north on the western slope of the escarpment area (< 4 m in the south, up to 10-17 m in the northern area), while on the top of the central portion of the escarpment, the height ranges between 4-6 m.

No living CWC were observed and, thus, the mounds experience today no active aggradation. First U/Th dating on fossil coral skeletons revealed that the CWC have thrived on the mounds until the Mid-Holocene. Water column information provided a potential explanation for the extinction of the Namibian CWC: at the water depth of the coral mounds (160 – 240 m), dissolved oxygen concentrations of mostly below 0.5 ml/l are likely too low with respect to the oxygen thresholds (ca. 3-7.2 ml/l) described for *L. pertusa*. These low dissolved oxygen concentrations relate to the well-developed Oxygen Minimum Zone (OMZ) off Namibia that in turn is related to the highly productive Benguela upwelling system.

This study provides a picture of the present-day setting of the Namibian CWC mounds, based on hydroacoustic surveys, ROV observations and hydrographic data (CTD). However, as the mounds are today solely covered by fossil corals, this indicates that the present-day setting is not suitable for the proliferation of CWC, while before the Mid-Holocene more suitable conditions for CWC must have prevailed allowing to thrive off Namibia. With dissolved oxygen being the most likely limiting factor for the CWC nowadays, it is hypothesised that better ventilated conditions in the past, possibly triggered by spatio-temporal variation of the Benguela Upwelling System causing a less developed OMZ, allowed the proliferation of the CWC in the Early Holocene.

Evolution of a Contouritic Depositional System beneath and around Cold Water Corals at the Angola upper continental slope (SW Africa)

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Content

The relationship between contouritic deposition and the distribution, appearance and dimension of mostly unexplored Cold Water Coral (CWC) mounds at the Angola continental margin was investigated during R/V Meteor Cruise M122 in 2016. Densely spaced bathymetric, PARASOUND sediment echosounder and high-resolution multichannel seismic data have been acquired to investigate the spatio-temporal evolution of sedimentary architecture as well as CWCs, which occur in chains in water depths between 200 and 500 m, comprising heights up to >100 m and widths between 400 and 1000 m.

In the study area indicators for an active bottom current regime are identified, including contourite channels, separated mounded drifts and erosional surfaces, from the seafloor to 300 mbsf. Furthermore, active and buried faults, related to extension due to salt rafting, are ubiquitous in the study area. CWCs appear to be rather recent features since only few superficially buried mounds have been found restricted to shallow water depth (<300 m). The architecture of the Contouritic Depositional System (CDS), however, is older and CWC growth starts late within the active CDS, indicating that it has developed a habitable environment for CWCs. This study provides a detailed analysis of the contourite channels and separated mounded drifts on both sides of the most prominent mound chain. The so-called Anna Ridge is 13 km long and appx. N S oriented. The eastern channel was formed much earlier than the CWCs and underwent several cycles of channel filling and erosion, suggesting significant changes in the regional current regime over time. Contrastingly, the western channel and drift succeed CWC formation, which suggests that it is formed by the interaction of bottom currents with the CWC mounds. This study focuses on CDS evolution on the upper continental slope in shallow water in response to paleoceanographic changes, discusses the onset of CWC growth as well as the role of salt driven tectonics and analyzes the interaction of bottom currents with the changing morphology.

Session 7.4: Carbonate mounds: Talk

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A comparison of Late Quaternary cold-water coral and coral mound development between two coral provinces in the southeastern Alboran Sea

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Content

The comparison of past cold-water coral (CWC) occurrence and coral mound development between two different mound provinces in the southeastern Alboran Sea, namely the East and West Melilla Cold-water Coral Provinces (EMCP, WMCP), reveals some striking similarities and also some discrepancies since the Late Pleistocene. In both provinces, CWCs experienced a pronounced proliferation between 14 ka BP and 8 ka BP, which was associated with high coral mound aggradation rates $>500 \text{ cm kyr}^{-1}$ during the Bølling-Allerød and the Early Holocene. However, within this period reduced mound aggradation is documented for the Younger Dryas. The periods of enhanced coral mound aggradation coincide with a decreasing trend in the benthic foraminifera $\delta^{13}\text{C}$ values that probably reflect a gradual change in the water column structure in the Alboran Sea, when the dominant water mass at the level of coral mound tops changed from an intermediate water mass to a deep water mass (in comparison to the present-day regional $\delta^{13}\text{C}_{\text{DIC}}$ depth profile). This long lasting trend associated with significant fluctuations points to an extended period of enhanced interactions between the involved water masses most likely resulting in a strengthened hydrodynamic setting as commonly observed along water mass boundaries. Stronger hydrodynamics enhance the important lateral food supply to the CWC, which is supported by high export productivity as reflected by high benthic foraminifera accumulation rates. However, the coral mound tops have been bathed in the deep water mass since $\sim 8 \text{ ka BP}$, as reflected by low benthic foraminifera $\delta^{13}\text{C}$ values. The reduced coral mound aggradation in this period indicates a deteriorated setting. In addition, computed tomography results exhibit a distinct change in the coral community in the WMCP at $\sim 8.4 \text{ ka BP}$. The coral assemblage changed from a *Lophelia pertusa*-dominated lower section (mainly accompanied by *Desmophyllum dianthus*) to a *Madrepora oculata*-dominated upper section (mainly accompanied by *Dendrophyllia* sp.). Overall, our data clearly point to a main role of the water column structure in influencing CWC proliferation and mound formation as well as CWC assemblage composition. The main difference in CWC proliferation between the two provinces occurred since 5 kyr BP, when CWCs seem to have vanished in the WMCP, while sparse CWCs continuously occurred in the EMCP (even until today).

Late Quaternary development and cessation of Mauritanian cold-water coral mounds obtained by U-series dating

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Content

The Mauritanian margin represents an exceptionally vast cold-water coral (CWC) mound area formed by the prominent scleractinian coral *Lophelia pertusa*. Between Cap Timiris and the Senegalese border, up to 100-m-high coral mounds are arranged as two slope-parallel chains in water depths of 400-550 m almost continuously running over ~400 km. CWC were also abundantly found in the numerous Mauritanian canyons and even isolated coral mounds are developed on top of some canyon flank. Today, living corals are rather sparse, while the widespread and massive deposits of fossil corals point to their far more successful proliferation in the geological past. Yet, the knowledge about the timing of cold-water coral colonisation and in particular the development of the Mauritanian coral mounds to date is still limited. This study provides a new extended data set of 77 U-series ages obtained from *Lophelia*-samples, which were collected from various canyons and coral mounds. The data clearly indicate that mound formation ceased with the onset of the Holocene and experienced no reactivation until today, which probably is a consequence of dramatic environmental changes related to the rapid deglacial sea level rise. Most prolific periods for CWC resulting in enhanced vertical mound aggradation with maximum rates of up to ~1600 cm kyr⁻¹ are identified for the last glacial and deglaciation. CWC are also documented for the last interglacial, although as reduced occurrences. Coral mound formation varied partly considerably between the individual mounds revealing a water depth-dependent pattern, which was likely controlled by changes in central water mass circulation that in turn controlled productivity and dissolved oxygen conditions. The occurrence of CWC in the canyons during the Late Holocene points to the potential role of canyons acting as a regional refuge for CWC, from which larvae were supplied that triggered the recent re-colonisation pulse along the open slope.

Mediterranean cold-water corals – an important regional carbonate factory?

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Content

Cold-water coral ecosystems and deposits, dominated by *Lophelia pertusa* and *Madrepora oculata*, are wide-spread in the Mediterranean Sea, which resulted in their description as independent benthic community, called white coral community. To evaluate their role as carbonate factories, we investigated aggradation rates and carbonate accumulation rates from three different cold-water coral sites that differ in their regional and geomorphological settings: (i) a cold-water coral ridge (eastern Melilla coral province, Alboran Sea), (ii) a cold-water coral rubble talus deposit at the base of a submarine cliff (Urania Bank, Strait of Sicily) and (iii) a cold-water coral deposit rooted on a predefined topographic high overgrown by cold-water corals (Santa Maria di Leuca coral province, Ionian Sea). The mean aggradation rates of the respective cold-water coral deposits vary between 10 and 530 cm kyr⁻¹ and the mean carbonate accumulation rates range between 8 and 396 g cm⁻² kyr⁻¹. The studied cold-water coral sites reveal significantly higher carbonate accumulation rates than other deep-water depositional environments. Furthermore, the observed rates were even in the range of the highest productive shallow-water Mediterranean carbonate factories (e.g., *Cladocora caespitosa* coral reefs). This clearly indicates the potential of cold-water corals as important carbonate factories and regional carbonate sinks within the Mediterranean Sea.

Thousands of Late Quaternary carbonate mounds along the Moroccan continental margin

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Content

Whereas Morocco is well-known for long time for hosting a large variety of Paleozoic and Mesozoic carbonate mounds, the discovery of Quaternary mounds built-up by framework-forming cold-water corals is still an ongoing process. The Quaternary Moroccan cold-water coral mounds occur in water depths of 200-400 m in the Mediterranean Sea and in 600-1000 m along the Moroccan Atlantic margin. Depending on the location, the occurrence of living corals ranges from common to absent, with specifically the region of NW Morocco is characterised by a complete lack of living cold-water corals. There, fossil corals cover the mounds, mostly dating back to the last deglacial period or even beyond. The mounds along the Moroccan margins rarely exceed 20 m in height, although in the Mediterranean Sea ridges made up by cold-water corals can reach heights of >100 m.

An extremely high accumulation of coral mounds has recently been discovered off NW Morocco between 35°N and 35.5°N. A detailed mapping revealed the presence of >3000 cold-water coral mounds between ~700 m and ~1000 m water depth. In addition, new hydroacoustic subseafloor data show that in this region more than 600 buried mounds that have no expression at the seafloor exist. As these ~600 buried mounds correspond to ~100 still exposed mounds along the investigated hydroacoustic lines, the number of >3,000 mounds detected in the swath bathymetry data imply that the number of all, buried and unburied, mounds in the ~1300 km² of mapped area might reach ~20,000. Furthermore, the hydroacoustic data reveal 10 distinct subseafloor reflectors that serve as a “settling ground” for mounds. The same reflectors also can bury mounds, grown upward from deeper reflectors. Often several generations of mounds can occur on top of each other, whereas in other places buried mounds and mounds still piercing the sea floor occur side-by-side while they originate from the same reflector. Thus, off the Moroccan Atlantic margin, it appears that only little differences between the mounds decide on their fate: getting buried or keep on growing during the next phase of coral growth. This variable response combined with a dynamic paleoenvironmental setting creates a diversity in individual mound histories that has never been described before. More and more it becomes obvious that cold-water coral mounds are ubiquitous sea floor structures capable of adopting to a variety of settings – sometimes successful, sometimes not.

Session 7.5: From source to sink: Environmental signal propagation into the stratigraphic record.: Poster

Session 7.5: From source to sink: Environmental signal propagation into the stratigraphic record.:
Poster
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Denudation rates in slate lithologies from meteoric $^{10}\text{Be}/^9\text{Be}$ ratios along a small mountainous sediment-routing system

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Content

More than 1/3 of the modern suspended load into global oceans is derived from high-standing islands in southern Asia and Oceania [1]. Different from large sediment-routing systems with large buffering zones, small mountainous source-to-sink systems, like Taiwan rivers, are very sensitive to environmental perturbations such as earthquakes and typhoons, and thus characterized by high denudation rates. Although centennial denudation rates from in situ ^{10}Be (D_{insitu}) are commonly the first choice, slate lithologies and very rapid denudation in the West Central Range of Taiwan impede its application. Hence, we test a promising denudation proxy, the meteoric $^{10}\text{Be}/^9\text{Be}$ ratio, as an alternative choice for determining denudation rates [2] [3]. This new proxy combines a known atmospheric flux tracer, meteoric ^{10}Be , with ^9Be released from rocks by weathering, and can be measured on small (<1 g) sample amounts and quartz-free lithologies [4]. We analyzed ^{10}Be and ^9Be concentrations in the 30-63 μm fractions of bedload sediments along the Choshui River Basin, whose headwaters drain slate lithologies. To first assess ^{10}Be steady state conditions that are a prerequisite for the application of the meteoric proxy, ^{10}Be fluxes exported from the basin by river transport must equal their production by deposition. We determined the exported meteoric ^{10}Be flux by multiplying ^{10}Be concentrations with an independent erosion rate from in situ ^{10}Be , and compared it with the depositional ^{10}Be flux derived from general circulation models. The ratio of exported to produced ^{10}Be flux varies from 0.3 to 2.2 in the Choshui River, with the average value of 1.2, which may indicate a quasi-steady state of the ^{10}Be flux ratio. Hence, we calculate meteoric-derived denudation rates D_{met} . Downstream of the slate-dominated headwaters, our D_{met} agree with published D_{insitu} [5], where both methods yield rates on the order of 1-2 mm/yr. In comparison, the meteoric-derived denudation rate in the slate region is somewhat higher, corresponding to steeper slopes and more erodible bedrock. We conclude that in comparison with more traditional methods, the $^{10}\text{Be}/^9\text{Be}$ ratio is a promising tool to derive denudation rates in regions with rapid erosion and claystone lithology.

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Evolution of hillslope erosion rates during fluvial aggradation in the Yamuna catchment, northern India

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Content

The influence of climate change on fluvial transport capacity, sediment supply and hillslope erosion is fundamental for understanding landscape evolution and surface processes. Deposition of fluvial sediments and the incision of rivers into its bed are supposed to be a result of changes in sediment supply and transport capacity. Therefore the study of fluvial river terraces is important to understand the processes, which lead to aggradation and incision.

Changes in paleo-erosion rates during an aggradation episode provide us with information about changes in sediment supply. In rapidly eroding landscapes, landslides are considered the main process of hillslope sediment supply. Landslide frequency is set by the rate of river incision, which oversteepens adjacent hillslopes and makes them susceptible to failure [1][2]. It was recently suggested that during aggradation periods, when incision ceases and valley bottoms increase, the probability of landslides is reduced and thus hillslope erosion rates are forced to decrease [3]. This mechanism provides a negative feedback on the response of landscapes to climatic changes that has not been tested.

To test this hypothesis, we sampled a 120 m high fluvial fill terrace with an estimated age of ~20 ka [3] in the Yamuna catchment, northern India, and analysed the in situ ¹⁰Be concentration in sand and pebbles to estimate paleo-erosion rates. Preliminary results indicate that ¹⁰Be concentrations in the fill terrace are by a factor of two lower than concentrations in recent river sediments, suggesting generally higher paleo-erosion rates. Additional ¹⁰Be samples of the fill terrace that are currently being measured shall allow us to assess whether paleo-erosion changed during the aggradation periods, while optically stimulated luminescence samples will constrain the time period of aggradation.

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High-resolution modeling and characterisation of boulder deposits using terrestrial laser scanning (TLS)

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Content

The coastline of Oman is affected by extreme wave events. Two relevant ocean wave hazards, storm surges triggered by tropical cyclones and tsunamis, are known to occur in the region but were rarely instrumentally recorded in the past. Hazard potential and return periods therefore still remain enigmatic and are under discussion.

Geological remnants of paleo extreme wave events are archived along the coast. The most prominent deposits primarily consist of blocks and boulders ramparts composed of local limestone and beachrock clasts. Often, the clasts are organised in coast-parallel imbricated boulder trains, some on cliff platforms of over 10m a.s.l.. 14C dating results suggest at least two extreme wave events in the past 1300 years are responsible for the deposits.

We investigated the 3D-distribution and characteristics of those extreme wave event deposits using a high-resolution TLS survey. We focused on a high-precision modeling of parameters as vertical uplift, inland transportation, exact mass, and quarry location. Furthermore, the TLS data was used to distinguish between the various boulder lithologies. The high spatial resolution allowed a comprehensive boulder surface analysis. Variations of surface roughness are interpreted as a result of weathering processes and can serve as an indicator for exposure time. This allows to identify various generations of extreme wave events and therefore hint on a relative dating of deposits.

Altogether we analysed 332 boulders from two different sites. We identified two boulder ridges and an inland and upward fining of clast size. The largest block with a mass of 105.1t was vertically uplifted by 1.41m and experienced an inland transport of 17.6m, while another block of 47.3t was uplifted for 2.75m. The clasts show different shapes and orientation depending on their lithology. Our results allow a clast classification based on surface roughness. Identification of the quarry sites of individual boulders suggests a predominant transportation in SSW-direction, which hints on a wave origin at the Makran Subduction Zone.

We conclude that the Omani coast is prone to high-magnitude extreme wave events which are capable of dislocating blocks of over 100t on elevated cliff platforms. Our results suggest multiple events captured in various boulder trains. TLS proved to be a useful tool for high-precision modeling of extreme event deposit characteristics and differential surface analysis.

Numerical modelling of fluid pressure generation from deep aquifer systems to the seafloor: conceptual model of flow related pressure pattern and instability

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Content

Submarine landslides are related to several trigger mechanisms such as earthquakes, rapid sedimentation and groundwater flows. Those have the potential to affect prevailing pore water pressure conditions; and although in the focus of research since decades, no general conceptual models exist for the interaction between pore pressure changes along an embedded aquifer and the subsequent surface slope destabilization for various aquifer hydraulic conditions.

The major aim of our study was to develop a 3D numerical model to simulate pore pressure changes along aquifers as potential trigger of slope failure. Therefore, we coupled two modelling techniques (I) the Finite Difference Method (FDM) and (II) the Discrete Element Method (DEM). The FDM model is used to simulate hydraulic conditions or pore pressure pattern respectively that forces the DEM model which simulates the sediment physical behavior or slope sediment deformation resp..

Our model mimics a 5 km long and 1 km thick, 10° dipping continental slope with an embedded 50 m thick aquifer system located at 850 m in depth. Initially, the model is fully saturated under stable hydrostatic conditions. A constant flow streaming seaward towards the aquifer toe is initiated at the top of the aquifer. Resulting pore pressure pattern were adopted to the DEM model. In doing so, stress conditions in the DEM model vary which can cause e.g. slope failure. Aquifer permeabilities from $1 \times 10^{-15} \text{ m}^2$ to $1 \times 10^{-12} \text{ m}^2$ were tested whereas slope permeability was fixed to $1 \times 10^{-16} \text{ m}^2$.

Our model enables to simulate the effect of permeability contrast on slope stability in case of an aquifer scenario. There is a significant pressure migration seaward if the permeability contrast of aquifer and confining slope is in the order of two magnitudes or even more. This gradient affects the stability by increasing pore pressure at sites where low sedimentation rates occur and lead to estimate retrogressive failure. In contrast, permeability contrast of one magnitude influence regions with high sediment loading more efficient than regions with lower loading.

Consequently, transient pore pressure changes result in different fluid flow pattern within continental margins. Our results allow to estimate the potential of failure onset at specific sites of the slope due to the influence of lateral fluid flow and associated pore pressure generation. Two conceptual flow-focusing models which affect the slope stability in different pattern are identified.

Propagation of Alpine uplift signals into the deep marine Austrian Molasse Basin: First results of the interpretation of 3D seismic-reflection data and heavy mineral analysis

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Content

The sedimentary fill of peri-orogenic basins is a product of the interplay between tectonics, climate, as well as sediment transport and transient storage processes. It can therefore serve as an archive to reconstruct mountain building, past climatic variations and sediment-transport systems in four dimensions. However, the reconstruction of Earth-surface response to climatic or tectonic variations and the propagation of this response signals into the stratigraphic record is a matter of vital ongoing debate. A key area to investigate such signals is the Northern Alpine Foreland Basin due to its large amount of available data in the Alpine source area and its foreland.

Three major tectonic uplift events occur during late Oligocene to middle Miocene times in the Alps: the uplift of the Lepontine Dome, the Tauern Window, and the Northern Calcareous Alps east of Salzburg. We will investigate how and at what tempo these tectonic signals propagate into Late Oligocene to Miocene sediments. Therefore, the sedimentary successions in the Upper Austrian Molasse Basin will be investigated by the use of 3D seismic-reflection data, sediment core analyses, and heavy mineral-assemblage analyses combined with apatite geo- and thermo-chronology (U/Pb, AFT, AHe). For the determination of lag times between the uplift event in the Alps and the arrival of its sedimentary response in the basin, the marine biostratigraphy of the basin will be reevaluated using foraminifers, nanofossils and $\delta^{13}\text{C}$ stratigraphy. Initial sampling strategy focused samples from the northern and southern flanks of the basin, where sediments are sourced from different parts of the Alps. Sediments from the northern flank are interpreted as overbank deposits of turbidity currents and debris flows in a submarine channel belt, which were sourced from a delta close to Munich and by the paleo-Inn, representing sediment sourced from the Eastern and Central Alps. On the southern flank, northward directed submarine fans developed, which were sourced from the Augenstein Gravels, which covered the Northern Calcareous Alps east of Salzburg during the Oligocene and Miocene.

We will present initial results from the sedimentological investigation based on the re-interpretation of 3D-seismic-reflection data, sediment core analyses and point-counting of heavy minerals. Our results will provide new insights into the propagation and preservation of uplift signals into and through a foreland basin in geological deep time.

Quaternary sea-level variations along the coastline of Oman: facies analysis and petrography on uplifted beach rock deposits (Northern Indian Ocean)

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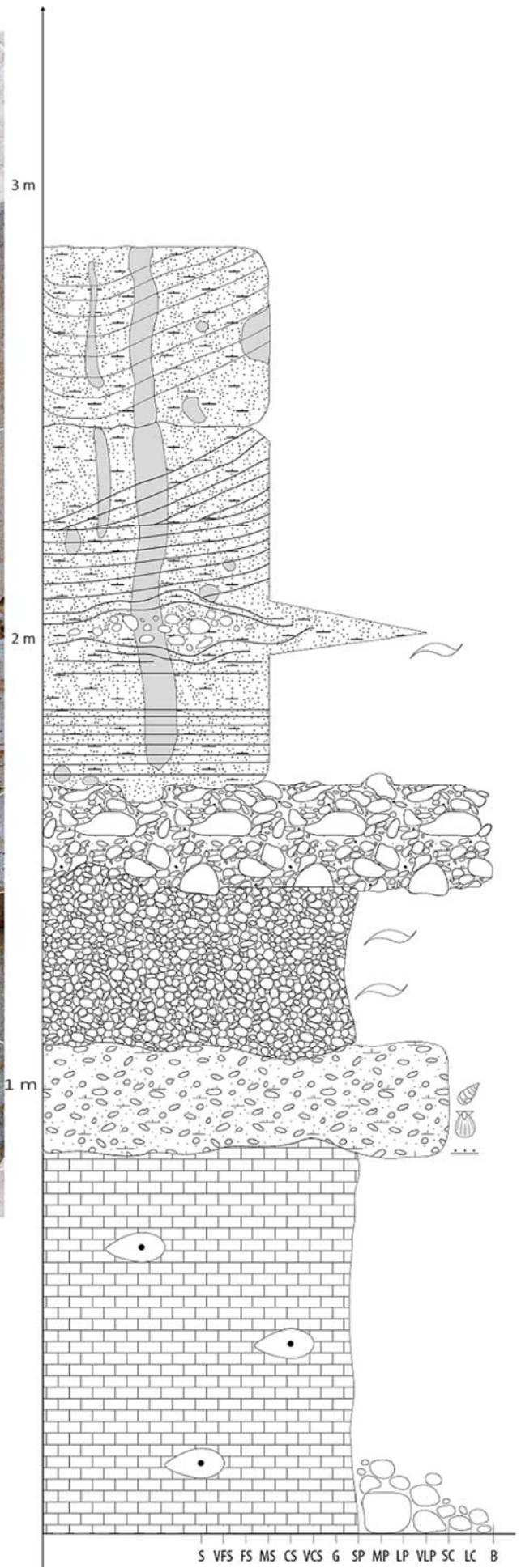
Content

Any beach rock location above or below present sea level can be interpreted as evidence for eustatic, isostatic or neotectonic movements. Analyses of beach rock deposits are used to reconstruct regional sea level changes and hold the potential of completing coral-based reconstructions [1]. Sedimentological features of beach rocks allow detection of the exact water depth during their formation in contrast to the wide vertical living range of corals. Despite the potential of interpreting facies variations in beach rocks and the need for knowledge of their initial position, detailed facies analyses of beach rock have received little attention [2].

The NE coastline of Oman shows geomorphological evidence of neotectonic activity and presents us with a unique setting for the investigation of beach rock: six raised marine terraces with erosional remnants of paleo beaches along their former shoreline angle. The terraces formed as wave-cut platforms in times of sea-level highstands during MIS 5-13. The aim of the project is to quantify the uplift rates of the area and the timeframe of its occurrence.

Outcrops on three terrace levels were logged and sampled. Analysis of the sedimentological features allows us to identify lateral facies relationships, energy level, sediment entry, and beach morphology. Thin section-based petrographic microscopy helps to recognise cementation cycles and mineralogy.

The results show that all beach rocks in the area classify as calcarenites or calcirudites. Their sedimentological features have been assigned to a variety of depositional environments, including high energy wave-controlled gravel pockets on rocky coastlines or sandy backshores influenced by terrestrial mass flow events. Major sediment components are extraclasts, as well as peloids and fossils, whereas Quartz is secondary. In the majority of the samples, over 50% of the grains have been leached. The oldest beach rocks show complete porosity inversion. In all samples multiple stages of cementation can be observed, the cement is calcitic or aragonitic and occurs as isopachus or irregular crust cement, passive cement, meniscus cement, or microstalagmites.



Typical log section from an elevated beach rock profile near Bimma (Oman), debris flow deposit is overlain by sandy backshore sediments showing trough cross bedding, parallel lamination, coarse grained lag deposits and *Psilonichnus* burrows.

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Young vs. old onshore tsunami records in Central Chile

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Content

High seismic earthquakes and tsunamis originate frequently from the subduction zone along the Chilean active plate margin. In view of these hazards, it is important to understand the complex tsunami history of Central Chile which can be deciphered by studying the tsunami deposits preserved in the geological record. Here, we present first results of two localities, Pelluhue and Chovellen (35°52'S and 35°48'S), studied in the course of a regional survey of paleotsunami deposits at the coast of Central Chile. At both coastal localities, we studied sections exposed in the river bank. Outcrops and cores were sampled for a sedimentological and geochemical analysis, including grain-size analysis, and dating by optically stimulated luminescence (OSL) using the SAR-protocol for quartz grains. At both localities, we observed sand intercalations (medium to coarse sand) with erosional lower contacts and grain sizes coarser than the surrounding river bank and river floodplain sediments (silty fine sand); the grain size differences of the intercalations and fluvial sediments range mostly from 0.5 to 1.0 ϕ suggesting deposition from different flow velocities. Also these layers show significant landward thinning and fining. Geochemical analysis (FUS-ICP) show merely a slightly decreased LOI within the sand intercalations indicating less organic matter within these layers which is common in tsunami deposits.

The OSL-ages of Pelluhue revealed depositional ages of all sand intercalations younger than 1950. The sand layer 3 yields younger ages than sand layer 2 indicating a multiple-layer deposition during this one tsunami event revealed by the age inversion.

At Chovellen, nearly all the sand intercalations were deposited in 1954 ± 4 yrs. All these sand layers show a similar age range which might indicate that these layers were deposited during one tsunami event.

Comparing the findings of these localities to the onshore tsunami record of Tirúa in South-Central Chile (38°20'S), we can point out six different tsunami events over the last 1,500 years preserved within the uppermost 2 m of riverflood plains. These significantly different onshore tsunami records in Central Chile depict the complex interaction of vertical neotectonic movement during and after earthquakes with subsequent tsunami inundations and preservation of their deposits at highly active plate margins.

Session 7.5: From source to sink: Environmental signal propagation into the stratigraphic record.: Talk

Keynote speaker

A-227

Environmental signal propagation into the stratigraphic record of small mountainous rivers feeding submarine canyon-fan systems, southern California

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Content

Sediment supply delivers environmental signals that originate in erosion zones to submarine fans in continental-margin sediment-routing systems. Sediment and signal propagation can be reconstructed from a source-to-sink sediment budget. A sediment budget accounts for the spatial and temporal partitioning of sediment removed, transferred, and deposited within a sediment-routing system. We calculated sediment budgets in two small, tectonically active sediment-routing systems of southern California using cosmogenic radionuclides from the Transverse (north) and Peninsular (south) ranges for denudation rates, and submarine-fan deposition rates since the last glacial maximum, ~20 ka. The surface areas and headwater elevations of the Transverse and Peninsular ranges catchments are similar; however, the Transverse ranges are composed of rapidly uplifting and more easily eroded Plio-Pleistocene sedimentary rocks compared to the Peninsular ranges. Accordingly, the denudation rates of the Transverse ranges and deposition rates in submarine fans are ~3 times greater than the rates of the Peninsular ranges and submarine fans in the south. In both sediment-routing systems, submarine-fan deposition exceeds terrestrial denudation by a factor of ~1.5. This suggests complete transfer of denuded mass to the deep sea during millennia. Additional sediment supply to the submarine fans might be from unaccounted transgressive erosion of shelf deposits. Thus, small mountainous rivers can rapidly transfer sediment and environmental signals to submarine canyon-fan systems, but transfer might be modulated by eustasy. In these “reactive” sediment-routing systems, changes in deposition rates might reflect external forcings operating in the erosion zone, as well as changes in sediment dispersal pathways as a result of sea-level fluctuations. Future work will compare detrital-zircon U-Pb ages from rivers draining the Peninsular ranges and the offshore latest Pleistocene-Holocene submarine fans in southern California (1051 grains from eight samples) to evaluate the variation in sediment dispersal and provenance signals in response to sea-level fluctuations. Preliminary results suggest that signals of fluvial input versus beach-cliff erosion can be deciphered from the stratigraphic record of submarine fans.

A newly identified Sediment Sink for the Ems Estuary based on Persistent Scatterer Interferometry (PSI)

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Content

The Ems Estuary flows into the North Sea between the Netherlands and Germany. The Estuary has vast tidal flats consisting of fine grained Sediment. It is highly modified e.g. for land reclamation, coastal protection and navigability. Thus natural sediment sinks vanished. This is assumed to be an important reason for a prominent increase in the suspended sediment concentration and change of tidal behaviour. Since large harbours, ship yards, population centers, important nature reserves, waterways and recreational areas cluster around this waterbody, extensive research is going on to even better understand the hydraulic and morphodynamic system to maintain the area in a stable state while balancing the varying concerns and interests and preparing for a future rising sea level. Therefore calculations of sediment budget and morphodynamic modellings are performed accounting for all known sediment sinks and sources like dredging or land reclamation as well as for hydrodynamic influences like fairway deepening or changes of hydraulic structures (e.g. [1], [2]).

Analysis and interpretation of PSI-data of the new satellite based InSAR Ground Motion Service Germany (BBD) extended with thematic data covering the land west of the Ems shoreline led to the identification and quantification of a new significant sediment sink. The subsidence of land above the Groningen natural gas field is well known. In this study we computed the extension of the subsiding area to the seafloor of the Ems Estuary. We combined information about the extension of the gas fields, the PSI-derived subsidence on both banks of the estuary and checked against GPS-stations e. g. mounted on gauges in the estuary. The seafloor subsided between 1992 and 2001 up to 42 mm and an area of approximately 200 km² is affected by a subsidence rate > 2 mm a⁻¹.

The volume change between the seafloor of 1992 and the one of 2001 is about 5.5 Mil. m³. The resulting average volume change of ca. 0.6 Mil m³ a⁻¹ is in the same order of magnitude as the estimated annual sediment sink of the total Ems Estuary between 1994 and 2015 [1]. We recommend, to take this newly identified sediment sink and in general the subsidence of the seafloor and tidal flats due to natural gas and oil extraction into account in future sediment budget calculations and morphodynamic modelling approaches.

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Climate-tectonic interaction at the Southern Alaska continental margin: insights from a single grain provenance approach

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Content

The formation of the Cenozoic Chugach-St. Elias Mountains, the highest costal mountain range on Earth, coincides with glaciation of variable degrees along the Southern Alaska continental margin. Its proximity to the ocean and missing onshore sediment traps allow transport of orogenic sediments into the Surveyor Fan system in the Gulf of Alaska. These sediments supply a complete record of Miocene to Pleistocene detritus giving information on onshore mountain building and denudation processes. We present results of a single-grain provenance study, using U-Pb LA-ICP-MS geochronology of zircon together with (U-Th)/He, REE and laser ablation Hf isotope analysis, amphibole and garnet geochemistry and Ar/Ar dating of amphibole and mica on two IODP 341 sites on the distal and proximal Surveyor Fan (sites U1417 and U1418, respectively). Two zircon U-Pb age components around 50 Ma and 70 Ma and single Precambrian ages characterize all age spectra. The 50 Ma component matches the metamorphic rocks of the Chugach metamorphic complex (CMC) and the intrusions of the Sanak-Baranof plutonic belt (SBPB). The age distribution of all older grains strongly resembles the non- or low-grade metamorphic rocks southward of the CMC. Geochemical compositions of amphibole and garnet imply source rocks of mostly amphibolite facies metamorphic conditions together with variable igneous and greenschist facies metamorphic input, supporting a Chugach-Prince William and Yakutat provenance.

Starting with a CMC/SBPB dominated provenance in the Miocene the provenance changes to more input from low grade metamorphic areas at the southern flanks of the orogen in the Pliocene, coinciding with the advance of glaciers to the tidewater line.

In the Pleistocene, geochemical data define a dominant amphibolite facies metamorphic and igneous provenance from the CMC and SBPB where the exhumation rate is considered to be very high as a result of focused tectonic uplift. Increased glaciation after the middle Pleistocene transition did not result in significant changes in the provenance signal.

We conclude that the Chugach-Prince William and Yakutat terranes form the main and long-standing sediment sources for the Surveyor Fan sediments. Sediment was delivered via the Bering and Malaspina glacial systems throughout different tectonic and glacial phases with glaciers occupying essentially the same regions as today. The volume and rate of input from this area is modulated by glacial as well as tectonic processes.

Cosmogenic nuclide-derived denudation signals from global large river basins

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Content

Large rivers contain extensive floodplains, which are known to act as buffering agents for climate-driven denudation signals from the source area as the sediments can be transiently stored in the lowlands. Our new dataset of 60 in situ cosmogenic nuclide- and bedload chemistry-samples from detrital sediments of large rivers disentangles the cause (climatic or orogenic) of the signals that are propagated downstream. The dataset integrates over ~30% of Earth's terrestrial surface, distributed over a variety of climatic zones across all continents, and represents the millennial-scale denudation rate of the sediment's source area.

We show that sediment loads from cosmogenic nuclides do not respond to climate forcing, but faithfully record orogenic forcing, when analyzed with respective variables like mean local relief, climatic data (runoff, temperature, precipitation) and floodplain transfer times. In contrast to this, changes in elemental bedload chemistry respond to climate-related variables (precipitation, runoff) and floodplain transfer times. Similarly, published compilations of decadal-scale river-gauged sediment loads are also climatically controlled (e.g.[1]). These findings together imply that the climatic response to changes in sediment supply can be preserved in the chemistry of detrital sediment of large rivers. However, this response is likely imprinted during transfer through the lowlands, for example through floodplain weathering, because in contrast, sediment loads from cosmogenic nuclides robustly preserve the orogenic forcing of the source area despite being transported over the same distance through the lowland basin. Conversely, published compilations of cosmogenic nuclide-derived denudation rates (e.g.[2]) from small (<10000 km²) river basins show a response to climate variables. Hence, we ascertain that sediment loads from cosmogenic nuclides in large rivers are weakly responsive to climate changes, making this method highly suitable to detect orogenic forcing even in their paleo-sedimentary records.

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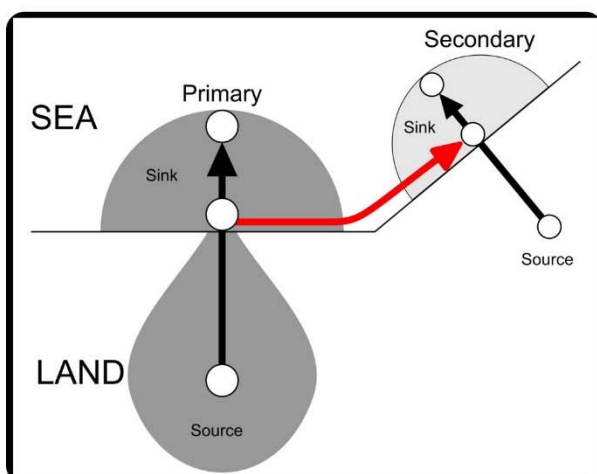
Hierarchy of source-to-sink systems — Example from the Nile distribution across the eastern Mediterranean

Schattner, U.

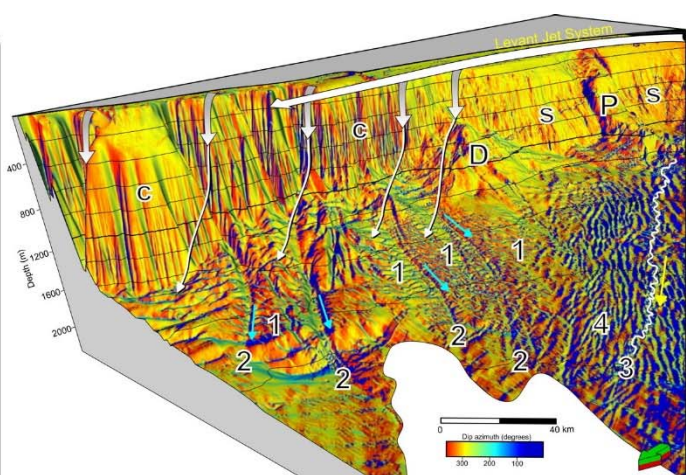
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Content

A standard source-to-sink approach examines sediment transport along an imaginary axis (regarded here as primary) extending between land, the continental margin and a nearby basin. This approach oversimplifies the development of depositional environments located off the axis (regarded here as secondary). Similarly, it imposes that factors affecting the primary source (e.g. climate) will directly be reflected in the secondary sink. The current study examines this suggested hierarchy in a confined basin, where the sedimentary budget remains closed. It evaluates the mechanism connecting between the primary and secondary axes. The study focuses on the Nile sedimentary system, across northeastern Africa and the eastern Mediterranean basin (primary axis) and the Levant depositional system (secondary sink). We hypothesize that since secondary river input into the Levant basin is negligible, the main secondary source is seafloor currents. The Levant Jet System (LJS) transported sediments from the Nile cone along the Levant margin at depths between 0 and 350 m, during the Holocene and until today. Once the LJS reaches its capacity to transport sediments, the surplus falls downslope to the deep basin. By integrating seismic and bathymetric data, this paper suggests a unifying mechanism integrating deposition, erosion, and transport of sediments across the Levant margin and basin throughout the Quaternary. Results show that during both highstand and lowstand conditions the primary source-to-sink axis delivers sediments to the deep basin via south to north meandering channels. The LJS transports sediments that build the shelf, while unconfined overflows slide downslope to accumulate across the continental rise. However, when sea levels drop, the capacity of the LJS weakens. This results in a drastic decrease in sedimentation across the shelf and rise, accompanied by confined downslope turbidity flows into the deep basin. In principle, seafloor currents serve as an immediate supplier from the mouth of the primary source to the off-axis system. Variations in seafloor current dynamics and their capacity to transport sediments will be directly reflected in the secondary sink. The primary continental source is expected to have only an indirect effect on the secondary sink.



Hierarchy of source-to-sink systems



In situ and meteoric cosmogenic nuclides in large lowland basins- Concepts, similarities, and implications for sediment routing

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Content

In order to quantify global geochemical cycles, we need to understand how sediment supply signals from source areas are modified from sediment routing through lowland river basins. Large basin such as the Amazon and Ganga basins provide several opportunities: They are globally relevant for their discharged sediment fluxes and are well-studied for their millennial-scale denudation rates from in situ ^{10}Be (Wittmann et al., 2011a; Lupker et al., 2012). In both these basins, in situ $^{26}\text{Al}/^{10}\text{Be}$ (Haedke et al., in prep.; Wittmann et al., 2011b) provide information on the age of deep intermittent storage. Moreover, the meteoric cosmogenic ^{10}Be to stable ^9Be ($^{10}\text{Be}/^9\text{Be}$) ratio recently applied to these basins (Wittmann et al., 2015; Rahaman et al., 2017) combines the atmospheric flux tracer meteoric ^{10}Be with ^9Be released from rocks by weathering, from which millennial-scale denudation rates can be calculated.

For both these basins, in situ ^{10}Be nuclide concentrations from fine sandy grain sizes are uniform from the Himalayan and Andean source areas to the rivers' outlet, hence tracing the upstream produced sediment supply signal. In coarser Amazon sediment mainly derived from floodplain sources, $^{26}\text{Al}/^{10}\text{Be}$ lower than the surface nuclide production ratio (6.75) indicate that a substantial fraction of sediment is deeply stored for several Myr in the floodplain. In the Ganga basin, $^{26}\text{Al}/^{10}\text{Be}$ of 6.75 indicate that sediment burial is too short to lead to significant radioactive decay. When comparing exported meteoric ^{10}Be fluxes by riverine erosion to those produced by atmospheric deposition, we detect a deficit in ^{10}Be export in the Amazon basin, attributed to ^{10}Be decay during Myr-scale sediment burial. In the Ganga basin, absence of long-term burial is supported by exported vs. deposited meteoric ^{10}Be fluxes that are balanced. However, at the same time, $^{10}\text{Be}/^9\text{Be}$ are modified from source to outlet in both basins, overall resulting in lower sediment fluxes than those from in situ ^{10}Be . This indicates that the meteoric system rather reflects a basin-wide denudation signal, where high-relief zones, cratonic areas, and floodplains all contribute to the meteoric budget. We conclude that even though large similarities exist in the systematics of in situ and meteoric nuclides, meteoric nuclides are more sensitive to be modified from sediment routing. When applied to terrestrial archives to measure paleo-erosion rates, this behavior must be taken into account.

**Session 7.5: From source to sink: Environmental signal propagation into the stratigraphic record.:
Talk
A-310**

Latitudinal variation (15°-23°S) in denudation along the Western Andean Margin (Peru and Chile): Insights from cosmogenic ^{10}Be .

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Content

Previous studies of syntaxial regions in the Himalaya and Alaska document localized and rapid deformation and denudation due to vigorous fluvial or glacial erosional processes. This study quantifies latitudinal variation in denudation rates along the Andean Coastal Cordillera and Western Cordillera around an arid end-member syntaxial orogen in South America to understand the interactions between climate and tectonic processes in localizing denudation.

We present 32 new cosmogenic ^{10}Be analyses of river sediments of southern Peru combined with 34 new ^{10}Be analyses from northern Chile. The controls on the denudation rates are evaluated with a multivariate statistical factor analysis that identified correlations and covariation between denudation rates with climate, vegetation, topography, and fluvial steepness index (among other things). Measured cosmogenic derived denudation rates range from 0.5 - 168 m/Myr. The denudation rates generally decrease from the 15°S (near Nasca, Peru) to 23°S (near Antofagasta, Chile) and from the Western Cordillera to the Coastal Cordillera.

Results from the factor analysis indicate that (1) the main controls on denudation rates are local tectonic driven processes indicated by the strong correlation and covariation of the denudation rate to the channel steepness in the arid northern Chile. (2) In southern Peru the denudation rates are mainly controlled by the intensity of vegetation and show strong covariation of denudation rates, vegetation cover and precipitation. (3) Regional trends in topography in this arid to hyper-arid region suggest a decrease in maximum elevations away from the syntaxis. This trend in topography is suggestive of the rock uplift effects in response to the 3D plate geometry of the subducting plate. Thus, although the topography seems to display a north to south slightly decreasing plate corner topographic trend, it is not reflected by localized denudation rates, most likely due to the low precipitation rates in the region (mean annual precipitation rates between ~50-300 mm/a). The covariation of denudation rates with steepness index in northern Chile suggest that local tectonic controls (faulting) play an important role on millennial scale denudation in this region.

**Session 7.5: From source to sink: Environmental signal propagation into the stratigraphic record.:
Talk
A-787**

Reactive versus Buffered Sediment Routing Systems: The Paleogene Record in the Greater Gulf of Mexico Basin

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Content

Previous work on small, spatially restricted source-to-sink systems like the Holocene of southern California have interpreted rapid propagation of climatic signals from terrestrial to submarine segments. These reactive systems contrast with larger drainage basin to abyssal plain sediment routing systems that are expected to show a more buffered response, reflecting transient sediment storage and/or autogenic variability that produce lags in, or obscure, allogenic forcing. Paleogene strata of the greater Gulf of Mexico (GoM) basin, preserved in both outcrop and subsurface datasets, includes both large (>1000 km long) and small river systems (<500 km long) allowing a unique test of expectations. Paleogene systems documented by well penetrations and reflection seismic data in the northern GoM show large submarine fans with run-out lengths and widths that would rank among the largest deep-sea systems known in the modern world. Southern GoM source-to-sink systems tend to generate fewer fans and more common deep-water channel-belt assemblages that reflect lower sediment flux as a function of more limited drainage areas. However, both types of systems tend to faithfully preserve a high-fidelity record of the hinterland climate, bedrock composition, and tectonics. One explanation is the globally high sea level and reduced frequency of eustatic changes in the greenhouse Paleogene allowed longer-lived connections between sediment source and basinal sink in both small (reactive) and large (supposed buffered) systems. Of particular importance to hydrocarbon exploration and paleogeographic reconstructions is the observation that dimensions of submarine fans and channel-belt assemblages is a faithful representation of the scale of the catchments in both systems and thus predictable at the first order. Our work demonstrates that this holds true in both the northern and southern GoM, where the tectonic style of the source terranes varies from thick-skinned to thin-skinned contractional tectonics, respectively, during the Paleogene.

Up-stratigraphic provenance variations of Palaeozoic siliciclastic rocks from the Ellsworth Mountains in West Antarctica, as determined by detrital zircon geochronology

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Content

The Ellsworth-Whitmore Mountains block is one of the most isolated fragments forming West Antarctica. This block is most extensively exposed in the Ellsworth Mountains, where there is an extensive record of sedimentation from early Cambrian to Permian times. However, its tectonic history and palaeogeographic significance remain enigmatic. The active continental rift sediments of the Cambrian Heritage Group have main zircon components of late Mesoproterozoic–early Neoproterozoic age (ca. 1300–900 Ma) with little to no contributions from older cratons. Two meta-volcaniclastic samples of the lower Heritage Group have U-Pb zircon ages of ca. 675 Ma indicating proximal Cryogenian volcanism. Igneous and metamorphic zircons of late Neoproterozoic–early Cambrian age (650–530 Ma) are a secondary component in the upper part of this group. The passive margin sediments of the overlying upper Cambrian–Devonian Crashsite Group record an up-sequence increase in late Neoproterozoic–Cambrian detrital zircons (ca. 650–480 Ma). The youngest detrital zircons are ca. 480 Ma with major peaks at ca. 530 and 500 Ma. Similar patterns are recorded in the Permian–Carboniferous Whiteout Conglomerate, with main components at ca. 650–500 Ma, and an absence of detrital zircons younger than Cambrian. The results suggest that sediments of the lower Heritage Group were derived from the palaeo-Pacific margin of the Australo-Antarctic plate. Cryogenian igneous zircon ages from the lower Heritage Group indicate proximal rift-related magmatism, which is recognised in the Transantarctic Mountains and related to the break-up of Rodinia. Sediments from the upper Heritage Group were derived from proximal sources, likely in Coats Land and Dronning Maud Land, with possible extensions into the Shackleton Range. This area was probably uplifted during the final amalgamation of Gondwana, which restricted the supply of sediment from older cratons. Sediments from the Crashsite Group allow for a more expansive source region, which could have been located in Dronning Maud Land, the Shackleton Range, the Transantarctic Mountains and/or Southern Africa. Sediments of the Whiteout Conglomerate indicate that deposition during the Permian–Carboniferous was similar to that in the Transantarctic Mountains. Our data support that the Ellsworth-Whitmore Mountains crustal block was once part of the Australo-Antarctic plate rather than the southern African sector.

Session 7.6: From source to sink: Environmental signal propagation into the stratigraphic record.: Talk

**Session 7.6: From source to sink: Environmental signal propagation into the stratigraphic record.:
Talk
A-796**

A probabilistic model to quantify sediment mixing across alluvial landforms with aggradation-incision cycles.

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Content

The accurate interpretation of ever finer clastic sedimentary records hinges on a good understanding of the timescale and mode of sediment transport from source to sink. An environmental signal can be accurately recorded in the stratigraphy if it is transported quickly without being mixed with older sediments or it can be entirely altered by slow transport (phase lag) and significant mixing (gain) along the way. Both transformations happen in any alluvial landforms where sediments are intermittently deposited and remobilized.

We use the north piedmont of the Tian Shan (NW China) to explore and quantify the consequences of intermittent storage and mixing of sediment. The piedmont undergoes aggradation-incision cycles on a precessional tempo. We establish that the coarse fraction of a post-glacial sediment pulse is delivered to the endorheic basin with a 7-14 kyrs delay due to transient deposition on the piedmont, whereas the dissolved and the fine loads are delivered almost immediately to the basin. Aggradation and incision mix sediment deposits as old as 0.5 Ma into the modern sediment flux that builds the basin's stratigraphic record.

The phase lag and gain of the environmental signal across an alluvial landform depend on four characteristics that can be measured in the field and remotely: 1) net aggradation rate, 2) depth of incision, 3) river lateral migration, and 4) period of aggradation-incision. These values inform a probabilistic model that predicts the degree of local mixing in the environmental signal. Our model can be used to predict the pattern of signal alteration across landforms with important vertical dynamics such as high mountain valley fills, alluvial piedmonts, or coastal systems forced by sea level.

Session 8.1: Hydrothermal systems and related mineral and geothermal resources.: Poster

Session 8.1: Hydrothermal systems and related mineral and geothermal resources.: Poster A-779

Fluid sources and variations along a large quartz vein system – the Bavarian Pfahl

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Content

Hydrothermal veins are abundant both in the continental and in the oceanic crust of the Earth and indicate the flow of hydrous fluids through the crust. In the upper crust, fluid flow is localised and pre-existing shear and fault zones are used as pathways. One impressive example is the more than 150 km long Bavarian Pfahl zone where fluids have infiltrated a late-Variscan shear zone. The initial quartz vein formation is followed by repeated fragmentation, healing and precipitation of younger quartz. This multi-stage mineralisation can be subdivided into an early fine-grained and reddish to dark greyish quartz phase and a younger white quartz phase which forms massive veins with larger grain-size. These veins predominantly mineralised vertically and parallel or at a low angle to the NW-SE trending Pfahl shear zone. A younger generation of N S trending fractures is partly mineralised with white quartz and cross-cuts all other quartz units. We have sampled the different mineralisation phases along a length of 100 km to study the structural and geochemical evolution of this large-scale hydrothermal system. O-isotope, He-isotope and trace element studies are carried out to record the heterogeneity of the Pfahl quartz system and characterise the fluid sources. The interaction with different wall rocks (sedimentary units and crystalline basement) may also influence the geochemical signatures of the quartz along the shear zone. The results are compared to geochemical data of quartz veins of the sub-sedimentary basement in the northwestern continuation of the Bavarian Pfahl. Another focus of this study is the relationship of the Pfahl quartz to the fluorite mineralisation of Wölsendorf and associated quartz veins. Preliminary data suggest that the Wölsendorf quartz veins have higher contents in elements like Ba, Zn, the rare earth elements, and U than those of the Pfahl in agreement with previous findings (Peucker-Ehrenbrink & Behr, 1993, Chem. Geol. 103, 85-102). Thus, the fluids precipitating quartz in the Wölsendorf area had a different source and carried a higher element load than the fluids flowing further to the south along the Pfahl vein system.

Ni and Pt in high-temperature H₂O+HCl fluids

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Content

In hydrothermal environments, Ni and Pt occur mainly in divalent oxidation state as arsenide and sulfide minerals. The solubility of Pt in hydrothermal, generally Cl-bearing, fluids appears to be much lower than that of Ni. A few occurrences of PtAs₂ (sperrylite) are suggested to be related to hydrothermal fluids [1] as well as an overall enrichment of Pt relative to Ni, e.g. in the footwall-type deposits of the Sudbury District [2]. This suggests that As may foster precipitation of Pt ore minerals. The role of S and As ligands on the solubility and complexation of Ni and Pt in hydrothermal fluids is addressed in this study by in-situ synchrotron XRF- and XAS- and Raman spectroscopy on solubility experiments. The solubility experiments were carried out with NiS and NiAs (nickeline) at 80 MPa in 0.1 and 1 molal HCl at 400 °C and with PtAs₂ and Pt metal in 1 and 6.86 molal HCl at 500 °C.

The amount of Pt in the fluid was very low, max. $8 \cdot 10^{-5}$ molal by dissolution of Pt metal in 6.86 molal HCl. NiS dissolved congruently from $7.2 \cdot 10^{-3}$ to $8.72 \cdot 10^{-2}$ molal Ni with increases in HCl from 0.1 to 1 molal. NiAs dissolved incongruently with slightly more As dissolved than Ni. Even after >16 h Ni and As contents were still rising to max. $3.6 \cdot 10^{-3}$ and $2.7 \cdot 10^{-2}$ molal Ni and $2.5 \cdot 10^{-3}$ molal and $2.0 \cdot 10^{-2}$ molal As in 0.1 and 1 molal HCl, respectively.

XANES spectra indicate the presence of As as oxidized As(V) and of Ni as Ni(II) and, supported by literature data [3] and [4], no complexation of Ni with As or S.

Raman spectra of HCl solutions reacted with NiS up to 600 °C and 1.15 GPa showed Ni-Cl complexation with contact ion pairing at ≥ 300 °C and below 600 MPa. No complexation of Ni with S was detected.

These results show that Ni is readily mobilized from NiS and NiAs by acidic chloridic hydrothermal fluids and that Cl is the dominating complexing anion. That Pt remains nearly immobile suggests that the Pt enrichment relative to Ni and the occurrence of sperrylite in the Sudbury deposits are rather related to magmatic than to hydrothermal processes. The results indicate that arsenate species are more stable in hydrothermal fluids than previously thought and that the redox reactions involving As may be crucial for the mobilization and precipitation of arsenide ore minerals.

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REE-mineralization with bastnaesite and britholite in a fenitized monzogranite at Rodeo de Los Molles, Central Argentina.

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Content

An unusual REE-bearing assemblage was identified in a hydrothermally altered (fenitized) biotite-monzogranite at Rodeo de Los Molles, which is part of the Devonian Las Chacras-Piedras Coloradas Batholith in San Luis province, Central Argentina. The fenitization occurs in an elliptical, NNE-SSW trending zone that may be fault-related. Fenitization is characterized by metasomatic gain of Na and K as well as loss of Ca and Sr, leading to the transformation of monzogranite to quartz alkali-feldspar syenite and alkali-feldspar syenite composition. The fenitized zone is locally enriched in light rare earth elements and has been subject to a mineral exploration campaign. [1] Drill-core samples from that campaign and new surface samples are the basis for the present investigation, which aims to decipher the fluid evolution and REE-mineralization.

The typical REE-rich assemblage at Rodeo de los Molles occurs as irregularly patches of intergrown primary britholite $(\text{Ce,Ca})_5(\text{SiO}_4, \text{PO}_4)_3 (\text{OH}, \text{F})$, allanite, apatite, aegirine-augite, sphene, fluorite, bastnaesite and quartz as well as complex thorium-rich minerals. In more intense metasomatically altered areas the assemblage also includes secondary clinochlore, spherulitic quartz, calcite, kaolinite, hematite and phlogopite. Britholite is a rare mineral, isostructural with the apatite group, and typically described as an accessory mineral related to late-magmatic crystallization or alteration of primary minerals in alkali-rich granites. [2] Rodeo de los Molles is one of only three localities in the world where britholite occurs in ore quantities [3], and the origin of britholite forms one focus of this study.

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Zircon as a magma monitor: examples of zircon saturation and Ti-in-zircon thermometry applied to felsic volcanics of the Iberian Pyrite Belt

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Content

The Iberian Pyrite Belt (IPB) is one of the outstanding metallogenic provinces worldwide, hosting great volumes of polymetallic massive sulphides. Felsic rocks account for up to 70% of the volcanic exposures in IPB and are the host of many sulphide orebodies.

The Ervidel-Roxo (ER) and Figueirinha-Albernoa (FA) volcanic sequences (at the IPB northern sector, in Portugal) form two elongated and independent exposures roughly running WNW-ESE. The ER sequence is mainly composed of rhyolites with subordinated rhyodacites and rocks of intermediate composition, while the FA succession comprises mostly rhyodacitic to dacitic rocks. Rhyolitic and rhyodacitic magmas resulted from distinct degrees of melting of quartz-feldspar crustal rocks, while magmas of intermediate composition developed independently, representing outcomes of variably crustal contaminated basaltic magmas.

The zircon saturation temperature ($T_{\text{Sat}}^{\text{Zrn}}$) and Ti-in-zircon thermometry were jointly used to assist the separation of volcanic series linked to high-temperature hydrothermal systems from those formed at lower temperature conditions, thus setting the ER and FA within an extensive regional database. The ($T_{\text{Sat}}^{\text{Zrn}}$) was estimated according to the zircon solubility model reported in [1] and applying a regional database of whole-rock analyses with $\text{SiO}_2 > 60\%$ and compositional factor M ranging from 1 to 1.9. The zircon crystallization temperatures (Ti-in-zircon) were estimated from measured Ti contents following the model proposed by Watson et al. [2] as modified by Clairborne et al. [3]. The combination of $T_{\text{Sat}}^{\text{Zrn}}$ and Ti-in-zircon results suggest that the rhyolitic magmas feeding volcanic centers that host ore-forming systems mostly resulted from sources with minimal inherited zircon at high temperature ($T > 800^\circ\text{C}$). In contrast, barren or weakly mineralized felsic volcanic sequences (rhyodacitic to dacitic) mainly preserve a large fraction of inherited zircon and formed under lower temperature conditions ($< 800^\circ\text{C}$, clustering at $700\text{--}750^\circ\text{C}$).

The combination of both methods proved to be a useful exploration tool to assist in the discrimination of felsic volcanic series in terms of potential heat sources for initiating, driving and sustaining long-lived, high-temperature hydrothermal systems.

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Session 8.1: Hydrothermal systems and related mineral and geothermal resources.: Talk

Session 8.1: Hydrothermal systems and related mineral and geothermal resources.: Talk
A-424

Beryllium speciation in hydrothermal and magmatic fluids - new insights from first principles molecular dynamics

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Content

Beryllium is a strategic element [1] and, because of a low absorption cross-section for thermal neutrons, it is used in nuclear reactors. Furthermore, the geochemical behavior of Be^{2+} in late magmatic fluids is poorly known [2].

In hydrothermal beryllium deposits and pegmatites beryllium minerals are frequently associated with fluorite and topaz, which suggests that Be^{2+} is commonly transported in fluoride-rich aqueous solutions in geological environments [3].

It is the aim of this study to make predictions of the speciation of beryllium in geological fluids from ambient conditions up to 700 °C and 600 MPa with focus on monomeric complexes of beryllium with fluoride.

As Be is poisonous for people and invisible to x-rays, Be is difficult to study experimentally. Here, first-principles molecular dynamics simulations in combination with thermodynamic integration (TI) were used to derive equilibrium constants of dissociation reactions of different Be-F species.

We were able to reproduce experimental stability constants [3] of Be-F complexes at room temperature and to interpolate our data in pressure-temperature space with electrostatic models of ion association.

Our results indicate that at high temperatures Be^{2+} prefers a trigonal coordination environment in aqueous solution compared to a tetrahedral coordination geometry at ambient conditions. Moreover, we predict that at high fluoride activity $\text{BeF}_{2(\text{aq})}$ and $\text{BeF}_{3(\text{aq})}^-$ are the majority species in late magmatic fluids. At high temperatures the thermodynamic data extracted from thermodynamic integration appears to be more accurate compared to extrapolations from measurements at ambient conditions [5]. In support of this we see a better agreement of our data with high temperature experiments for $\text{BeF}_{2(\text{aq})}$ [6,7] species. With this result we can shed new light on the behavior of beryllium during late magmatic evolution, which needs to be understood to interpret field observations [2].

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Decoding the mineralogical variability of five-element veins: Comparative evaluation of an Alpine multi-stage system

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Content

Five-element veins typically display dendritic native metals (Ag, Bi, As) enclosed by later Fe-Co-Ni arsenides. Recent studies propose reduction due to hydrocarbon influx to be essential for the formation of the native metals and arsenides. Although mineral successions reveal the natural subdivision into native As-, native Ag/Bi- or arsenide-dominated vein types, the variations in Fe-Co-Ni among the arsenides are not well understood yet.

The present study evaluates ore textures, mineral chemistry, fluid inclusion compositions (microthermometry and Raman) and in-situ U-Pb age determinations to interpret formation processes and the geologic history of various five-element veins from one district in the Swiss Penninic Alps. Ore textures and U-Pb ages constrain a primary formation of löllingite-skutterudite-dominated ores at 233 ± 10 Ma and niccolite-gersdorffite-skutterudite-dominated ores at 188 ± 32 Ma. Both ages relate to crustal thinning caused by the breakup of the Alpine Tethys. Fluid inclusions imply that all investigated veins precipitated from Na-Ca-Cl fluids with fluctuating temperatures, salinities and molar Ca/(Ca+Na) ratios, suggesting different degrees of water-rock interaction due to variable formation depths, cover rock lithologies and resulting fluid pathways. Raman results do not support the presence of hydrocarbons in this Alpine ore district. Dissolution of earlier siderite and precipitation of magnetite imply, however, the oxidation of Fe²⁺ to Fe³⁺ as the required redox couple producing Bi⁰, As⁰ and As⁻¹ from their oxidized aqueous species Bi³⁺+Cl⁴⁻, and As³⁺+(OH)₃

Comparison of hydrochemical and mineralogical trends of five-element veins worldwide reveals a complex mineralogical relationship between mono-, di- and triarsenides and their Fe-Co-Ni signatures. Generally, Ni-diarsenides predominate under the most oxidized fO₂ conditions, followed by Co-diarsenides and lastly Fe-diarsenides with decreasing fO₂. Equal fluid concentrations of Fe, Co and Ni, therefore, result in the evolution from Ni- to Co- and finally Fe-dominated compositions. High pH and low arsenic concentrations, however, favor the monoarsenide niccolite instead of the diarsenide rammelsbergite. Slightly variable pH during ore formation may affect the dominance of skutterudite over safflorite.

Formation of epithermal Sn-Ag(-Zn) mineralization at the Pirquitas deposit, Jujuy Province, NW Argentina – Fluid inclusion and isotopic constraints

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Content

The Pirquitas epithermal Sn-Ag(-Zn) deposit is located near the Bolivian border in the Argentine Puna Plateau and has been a major source of Sn and Ag, with both primary Sn-Ag sulfide mineralization. The Pirquitas deposit is considered to be an analogous of the Bolivian Sn-Ag epithermal deposits, but the origin of the ore-bearing fluids is still controversial and no direct association with magmatism has been observed so far. The closest intrusion is the granodioritic Cerro Galán, some 12 km to the east of Pirquitas mine. Our fluid inclusion studies in quartz, Sn-Ag ore minerals and sphalerite from the Oploca vein system in transmitted and near infrared light show variable salinities from 10.6 to 0.8 wt.% NaCl equiv. and homogenization temperatures (Th) in the range between 274° and 190° C, probably due to mixing of saline metal-rich fluids with meteoric water. Fluid inclusion evidence for boiling was suggested in previous studies from the nearby Cortaderas breccia body [3] but this was not observed in our samples from the Oploca vein system. The fluid compositions and temperature results are in agreement with data from Bolivian epithermal Ag deposits, such as Potosí, with Th and salinity values of 174° - 311° C and 6.6 - 9.5 wt. % NaCl equiv. , respectively, and San Rafael with Th between 157° and 317° C and salinity between 1.2 and 16 wt% NaCl equiv [4] .

Helium isotope analyses of fluids trapped in Sn-Ag and Zn ore minerals yielded ratios ³He/⁴He ratios between 2.1 and 2.7 Ra suggesting a mixture of mantle and crustal- derived He. Sulfur isotope analysis of Sn-Ag and Zn ore mineral separates yielded δ³⁴S values between 0 and +4 ‰ for the majority of samples, which fall in the typical range for magmatic sulfur [2] . Lead isotope measurements in Pirquitas Sn-Ag and Zn ore minerals are homogeneous and suggest an upper crustal source of lead similar to that which is found in the Central Andes volcanic arc and its metasedimentary basement [1].

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Quantifying the history of hydrothermal activity using low-temperature thermochronology and numerical models

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Content

Knowledge of the timing and duration of flow events can provide key information on the interaction of hydrothermal activity with geological processes such as fault movement and seismic activity. However, the duration of flow events is often difficult to quantify using current dating methods, especially in the case of relatively short events. Here we present a new approach to constrain the history of hydrothermal activity that combines low-temperature thermochronology, subsurface temperature data and inverse thermal modelling. We present recent results from the Beowawe geyser field in the Basin and Range Province, where new apatite U-Th/He data and models provide constraints on episodic flow events that are linked to seismic activity.

Session 8.2: Structure, properties, and applications of crystalline materials.: Poster

Session 8.2: Structure, properties, and applications of crystalline materials.: Poster A-609

Application of a new split Pseudo-Voigt function improving the refinement of crystal-structure parameters in BRASS

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Content

The profile function for the matching of reflection profiles in X-ray powder diffraction patterns as used in BRASS [1], the Bremen Rietveld Analysis and Structure Suite, has been revised (more details in [2]). The main target was to improve matching of asymmetric low diffraction angle profiles by new parameters in the split Pseudo-Voigt function (sPV) to allow for more accurate determination of the reflections' integral intensities to yield a more accurate determination of crystal-structure parameters. As the asymmetry is usually governed by instrumental contributions appropriate new terms with new parameters were added to the instrumental part of the FWHM (full width at half maximum) in the sPV profile function:

$$FWHM_G(2\theta) = \sqrt{U_G \cdot \tan^2\theta + V_G \cdot \tan\theta + W_G [X_G \cdot e^{Y_G \cdot 2\theta} + Z_G \cdot \sin^4 2\theta]}$$

$$FWHM_L(2\theta) = U_L \cdot \tan\theta + (V_L \cdot \sqrt{\tan\theta}) + W_L [X_L \cdot e^{Y_L \cdot 2\theta} + Z_L \cdot \sin^2 2\theta]$$

with G = Gaussian, L = Lorentzian, U,V,W = usual instrument parameters, [] = new part: X, Y = new parameters for low-angle asymmetry and Z = new, accounting for asymmetric sample transparency. Note: in sPV two complete sets of these two functions are used separately for the right & left halves of the reflections. The new X and Y parameters provide the needed flexibility in the low-angle region.

This is especially needed for the analyses of many zeolites, which are phases with low-density aluminosilicate frameworks including large cavities and/or channels which may be populated by non-framework atoms, i.e., ionic species with low charges (e.g., Na⁺) and neutral molecules (e.g., H₂O). Due to their frequently large unit-cell parameters they often exhibit the strongest reflections at very low diffraction angles. Since the non-framework atoms often have large displacement parameters (due to large vibration amplitudes) they often contribute only to low-angle reflections significantly while their impact quickly diminishes towards higher diffraction angles. On top, since these atoms are often located on partially filled crystallographic sites, often have similar scattering powers (e.g., Na⁺ and H₂O) and have a weak bonding to the framework they are often ill defined in diffraction analyses. The impact of low-angle asymmetry on crystal-structure parameters of zeolites in BRASS can now be studied in more detail and potentially with better accuracy.

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Can density-functional calculations deliver accurate heats of formation for materials relevant in Geosciences?

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Content

In internally consistent thermodynamic data bases used in Geosciences the entropy (S) and the heat of formation (ΔH_f) are estimated in many cases due to the lack of appropriate calorimetric and phase equilibrium data. There are also cases, where these quantities are experimentally not accessible, e.g., mineral end members that cannot be synthesized because the compositional range is restricted to the solid solution (Al-rich end members of biotite). The relative uncertainties of ΔH_f for well-studied minerals given in internally consistent thermodynamic data sets are in the order of 0.1%. It is the purpose of this contribution to evaluate, if ΔH_f -values calculated by the density functional theory (DFT) are accurate enough for phase stability calculations in Geosciences, i.e., if such values do not deviate much more than 0.1% from those of the thermodynamic data sets. DFT-calculations yield energies that are not directly comparable to those of thermodynamic data sets, because the enthalpies of the elements are not set arbitrarily to zero as done in classical thermodynamics. To make the DFT results available to a broad range of applications, they have to be integrated into the existing thermodynamic data sets. It is, therefore, necessary to investigate the DFT energies of the elements too, in order to formulate the formation reaction of a compound. The results show deviations in the range of a few percent comparing DFT calculated with tabulated ΔH_f 's and are thus disappointing. We show, however, that DFT results are better, if the formation from the oxides is considered. We calculated the heat capacity, the internal energy and the entropy of 18 reactions describing the formation of well-studied minerals from the oxides. The investigated minerals were the aluminosilicates, feldspars, pyroxenes, garnets, forsterite, fayalite, layer silicates, perovskite and amphibole. Using literature ΔH_f 's of the oxides, ΔH_f 's from the elements at 298.15 K were calculated. They do not deviate more than 1% from reference values. Most ΔH_f -values are within 0.5%. The calculated entropies deviate less than 4% from reference values. Finally, the Gibbs free energy (ΔG) was calculated, because it is the relevant quantity for phase stability calculations. The errors in ΔH_f and S are partly compensated delivering deviations of ΔG from reference values that are small and lie at and below 0.3% in most cases.

Computational study of the fully hydrated, partly hydrated, and dehydrated forms of $\text{AlPO}_4\text{-H}_3$, an aluminophosphate zeotype

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Content

Porous aluminophosphate zeotypes (AIPOs) have received considerable attention as adsorbents for thermal energy storage using water adsorption-desorption cycles. Using NMR spectroscopy, it has been shown for various AIPOs that some adsorbed water molecules coordinate to framework aluminium atoms upon hydration, leading to the formation of five- or six-coordinated Al atoms.(1,2) For the chabazite-type AIPO-34, a previous computational study indicated that hydrogen bonds to non-coordinated water molecules in the pores play a crucial role in stabilizing the Al-coordinated water molecules.(2) As this additional stabilization is missing in systems containing only Al-coordinated water, these partly hydrated AIPOs were predicted to be unstable. However, it is unclear to what extent these findings can be generalized, especially to AIPOs with smaller pores.

The present contribution uses electronic structure calculations in the framework of dispersion-corrected density-functional theory (DFT-D) to study fully hydrated, partly hydrated, and dehydrated $\text{AlPO}_4\text{-H}_3$ (termed $\text{AlPO}_4\text{-C}$ in its dehydrated form). This small-pore AIPO is a well-suited model system because crystal structure data for the fully hydrated phase are available.(3) Moreover, there are only three non-equivalent water molecules in the structure (two Al-coordinated and one non-coordinated), facilitating the generation of partly hydrated structure models.

After performing full DFT-D geometry optimizations of all models, the interaction energy per water molecule was evaluated. As in the case of AIPO-34, mentioned above, the interaction in partly hydrated systems is weaker than in the fully hydrated $\text{AlPO}_4\text{-H}_3$ phase, indicating that partly hydrated phases are metastable, and that hydration is likely to occur as a one-step process from the dehydrated to the fully hydrated phase. In addition, phonon calculations were carried out in order to predict the IR and Raman spectra. These calculations can serve to identify “fingerprint” modes that are indicative for different types of adsorbed water molecules (Al-coordinated vs. non-coordinated), and for the presence of five- or six-coordinated aluminium atoms.

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Crystal growth and characterization of Mn-doped melilites

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Content

The large family of tetragonal, noncentrosymmetric melilite-type compounds represents an interesting class of materials due to its magneto-electric and multiferroic properties. The chemical variability of the melilite family of crystal structures offers a wide range of possibilities for the design of new crystalline materials [1]. The general composition is given by the formula $M_2^{[8]} T^{[4]} T_2^{[4]} X_7$ with $Ca_2MgSi_2O_7$ for the mineral åkermanite. Interesting magnetic, optical, and dielectric properties have been reported for Mn-containing melilites. In order to systematically study the magnetic structure as well as the physical and chemical properties, large single crystals of Mn-doped melilites are needed. We have successfully grown single crystals of the host mineral åkermanite ($Ca_2MgSi_2O_7$) using the Czochralski method. In first experiments Mn-doped single crystals were grown from melts containing 0.2-1.5 mol % MnO. Crystals were grown under reducing conditions with forming gas (98% N_2 /2% H_2). Difficulties arose by an increased solubility of forming gas in the melt thus complicating the growth process. X-ray microscope tomography was used to check the quality of the crystals grown (Fig. 1).

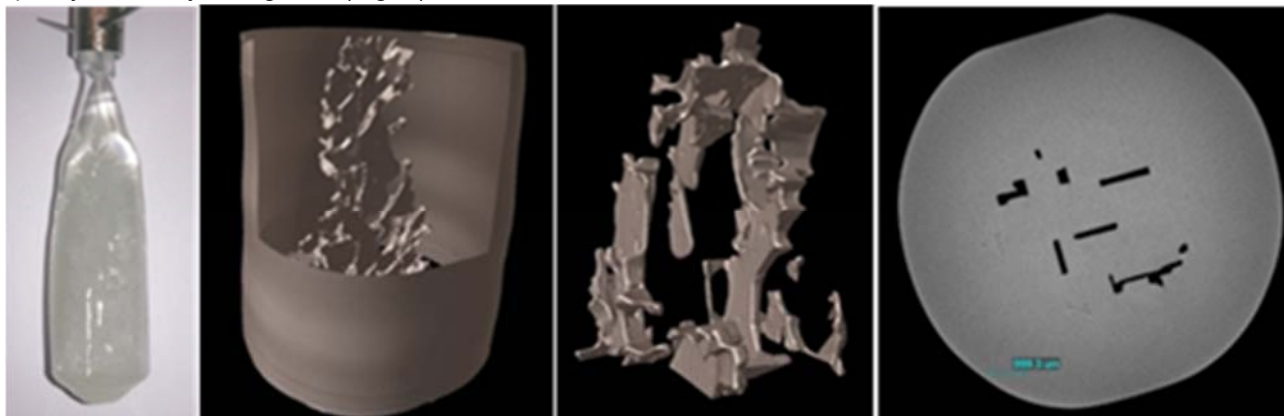


Fig.1: X-ray microscope tomography of a crystal grown under reducing atmosphere exhibiting large interconnected tubular structures indicating continuous absorption of gas bubbles.

Finally single crystals were grown with very low growth rates (0.5 mm/h) to avoid the incorporation of gas bubbles into the crystal. Mn-incorporation was confirmed by microprobe analyses and UV-vis spectroscopy was applied to distinguish between Mn II and Mn III. In principal grown crystals exhibit the general composition of åkermanite and contained 0.21-0.31 mol % MnO grown from melts with 0.75-1.5 mol % MnO. Spectroscopic analysis showed the presence of Mn II in crystals grown under forming gas in contrast to crystals grown under pure N_2 which contained only Mn III.

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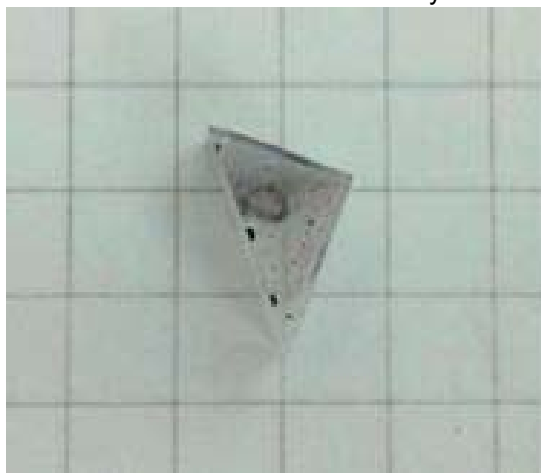
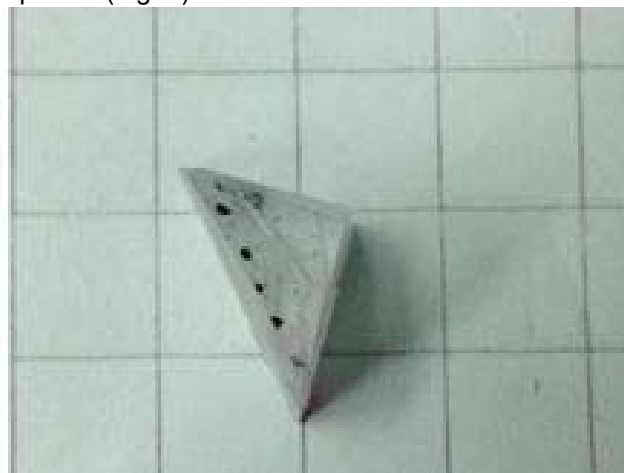
Optical dispersion and electronic polarizability of synthetic mullite

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Content

Mullite with general composition $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ is a rare mineral but a common synthetic compound in high-temperature ceramics. The crystal used here for optical studies was grown by the Czochralski method at the Leibniz Institute for Crystal Growth in Berlin. Its chemical composition derived from electron microprobe analysis is $\text{Al}_{4.75}\text{Si}_{1.25}\text{O}_{9.625}$ ($x=0.375$) close to a 2:1 ($2\text{Al}_2\text{O}_3 : \text{SiO}_2$) composition. Two pieces of about centimeter size were cut from the crystal and polished to prisms (Fig. 1)



Mullite prisms with (100) as plane of incidence and [010] as refracting edge (left), and correspondingly (001) and [100] (right).

. The orientation of the prisms relative to the crystallographic axes of the orthorhombic crystal was checked by X-ray diffraction methods. For each of the prisms two dispersion curves were recorded, n_x and n_y for the first prism, and n_y and n_z for the second one. A Sellmaier fit through 15 points measured between 400 and 700 nm clearly shows that the slope of the dispersion curves is much lower than determined by Guse and Saalfeld [1]. The mean refractive index $\langle n \rangle$ at 589 nm can be calculated from the individual electronic polarizabilities of Al and Si [2] using the additivity rule and calculating the refractive index from the Anderson-Eggletton relationship $n = \sqrt{4\pi\alpha / ((2.26 - (4\pi/3))\alpha + V_m) + 1}$ where α AE = the total polarizability of a mineral or compound, n_D = the refractive index at $\lambda = 589.3$ nm, V_m = molar volume in $\text{\AA}^3$, and $c = 2.26$ representing the electronic overlap factor. The calculated value of $\langle n_{\text{calc}} \rangle = 1.640$ is in excellent agreement with the observed value of 1.644 with a deviation $\langle n_{\text{obs}} \rangle - \langle n_{\text{calc}} \rangle / \langle n_{\text{obs}} \rangle$ less than 0.3 %. The results are compared with other mullite-type (sillimanite and andalusite) and olivine-type (forsterite, fayalite, sinhalite) compounds having similar chains of edge-sharing octahedra.

We thank the DFG for funding this project under grant Fi442/21-2.

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Polarizability deviations from the additivity rule in $M^{2+}SO_4 \cdot nH_2O$, bloedite, and kieserite-related minerals with sterically strained structures

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Content

Shannon and Fischer [1] have recently evaluated the dynamic total polarizabilities α_{AE} of minerals and synthetic compounds using ~2600 measurements of refractive indices (n_D) at $\lambda = 589.3$ nm to yield a unique set of individual electronic polarizabilities $\alpha_e(\text{ion})$ of ions which can be used for the prediction of total mineral polarizabilities and mean refractive indices of the vast majority of minerals and synthetic oxides. The total polarizabilities are defined by the Anderson-Eggleton relationship

$\alpha_{AE} = ((n_D^2 - 1) V_m) / (4\pi + (4\pi/3 - c)(n_D^2 - 1))$ where α_{AE} = the total polarizability of a mineral or compound, n_D = the refractive index at $\lambda = 589.3$ nm, V_m = molar volume in $\text{\AA}^3$, and $c = 2.26$ representing the electronic overlap factor. If the chemical composition is known, the total polarizability α can be calculated from the individual electronic polarizabilities $\alpha_e(\text{ion})$ [1] using the additivity rule where the sum of individual polarizabilities corresponds to the total polarizability of the compound. Applying this scheme, we found that the calculated mean values of $\langle \alpha_{AE} \rangle$ and $\langle n_D \rangle$ for 54 common minerals and 650 minerals and synthetic compounds differ by less than 3% and 2%, respectively, from the observed values. However, deviations from the valence-sum rule at cations in some minerals are associated with large deviations of observed from calculated total polarizabilities. We have identified several groups of minerals and compounds where deviations from the valence-sum rule at cations lead to polarizability deviations of 2-5%: $M(SO_4) \cdot nH_2O$, $n = 1-6$, bloedite-group minerals $[Na_2M^{2+}(SO_4)_2 \cdot 4H_2O]$, and the kieserite-related minerals: isokite, panasqueiraite and tilasite. In these minerals, the environment of the M ions contains both O and H_2O : $Mg[O_4(H_2O)_2]$ in kieserite, szmikite, and szomolnikite; $Mg[O_2(H_2O)_4]$ in starkeyite, ilesite, and rozenite, and $Mg[(H_2O)_6]$ in hexahydrite. Deviations from the valence-sum rule in compounds where the ligands are only H_2O , the $M(H_2O)_6$ groups do not result in significant polarizability deviations. A possible explanation for this different behavior is that bond-valence theory treats O and H separately whereas polarizability calculations treat the polarizability of the entire H_2O molecule.

We thank the DFG for funding this project under grant Fi442/21-2

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Promoting the catalytic performances of HZSM-5 zeolite by impregnation with phosphoric acid: An insight into the interactions between phosphorus and HZSM-5 framework

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Content

HZSM-5 is a zeolite largely used as a solid acid catalyst in petrochemical processes such as Fluid Catalytic Cracking (FCC). Catalysis over HZSM-5 zeolite is carried out by the strongly acidic bridging hydroxyl groups (Si-OH-Al) in the porous framework, which are Brønsted acid sites. However, during catalytic reactions, the presence of water combined with high temperature conditions ("steaming") can cause the breaking of the Si-OH-Al bonds, leading to framework dealumination and consequent deactivation of the zeolite-based catalyst. Therefore, hydrothermal stabilization of HZSM-5 is crucial to enhance the effectiveness of this acid-catalyst for industrial applications.

Impregnation with phosphoric acid represents an efficient and relatively inexpensive post-synthesis route to promote the hydrothermal stability of HZSM-5. Although phosphorous treatment of HZSM-5 is largely applied on the industrial scale with evident beneficial effects, the nature of the interactions between phosphorus and HZSM-5 framework are not fully understood.

To this end, we have investigated the physicochemical modifications induced by phosphorus on HZSM-5 zeolite by means of atom probe tomography, X-ray diffraction (XRD) and ¹H, ²⁹Si, ²⁷Al, ³¹P Magic Angle Spinning (MAS) solid-state Nuclear Magnetic Resonance (ssNMR) spectroscopy. These data show that phosphatation followed by thermal treatment induces the breaking of Si-OH-Al bridging groups and consequent partial dealumination. Therefore, one could expect a decrease in strong acid sites after phosphatation. Nevertheless, the formation of new types of Brønsted acid sites was confirmed by ¹H MAS ssNMR and, together with the results obtained from ³¹P NMR spectra, we have been able to understand the mechanism responsible for the enhanced cracking activity of phosphorus-treated HZSM-5.

Radiation damaged pyrochlore – metastable short range order

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Content

Radiation damaged pyrochlores are heterogeneously disordered on different length scales as a result of intrinsic decay processes by uranium and thorium nuclei. Such structural damages are metastable and influence the macroscopic properties drastically. Thermal annealing re-establishes the long-range structural order to a certain extent. This is of great interest for material sciences and in general for the better understanding of embedding materials for actinides in radioactive waste. [1], [2].

The analysis of pyrochlores exposed to different radiation doses on annealing using X-ray diffraction, Raman and IR spectroscopy respectively, gives insight into the structural damage and the recrystallization behaviour on different length scales [3].

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Screening phase compositions of LTO ($\text{Li}_5\text{Ti}_4\text{O}_{12}$)-dominated nano-particle powders produced by flame spray pyrolysis

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Content

LTO ($\text{Li}_5\text{Ti}_4\text{O}_{12}$) is a well-established material for energy storage [1]. Nano-crystalline LTO shows better performances than larger particles due to short diffusion path lengths compensating for LTO's rather low apparent chemical diffusion coefficient (e.g., [2]). The production of nanoparticles by flame spray pyrolysis (FSP) is cost-effective and allows for production of spherical particles with a narrow particle size distribution. However, cost-effectiveness depends upon the choice of metal precursor/ solvent combinations. In the present study numerous combinations of solvents and metal precursors for FSP synthesis were screened by Rietveld analysis (BRASS2, [3]) of powder diffraction data to find the combinations with highest yield of LTO phase. In total 25 combinations of five different Li-precursor/solvent pairs and 5 different Ti-precursor/solvent pairs were analyzed, of which 13 have phase fractions > 90 % but only two of these yielded phase pure LTO. In all cases the Rietveld-based LTO average particles sizes are 4-7 nm, matching well those observed by TEM and BET. Considering the extreme broadening of the reflections it was quite astonishing that even structural parameters could be refined to reasonable values. Further results indicate that separate dissolution of the precursors and that the degree of solution homogeneity are the key factors: The quality of dissolution was studied by timely high-resolution imaging of the explosion of single-droplets on sudden heating. Further materials properties such as battery performances of the as-synthesized materials are reported in [4].

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Stability of monoclinic malayaite by first principle calculation and Raman spectroscopy

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Content

Malayaite, CaSnSiO_5 , is the Sn analogue of titanite, CaTiSiO_5 . While the ground state structure of titanite is distorted in space group symmetry $P2_1/c$, transforming to the $C2/c$ aristotype structure only at elevated temperatures, a similar distortion is not known in malayaite. Accordingly malayaite occurs in space group symmetry $C2/c$ at room temperature, while low temperature data so far have been unavailable. The structure is known to transform to triclinic symmetry under high pressure conditions [1].

Here we report phonon dispersion of malayaite, calculated using the variational density functional perturbation theory (DFPT) as implemented in the CASTEP electronic structure code. For the $C2/c$ crystal structure of malayaite, imaginary frequencies are obtained at several wavevectors. The associated phonon modes are dominated by motion of the Ca atoms. At the Γ -point an unstable, Raman active B_g -mode is predicted by the DFPT calculations. Structure optimization in triclinic symmetry $P-1$ yields a crystal structure that is similar to the known triclinic high-pressure phase of malayaite. The calculated phonon dispersion of this triclinic polymorph does not indicate any further instabilities.

Softening of a phonon mode from 55 cm^{-1} at 290 K to 45 cm^{-1} at 90 K is observed by polarized Raman scattering experiments of a natural malayaite crystal. Implications of the mode softening for the existence of a triclinic low temperature polymorph of malayaite and possible relation of this mode to the unstable modes predicted by DFPT are discussed.

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Synthesis of strontium and calcium rare-earth aluminates

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Content

Luminescent materials based on MAlO_4 and MR_2O_4 ($\text{M} = \text{Ca}, \text{Sr}$; $\text{R} = \text{Rare Earth Elements}$) as host lattice are gaining more interest due to their smooth emission spectra and long lifetimes.

The abstract reports on the results of studies on solid solution of $\text{MEu}_{2-x}\text{Al}_x\text{O}_4$ ($\text{M} = \text{Sr}, \text{Ca}$). The compounds MAlO_4 ($\text{M} = \text{Ca}, \text{Sr}$; $\text{R} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Y}$ and Yb) are prepared by sol gel based Pechini method and are studied by PXRD, IR, TG and REM. Furthermore their hydraulic behaviour is studied by isoperibolic calorimetry.

The gels required for Pechini method were prepared using stoichiometric amounts of analytical-grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and R_2O_3 ($\text{R} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Y}$ and Yb). Additionally citric acid as a complexing agent and ethylene glycol as a dispersing agent was added to form the gel. The annealing temperature for each compound varied between 1000 and 1500 °C.

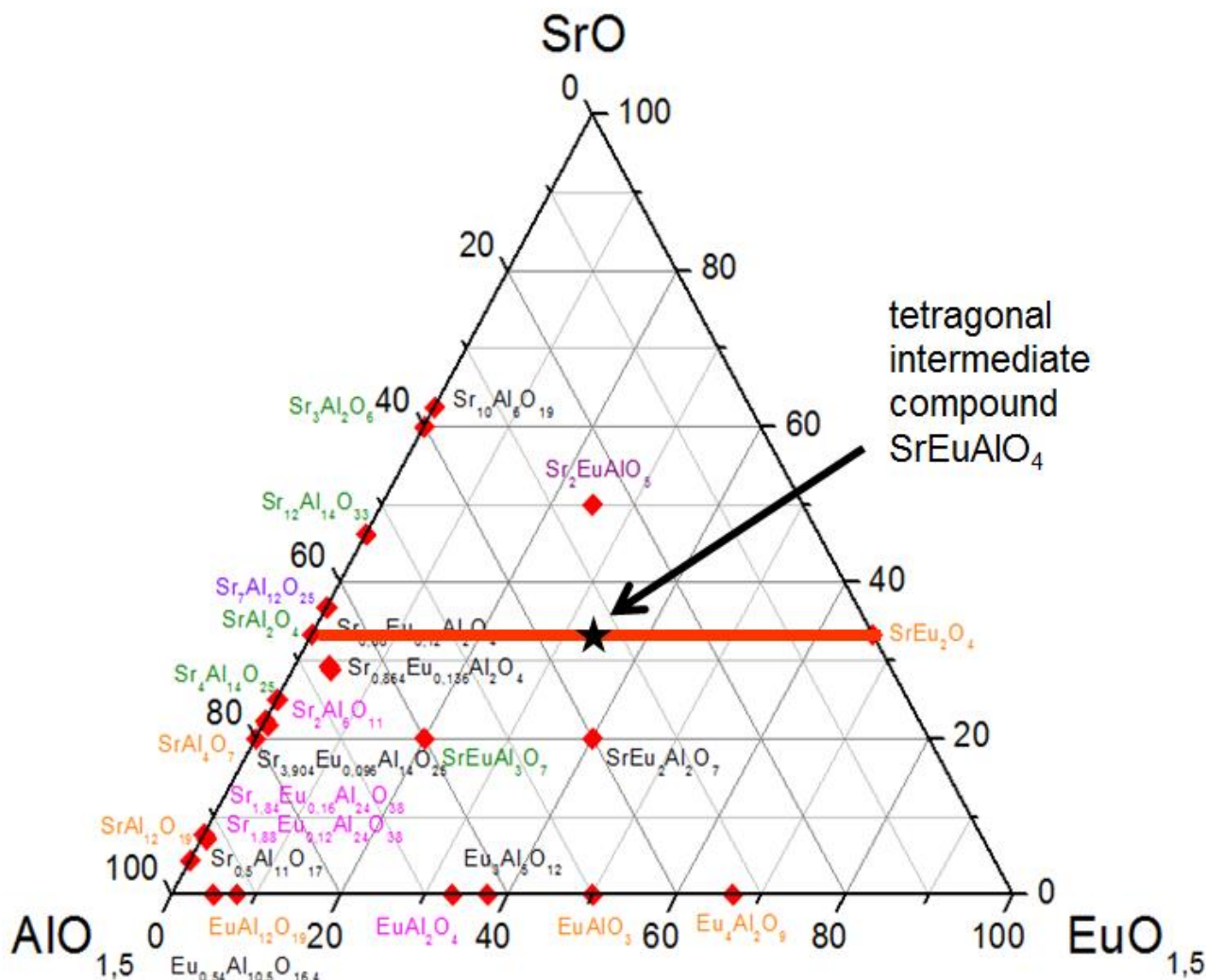


Figure 1: Ternary diagram of SrO-AlO_{1.5} - EuO_{1.5} (red line: studied system)

The study of the system of $\text{SrEu}_{2-x}\text{Al}_x\text{O}_4$ (Figure 1) showed that when $x = 1$ an intermediate phase with composition SrEuAlO_4 crystallizes. Phases with composition MRAIO_4 ($M = \text{Sr, Ca}$; $R = \text{Nd, Sm, Eu, Dy, Y}$ and Yb), isotypic to SrEuAlO_4 , are not all stable depending on the ionic size of alkaline earth and rare earth elements.

The results on the investigation of hydraulic behaviour of components and intermediate phase of the system $\text{SrEu}_{2-x}\text{Al}_x\text{O}_4$ with isoperibolic calorimetry are shown in Figure 2. The special cement phase SrAl_2O_4 reacts with water immediately, forming SrAl -garnet and amorphous hydration phase at 20°C . No heat flow was detected with the intermediate phase SrEuAlO_4 . The XRDs before and after hydration showed no difference, hence SrEuAlO_4 seems to be stable against water. The REE component SrEu_2O_4 reacts with water and a new amorphous phase is formed.

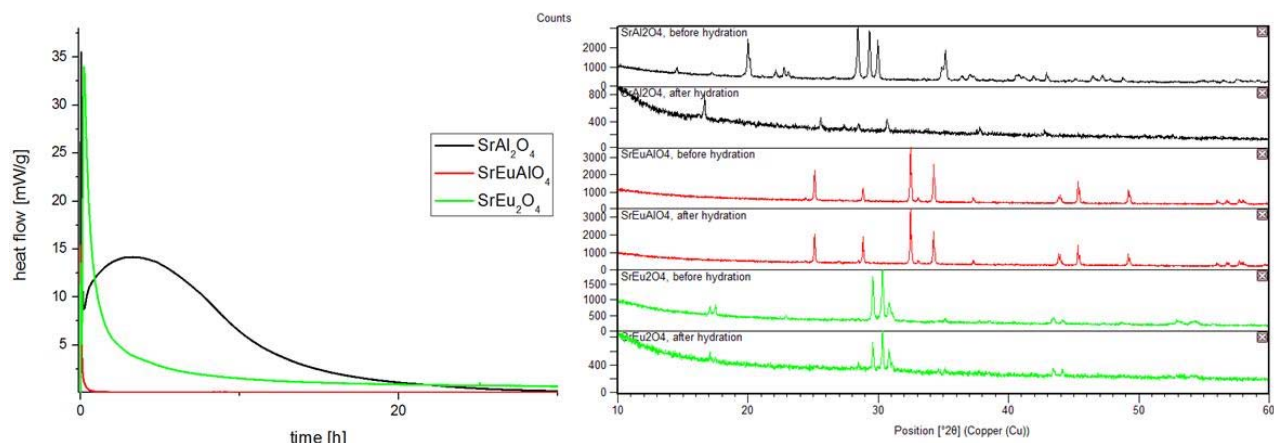


Figure 2: a. Isoperibolic heat flow calorimetry of SrAl_2O_4 , SrEuAlO_4 , SrEu_2O_4 water/aluminate-ratio: 1 b. XRDs of SrAl_2O_4 , SrEuAlO_4 , SrEu_2O_4 before/after calorimetry

The present study demonstrates the synthesis of monophasic MRAIO_4 ($M = \text{Sr, Ca}$; $R = \text{La, Nd, Sm, Eu, Dy, Y}$ and Yb) by sol gel based Pechini method. The stability of compounds depends highly on the ionic size of incorporated REE and alkaline earth. Different stability of alkaline earth rare earth compounds against water is studied as well.

Temperature-induced structural transformations in the ferroelectric (1-x)PbTiO₃-xBiMg_{0.5}Ti_{0.5}O₃

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Content

Piezoelectric ceramics with the perovskite structure type (ABO₃) play a key role in the development of new electronic devices, with lead zirconate titanate (PZT) being currently one of the most used piezoelectric ceramic materials worldwide. However, in the past few years, the negative effects of Pb on the human health led to new EU regulations, which restrict the use of lead. Therefore, the major challenge that the ferroelectric community is currently facing, is to find lead-free and lead-poor ferroelectrics suitable to replace PZT. Very promising candidates are the (1-x)PbTiO₃-xBiMeO₃ solid solutions with Me = Sc, In, Mg_{0.5}Ti_{0.5}, Ni_{0.5}Ti_{0.5}, Co_{1/2}Ti_{0.5}, Mg_{0.5}Zr_{0.5}, Ni_{0.5}Zr_{0.5}, which exhibit piezoelectric and electromechanical properties approaching those of PZT. Similar to PZT, (1-x)PbTiO₃-xBiMeO₃ compounds have a morphotropic phase boundary (MPB) corresponding to the composition xMPB, at which a transition between a tetragonal and a rhombohedral/monoclinic ferroelectric phase takes place. The properties of (1-x)PbTiO₃-xBiMeO₃ depend on the chemical characteristics of the dopant elements. In order to better understand the relation chemistry-structure-properties, it is necessary to study in detail the temperature-induced structural transformations at a mesoscopic scale. Hard-mode Raman spectroscopy is a very appropriate method to study ferroic coupling processes in these materials. In this contribution the composition effect on the temperature-induced structural changes in the solid solution (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ (PT-xBNT) studied by Raman scattering is reported. PT-xBNT has a morphotropic phase boundary at x = 0.55, relatively high Curie temperature ~ 673 K and longitudinal piezoelectric coefficient d₃₃₃ = 260 pC/N at xMPB. Raman analyses were performed for compounds with x = 0.20, 0.50, 0.55 and 0.70 in the temperature range 100 - 870 K. The results reveal the presence of polar displacements of the A-site and B-site cations above the transition temperature for all compounds, indicating strong order-disorder phenomena on the local scale. The doping strongly affects the type of temperature-driven structural transformations and especially the coupling processes within the A-site cation system, which in turn changes the long-range ferroelectric order from tetragonal to pseudorhombohedral and the type of the paraelectric-to-ferroelectric phase transition from predominantly displacive to predominantly order-disorder.

Thermal expansion of Co and Ni olivine: A comparison with Mn and Fe olivine and an assessment of equations-of-state

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Content

To complete the data basis for comparing the thermal behaviour of end-member olivines containing cations of the transition element series Mn (3d5), Fe (3d6), Co (3d7), Ni (3d8 subshell) the thermal expansivity of Co and Ni olivine has been studied by powder diffraction at ambient pressure and temperatures between 25°C and 1000°C. The anisotropy of the thermal expansion was analysed using various isothermal equations-of-state (EoS) coupled with the thermal Mie-Grüneisen EoS.

Axial expansivities α are controlled by compressibilities β_T and thermal pressures $(\partial P/\partial T)_V$ according to $\alpha = \beta_T (\partial P/\partial T)_V$. For olivines, the structural features suggest a sequence of compressibilities with $\beta_{T,b} > \beta_{T,c} > \beta_{T,a}$ (SG Pbnm). Usually, a similar ranking is also found for the axial expansivities. In this case of olivines, however, only Mn and Mg olivine meet the expectation, contrary to Fe olivine and to a lesser degree to Co and Ni olivine. The reason for the unusual behaviour is found in the specific anisotropies of the axial thermal pressures.

Based on our expansion data, we have compared the high temperature extrapolation behaviour as predicted by two groups of EoSs. The first one included five EoSs which were originally designed to model high-pressure behaviour at ambient temperature (Birch-Murnaghan etc.). The second group consists of two expressions explicitly devised in order to describe thermal expansion at ambient pressure (Suzuki, Wallace). The first group of EoSs was found to deliver closely related results upon extrapolating α up to 3000 K, whereas the results of the second group clearly deviate.

The ambient-pressure high-temperature performance of an EoS can be judged by comparing bulk moduli K_T predicted by the respective EoS with the corresponding values derived from experimental elastic moduli. The K_T values obtained from the Wallace and Suzuki EoSs severely deviate from measured K_T , while good agreement is found for the first five EoSs. Thus, we have the paradox situation that those expressions, which were designed to describe thermal expansion, fail on extrapolation, whereas the "high-pressure EoSs" do properly perform with respect to K_T .

Thermal expansion of coesite determined by in-situ X-ray diffraction at high pressures

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Content

Among the SiO₂ polymorphs, coesite is the stable modification in metamorphic rocks formed at ultrahigh pressure conditions (e.g. >3 GPa). Pressure-volume-temperature (P-V-T) equations of state are essential to model equilibrium P-T phase diagrams for such rocks. Available data for coesite include thermal expansivity at ambient pressure, $\alpha_0 \sim 7.5 \times 10^{-6} \text{ K}^{-1}$ [1], and bulk modulus / compressibility at ambient temperature, $\kappa_0 \sim 100 \text{ GPa} / \kappa'_0 \sim 4$ [2]. However, data at combined high P and high T are not reported in literature. Several thermodynamic datasets utilize either these values or optimized values, resulting in different predicted coesite unit cell volumes at P and T. Remarkably, the value used for thermal expansivity in the recent Holland & Powell database [3] is 60% higher compared to the experimentally determined value.

We here present new in-situ unit cell volume measurements of coesite at combined high P and T aiming to establish an experimentally validated equation of state. A polycrystalline coesite sample was synthesized from SiO₂ glass in a large volume multi-anvil press at 7 GPa and 1873 K. Octahedrons with 18 mm edge length and tungsten carbide anvils with 11 mm truncated edge length (OEL/TEL 18/11) were used. For measuring unit cell volumes, in-situ synchrotron experiments were conducted in a large volume multi-anvil press (OEL/TEL 14/8) at beamline BL04B1 (SPring-8/Japan). The coesite sample and the P marker (NaCl+MgO) were analyzed at various P's and 300-1300 K with X-ray diffraction. T was monitored with a thermocouple. Unit cell volumes of coesite and NaCl+MgO were determined by Rietveld refinement of X-ray spectra. Equations of state for NaCl+MgO were used to calculate experimental P's (0 - 8.2 GPa).

Preliminary data evaluation yield $\kappa_T' \sim 4$ and $\alpha_P \sim 12\text{-}15 \times 10^{-6} \text{ K}^{-1}$, the latter being higher at higher P. While κ_T' closely matches literature values, α_P is about two times the reported thermal expansivity at ambient pressure [1]. This might indicate that thermal expansivity increases with P and is maybe even higher than the optimized value used in the Holland & Powell database [3]. These results can potentially improve the P-V-T equation of state for coesite.

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Session 8.2: Structure, properties, and applications of crystalline materials.: Talk

Keynote speaker

A-161

High-pressure nano-confinement in zeolites: innovative materials from the Mineral Science know-how

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Content

The scientific research on zeolites – an important class of minerals and synthetic materials – represents an example of fruitful symbiosis among mineralogists, crystal chemists, industrial scientists and engineers. In fact, zeolite properties – among which selective cation-exchange, hydration/dehydration, molecular sieve efficiency and catalytic activity – have made these materials interesting for advanced technological applications, spanning from water treatment, soil remediation, gas and solution separation, animal feeding, biomedical applications to catalysis and nuclear-waste processing. This contribution will review some recent studies on the penetration of guest molecules in porous materials, performed combining the matrix shape and space constraints with the effects of an external pressure. In particular, the use of a multi-technique strategy based on synchrotron X-ray powder diffraction experiments and modeling studies [1], has showed that HP applied on a hydrophobic all-silica ferrierite is able to separate an ethanol–water liquid mixture into ethanol dimer wires and water tetramer squares (Fig. 1). These confined supramolecular blocks, alternating in a binary two-dimensional architecture, remain stable upon P release. HP can also be exploited to force the intrusion of water or aqueous salt solutions into a hydrophobic porous material. During this intrusion, the mechanical energy can be converted into interfacial one. Depending on various physical parameters of the porous material, when P is released the “zeosil-water” system is able to restore, dissipate or absorb the supplied mechanical energy accumulated during the compression step, displaying a spring, shock-absorber or bumper behavior, respectively. The energetic performances of pure-silica ferrierite [2] upon intrusion/extrusion experiments with water and MgCl_2 electrolytic aqueous solution will be discussed.

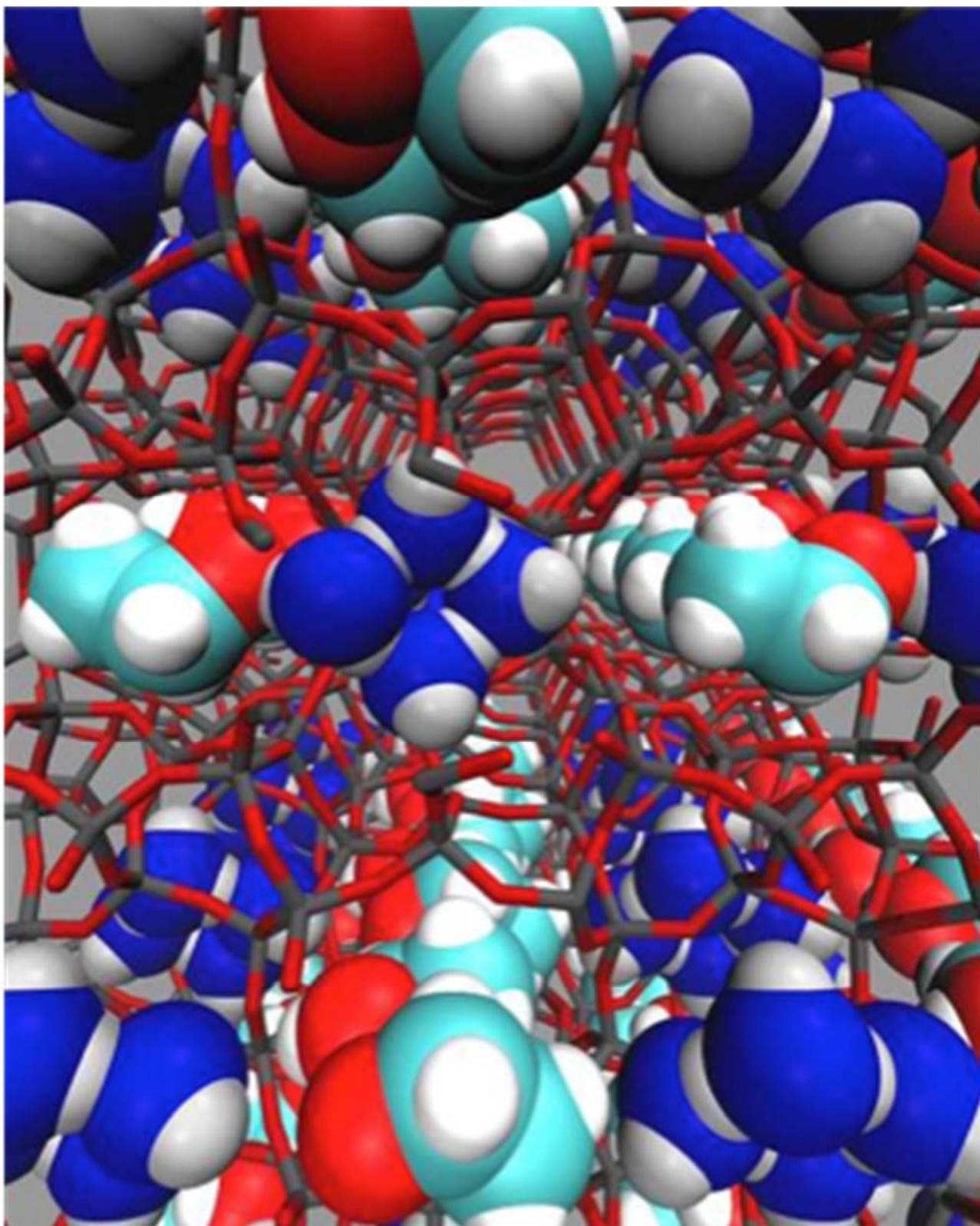


Figure 1 - High pressure-induced supramolecular aggregates in Si-ferrierite: ethanol dimer wires and water tetramer squares.

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Fast Li-ion conduction in Fe-doped Li-oxide garnets

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Content

The rise of new technologies leads to an increased demand for safe high-performance energy storage devices. The application of solid electrolytes is one approach to realize such novel battery concepts. Li-stuffed oxide garnets such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) are among the most promising materials to be used as solid state Li^+ electrolytes. Besides its high lithium ion conductivity, LLZO also shows electrochemical inertness over a wide potential window. Another advantage of LLZO is its stability against lithium metal. Thus, LLZO is particularly suited to be used as solid lithium electrolyte.

Pure LLZO shows a tetragonal crystal structure with space group $I4_1/acd$ (no. 142). Around 650°C , the material undergoes a phase transition to the cubic garnet-type modification with space group $la-3d$ (no. 230). Compared to conventional garnets with general formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$, Li^+ does not only occupy the tetrahedrally coordinated C-site (24d), but also additional sites, resulting in a three-dimensional network of partially occupied lithium sites which form a threedimensional diffusion pathway.

For application as solid-state electrolyte, the cubic modification is preferred, as it shows a higher lithium ion conductivity compared to the tetragonal modification. A stabilization of the cubic garnet-type modification at room temperature can be achieved by the introduction of supervalent cations. These supervalent cations cause the formation of lithium vacancies, which lead to a disorder in the lithium ion distribution; resulting in a higher symmetry. It was shown that the substitution $3 \text{Li}^+ \rightarrow \text{Ga}^{3+} + 2 \square_{\text{Li}}$ leads to the formation of another structural modification, showing the acentric cubic space group $la-3d$ (no. 220). The reduction in symmetry, compared to the common garnet structure, is caused by the site preference of Ga^{3+} . A recent study showed that the introduction of Fe^{3+} as substituent also causes the formation of the acentric garnet-similar $la-3d$ modification. The crystal structure of Fe^{3+} -substituted LLZO has been characterized by powder and single crystal X-ray diffraction as well as by powder neutron diffraction. In addition, ^{57}Fe Mößbauer spectroscopy has been applied to study the distribution of Fe^{3+} over different crystallographic sites. Electrochemical impedance spectroscopy of Fe^{3+} -substituted LLZO showed a lithium ion conductivity of up to $1.38 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, which among the highest values ever reported for lithium-stuffed oxide garnets.

First crystal structure investigations of natural mullites

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Content

Synthetic mullite ($\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$) has attracted the interest of many researchers because of its outstanding thermal resistance and mechanical strength. It can be obtained as a synthetic product for technical applications but also occurs as a rare mineral in nature. In contrast to its synthetic counterpart the natural mullite is not very well characterized. To contribute to the investigation of that mineral we present here the first crystal structure refinement of natural mullites. Therefore, three single-crystals of SiO_2 -rich mullite minerals were examined by X-ray diffraction methods and electron microprobe analyses. Two isometric crystals were obtained from a rock sample from the Bellerberg, Eifel area, Germany (specimen M1_3c and M1_4b). The other sample is from Kladne, Czech Republic (161101-2a) and exhibits a needle-shaped habit. The microprobe analyses yielded the following chemical compositions expressed as the corresponding mineral formulas: $\text{Al}_{4.30}\text{Fe}_{0.12}\text{Si}_{1.53}\text{Ti}_{0.05}\text{O}_{9.79}$ for M1_3c referring to an x -value of $x = 0.21$ for M1_3c; $\text{Al}_{4.21}\text{Fe}_{0.11}\text{Si}_{1.63}\text{Ti}_{0.05}\text{O}_{9.84}$ for M1_4b with $x = 0.16$; $\text{Al}_{4.36}\text{Fe}_{0.02}\text{Si}_{1.62}\text{O}_{9.81}$ for 161101-2a with $x = 0.19$. Here it is assumed that Fe appears as ferric iron. The chemical analyses show that all three minerals exhibit a higher concentration of SiO_2 than stoichiometric 3/2-mullite ($x = 0.25$). Natural mullites show the same characteristic structural features as synthetic crystals and also crystalize in the orthorhombic space group $Pbam$ with $Z = 1$. The lattice parameters are: $a = 7.5542(3) \text{ \AA}$, $b = 7.6998(3) \text{ \AA}$, $c = 2.8935(1) \text{ \AA}$, $V = 168.31(2) \text{ \AA}^3$ for M1_3c; $a = 7.5353(3) \text{ \AA}$, $b = 7.7018(3) \text{ \AA}$, $c = 2.8928(3) \text{ \AA}$, $V = 167.89(4) \text{ \AA}^3$ for M1_4b; $a = 7.5439(3) \text{ \AA}$, $b = 7.6958(3) \text{ \AA}$, $c = 2.8879(1) \text{ \AA}$, $V = 167.66(1) \text{ \AA}^3$ for 161101-2a. Furthermore, hkl sections in reciprocal space were generated from the X-ray diffraction data. These revealed that also natural mullites show the characteristic diffraction pattern which is composed of strong main reflections, weak satellite reflections and diffuse X-ray scattering. However, the relative intensities of the satellite reflections and the diffuse scattering are decreasing with increasing SiO_2 concentration. For the SiO_2 richest samples (M1_4b and 161101-2a) almost no diffuse scattering was detected.

High transparent low crystal symmetry nano-ceramics

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Content

Highly transparent solids are optically isotropic. Examples are glasses and cubic single crystals. Since most of these materials are fragile, polycrystalline materials become increasingly important, e.g., as optical lenses or in high-energy lasers, because their microstructure can enhance their physical properties [1]. Most of transparent polycrystalline ceramics consist of cubic crystals and could not be produced so far from more commonly occurring low symmetric, optical anisotropic, birefringent crystals [1] [2]. The present study demonstrates for the first time the synthesis of a fully dense highly transparent polycrystalline kyanite based ceramic with the lowest possible (triclinic) crystal symmetry.

Composites of Al₂SiO₅ (kyanite) with small amounts of bulk Al₂O₃ were synthesized from glasses at high pressure (10 GPa) and high temperature (1200-1600 °C) in a large volume multi-anvil press. Synchrotron X-Ray diffraction indicates that the glass completely transformed into kyanite and minor Al₂O₃. Transmission electron microscopy shows, that the ceramic synthesized at 1200 °C exhibits nano-sized grains of 33 ± 13 nm. In the visible light range, the transparency of this nano-polycrystalline ceramics is excellent (Figure 1) and was determined with 60-80 % to be close to that of highly transparent cubic polycrystalline ceramics. The increases of average grain size with the synthesis temperature results in decreases of the transparency, so that the ceramics with the largest observed grain size (611 ± 170 nm) obtained at 1600 °C is opaque. The theoretical relationship of crystal birefringence, grain size, and transparency [3] well coincide with our results given full density and randomly orientated crystals. Thus, the sharp increase in transparency with decreases in the grain size mainly results from fading interaction of the incident light with the crystals. This study demonstrates that, regardless the optical anisotropy of constituting crystals, all ceramics without strong absorption in the visible-light region can be optically isotropic and hence be highly transparent.

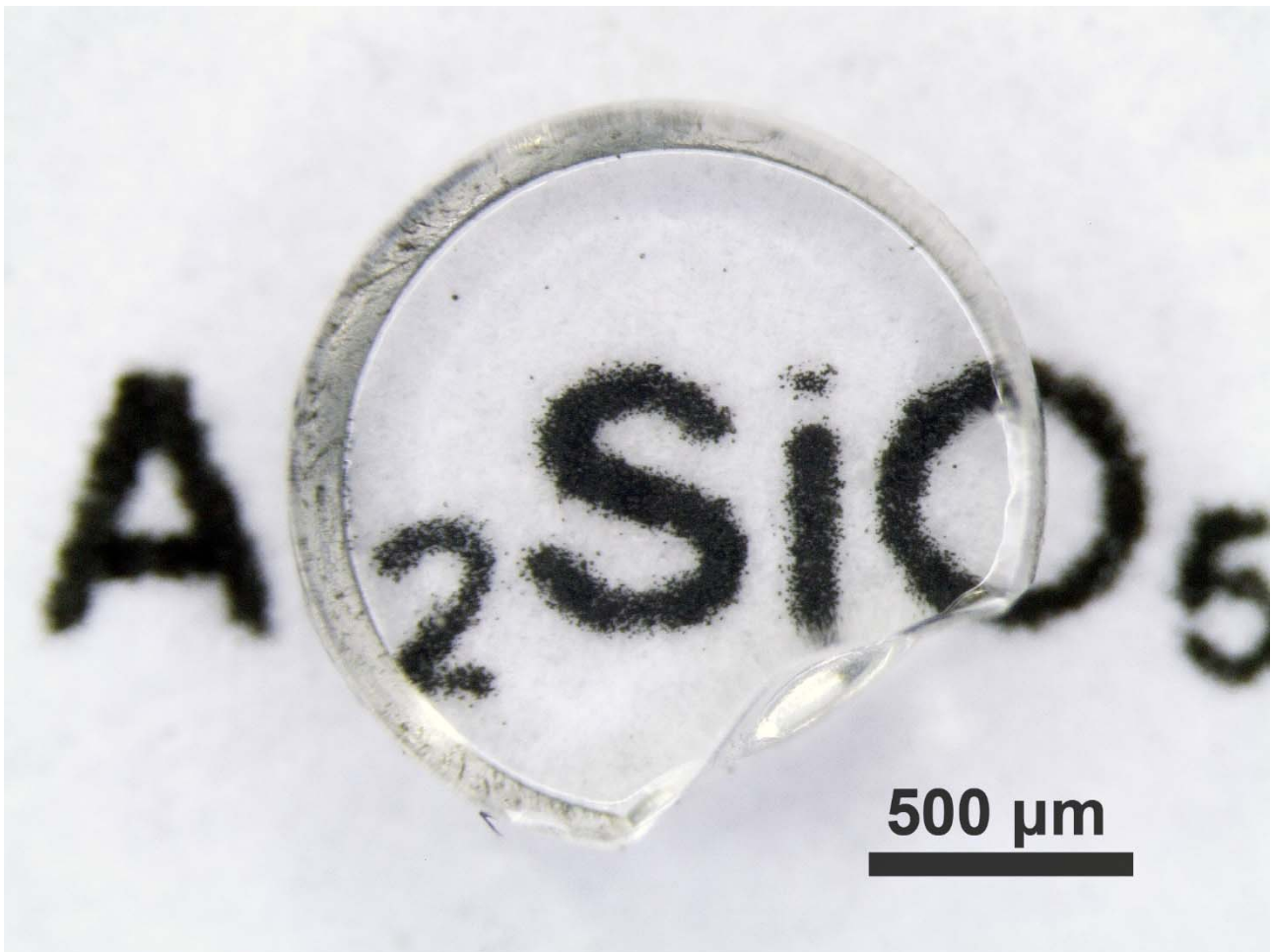


Figure 1: Optical appearance of the triclinic kyanite based nano-ceramic synthesized within this study.

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In-situ Raman spectroscopy and UV-C Laser stimulated luminescence spectroscopy of carbonate and phosphate minerals while irradiated with swift heavy ions

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Content

Raman spectroscopy is widely used in materials research as well as in geosciences. It has proved to be an excellent method to analyze mineral and structural changes of solids exposed to high-energy ions available at large accelerator facilities like the GSI Darmstadt [1] [2] [3]. Radiation-induced modifications are typically analyzed ex-situ. For a better understanding of dose dependent effects, a series of samples is exposed to different ion fluences. If, however, the material to be studied is anisotropic, it is impossible to analyze similar or identical crystallographic orientations for the different fluence measurements. To avoid these difficulties online and in-situ Raman spectroscopy were performed in the irradiation chamber prior to, during, and shortly after irradiation, in order to analyze how a given sample area changes as a function of ion fluence. The advantages of in-situ measurements are a flexible fluence management and above all a guarantee that the same area of the sample is being measured at all fluences and all measurements.

UV-C Laser stimulated luminescence spectroscopy is a new approach to visualize and quantify the defect concentration of minerals in a quick and non-destructive manner. In the past, calcite and apatite turned out as a sensitive natural detector for defects. Etching methods reliably reveal linear defects caused by irradiation with swift heavy ions or caused by natural fissioning (Fission Tracks). Additionally, crystals from the carbonate and phosphate family are known to luminescent under UV excitation. We thus exposed a with swift heavy ions irradiated calcite crystal (1×10^8 Au-ions/cm², 11.1 MeV/u) offline with UV-C light where the damaged area of the calcite crystal showed a thin line of greenish to yellowish luminescence. Further experiments were performed with a UV-Raman and photoluminescence spectrometer (UV-laser: 244 nm) of Jobin Yvon Horiba. Calcite irradiated with 1×10^6 Au-ions/cm² (11.1 MeV/u) show distinct photoluminescence with bands at about 520 and 545 nm. [4] [5]. With increasing fluence the amplitude of both peaks increases. To further investigate this effect, a UV-C Laser stimulated luminescence spectroscopy has been developed and set up in Heidelberg.

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Mesoscale twinning patterns in a mollusc shell: *Pinctada martensii*

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Content

Biominerals have caused huge interest in different disciplines (e.g. in material, medical and bio-geosciences) due to their complex organic-inorganic microtexture. In this work, electron backscatter diffraction (EBSD) and topological analysis of pole figures show that aragonite nacreous layers of *Pinctada martensii* (marine bivalve) shells have a mesocrystalline organization, which consists of at least a two-level domain structure. Primary domains are related by twin laws. The twinning between the primary domains is described as “mesotwinning”. Each domain is twinned by (110) planes. Angles between primary domains are ca. 63.5° or 52.5°. Secondary domains inside the primary domains are submicrometre units, ranging from several to hundreds of microns in dimension. The secondary domains are separated by low-angle grain boundaries. Angles between secondary domains range from 5° to 12°. The twin relationship is quantified and twin boundary patterns are discussed.

Neutron scattering as a gateway for understanding the anomalous temperature dependence of optical properties of sanidines from Eifel

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Content

The optical angle 2V of sanidine megacrystals from the Eifel volcanic field irreversibly changes when heated above about 750 °C [1]. Thus far, this anomaly has been attributed to rapid changes in the Si/Al ordering [1]. Recent investigations of bond-lengths in such sanidines gave rise to doubt on this interpretation [2]. Therefore, we performed single crystal neutron diffraction experiments on sanidines from Volkesfeld (Eifel) and Madagascar on the 4-Circle Diffractometer E5 at Helmholtz-Zentrum Berlin to determine the Si/Al order state before and after annealing the samples. Furthermore, using the Flat-Cone Single Crystal Neutron Diffractometer E2, possible real-structure phenomena associated with the irreversible changes were studied in-situ at temperatures up to 1050 °C.

The Si/Al order state of sanidines from Eifel and Madagascar changes similarly at high temperatures, confirming that the Si/Al ordering is not causing the anomalous optical behavior that only appears in sanidines from Eifel. The neutron diffraction patterns recorded at E2 show structured diffuse scattering far from Bragg peaks. The intensity of the diffuse scattering phenomena decreases strongly from 700 °C to 900 °C and recovers only partly upon cooling to room-temperature. This indicates that different structural features contribute to the diffuse scattering pattern, one of which vanishes in the expected temperature range and is, thus, likely associated with the irreversible change.

The unusually high Ba²⁺ and water content of sanidines from Eifel [3], the latter does not decrease significantly even when annealed at 1050 °C [2], suggests that H₂O may occupy regular lattice sites following the substitution 2(Na,K)⁺ → Ba²⁺ + H₂O [4]. This would result in compressive lattice strain in regions adjacent to the H₂O, which is attractive for the relatively small Na⁺ ions. This leads to an enrichment of Na⁺ cations in the vicinity of the H₂O defects. These clusters may contribute to the anomalous optical behavior, i.e. the irreversible change at 750 °C is possibly the result of temperature-induced dispersion of the clusters. The reformation of the clusters at lower temperatures is beyond laboratory timescales.

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Radiation damage in zircon: Structural response and damage accumulation

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Content

From dose-dependent ($0 - 6.8 \times 10^{18}$ alpha-decays/g) nanoindentation measurements and calculations a radiation damage related decrease in hardness (48%) and stiffness (54%) and an increase in the Poisson's ratio (54%) could be revealed for natural zircon with increasing dose (Beirau et al. 2016). This relationship between the structural damage (due to the alpha-decay of natural U and Th impurities) and the mechanical properties will be shown in detail. Furthermore, deeper insights into the underlying damage accumulation process and the radiation-induced anisotropic to isotropic transition of the mechanical properties will be provided. Their direct correlation with the amorphous fraction could be verified. The presented results indicate the importance of acquiring better knowledge about the mechanical long-term stability of radiation damaged materials in general.

Beirau, T., Nix, W.D., Bismayer, U., Boatner, L.A., Isaacson, S.G. and Ewing, R.C. (2016) Anisotropic mechanical properties of zircon and the effect of radiation damage. *Phys Chem Minerals* 43:627–638

Structure- property relations and structural instabilities in high-temperature piezoelectric materials of the oxoborate-family $RX_2Z_2O(BO_3)_3$

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Content

Many modern electronic components like sensors, frequency control elements and signal processing filters make use of bulk or surface acoustic wave properties of piezoelectric single crystals. In this context, α -quartz is the most widely used piezoelectric material because of its favorable chemical and mechanical stability in combination with high availability at relatively low costs. At non-ambient conditions, however, phase transitions, chemical decomposition, increasing electrical conductivity and/or high loss factors caused by anelastic processes restrict the application of α -quartz and of most of its synthetic alternatives. Nevertheless, there is an increasing demand for the development of piezoelectric materials capable of operating in harsh environments, particularly at high temperatures in oxidizing atmospheres. Examples are devices for active combustion and gas flow control in engines and turbines. The lack of appropriate synthetic materials led to a temporary renaissance of natural tourmaline, one of the longest known piezoelectric materials, which decomposes at about 1050 K. Promising candidates to overcome these limitations are members of the family of rare earth calcium oxoborates (RCOBs) crystallizing in the monoclinic space group Cm. These crystal species combine high melting points at around 1770 K with high piezoelectric sensitivity and low electric resistivity [1]. Moreover, different possibilities of cation substitution allow for a large variability in chemical composition and tuning of certain physical properties.

GdCa₄O(BO₃)₃ single crystals were grown from melt using the Czochralski method and their electromechanical properties were studied from 100 K to 1500 K using resonant ultrasound spectroscopy, differential scanning calorimetry and dilatometry. The 13 and 10, respectively, independent components of the elastic and piezoelectric tensor of both compounds could be determined. Above about 600 K more or less pronounced anomalies [2] are observed in the temperature dependence of the investigated physical properties, which are probably related to order/disorder processes on certain cation sites.

Acknowledgements: The authors gratefully acknowledge the financial support of the DFG PAK921/1, SCHR 761/4: Structure/property relationships and structural instabilities of high-temperature piezoelectrics of the oxoborate family.

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Viscoelastic properties of quartz at the alpha-beta phase transition: What we know, what we don't know, and what we could do to broaden our knowledge

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Content

Quartz is one of the most common rock-forming minerals of the Earth's continental crust and used in many technical applications. Detailed knowledge of the atomic structure and physical properties of quartz, related to a broad range of physical conditions, is important to understand geodynamic processes and enhance technical uses. This particularly holds for an apparently distinctive minimum of elasticity at the alpha-beta phase transition that is supposed to provide an in situ thermometer for seismic studies in thick, hot, and quartz-rich crustal areas. The interpretation of seismic data, however, is not always straightforward and low velocity zones can also be attributed to partial melting.

High-temperature dynamic mechanical analyses (DMA) of quartz indicate a viscoelastic behavior in the vicinity of the alpha-beta phase transition at around 573 °C. In DMA, measurements of stress, strain, and phase lag from sinusoidal three-point bending between 0.1 and 20 Hz enable us to determine the complex Young's modulus. At constant temperature just below the alpha-beta phase transition, quartz shows an increasing stiffness with rising loading frequency and a dissipation maximum around 1 Hz. The observed viscoelastic properties are mostly likely caused by the development of Dauphiné twin domains and can be described by a three-element equivalent circuit composed of two springs and a dashpot. Investigations on specimens with different crystallographic orientation allow the three-dimensional characterization of the complex Young's modulus. Using a set of estimated boundary conditions, both a frequency-dependent elasticity tensor and elastic wave velocities are assessed. Compressional wave velocities derived in this way are in agreement with DMA data of an elastically isotropic quartzite from Dalsland, Sweden.

The temperature of the alpha-beta phase transition increases with pressure and shifts the elasticity anomaly linked to it. The pressure-dependence of the viscoelastic properties of quartz, however, remains an enigma. Thus, there is a substantial gap between the available DMA data and its application as in situ thermometer in seismic studies. To broaden our knowledge and close this gap we could do dynamic experiments under pressure. Opportunities to do this, however, are currently rare. Thus, high-pressure studies of the viscoelastic properties of quartz, and other minerals, require the development of new devices.

Session 8.3: Economic Geology of Critical Raw Materials.: Poster

Session 8.3: Economic Geology of Critical Raw Materials.: Poster A-112

A study on the soundness of parent rocks in Sri Lanka

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Content

The quality of construction works in Civil Engineering largely depends on the properties of materials. The properties of rock aggregates depend upon the natural condition of different rock types. Therefore studies on the engineering properties of different rock types provide a prior knowledge on the quality of such rock types as well as potential locations of suitable sources for the industry. Soundness of aggregates is the ability of aggregates to resist change of volume due to change of physical condition. The property "soundness" of a material measures the tendency to split into pieces similar to physical weathering during expansion and contraction processes within it. Estimation of soundness of aggregate for use of concrete and other purposes indicates a quality and its' suitability. This soundness varies according to the type of minerals in a rock and its' origin. Geologically nine tenth (90%) of Sri Lanka is made up of high grade metamorphic rocks of Precambrian age. The remaining rocks are sedimentary rocks of predominantly Miocene age and a few intrusive rocks. The objective of this study is to classify different rock types found in Sri Lanka on the basis of their soundness and recommend the suitable rock types as aggregates for the construction industry.

Fresh rock samples of different rock types (metamorphic, intrusive rocks and sedimentary) were collected from quarries and exposed rocks in different localities in the Island, and were tested for their soundness property in the geotechnical engineering laboratory. Sodium sulfate was used to prepare the recommended solution according to the Standard Method ASTM C88-99a (1999). It takes fifteen days for one test on one rock type.

The range of soundness (loss of weight percentage) for each metamorphic rock can be mentioned as
Charnockite/ charnockitic gneiss 0.24-1.2
Charnockitic garnet/ hornblende/ biotite gneiss 0.34-2.82
Microcline/ Granitic gneiss 0.78-1.1
Garnet/ biotite gneiss 2.4-3.5
Marble 2.5-5.2,
Hornblende biotite gneiss 3.5-9.5
Quartzite 5.0-6.88

Soundness of two intrusive rocks, pegmatite and pink granite was 3.79 and 0.75 respectively. Range of Miocene sedimentary limestone was very high as 25-30. Accordingly charnockite/ charnockitic gneiss and pink granite are the highly suitable rocks and Miocene limestone is the highly unfavourable rock. The soundness limits depends on the type of the concrete or the type of its application.

Analysis of a tungsten mineralization using portable XRF and reflectance spectroscopy at the skarn occurrence Delitzsch, Central Germany

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Content

In this study, a drill core section from the western contact aureole of the Delitzsch plutonic complex was investigated. Due to intense contact metasomatism related to the intrusion of granitoid melts, sequences of pelitic to calcareous Cambrian sediments were converted to skarns. Additionally, the upper parts of the skarn system were strongly altered and oxidized. A historical exploration campaign in the 1970s revealed tungsten concentrations up to 3.44 % of WO₃ with a total estimated reserve of 52,000 tonnes [1] .

A detailed localization of tungsten-rich zones and accompanying elements was performed. Additionally, the influence of weathering and possible hydrothermal processes on the element and mineral distribution were assessed. Furthermore, the applicability of selected analytical methods for the geochemical characterization of weathered skarns was tested. The drill core was described macroscopically and the general mineral association was determined by optical microscopy on thin sections. Detailed profiles (interval spacing of 10 cm) regarding the distribution of tungsten, iron, calcium and base metals were generated on the basis of handheld XRF analyses and validated using XRF lab geochemistry performed at ALS Ireland. Sections of the core were subsequently analyzed using reflectance spectroscopy to detect alteration phases, such as clay minerals and Fe-oxihydroxides. For the verification of the results, x-ray powder diffraction was carried out exemplarily. Strongly altered zones exhibited a tenfold increase of the Ca/Fe-ratio compared with areas of the less altered skarn zone. Local maxima and minima in the tungsten content appear to occur erratic. Trends for the distribution of tungsten obtained by portable XRF correspond well with historical lab results of interval samples. The dominant mineral paragenesis is represented by hematite and goethite as well as carbonate minerals and minor chlorite. The occurrence of different iron phases correlates well with the measured iron maxima and minima. Kaolinite and halloysite were determined by reflectance spectroscopy in the highly weather zone. Quartz, garnet and scheelite could only be determined macroscopically, in thin sections or by UV fluorescence.

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Assessing the ecological impacts of deep-sea mining on Crustacea.

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Content

The deep-sea represents the largest ecosystem on the planet, yet our knowledge of its fauna remains limited. As part of the JPI Oceans project “Ecological aspects of deep-sea mining”, our research group is studying and comparing the long-term impacts of mining of ferro-manganese nodules on deep-sea crustaceans in two oceanic basins; (1) the Clarion-Clipperton fracture Zone (CCZ) a manganese nodule province in the NE Pacific and (2) the DISturbance and Re-COLonisation (DisCOL) Experimental Area (DEA), a disturbance proxy in the SE Pacific.

More than 60,000 specimens of Amphipoda were collected from the CCZ and DEA using baited traps in 2015. The greater than 15mm fraction has been morphologically sorted and 12 species have been identified thus far, including several undescribed species. We observed reduced biodiversity in the disturbed DEA with the domination of one amphipod species.

The two amphipod target species *Paralicella caperesca* and *Abyssorchomene gerulicorbis* were then selected for genetic analysis of connectivity and varied dispersal potential within and between the two research areas. For 200 specimens, we successfully obtained DNA sequences of part of the mitochondrial COI gene and the genetic results are presented here, providing evidence for cryptic diversity at a local scale in both species as well as connectivity over 3000km.

Next, we plan to use next generation double-digest Restriction-site Associated DNA sequencing (ddRAD-seq) to obtain population genomic data at a much finer resolution, to further contribute to the delimitation of the species within this diverse deep-sea amphipod group, and to test for population connectivity at smaller spatial scales.

Our molecular data will significantly contribute to the JPIO integrative data analyses which will be targeted towards formulating recommendations to policymakers for future deep-sea mining activities.

Hydrothermal tin deposits: experimental information from in-situ Raman spectroscopy

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Content

Experimental studies that aim to constrain formation conditions of hydrothermal tin deposits are in good agreement on solubility and fluid-melt partitioning [e.g. 1–4], but oxidation state and speciation of tin in hydrothermal fluids are not fully established yet. Here, an in situ technique, Raman spectroscopy and a Bassett-type hydrothermal diamond-anvil cell, was used to determine the speciation of Sn(II) and Sn(IV) and the solubility of cassiterite in H₂O+HCl at temperatures to 600 °C and to obtain information on the partitioning of tin between H₂O+HCl fluid and melt produced from Macusani glass.

The most abundant Sn(II) species was [SnCl₃][–]. The aqueous Sn(IV) species included mainly [SnCl₄(H₂O)₂]⁰, with additional [SnCl₃(H₂O)₃]⁺ and [SnCl₅(H₂O)][–]. Cassiterite solubility increased with HCl concentration and reached about 0.6 molal Sn at 500 °C and 3 molal HCl, with no strong dependencies on temperature, pressure, or redox conditions. The Sn(IV) concentrations at 500 and 600 °C determined from the integrated ν_1 [Sn(IV)–Cl] band intensity are in good agreement with literature data on the cassiterite solubility in H₂O+HCl at oxygen fugacities along the hematite-magnetite buffer [2] and are about two orders of magnitude higher than the solubility in equimolal NaCl solutions [1]. The integrated ν_1 [Sn(IV)–Cl] band intensities in fluid and coexisting melt observed at 700 °C suggest that tin partitions into the fluid at high HCl concentrations, but increasingly into the melt with decreasing HCl molality.

The solubility and speciation data point to removal of HCl as efficient mechanism for cassiterite precipitation, e.g. via dilution or reaction with the wallrock. The available fluid-melt partitioning data [3, 4, this study] indicate that magmatic fluid is not the primary source of tin in hydrothermal deposits. Instead, the HCl-bearing aqueous fluids exsolved from peraluminous granitic melt act as agent to mobilize tin from the exocontact of the intrusion. This implies that pre-enrichment of Sn in these wall rocks is a controlling parameter for the formation of a hydrothermal tin deposit, which is in full agreement with geological observations [5].

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Meeting future PGE demand: Optimization of a leaching technique for oxidized ores from the Bushveld Complex

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Content

The demand for platinum group elements (PGE) is constantly increasing due to their application in the high-tech sector and their unique properties as catalytic converters. The Bushveld Complex in South Africa hosts some of the largest PGE deposits in the world. It is a mafic-ultramafic layered intrusion and the PGE in the Bushveld are currently mined from the Merensky Reef, the Platreef and the UG-2 chromitite. While mining operations concentrate on the pristine (unweathered) sulphide ore, there are large surficial resources of oxidized Platreef ore with Pt concentrations of up to 4 g/t. The pristine, sulphide-bearing ores are mined and treated following conventional metallurgical practice. The oxidized PGE ores, however, are not mined with conventional processing techniques due to very low recoveries. The challenges during the processing of oxidized ores are related to the complex and polymodal mineralogy of the PGEs and the host minerals. In this study, a brine-based leaching protocol was developed and applied to oxidized Platreef PGE ores in order to enhance hydrometallurgical extraction of PGE from oxidized ores. This process was optimized in terms of mobilization efficiencies, as well as reagent consumption and time efficiency. Upscaling experiments were conducted at room temperature and at elevated temperatures in order to assess the large-scale applicability of the technology. The investigated ore samples mainly consisted of pyroxenes and clay minerals. No sulphides were detected. In oxidized ores, the PGE are mostly present within hydroxide minerals and as PGE oxides. The investigated samples yield average Pt+Pd+Au grades of 2.30 g/t. In our experiments, up to 78% Pt, 55% Pd and 92% Au were mobilized with the leach. Oxidized PGE ores have great, yet still unexploited potential to satisfy the increasing PGE demand. While exploitation has been uneconomic due to insufficient recoveries, chemical leaching technology may close this gap and provide a solution for meeting the future demand for PGE.

Mineralogical and geochemical characterization of the drill core SES1 of the “ultramafic carbonatite complex” (UCC) Delitzsch, central Germany

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Content

The UCC Delitzsch is a late Cretaceous ultramafic intrusive body, which is located 20 km north of Leipzig at the border between Saxony and Saxony-Anhalt. It contains areas of carbonatitic intrusive breccias, carbonatite pipes (beforsite, alvikite, ferrocarbonate) and lamprophyres (alnoeite, aillikite, monchiquite), which are enriched in rare earth elements [1]. The examined part of the drill core is located from 240 m to 270 m depth and begins approximately 120 m below the old pre Cenozoic land surface. This section includes the intrusive breccias, carbonatite sills and lamprophyric sills, as well as non-mineralized porphyritic wallrock. Macroscopically, especially the intrusive breccias are very heterogeneous and indicate different stages of alteration.

During the scope of this study, geochemical and mineralogical characterization of the core section was first examined by mobile XRF (Thermo Scientific Niton XI3t, resolution at least 20 cm) and secondly selected core section were analysed by certified geochemistry data (ALS Ireland). Within the mobile XRF analyses, small spot setting (detection field 3 mm diameter) allowed to distinguish small heterogeneous areas such as the matrix and the clasts of the intrusive breccia separately. A detailed log could be created for selected rare earth elements such as Lanthanum or Cerium, but also for pathfinder elements such as Strontium. Compared with reference samples, the XRF measurements for these elements are reliable by normalization with reference samples. Thus, it is possible to identify REE - enriched areas in the drill core and distinguish between enriched and non-enriched lithotypes as shown in figure 1.

Geochemical and mobile XRF data examination have shown that the REE-mineralization is predominantly associated with carbonatite veins, lamprophyres and the matrix of intrusive breccias, while clasts of the wall rock fragments within the breccia and the porphyry wall rocks contain no significant REE mineralization.

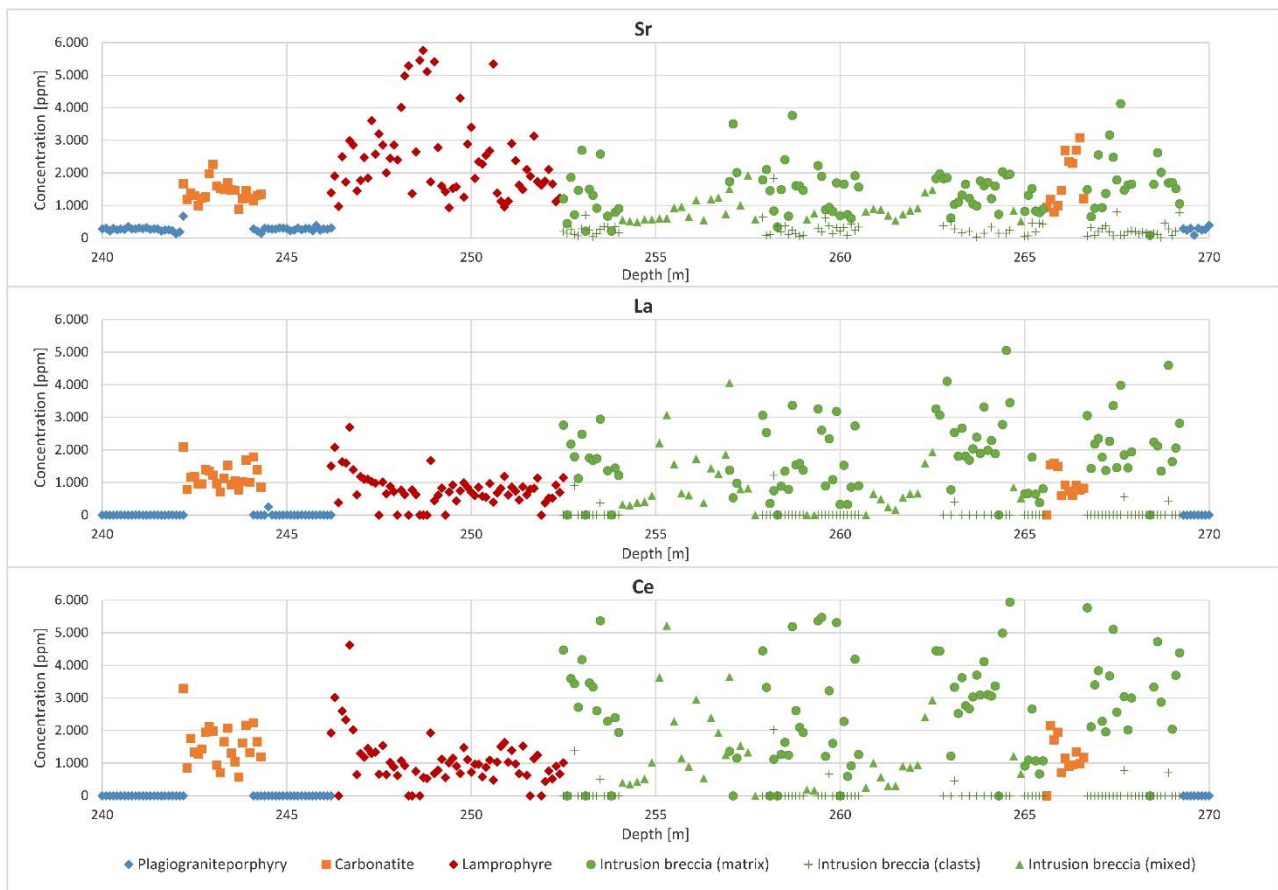


Figure 1: Concentration of Sr, La and Ce in the SES1 drill core measured with mobile XRF (concentrations lower than detection limit are indicated by 0)

References:

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Mineralogical and geochemical investigation of Fe-Ni-ores of Agios Athanasios area (Kastoria-Greece)

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Content

There are significant deposits of Fe-Ni-ores in Greece, which are exploited by LARCO GMMAE Company. The annual production of over 18,000 tons nickel ranks the company among the significant Fe-Ni alloy producers in Europe. The Agios Athanasios deposit located southwest of Kastoria is developed in form of layers over serpentinitised ultramafic rocks (ophiolites). There are successive layers of silicate ore, saprolithic ore, clay ore and iron ore zone (limonite iron ore and manganese oxides iron ore) above the underlying rock. The deposit is covered by molassic conglomerates. The Fe-Ni-ores of the wider Kastoria area are considered as litho-stratigraphic, equivalent to those of Mainland Greece, Euboea and Albania.

Hematite and goethite are the significant iron minerals and occur mainly in the form of veins and individual grains in the binder material of the ore. Garnierite, lizardite, saponite, willemseite, sepiolite and nepouite compose mainly the binder material and fill the gaps between the solid quartz masses. Additionally there were observed individual clastics chromite grains as well as calcite is encountered in form of veins within the binder material and is considered of secondary origin. Micro-analyses in the binder material confirmed the presence of lizardite and garnierite, submitted partially to be replaced by ferrous solutions. It is often observed that grains of goethite alter progressively into hematite due to dehydration.

The geochemical examination of the ore showed the presence of two groups of elements corresponding to the distribution along the section. 1. Fe₂O₃, Cr₂O₃, Al₂O₃, MnO, CoO and 2. SiO₂, NiO, CaO, MgO. The data from the 1st group show a positive correlation with each other, as well as those of the 2nd group. On the other hand, the elements of the 1st group are negatively correlated with those of the second group. The distribution of iron is exactly opposite to that of silicon, which is generally recorded in Fe-Ni-ores. Nickel is found mainly in mineral garnierite, willemseite and nepouite and is mainly recorded in the layers of clay, saprolithic and silicate ore with up to 4.1% w.t. NiO in the silicate ore.

According to the chemical analysis of the Fe-Ni-ore of Agios Athanasios (Kastoria), the concentrations of SiO₂, Al₂O₃, Fe₂O₃ and MgO correspond to those encountered in ultrabasic rocks, taking into account the enrichment rates of the elements, due to the lateritization of these elements.

Minor and trace element distribution in sphalerite/wurtzite from the district of Aachen/La Calamine (Germany/Belgium)

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Content

The mining district of Aachen and La Calamine is located in the westernmost part of the Rheinisches Schiefergebirge. Here, the dominating ore type of epigenetic lead-zinc mineralization in Paleozoic rocks is represented by post-Variscan carbonate-sulfide mineralized veins that are hosted by Upper Devonian to Upper Carboniferous shales and carbonates. Ore samples are composed of sphalerite/wurtzite ("Schalenblende"), galena, and pyrite associated with quartz and siderite. The recent study focuses on the major and trace element distribution in sphalerite/wurtzite from seven locations of historic deposits including two of the largest ore mines Diepenlinchen and Albertsgrube.

Sphalerite is the most common zinc-bearing mineral and therefore plays an important role as a possible source for critical electronical metals for high-tech applications, such as germanium, indium, and gallium. The abundance of these trace elements in the crystal structure is controlled by coupled substitution mechanisms. Especially the incorporation of germanium is correlating with the iron content in the ZnS lattice [1]. In total, 19 samples of zinc-rich ores were analyzed to determine the zonal distribution of iron using the μ -EDXRF method (M4 Tornado, Bruker). Schalenblende is mainly characterized by collomorphous textures with alternating bands of varying color from light brown/beige to dark brown. Iron content in the ZnS is generally low; however, almost all samples show areas hosting increased iron contents (> 2 wt.%) represented by dark brown bands. It is suggested that germanium concentration in sphalerite/wurtzite from the district of Aachen/La Calamine is correlated with incorporation of iron and reaches values up to 0.1 wt.% [2]. Further measurements of the trace element contents in the ZnS applying a quadrupole laser ablation-ICP-MS and using a matrix-matched sphalerite reference material (MUL-ZnS-1) will be used to extend and verify the existing data base [3]. This study contributes to the projects RoStraMet (BGR) and HTMET (FKZ033R131) funded by the German government (BMBF).

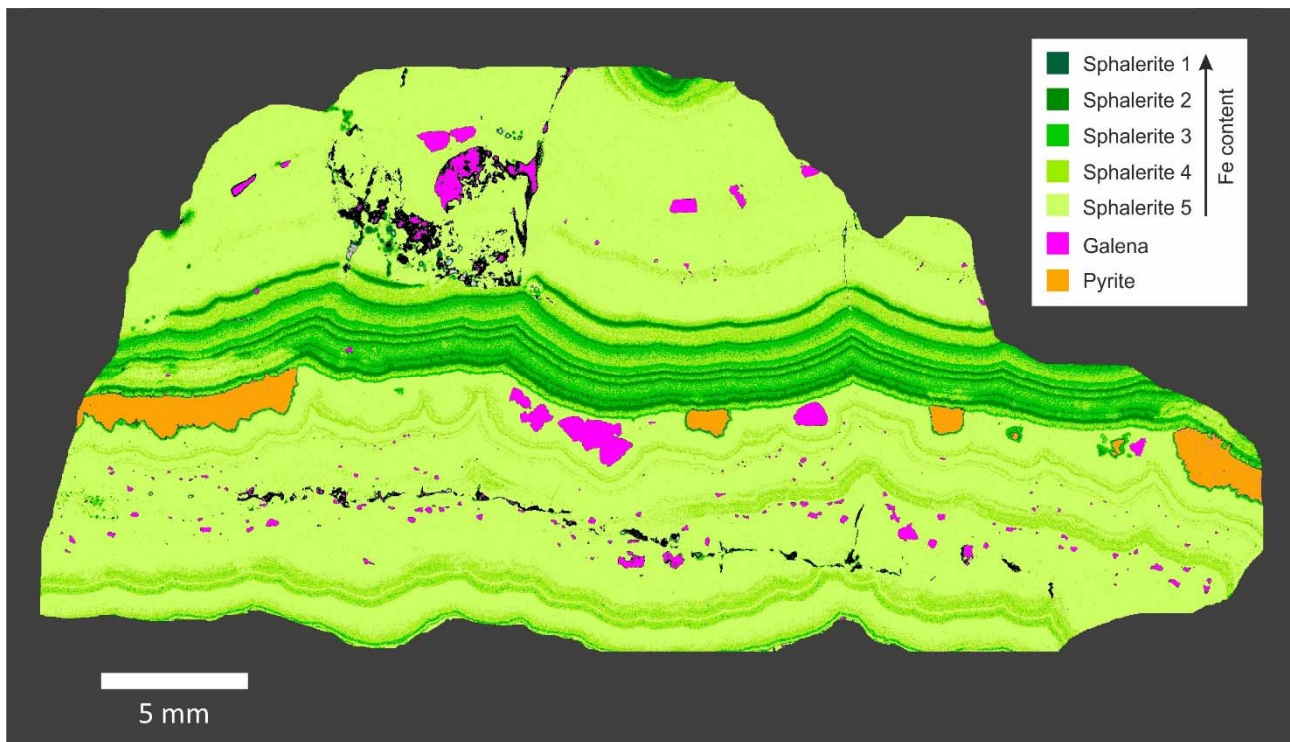


Fig.1: μ -EDXRF-mapping of ZnS-rich ore from the mine Albertsgrube showing a collomorphic texture correlated to the iron distribution in the mineral; granular galena and pyrite are associated.

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R&D projects focusing on innovative technologies for exploration, mining, and ore processing – Increasing the security of supply with metals of strategic economic importance

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Content

A sustainable supply of raw materials is an essential requirement for the high-tech industry in Germany. By giving up mining of metallic ores in the early 1990s, Germany became entirely dependent on imports of economically strategic metals associated with a high uncertainty of supply. The development of new methods and concepts for exploration, mining, and processing of polymetallic ores is bringing traditional German mining regions, such as the Erzgebirge, the Harz Mountains, the Schwarzwald and the Siegerland back into focus of scientific and, possibly, economic interest. A domestic supply of raw materials of strategic economic importance would reduce the German import dependency on metals that is associated with concerns on a reliable and undistorted access to raw materials.

Main purpose of the funding measure “r⁴ – Innovative Technologies for Resource Efficiency – Research for the Provision of Raw Materials of Strategic Importance”, which was initiated in 2015 by the German Federal Ministry of Education and Research, is to decrease the supply risk of these strategic metals. Nine projects are focusing on (a) the assessment of raw materials potentials in Germany, on (b) deciphering formation conditions of Sn/W deposits, and on (c) enhancing geophysical methods for the prospection. Furthermore, seven projects are developing sustainable technologies for the highly selective, economic, and eco-friendly mining of polymetallic ores from known mineral deposits or enhancing existing ore treatment processes.

Within the scope of the research-supporting integration and transfer project r⁴-INTRA, we aim to evaluate the contribution of the r⁴ research projects on the security of raw materials supply. Moreover, we evaluate the economic potential of the research results by applying newly developed assessment criteria for mining projects. For projects developing innovative exploration concepts, cost savings due to a then reduced number of failed prospections can be quantified. Moreover, exploration expenditures can be reduced by enhancing existing methods in terms of a faster exploration or a higher accuracy in locating ore deposits. For the evaluation of projects dealing with new mining and processing methods, we are determining the mass flows of the actual and the target state. All results will be summarized for a general view on the potential of primary metallic raw materials in Germany and the contribution to the security of supply.

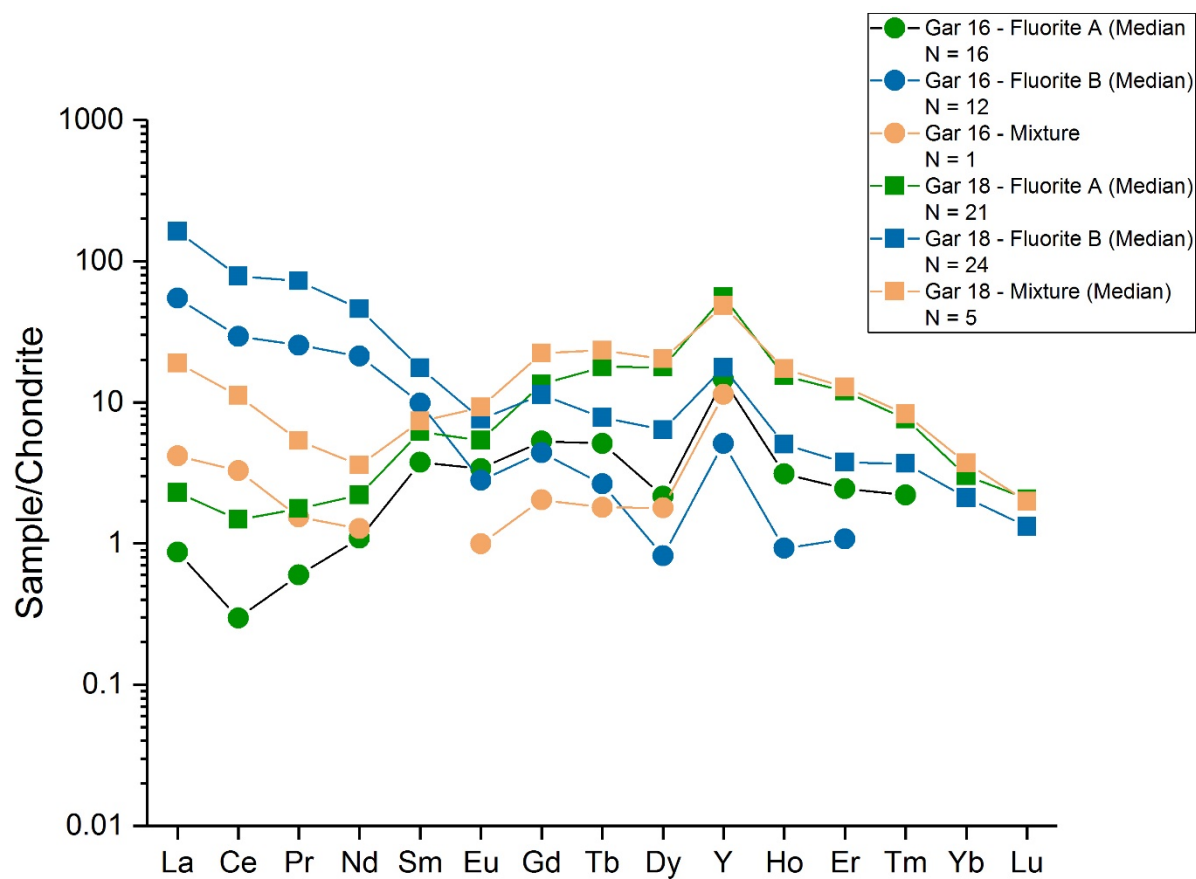
Trace element analyses of fluorite and barite combined with stable isotope analyses ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) of carbonates—toward a genetic model for hydrothermal mineralization in the North German Basin (NGB)

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Content

Fluorite and barite were discovered in E&P wells in Permian sediments in the NGB. The BMBF-funded project “MinNoBeck” is undertaking geochemical investigations of mineralized zones with special attention to strategic elements such as REE. The aim is to develop new concepts for the exploration of deeply covered deposits and to gain a better understanding of the formation of the hydrothermal mineralization. This study focusses on petrographic and geochemical analyses of fluorite and barite from the Altmark sub-basin compared with hydrothermal veins in the Harz mountains. Additionally, stable isotope ratios ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) of carbonate host rocks and veins were measured. Samples were studied with transmitted- and reflected-light microscopy, supported by scanning electron microscopy (SEM). Major- and trace element compositions were measured with EPMA and LA-ICP-MS. Carbonates or sandstones, interrupted by cm-wide veins of fluorite occur in the Altmark. Samples in other parts of the NGB show less fluorite in form of small isolated disseminated grains surrounded by fine grained wall rocks. Fluorite shows sharp boundaries to wall rock minerals. Boundaries to neighboring carbonates are curved or display bays, indicating disequilibrium. Barite occurs in thin veins or as massive pore fillings with sharp boundaries to neighboring minerals. Apart from Ca and F, EPMA measurements of fluorite do not show element contents above the detection limit (ca. 500 ppm). Barite shows detectable levels of substituting Sr (up to 5.8 wt%). LA-ICP-MS analyses discovered two generations of fluorite, distinguishable by divergent behavior of light REE. This was confirmed by different grey scales in SEM-BSE imagery and variant CL signals. Europium anomalies are negative or absent in both fluorite generations. Yttrium shows a positive anomaly in the samples without a clear trend for different generations of fluorite. Isotope analyses of carbonate (re-)crystallizations show that there were either two fluids with different sources or two generations of fluids from the same source circulating. SEM-BSE imagery shows euhedral, recrystallized dolomite crystals, an outcome of a fluid with high Mg content.



REY plot based on LA-ICP-MS data for fluorite from the Altmarm Basin. All samples are normalized on chondrite after McDonough and Sun (1995). A and B stands for two generations of fluorite. Mixtures are outcomes of resolution limitations

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Session 8.3: Economic Geology of Critical Raw Materials.: Talk

Session 8.3: Economic Geology of Critical Raw Materials.: Talk
A-571

High tech trace element distribution in sulfides from the Ruhr district and comparison with data from the Bergisches Land district

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Content

The Ruhr district is rated as the center of German coal mining, whereas numerous hydrothermal base metal ore deposits cutting the Carboniferous mud- and sandstones are less well-known. Ore prospection work initiated in the 1930s was discontinued in the late 1950s due to low commodity prices. Several million tonnes of known Pb-Zn ore resources are still present in the deposits. The recent study focused on the most important metal ore deposits of the Ruhr district. Samples from eleven Pb-Zn deposits were analysed with special focus on mineralogy, concentration and distribution characteristics of the high tech (HT) trace elements Ge, Ga and In in sphalerite and chalcopyrite. The proportions between sulfide and gangue minerals were determined by μ -EDXRF and the sulfides were further studied by optical and scanning electron microscopy. The quantitative analysis of trace elements was conducted *in-situ* by a quadrupole laser ablation-ICP-MS using an in-house sulfide reference material [1]. First results for the sphalerite indicate low Fe contents (< 2.5 wt.-%) and a rather large variability for the minor and trace elements (e.g. Cu 200 – 3100 ppm (sample median values), max. 0.9 wt.-%). The HT elements Ge and Ga generally occur in significant amounts (24 – 185 ppm (deposit median values; Fig. 1), whereas In (max. 0.2 wt.-%) is restricted to small domains in a few samples (confirmed by high resolution EMPA mappings). Correlation trends between Ge and Cu suggest a coupled substitution mechanism for Ge incorporation in sphalerite. Scarce chalcopyrite contains up to 210 ppm Ge.

A comparison of the geochemical data with 27 samples from the “Bergisches Land” district (eleven deposits) was carried out. Here, the concentrations of HT elements are generally much lower than in the Ruhr district in spite of similar host rocks and Fe content in sphalerite. We suppose an influence of the high enrichment of organic material in the host rocks of the Ruhr district on the elevated trace metal content of the mineralised systems.

This study contributes to the project RoStraMet of the BGR and the project HTMET (FKZ 033R131) funded by the German government (BMBF).

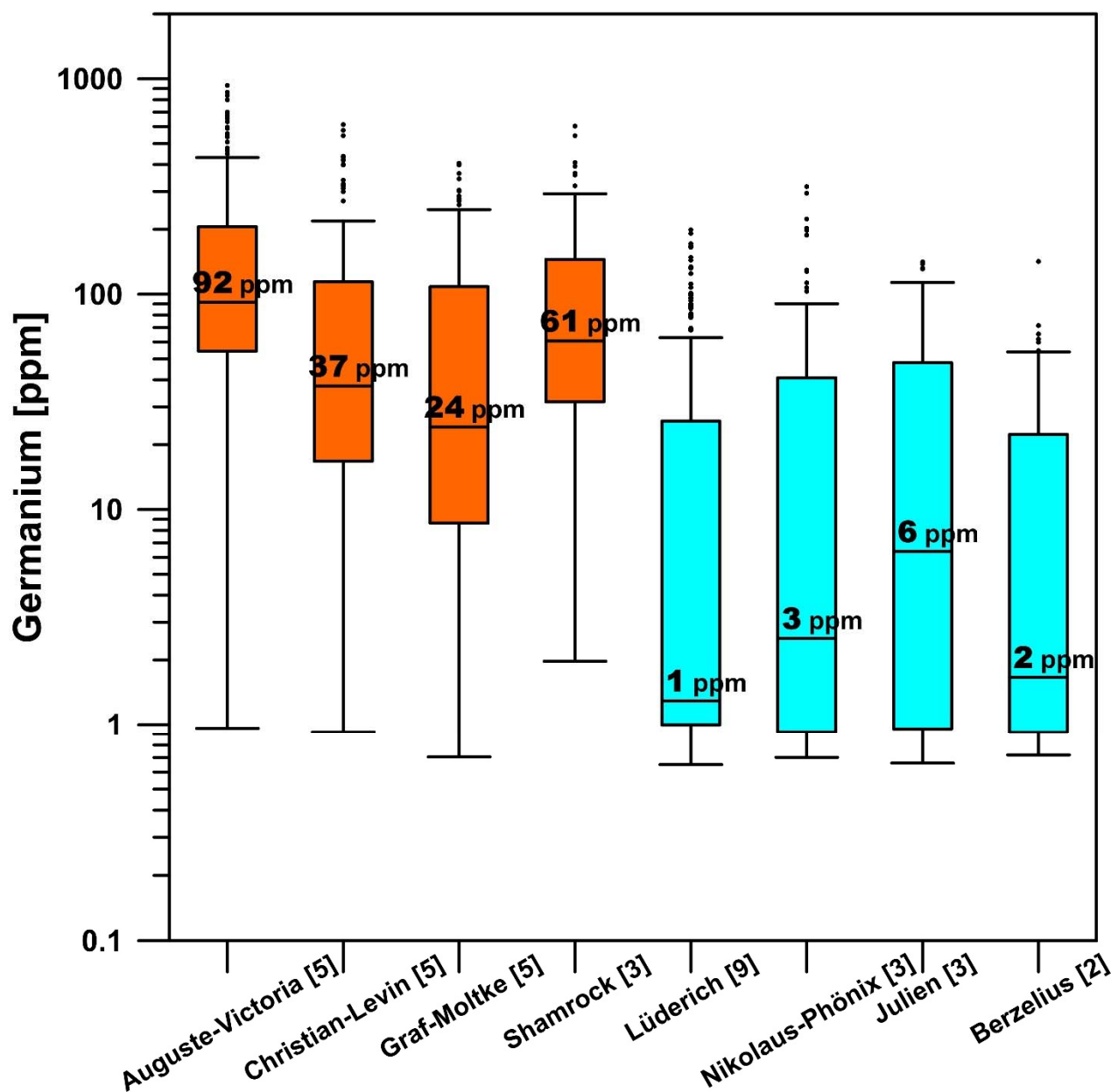


Figure 1: Boxplot diagram showing LA-ICP-MS data for Ge in sphalerite of selected deposits in the Ruhr district (orange) and the "Bergisches Land" district (blue). The median values are added and the number of samples is shown in brackets.

References:

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Chemical and $\delta^{11}\text{B}$ compositions of tourmaline from the Panasqueira W-Sn-Cu deposit, Portugal: considerations on fluid source and evolution

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Content

The chemical and stable isotopic compositions of tourmaline can be used to constrain fluid sources and fluid-rock interactions in granite-related W-Sn deposits. In this study, we analysed hydrothermal tourmaline from the Panasqueira W-Sn-Cu deposit in Portugal [1], which consists of a swarm of sub-horizontal, hydrothermal quartz, wolframite, sulphide veins hosted by a metasedimentary unit and spatially associated with a greisen cupola of a peraluminous, S-type, two-mica Variscan granite (Fig.1, [2]).

Tourmaline occurs as a ubiquitous mineral in wallrock alteration that predates the main ore stage [3] and in late-stage vugs within the ore veins, thus bracketing the time of Sn-W mineralisation.

We present results of an extensive set of in-situ electron microprobe and SIMS measurements showing the variations in chemical and boron isotopic compositions of tourmalines from three different settings within the Panasqueira deposit: (1) wall rock alteration zones, (2) mineralized veins (early and late stage tourmaline) and (3) post-ore fault zones. The tourmaline from Panasqueira is Li-poor and Fe-Mg-Na-Al-rich and belongs to the schorl-dravite series. It typically displays optical and chemical zoning with a Fe-F-Na-increase and Mg-Al-Ca-decrease from core to rim. The $\delta^{11}\text{B}$ values are remarkably homogeneous at -9 ± 2 ‰, in 90% of the samples. Although these values are permissive of a metamorphic or magmatic source, mass balance and geological constraints favour a fluid source from the S-type granite. The variations in tourmaline compositions from core to rim coupled with the B-isotope compositions can be explained by a combination of cooling and a transition from wallrock- to fluid-dominated conditions, which is also supported by variations in white mica geochemistry.

This work highlights the variable roles of wallrock, hydrothermal fluid compositions and co-precipitating mineral phases in tourmaline chemistry. Additionally, the similarity of chemical and $\delta^{11}\text{B}$ compositions of late-stage and early-stage tourmaline suggest a dynamic hydrothermal system with multiple injections of magmatic-dominated fluids.

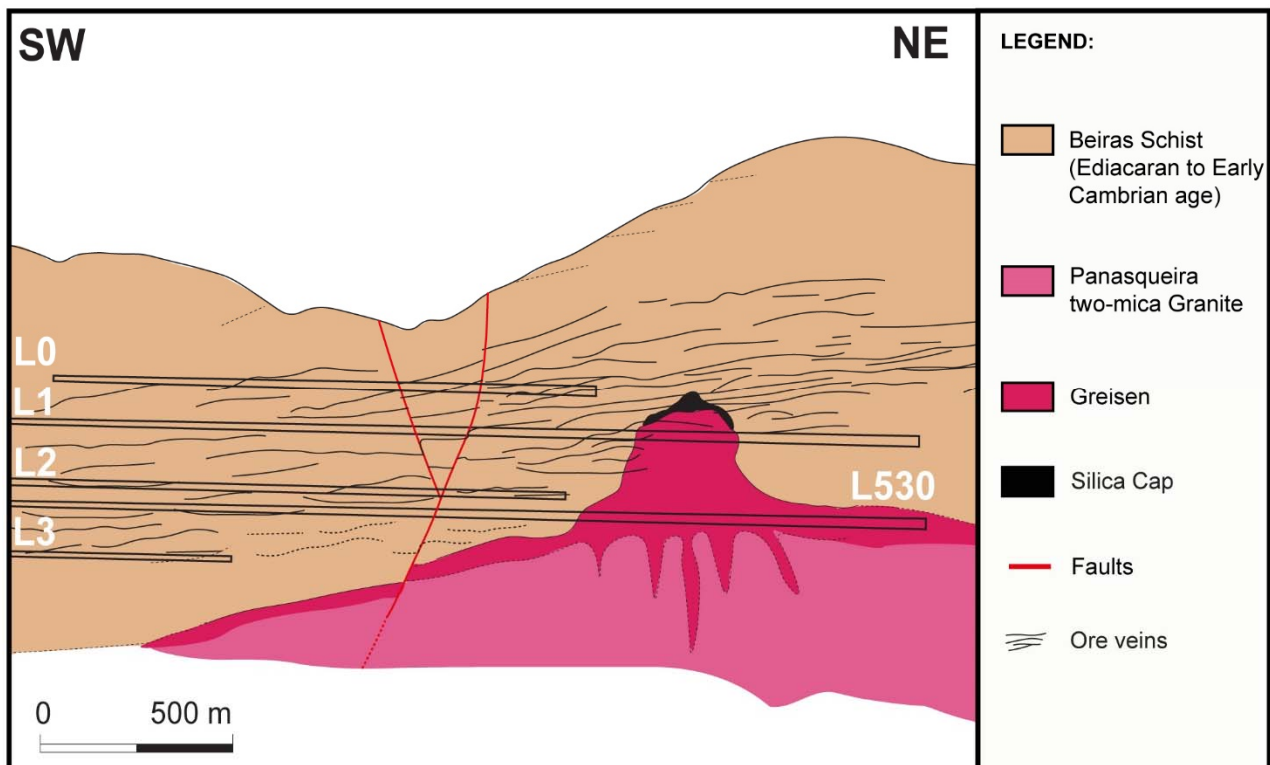


Fig. 1: Schematic cross section of the Panasqueira vein system, greisen and Panasqueira Granite (modified after [2]). L – Level.

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Evaluation of boosting algorithms for prospectivity mapping

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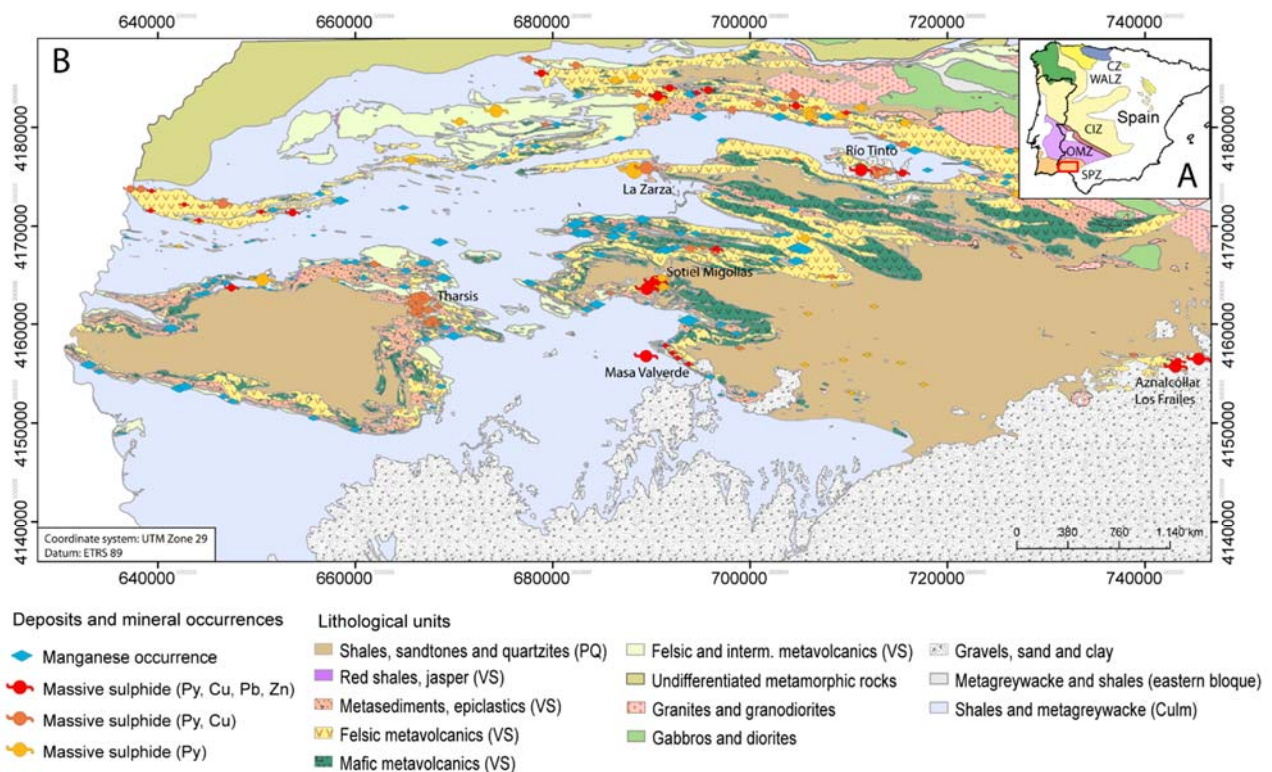
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Content

In the context of an increased need of critical materials, good predictive models that allow minimal invasive exploration are of uttermost importance. This research is part of the project “Mineral Prospectivity Modeler” of the Geological Survey of Finland in cooperation with Esri Germany. Its aim is to study different machine learning techniques such as boosting algorithms and to test them on real exploration datasets in terms of accuracy, performance, and robustness.

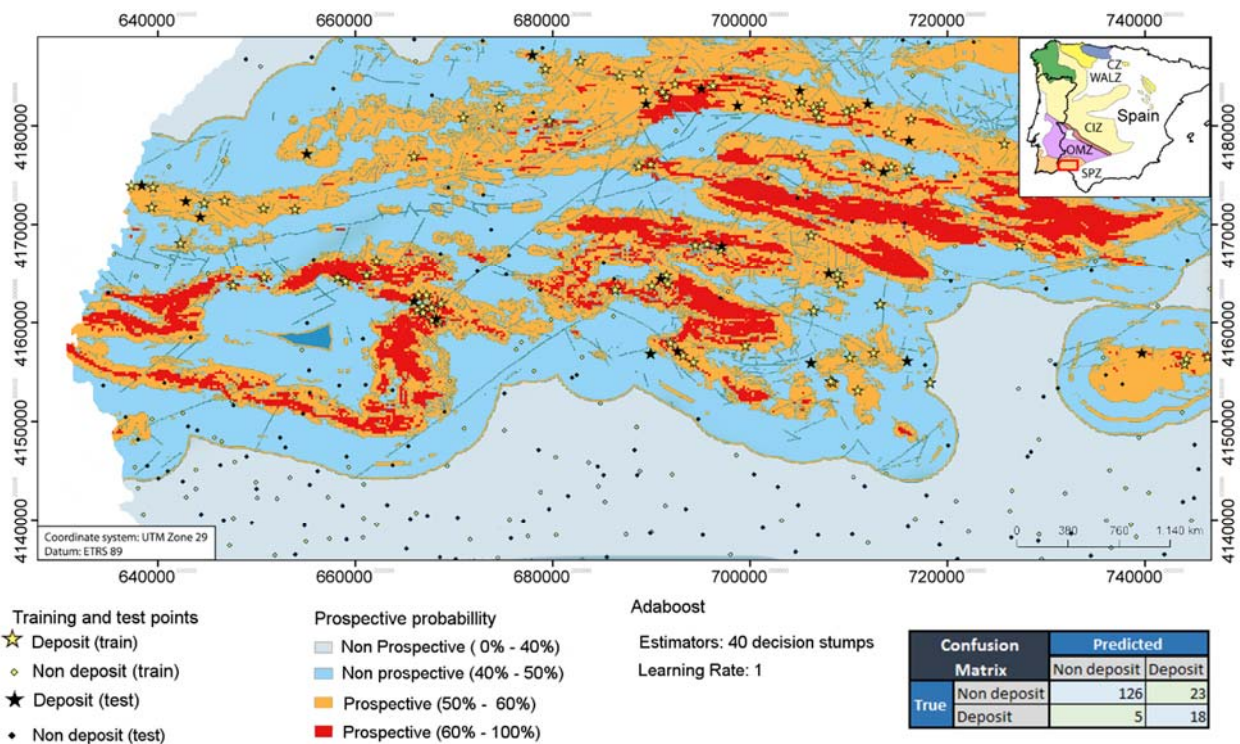
Boosting algorithms are ensemble methods used in supervised learning for regression and classification. They combine weak classifiers (classifiers that perform slightly better than random) to obtain robust classifiers [1].

Our test area is the Iberian Pyrite Belt (IPB), one of the oldest mining districts in the world that hosts giant and supergiant massive sulphide deposits. The spatial density of ore deposits, the size and tonnage make the area quite unique [2]. The IPB occupies the south-western part of the Iberian Peninsula from Portugal to Spain with a length of about 230 km and a width of 40 km.



A) Overview with the IPB (red box) B) Lithological map of the area with deposits and mineral occurrences of manganese and pyrite.

As predictors, we use total intensity of magnetic field, proximity to volcanic rocks, proximity to faults, total gamma radiation as well as lithology, projected in 232 training and 172 test points. Adaboost [3], the first and most popular algorithm of Boosting family, trained with 40 estimators and learning rate of 1 was used to create a prospectivity map, having an accuracy of 83.7% and an area under the curve of 0.889.



Train and test points with deposit occurrence probability using Adaboost with 40 Estimators and learning Rate of 1 and confusion matrix

In comparison to other machine learning methods, Adaboost shows ease of use, relatively short training time and higher resistance to overfitting. Furthermore, it allows working with continuous datasets unlike widely used methods in prospectivity mapping such Weights of Evidence. In preliminary results the Adaboost algorithm shows high accuracy in real datasets, making it an excellent data-driven alternative to model prospectivity maps.

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Exploring for Ni-Cu-PGE veins in the Sudbury Basin, Canada. Recognizing sulphide migration pathways by metamorphism and partial melting in container rocks.

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Content

The Sudbury Basin, located in the southern Canadian Shield, is the deformed remnant of a major meteorite impact structure that formed at 1.85 Ga. The Basin is a world class mining camp hosting massive deposits of Ni-Cu-PGE sulphides that accumulated along the contact of the deformed impact melt sheet, the Sudbury Igneous Complex (SIC), and the underlying country rocks. Sulphide mineralization within the country rocks occurs in ore zones made up of veins and disseminations. Drilling for this type of deposit is difficult due to the distributed nature of veins within these ore systems. Successful exploration, therefore, requires an understanding of the various host rocks and the petrological changes they undergo during emplacement of sulphide veins in order to recognize ore-bearing rock volumes.

The Capre 3000 ore zone in the East Range of the SIC was investigated. Representative drill core intervals were analyzed for mineralogical composition, structure, metamorphism and evidence for melting. Samples were collected outside the ore zone and at sulphide mineralizations. Petrographic analysis was conducted to investigate changes in crystallization patterns with regard to distance to mineralizations.

Emplacement of ore veins occurred mainly in mafic host rock. Brittle structures, impact breccias and lithological contacts were identified as important pathways for sulphide migration. Mafic rocks show little thermal reaction to the migration of hot sulphide fluids, whereas there is abundant evidence for melting of felsic host material in the vicinity of ore veins. Moreover, felsic country rocks exhibit pervasive static recrystallization. However, textures indicating rapid crystallization of felsic material and large (>100µm) intergrowths of quartz and feldspar can only be observed at sulphide mineralizations.

Distribution of thermal characteristics in host rocks of massive sulphide veins seems to show a distinct spatial pattern. Massive ore veins are found essentially at the bottom of their migration pathway, with the strongest partial melting of felsic rock occurring at the depth of mineralization and directly above it. Mobilization of felsic host rock may have provided space for the emplacement of sulphides. Recognizing these host rock characteristics during exploration drilling may help to identify migration pathways of sulphides and, thus, to target drilling campaigns more accurately.

Fluid evolution and ore formation in the Zinnwald Sn-W-Li deposit, Erzgebirge (Germany): insights from microthermometry and LA-ICP-MS of fluid inclusions

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Content

The Sn-W-Li deposit in the roof zone of the highly evolved Li-F Zinnwald granite in the Erzgebirge (Germany/Czech Republic) is associated with large Sn-bearing greisen bodies and sub-horizontal veins containing economical contents of cassiterite, wolframite and zinnwaldite [1]. The temporal and spatial evolution of the ore-forming hydrothermal system is still debated. In particular, the relation between the contrasting mineralizations in the greisen and veins remains elusive. We analysed fluid inclusions in gangue and ore minerals from samples of the German part of the deposit using conventional-, infrared-microthermometry and LA-ICP-MS. The analysed fluid inclusion assemblages (FIAs) were associated with the precipitation of the tin and tungsten ore and give insights into the hydrological and chemical evolution of the fluid.

The most common primary FI in the quartz veins show homogenization temperatures (Th) between 360°C and 380°C and high variability in salinity (1–8 eq. w(NaCl)). This FI type can be found throughout the entire veins in the deposit and can in places be petrographically related to ore deposition. Microthermometric measurements using IR microscopy of FIAs hosted in cassiterite and wolframite from the vein reveal slightly lower Th but higher salinities of about 12 eq. w(NaCl). In contrast FIA in quartz and cassiterite from greisen have similar Th (360–380°C) to the vein quartz and salinities between 5 and 8 eq. w(NaCl). Furthermore, a few quartz vein samples contain boiling assemblages of brine (up to 35 eq. w(NaCl)) and vapor-rich inclusions. Brine-bearing aqueous FI homogenize at temperatures between 300°C and 340°C. In contrast, some euhedral quartz crystals contain boiling assemblages showing higher temperatures of about 470°C and higher salinities of ca. 40–45 eq. w(NaCl), similar to those described by [2].

LA-ICP-MS data show that all elements required for forming a Sn-W deposit are included in the hydrothermal fluid (e.g. W, Sn, Fe, Mn). The results suggest that ore formation is controlled by two main processes: 1) invasive fluid rock interaction with the granite during greisen formation and 2) boiling and the resulting loss of HCl leading to ore precipitation in the veins, which are interpreted as former fluid pathways in the peripheral parts of the granite such as the German part of the deposit.

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Formation of TRS controlled MVT type Zn-Pb mineralization in Zechstein carbonate (Ca₂) in the Lower Saxony Basin, Germany

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Content

The Lower Saxony Basin (LSB) is a W-E-trending trough situated in the western part of the Southern Permian Basin (Central Europe). The Zechstein carbonate (Ca₂) unit, which is an important gas reservoir rock in the LSB, is locally a host for hydrothermal Zn-Pb mineralization. The Zn-Pb ores were accidentally drilled at great depths in the centre and at the western margin of the LSB during the gas and oil exploration campaigns in the second half of the 20th century. Similar mineralization was historically mined north of the Osning thrust zone, where the orebodies were exposed to the surface in the surroundings of uplifted Upper Carboniferous blocks.

This study aims to unravel the origin of the deeply buried Zn-Pb mineralization in the central and western LSB. Petrographic, fluid inclusion and stable isotopic studies of ore and gangue minerals from the focus areas were performed to constrain geochemical controls on the ore formation, in the frame of an integrated project founded by the Federal Ministry of Education and Research (BMBF).

Stratiform and vein-type Zn-Pb mineralization is dominated by bright yellow to dark brown, frequently zoned sphalerite, which is intergrown with gangue minerals, namely anhydrite, calcite and/or fluorite. Other sulphides such as chalcopyrite and pyrite occur subordinate. Homogenization temperatures of primary, two-phase (L+V) and three-phase (L+V+H) aqueous fluid inclusions hosted in sphalerites from the central LSB vary between 158 and 214°C and are slightly elevated compared to the temperature range of 151-171°C of sphalerite-hosted inclusions from the W-margin of the LSB. These inclusions show high salinities in both study areas.

Minimum temperatures of sphalerites precipitation (151-214°C) inferred from fluid inclusions and highly variable δ³⁴S values (-11.8 to +8.5‰) measured in various sulphides suggest TSR-derived origin of H₂S in the Zechstein carbonate reservoir. Therefore, mixing of reservoir H₂S with ascending metalliferous brines is proposed to explain the ore-forming processes in the Zechstein carbonate unit.

Geometallurgy: a key for evaluation and efficient use of polymetallic rare metal and REE deposits, the example of Khalzan Buregtei (Mongolia)

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Content

The polystage plutonic intrusion of Khalzan Buregtei (Mongolia) is a typical representative of a group of alkaline silicate magmatic complexes occurring in cratonic settings, which host significant rare metal and REE mineralizations. At Khalzan Buregtei enhanced concentrations of REE, bound to carbonates, and of Zr and Nb, bound to silicates and pyrochlore, respectively, can be observed. Mineralogical examination of surface samples and a set of 1884 whole rock compositions from surface and drill core samples shows the lithological diversity comprising nepheline- to quartz-syenitic as well as alkali-granitic to monzonitic compositions. Inspection of detailed surface profiles indicates small scale mineralogical diversity and textural heterogeneity confirming the importance of post-magmatic hydrothermal overprint for rare metal and REE enrichment also stated by previous investigators. Mineralogical and textural features represent an obstacle to economic mining operations. To become technically and economically viable, beneficiation strategies have to be developed and evaluated, which are optimized for different domains of the heterogeneous polymetallic deposit. The cross-discipline geometallurgical approach is an important step to successful beneficiation of such granitoid hosted deposits because it integrates mineralogical, mining engineering and processing knowledge as well as environmental and economic information (Fig. 1). Definition and generation of quantitative mineralogical parameters, which serve as key values for a geometallurgical concept, represent a field of mineralogical research with growing importance.

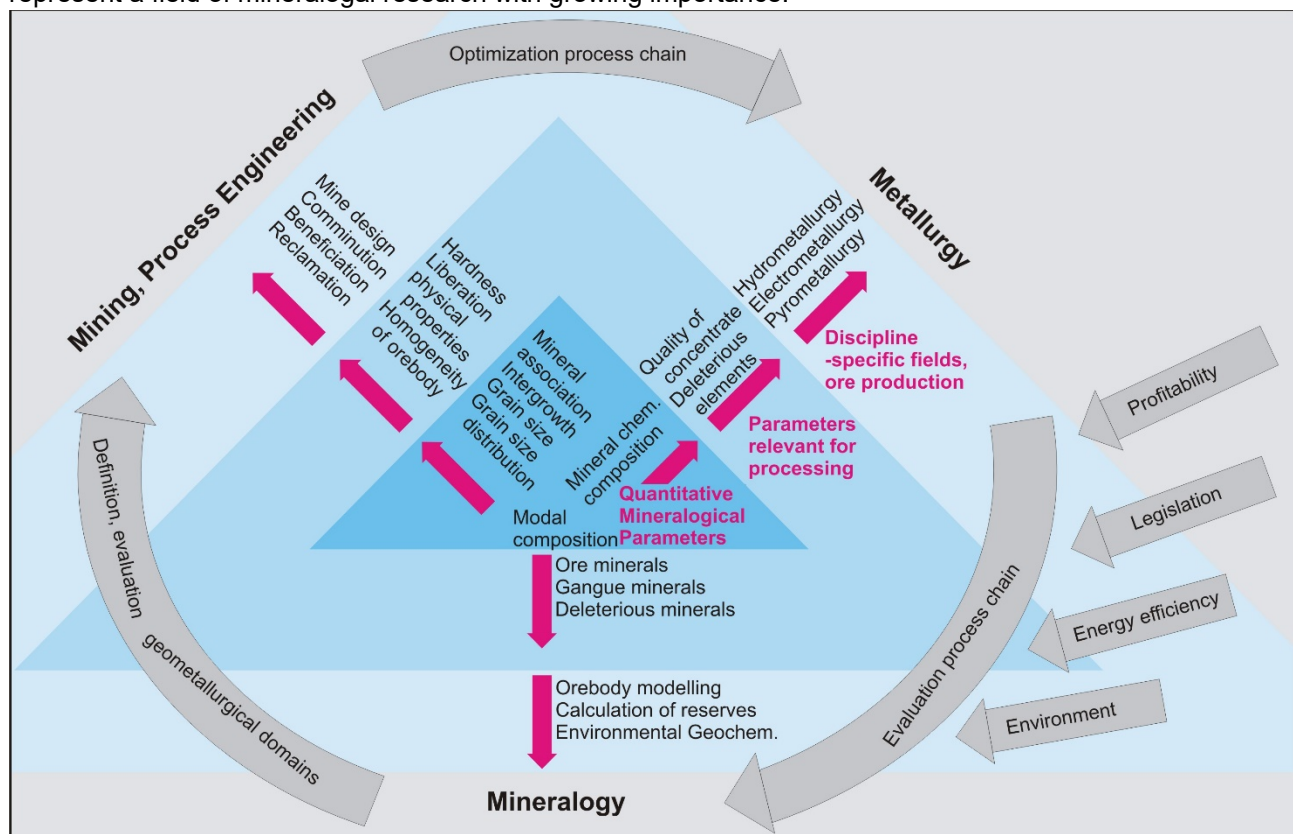


Fig. 1: Geometallurgy integrates mineralogical, mining engineering and processing knowledge to optimize a process chain. Quantitative mineralogy provides key parameters to this cross-discipline approach.

Hydrothermal base metal sulfide and fluorite-barite mineralization in the North German Basin

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Content

Minerals that host strategic elements such as Ge, Ga, In and REE have become a sought-after commodity due to limited developed resources and an increased demand. Evidence of hydrothermal base metal sulfide and fluorite-barite mineralization in Paleozoic sediments of the North German Basin (NGB) has emerged as early as the 1960s. E&P drill cores yield an extensive record of mineralized zones within the Paleozoic host rocks across the NGB. However, little is known about the fluid sources and the processes that led to the formation of these deposits and about their extent, distribution and economic potential regarding strategic mineral resources.

Here, we present first findings from detailed petrographic and geochemical investigations of indicator ore minerals such as sphalerite and fluorite and their host rocks. Electron microprobe, laser ablation ICP-MS, XRF and isotopic analyses have been employed to record and decipher compositional trends and patterns to obtain an inventory of the mineral chemistry of ore minerals and to gain insights into the formation history of the hydrothermal mineralization. Samples from mineralized veins from the Harz Mountains of similar age and mineralogy are also being investigated and compared to the NGB style mineralization to trace a possible genetic link.

First results indicate that the occurring mineralized zones are the expression of complex low temperature (< 250 °C) basinal brines that precipitated ore minerals in multiple stages. Several generations of pyrites, sphalerites and fluorites can be distinguished petrographically and by their unique chemistry. However, the overall trace element contents, especially of strategic elements, are low (Figure 1). Sphalerites yield only low concentrations of Ga, Ge or In (<10 ppm) and fluorite has conspicuously low concentrations of REE such as La or Ce. Our findings provide evidence that these mineralized zones could be the expression of a large MVT-type deposit at depths of around 3000 m in the NGB.

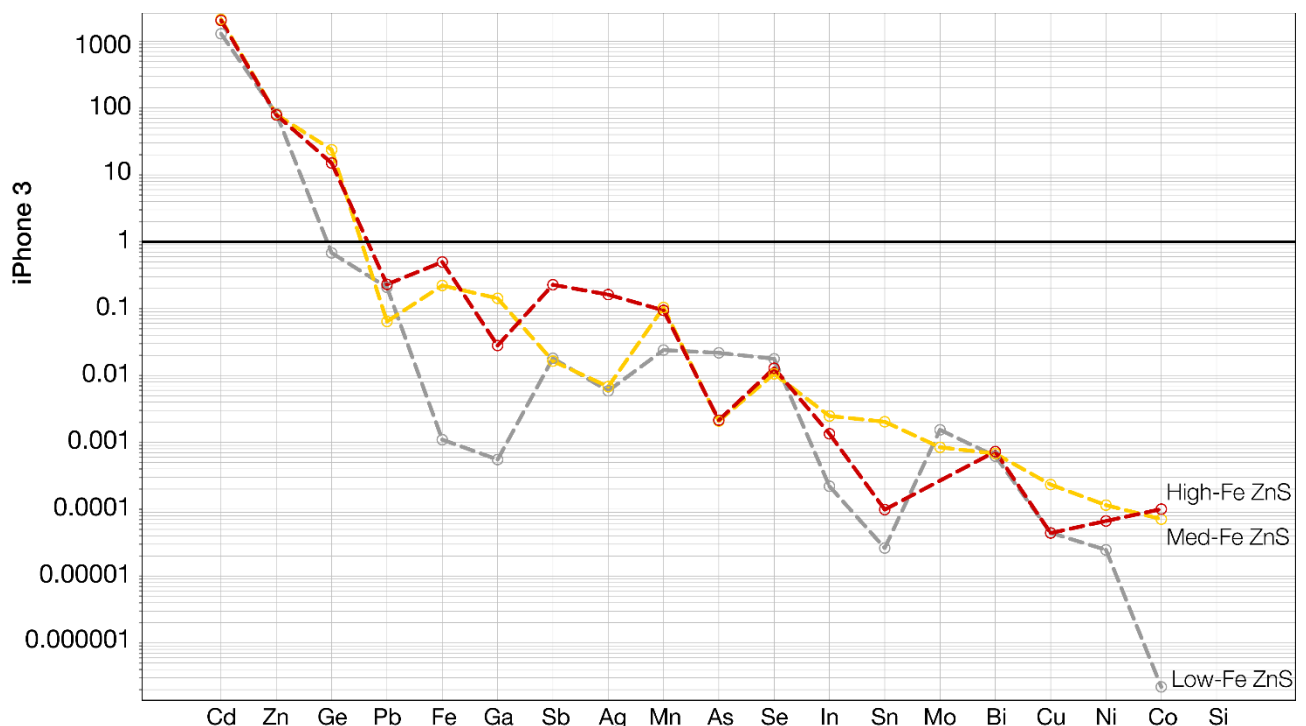


Figure 1 Median minor and trace element concentrations in three types (generations) of sphalerite (ZnS) normalized to an iPhone3.

Natural variability of geochemical conditions, biogeochemical processes and element fluxes in sediments of the eastern CCZ, Pacific Ocean

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Content

The abyssal seafloor in the equatorial Pacific Ocean bounded by the Clarion and Clipperton Fracture Zones (CCZ) is covered by polymetallic nodules. The International Seabed Authority (ISA) has granted exploration license areas in the CCZ and declared nine Areas of Particular Environmental Interest (APEIs). The APEIs are excluded from any mining activities and are designated for the protection of biodiversity and ecosystem functioning. However, little is known about the spatial variation in sediment geochemistry across the license areas and the APEIs. We present a comparative study on six sites on (1) the redox zonation in the sediments and (2) the dominating biogeochemical processes.

As part of the EU-BMBF funded JPI Oceans Pilot Action „Ecological aspects of deep-sea mining“, we visited five European license areas and the APEI3 located north of the CCZ during RV SONNE cruise SO239 in 2015. The recovered multiple and gravity cores were sampled for comprehensive pore-water and solid-phase analyses.

Due to low POC fluxes of $< 2 \text{ mg m}^{-2} \text{ d}^{-1}$ and low sedimentation rates of $0.18\text{-}1.15 \text{ cm kyr}^{-1}$ the upper oxic zone extends from 1 to $> 6 \text{ m}$ sediment depth. Aerobic respiration is the dominant process and accounts for 90% of the organic carbon degradation whereas denitrification is negligible. Below the oxygen penetration depth (OPD), Mn^{2+} is released into the suboxic zone and coexists with NO_3^- . At several sites the Mn^{2+} pore-water profiles indicate an upward diffusion of O_2 from the underlying basaltic basement.

The distinctly different geochemical conditions found in the six areas result from differences in (1) surface water productivity and POC flux, (2) sedimentation rates, (3) deep Mn reduction and (4) diffusive upward flux of O_2 from the basaltic basement. The conditions at the APEI3 site differ significantly from the geochemical settings in the investigated European license areas.

Paleo-stress field reconstruction and age determination of mineralized fractures within sedimentary rocks from the North German Basin using drill-core reorientation, hot-cathodoluminescence microscopy and radiometric geochronology

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Content

Mineralized fractures in sedimentary rocks not only preserve valuable information on paleo-fluid composition, formation pressures, or temperatures and thus give insight into ore forming processes. They also provide information on paleo-stress fields that were responsible for fracture formation during basin evolution. In combination, these data can be used to define structural, geophysical, and geochemical conditions during fluid mobilization and subsequent mineral precipitation along fault-related fracture systems in an intra-continental basin.

In this study, we present a combined core-based and microstructural approach to reveal paleo-stress fields as well as age correlations between fracture mineralizations in sedimentary rocks from two target areas in the North German Basin (a: Lower Saxony Basin, b: Altmark-Brandenburg Basin).

As a first step, continuous drill-core samples from various locations were reoriented in order to characterize different fracture sets (healed, sealed, open, natural or induced fractures) as well as to determine their spatial orientation. Reorientation was carried out by CORIAS using an electromagnetic goniometer developed specifically for geometrical drill-core analysis.

Another crucial step in paleo-stress field reconstruction is the analysis of age relations between different fracture sets and corresponding fluid-mineral systems. While microstructures and relative ages of fracture mineralizations are determined by hot-cathodoluminescence microscopy, specific ore minerals such as fluorite, sphalerite, and specularite are used for radiometric geochronological analysis in order to define absolute ages of respective mineralizations.

Finally, this data is supposed to serve as the basis for space and time resolved geomechanical models for both target areas, with a special focus on fault-related fluid migration and P/T evolution.

Rare earth elements (REEs) geochemistry of the Dorreh barite deposit, Esfahan Province, Iran

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Content

The Dorreh barite deposit is located 11 km southwest of Kashan city in central Iran. The aim of current study is to identify the conditions under which barite deposited using geochemistry of rare earth elements (REEs) hosted in mineral barite. The geological setting and mineralogy of the deposit are also investigated. The concentrations of REEs were determined in 6 barite samples using ICP-MS method. Geologically, the Dorreh barite deposit occurs in the Urumieh-Dokhtar magmatic zone, extending as a 100 km wide and 1700 km long belt from northwest to southeast Iran. Barite mineralization is found as layers with some lenses in the Dorreh deposit. The footwall rocks are composed of Eocene-Oligocene tuff and andesitic-basaltic lava beds. Barite mineralization also occurs as veinlets and open-space fillings in the footwall rocks. The andesitic-basaltic rocks have been undergone pervasive carbonatization and chloritization. The ore horizon is covered by a marly limestone bed with an Eocene-Oligocene age. Intense faulting caused brecciation at different scales in both footwall and hanging wall rocks. Barite is the main ore mineral forming anhedral to subhedral crystals with sizes ranging from fine to coarse. The fine crystals deposited directly from mineralizing fluids, whereas coarse crystals are resulted from recrystallization of the former ones. Calcite, malachite and iron oxides constitute the subordinate minerals. The value of Sr concentration in barites is low and varies between 0.14 and 0.24 wt. %. The amount of Rb, Zr, Y, Ta and Hf is also low (<4 ppm) in barite samples. The concentration of total REEs (Σ REE) is low in barites, ranging from 5.3 to 7.2 ppm. Chondrite-normalized REE patterns reveal light rare earth element (LREE) enrichment relative to heavy rare earth element (HREE). The NdN/YbN ratio (5.92) in one sample also reveals that barite is enriched in LREE with respect to HREE. Geochemical data indicate that seafloor hydrothermal fluids are most likely the source of mineralizing fluids. These hydrothermal solutions deposited barite on seafloor as they encountered sulfate-bearing seawater.

Recovery potential of Scandium and other critical raw materials from European industrial by-products

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Content

Technological evolution and modern advances in the field of renewable energies are connected to an increasing demand on critical raw materials and especially technological metals. Recently, interest in the element scandium (Sc) has started to grow due to its positive influence on material properties e.g. in high performance-alloys, solid-oxide-fuel cells and solid-state lasers. Therefore, a rise in value and demand is expected in the near future.

This study focuses on the reliable and sufficient methodology of measuring Sc and other critical raw materials in secondary waste products from the Al_2O_3 - and Ti_2O producing industry. It also targets the examination of Sc-bearing phases and their potential influence in the recovery of Sc from above mentioned materials. Essentially, chemical and structural analyses and characterization of European red muds and its Sc-bearing mineral phases are carried out. Furthermore, analogue investigations are performed for filter cakes and acid slurries that incur during TiO_2 production.

Red muds and TiO_2 filter cakes from several European countries have been analyzed by X-ray diffraction, X-ray-fluorescence, ICP-MS and -OES. Analytical procedures performed are based on previous studies [1] and different methods are tested and compared to ensure reliable data from ICP-MS and -OES measurements. Red mud samples were found to contain ~60-100 mg/kg Sc. Main mineral phases are Hematite, Gibbsite, Boehmite, Cancrinite, Diaspore, Perovskite, Rutile, Katoite and Quartz in variable amounts. Samples from TiO_2 -production contain up to 400 mg/kg of Sc and significant amounts of niobium and cerium. The main mineral phases are Rutile, Calcite, Quartz, Graphite and Iron-Oxide-Chloride. Generally, it is assumed that Sc is associated with iron and titanium-bearing phases such as Ilmenite and Rutile as it was found in REE deposits in China [2]. Hence, these phases are studied in more detail with advanced structural analyses such as X-ray absorption near edge structure (XANES) and point-based mineral chemistry analyses by electron microprobe. The study is incorporated in the SCALE project (GA No. 730105) funded by European Union's Horizon 2020 research and innovation program and aims to secure a European supply chain for Sc from metallurgical by-products.

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Short and medium duration impacts on polymetallic nodule ecosystem functioning following the removal of nodules and seafloor surface sediments

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Content

Methodologies to remove polymetallic nodules from the deep sea seafloor are currently under development. It is highly likely that the upper, most active layer of seafloor sediments down to several tens of centimetres depth will be strongly disturbed by sediment removal, compaction, or redistributed, either directly by the nodule collection system or as a result of the passage of the mining vehicle.

In 1989 the DISturbance and COLonisation (DISCOL) project was initiated in a polymetallic nodule ecosystem of the Peru Basin; The DISCOL Experimental Area (DEA). To simulate a potential mining event, the 'RV SONNE' pulled an 8m wide plough 78 times across a ~6km diameter region of seafloor. This plough removed nodules from the surface by ploughing them into the underlying sediments whilst simultaneously overturning the upper sediment layers, or even burying them beneath less active, initially suboxic, more compacted sediment layers.

In the summer and autumn of 2015 the new 'RV SONNE' returned to the DISCOL region twice. The initial cruise, SO242/1, carried out AUV acoustic and image mapping of the ploughed DEA, as well as deploying an epibenthic trawl in previously undisturbed regions of the DEA. The epibenthic trawl fully removed the upper 10 – 20 cm of bioturbated surface seafloor sediments, thus representing a more invasive anthropogenic seafloor impact than was made by the initial ploughing device. During the second cruise (SO242-/2) conducted six weeks later, a detailed visual survey of megafauna abundances within ploughed, epibenthic trawled and undisturbed regions of seafloor was made. Complimentary investigations of biogeochemical sediment characteristics and fluxes as well as microbial communities within these contrasting seafloor sediments was carried out with ROV deployed autonomous benthic chambers, profiling units, ROV pushcores and multicorers.

Microbial abundance, biogeochemical fluxes, organic matter degradation activity, respiration rates, microbial activity and megafauna abundances were observed to be generally lower in ploughed regions of seafloor than in the undisturbed areas, even 26 yrs after ploughing. The microbial and megafauna community structures within the recently ploughed EBS-tracks differed significantly from those associated with undisturbed surface sediments whilst the community structures observed within the old plough tracks showed some indications of recovery, though for megafauna, recovery was very low for sessile species.

The BMBF r4 Joint Research Project MinNoBeck: Resource potential of covered hydrothermal mineralizations in the North German Basin

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Content

The North German Basin is part of the Southern Permian Basin in Central Europe and is host to significant hydrocarbon deposits. Hence, the basin has been intensely studied in the course of hydrocarbon exploration since the 1950s. Gas exploration activities have drilled numerous carbonate-hosted Pb-Zn and F-Ba mineralizations in the Rotliegend and Hauptdolomite (Ca₂) units of the Zechstein as well as in the underlying basement of the Devonian and Carboniferous.

Within the BMBF-FONA-funded research project “MinNoBeck – Covered Hydrothermal Mineralizations in the North German Basin”, these mineralizations are, for the first time, systematically studied in order to gain information on the ages of the mineralizations, on potential fluid sources and structural controls. Besides Zn, Pb and F, these mineralizations may also contain elevated concentrations of critical high-technology metals such as Ga, Ge, In, and REE.

MinNoBeck will provide a first assessment on the inventory of critical resources such as rare earth elements (REE), F, Ga, Ge and In present in the covered hydrothermal mineralizations and will assess the resource potential of the North German Basin for critical metals. Additionally, formation waters of the Carboniferous, Rotliegend and Zechstein units are investigated in order to gain information on the geochemistry, their potential linkage to the mineralizations and their resource potential. These high-salinity brines may not only contain elevated amounts of strategically important metals, but may also represent the original Paleozoic formation waters, which could have been sealed from mixing with meteoric waters by the overlying Zechstein evaporate units.

MinNoBeck is a joint research project between Jacobs University Bremen (coordination; M. Bau, D. Kraemer), the Friedrich-Alexander Universität Erlangen-Nürnberg (R. Klemm, P. Nadoll), the Georg-August-Universität Göttingen (J. Kley, F. Duschl) and the GeoForschungsZentrum Potsdam (V. Lüders, M. Sosnicka). Exxon Mobil Production Deutschland GmbH, ENGIE E&P Deutschland GmbH, Vermilion Energy Germany GmbH & Co. KG and Wintershall Holding GmbH kindly provide the drill cores and the formation water samples.

Session 8.3: Economic Geology of Critical Raw Materials.: Keynote speaker

Session 8.3: Economic Geology of Critical Raw Materials.: Keynote speaker
A-116

Potential of Formation Waters in Permian and Carboniferous Stratigraphic Layers of the North German Basin as a Resource for Critical Metals

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Content

The North German Basin is a sedimentary basin located in central and western Europe and is a sub-basin of the Southern Permian Basin. It contains mostly Permian to Cenozoic sedimentary strata. Similar to the Polish Trough, which for example hosts the widely known Kupferschiefer mineralizations and Mississippi-Valley-Type deposits, the North German Basin may also be host to numerous similar mineralizations, albeit under significant sedimentary cover. During the last century, hydrocarbon exploration activities have inadvertently drilled a significant number of F-Ba-Pb-Zn mineralizations in the North German Basin, which are, for the first time, investigated in detail for critical metals and their mode of formation within the joint research project “MinNoBeck – Resource Potential of Covered Hydrothermal Mineralizations in the North German Basin”.

Within this project, formation waters are investigated for their potential as a future resource of certain critical metals. Previous research already indicated that formation waters from the North German Basin, especially those occurring in the Carboniferous and Rotliegend strata, may represent the original connate waters, i.e., did not mix with descending meteoric waters, due to sealing of the formations by the overlying Zechstein evaporite units. These basinal brines hence may represent analogues to the mineralizing fluids which lead to the formation of the sediment-hosted F-Ba-Pb-Zn mineralizations found in the drill cores of the North German Basin. The formation waters are extracted from the underground during oil and gas production and may themselves represent an important future supplier of critical metals. Formation waters are co-produced during oil and gas production and can be significantly enriched in high-technology metals, like for example lithium, which is needed for the production of rechargeable batteries used in smartphones and electric vehicles. “Petrobrines” may contain elevated concentrations of Li, depending on the sedimentary strata from which they originate, and are the target of several exploration efforts, for example in Canada, for a future supplier of lithium. MinNoBeck will help to establish an inventory of critical metals present in the formation waters of the North German Basin and address important research questions on the fluid evolution and the sources of the contained metals.

Session 8.4: Spectroscopic 2D-Methods: Multiscale imaging spectroscopy.: Poster

Session 8.4: Spectroscopic 2D-Methods: Multiscale imaging spectroscopy.: Poster A-365

Portable X-ray fluorescence analyzer - a method for mineralogical-geochemical analysis of rock salt samples in the field

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Content

The knowledge about the mineralogical-geochemical composition of salt samples, especially with respect to their content of minor and trace elements like bromide or potassium, is a safety relevant aspect for cavern constructions or during exploration drillings in salt mines. This study describes a method which can be applied in the field to determine the relevant major, minor and trace element contents of salt rocks by using a portable X-ray fluorescence analyzer (mXRF). The advantages of this analytical method are widely used e.g. in archaeology or exploration of ore deposits (1).

For the determination and calibration of the mineralogical composition and the trace element content, especially the content of bromide, different salt samples were tested by using the Niton XL3t mXRF from ThermoFisherScientific. The mXRF is equipped with a 50 kV Ag anode and allows the analysis of up to 30 elements from magnesium to uranium. The detection limit depends on the element of interest and varies between ca. 1 ppm and 1 wt.-% (manufacturer information). Powder samples, originating from the Gorleben salt dome (Staßfurt z2 Hauptsalz, Upper Permian), which were previously analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), provided as reference samples for the calibration of bromide. By comparing the evaluated data, the mXRF was calibrated for bromide concentrations between 50 and 2000 ppm, which covers a wide range of common bromide content in salt rocks. Additional measurements with the mXRF were carried out on rock salt samples from the Bernburg salt mine and on drilling cores from the Asse and Gorleben salt mines. The mXRF delivers, with the special calibration to bromide, excellent correlating values compared to measurements performed by ICP-OES.

mXRF is a simple and fast method to analyze on site and to preselect points of interest. It does not replace a professional equipped chemical laboratory, but it is a supplementary method in order to enable reliable assessments to the particular nature and quality of the tested salt samples. Further calibrations for other minor and trace elements like potassium, strontium or rubidium are on the way and will extend the analytical possibilities of the system.

1Potts, P.J. & West, M. (eds.) 2008. Portable X-ray Fluorescence Spectrometry – Capabilities for In Situ Analysis. RSC Publishing 2008, 291 pp.

Session 8.4: Spectroscopic 2D-Methods: Multiscale imaging spectroscopy.: Talk

Session 8.4: Spectroscopic 2D-Methods: Multiscale imaging spectroscopy.: Talk
A-347

Comparison of classification and quantification methods for μ -EDXRF, hyperspectral imaging and LIBS core scanning in a case study for drillcores from Bad Grund / Germany

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Content

Rare Earth Elements and other technologically essential elements like Germanium, Lithium, Indium and others are important for many products in our everyday life. To understand the formation of the deposits and to improve the industrial processing of the minerals and ores, it is important to have fast and precise analysis.

Laser induced breakdown spectroscopy, hyperspectral imaging and μ X-ray fluorescence are widely used and common as single devices in many fields of geoscience. Their combination could use the advantages and reduce some deficiencies of each of the methods.

The aim of the presented master project is to combine these methods in a case study of drill cores from the closed Pb/Zn mine Bad Grund in the Harz mountains. The base of the classification and interpretation is a hyperspectral approach with the software of ENVI.

Beside the combination of the methods we search for valuable metals in the gangue minerals of the ore, e.g. REE in the carbonates. In case of findings the next step will be the calculation of the economic potential of these resources.

The data formats of the individual methods are converted to a comparable format for further classification and quantification.

Geochemical and mineralogical mapping of tailing samples with energy dispersive X-ray fluorescence (EDXRF) and automated image analysis compared to Raman analysis

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Content

Since the aim of modern exploration technology is to generate more information with less effort, the efficiency of the μ -EDXRF elemental mapping was tested on different sample types. The analyzed samples were drill cores and grain concentrates from selected mine tailings in northern Chile. Geochemical mapping of the drill cores yielded a good result in a detection of zones of metal enrichment or depletion as well as different lithological zones in the cores. In turn, geochemical mapping of the grain concentrates revealed a positive outcome in a characterization of size, shape and texture as well as mineralogy of each grain. On basis of the element distribution maps, a lithological classification for the drill cores and mineralogical classification for the grain concentrates were performed by using spectral angle mapper (SAM), which is a supervised classification algorithm for hyperspectral images. End member spectra used for the classification were extracted from the maps. Resulted mineral distribution map of the grain concentrates were compared with Raman spectroscopic analyses. The principal primary and secondary mineral parageneses obtained from EDXRF and Raman spectroscopy showed acceptable qualitative agreement with each other. However, texture of grains and distribution of minerals within the grains differ due to different spatial resolution, penetration depth, and geometry of the two instruments. Additionally, effect of grain topography, fine mineral mixtures in grains, coatings on grain surface still remain as a challenge for future development. Since the EDXRF mapping is a fast and non-destructive method that allows the investigation of a relative large cut sample without any need for further sample preparation, it is an essential method for an early stage of resource exploration.

Hyperspectral Imaging Analysis for Mineral Exploration in the Iberian Pyrite Belt, Spain

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Content

The Iberian Pyrite Belt (IPB) hosts one of the world's largest polymetallic massive sulphide complexes with originally >1700 Mt of massive sulphides [1], [2]. The regional mining potential is still existing [3] and new exploration related to Cu-Pb-Zn-mineralisation has recently been started in Aznalcóllar. As prospection and exploration is expensive, new application-oriented methods to optimise the exploration process and to lower the costs need to be developed.

The massive sulphide complex of the IPB shows hydrothermal alteration patterns around the orebodies and in the underlying stockwork. They consist of an inner and intensely altered chlorite-rich and a peripheral muscovite-rich zone [4]. Thus, the distribution of these minerals can be a proxy for the location of ore bodies and stockworks. Mineral identification can be performed with hyperspectral imaging spectroscopy, which is a fast, non-destructive and application-oriented method. In this study, different metasediment and -volcanic rock samples from the ore hosting Volcano-Sedimentary Complex (VSC) are analysed in the laboratory with imaging spectrometers in the visible, near-, short-wave- and long-wave-infrared (VNIR, SWIR, LWIR) with a resolution of 128 µm (VNIR) and 400 µm (SWIR, LWIR). The mineral identification is focused on muscovite and chlorite based on the Spectral Angle Mapper Algorithm (SAM) as well as on the multi-feature-extraction approach. Mineral transitions from muscovite to chlorite with varying mineral mixture ratios can be detected. Imaging spectroscopy and the introduced method are also applied on an outcrop in Aznalcóllar for a more extensive mineral distribution analysis. In this context, 375 m of a drill core covering different lithologies of the VSC were spectrally analysed with a point spectrometer beforehand in order to determine and characterise their spectral variations. The spectral pattern in the core reveals a chlorite-rich zone near the ore body and in the underlying stockwork and a muscovite-dominated zone above the ore.

This result demonstrates that hyperspectral data can successfully be applied to detect mineral abundances which are linked to the location of ore bodies and stockworks in massive sulphide complexes.

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Modal mineralogy of plutonic rocks determined by energy dispersive X-ray fluorescence mapping compared to Mineral Liberation Analyser

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Content

Determination of modal mineralogy is important for many geoscientific questions. The classical way of determining mineralogy by microscopy and point counting for modal mineralogy is important and provides valuable information, but preparation and microscopy of thin sections is a time consuming process. In this study, a μ -EDXRF spectrometer is used to map 2D elemental distributions of plutonic rocks. The device is able to scan samples of up to 20 cm length, but in order to compare the results to microscopy and Mineral Liberation Analyser (MLA), thin sections were measured. The instrument is equipped with a Rh-tube operating at 50 kV and 600 μ A and two silicon drift detectors. The spot size of the polycapillary lens is about 20 μ m. The samples were mapped using a dwell time of 2 ms per pixel. In order to obtain mineralogical information, the samples were classified with the supervised classification algorithm Spectral Angle Mapper and the modal mineralogy was compared to results from the MLA. The comparison revealed fair overall accuracy with differences coming mostly from the resolution limit of the μ -EDXRF device. Therefore, this method provides a fast and objective way to obtain mineralogical information suitable for large sample sizes without the need of preparing thin sections.

Multi-scale imaging spectroscopy for mineral mapping on selected diamond drill core of the REE bearing Carbonatite Storkwitz, Saxony

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Content

Rare earth elements are some of the most important components of high tech products as well as for “green” technologies and are used for the production of e. g. batteries, lasers, lenses, magnets of wind power plant turbines, modern color displays as well as fuel cells. After a production decrease by the world leading REE supplier China in 2009, the EU commission declared REE as some of the economically critical raw materials. Therefore, new exploration technologies and methods have to be developed to characterize existing and to find new REE deposits, to secure the worlds need of REE oxides und to lower the dependency on a few major REE providers. In that scope, multi-scale hyperspectral imaging data were acquired from a selected sequence of a diamond drill core of the REE bearing carbonatite at Storkwitz to demonstrate a fast and non-destructive method for mineral mapping. Hyperspectral reflectance data were acquired by the SisuRock core scanner from SPECIM with a spatial resolution of 25 µm, 400 µm, and 1.4 mm per pixel in the visible, near infrared and shortwave infrared wavelength range (VNIR-SWIR, 0.4 – 2.5 µm), and in the long wave infrared wavelength range (LWIR, 7.7 – 12.5 µm). The drill core consists of a ~73 Ma old carbonatite intruded in Cambrian and Carboniferous sediments. The REE are mainly associated with fluorocarbonates. The spectral analysis is based on a multispectral feature extraction method and is applied on the VNIR, SWIR and LWIR data. In case of ambiguities in the mapping, a combination of diagnostic spectral features derived from the full wavelength range was applied. µEDXRF and LIBS data of selected areas on the drill core were used for validation. The results show carbonate, silicate, and phosphate minerals, as well as neodymium distributions. Mineral patterns indicate that more than two phases of mineralization occurred. Finally, the influence of spatial resolution on the separability of the mineral phases was investigated. All results are discussed in context to geology and the accuracy of the mineral maps are assessed by the validation data.

**Session 8.4: Spectroscopic 2D-Methods: Multiscale imaging spectroscopy.: Talk
A-682**

New perspectives for mineral exploration at the mesoscale

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Content

Mineral exploration requires fast chemical, mineralogical and textural data acquisition on different scales from remote down to sub microscopic levels. Mesoscopic two dimensional scanning methods are able to link information over a wide range, from drillcores down to polished thin sections. The methods applied, such as LIBS (Laser Induced Breakdown Spectroscopy with 200 µm resolution), EDXRF (Energy dispersive X-Ray Fluorescence Spectroscopy with down to 20 µm resolution), Hyperspectral imaging (VNIR, SWIR, both 1400 - 25 µm, and LWIR 1400-400µm resolution) and Raman (532 nm, 633 nm, 785 nm; with a resolution of 20 µm to < 1 µm) provide textural, mineralogical and chemical information.

Data from individual methods can be merged by a hyperspectral software such as ENVI to link chemical and mineralogical information even on individual pixel size level for better interpretation. The combination of the methods opens up new perspectives for data acquisition and validation as well as for selection of most diagnostic features on a more objective way for further detailed investigation. Even the methods applied are quite fast, the linking of data by pixel co-registration is a major and time consuming issue. Future perspectives therefore are partial automatization of the data analyses and evaluation process.

Session 8.5: Geothermal heat supply in areas of high population density.: Talk

Session 8.5: Geothermal heat supply in areas of high population density.: Talk

A-143

Dimensioning of Borehole Thermal Energy Storage Systems in Crystalline Rock

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Content

In the heating and cooling sector, borehole heat exchangers (BHE) have become increasingly popular for supplying renewable energy. When grouped in compact arrays, BHEs represent suitable thermal energy storage systems for fluctuating heat sources such as solar energy or district heating grids. Tapping into greater depth allows for storage operation on a higher temperature level. This so-called medium deep borehole thermal energy storage (BTES) is characterized by a slow thermal response and a large storage capacity, which makes it particularly suitable for seasonal heat storage applications. Medium deep BTES requires negligible groundwater flow in the reservoir rock and benefits from high thermal conductivities. Hence, crystalline rocks represent a wide-spread and suitable reservoir for this technology.

Operating experience with medium deep BTES in crystalline rocks is scarce. Hence, a priori numerical simulations are imperative for planning and designing such BTES systems. The Chair of Geothermal Science and Technology at TU Darmstadt employs dual continuum models (BASIMO, FEFLOW) for this task: a numerical model for the subsurface heat transport is coupled with an analytical solution of BHEs' thermal interaction. This allows for an efficient modeling of BHE under consideration of high physical detail. In combination with mathematical optimization algorithms it is possible to determine various parameters in an iterative procedure for an ideal system design.

The dynamic interaction between BTES systems and downstream heating facilities has a significant impact on the overall efficiency. Thus, the department's research also develops comprehensive simulation models, which include all relevant system components. The BTES and heating system are modeled with specialized software tools, respectively. Simultaneous computation and continuous exchange of key parameters results in a coupled simulation and facilitates reciprocal interactions between the systems. This approach allows for the assessment of various system architectures, size ratios and control strategies and their impact on the energetic system efficiency, the economic viability and the environment.

Experimental and numerical investigation of a scalable modular geothermal heat storage system

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Content

Heat storage is a key concept within the transition towards a renewable energy economy, as it offers means to resolve the problem of the temporal disparity between consumption and production of heat energy from renewable resources.

This study focuses on the simulation based design of a heat storage system, which aims for easy integration into heat supply systems in urban regions. It features a scalable, modular setup that can be either installed in cellars of, or directly into the ground near existing buildings, or function as a foundation for new buildings. Solar collectors supply the storage with heat at temperature levels of up to 90 °C. A single storage module consists of a helical heat exchanger in a fully water saturated, high porosity cement matrix. A lab-scale prototype storage module was set up in a thermally insulated plastic cylinder with a volume of 1 m³, equipped with temperature and moisture sensors as well as flux meters and temperature sensors at the inlet and outlet pipes in order to experimentally analyze the performance of the storage. Besides experimental work, numerical simulation serves as a tool for sensitivity analyses, optimization of material properties and system design (e.g. heat exchanger geometry). The experimental work thus provides a data basis for the validation of a spatially detailed high-resolution 3D numerical model of heat and fluid flow in the storage module.

Two experiments are analyzed and reported here. The first experiment consists of six days of thermal loading up to a storage temperature of 60 °C followed by four days of heat extraction and was designed for the determination of heat losses during a complete thermal loading and extraction cycle. The storage could be charged with 54 kWh of heat energy, 36 kWh could be regained during the extraction period, which translates to a heat loss of 33%.

The second experiment consists of six days of cyclic operation after constant thermal loading for five days and was performed to determine the storage performance during cyclic operation. Maximum heat loading and recovery rates of 3.8 and 5 kW were determined during the cyclic operation.

This contribution will present the laboratory setup, the results of both experiments as well as the modelling approach chosen for the numerical representation of the experiments and compare measured and modelled temperatures and heat balances for the heat storage prototype.

Predictability of hydrochemical effects of near-surface heat storage

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Content

Hydrochemical processes associated to near-surface heat storage can potentially effect storage efficiency and groundwater quality. To enable site-specific predictions of potential gas-phase formation, trace element and heavy metal release, influences on redox processes and mineral dissolution and precipitation, experimental methods and hydrochemical model calculations were optimised and evaluated with regard to their usability for future applications. For this purpose batch tests, flow-through and circular flow column tests with tertiary and quaternary sands, tempered to 10, 25, 40 and 70°C as well as hydrochemical model calculations and solid phase analysis (e.g. NaOH-extractions) were performed and examined for transferability of the results. Therefore, pH, Eh, main cat- and anions, in- and organic carbon, gas-phase formation ratios and 20 trace elements and heavy metals were measured in the experiments.

Heating of flow-through columns to 25, 40 and 70°C lead to gas-phase formation ratios of 0-1, 1-4 and 8-19 mL(gas)/L(groundwater) which were estimated with hydrochemical model calculation based on thermodynamic data with an uncertainty factor < 2 in 5 out of 6 columns, whereby deviations were less than 2.5 % at 70°C. Whether arsenic is released up to drinking water limits (>10 µg/L) already at 25, 40 or only at 70°C was sediment-specifically determinable from 1 week lasting circular flow column tests. Subsequent recooling to 10°C for another week showed the As release to be on average 67 % reversible. Changes in redox conditions were only sporadically observable in the flow-through columns with a sediment-water contact time of 36 h, in contrast, ongoing sediment-water contact in circular flow columns at 25, 40 and 70°C lead to stronger reducing conditions within 1 to 4 weeks. Carbonate precipitation observed in flow-through columns was roughly estimable by hydrochemical model calculations and the amount of Si dissolved over 8 months in flow-through columns approached the amount of readily soluble silica determined in a NaOH-extraction.

As exemplarily stated above, it is possible to predict relevant hydrochemical effects of heat storage in near-surface aquifers within a few months by appropriately combining experimental investigations with hydrochemical model calculations. Thus, usable temperature ranges can be defined site-specifically and potential risks can be minimized.

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Utilizing the accumulated geothermal heat of cities

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Content

In urbanized regions, the ground thermal regime is often significantly modified. A main reason is that during decades and often centuries of urban development, heat release from buildings and infrastructures increases the temperature beneath cities. This is augmented by accelerated heat flux from sealed ground surfaces and often from active heat input through operation of groundwater-based cooling systems. Consequently, in many cities we find large-scale so-called subsurface urban heat islands (SUHI) that expand in the entire urban subsurface and penetrate several tenths of meters. In this study, we report our findings of the special thermal regime in urban groundwater of central European cities. We reveal that the geothermal potential is different in each city, depending on the manifestation and intensity of the subsurface urban heat island, the physical properties of the ground and the local heat demand. By spatially resolving these parameters, the theoretical and technical geothermal potential can be determined for different city areas and districts. It is shown in case-specific densely populated examples that, for instance, by large operating borehole heat exchanger (BHE) fields, long term sustainable ground heat extraction can supply up to 40 % of the heating demand. A main factor is the accelerated heat flux from the ground surface, which is unique to urban environments and crucial for partial regeneration of shallow geothermal systems.

Session 9.1.: Archaeometry and monument conservation.: Poster

Session 9.1.: Archaeometry and monument conservation.: Poster

A-178

Firing conditions in Anagama kilns: constraints from the archaeometric study of kiln wall samples from the Nakadake-Sanroku archaeological site.

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Content

This contribution examines the firing conditions in 9th century sloping single-chamber tunnel kilns (Anagama), based on the study of ceramic transformations recorded in clayey kiln roof samples from the Nakadake archaeological site (Kagoshima prefecture, Kyūshū, Japan). Recent work on ceramic sherds (Sue ware) from the archaeological site suggests peak firing temperatures of ~1150 °C and a reducing atmosphere largely controlled by the Boudouard equilibrium ([1]Raith et al., 2016). Anagama kiln ceilings were built with a bamboo network that was plastered with clayey material rich in lithic and mineral clasts and tempered with rice straw. The studied sample provides a complete transect through the roof of the kiln, with its inside surface facing the hot and reducing atmosphere of the firing chamber, and its outside surface being exposed to the cool and oxidizing conditions prevailing outside the kiln. The expected steep temperature gradient is reflected in the changes of mineralogy, modal abundances of phases, and microfabric. While the outer part (0 to 6 cm) of the sample is soft and non-vitreous, its inner part (6 to 16 cm) is hard, highly vitreous and blistered; the color change from yellowish-red to dark grey reflects the concomitant change from oxidizing to reducing redox conditions. The soft to hard domain transition is characterised by the structural breakdown of dehydroxylated clay minerals (metakaolinite, metasmectite, metakillite) and the neoblastesis of FeMg-spinel and mullite, almost coeval with the onset of near-congruent melting of K⁺Na⁺ exchanged rims of K-feldspar clasts. The pronounced increase of vitrification towards the interface with the hot kiln chamber is coupled with the progression of alkali feldspar melting. The release of the fluxing components K⁺ and Na⁺ from alkali feldspar melt pools into the adjoining ceramic matrix [coupled by a reverse influx of (Ca,Fe,Mg)²⁺] boosted the vitrification reaction (K,Na)⁺ + mullite + silica/quartz → melt. Temperature estimates for the observed mineralogical changes, based on literature data, suggest a steep temperature gradient across the kiln roof, from 1100-1150 °C prevailing at its immediate contact with the hot and reducing kiln atmosphere to probably less than 800 °C near its exposure with the oxidising cold ambient air.

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Medieval wall paintings of the monastery church in Angermünde. Pigments, pigment changes and the identification of a “new” pigment

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Content

Keywords: painting analysis, mobile Ramanprobe, REM-EDX, vanadinite

The uses of the gothic church of the former Franciscan monastery in Angermünde (northern Germany) varied very much throughout its history. Nevertheless, its up to 700 years old wall paintings survived but were strongly affected by degradation effects and apparent colour changes. The vaulted ceiling in the vestry is decorated with heraldic lilies and stars mimicking a starry sky. Here, colour changes are especially noticeable.

Measurements on paintings on the ceiling of the vestry were performed on-site using our mobile Raman equipment in heights of up to 5.5 m above the floor to identify pigments and their degradation products.

Beside (common) lead- and copper-pigments and their degradation products, a “new” pigment was detected: vanadinite $\text{Pb}(\text{VO}_4)_3\text{Cl}$. This lead chlorovanadate is known to form orange, red, brown crystals, but is light yellow when ground into a powder. Small samples were taken from the painting layer of the contour of a lily to ascertain the nature of the yellow pigment. Both samples and vanadinite standards were studied in the laboratory with Raman spectroscopy and REM-EDX. The results confirm for the first time that vanadinite was used as a yellow pigment.

The importance of the finding that in the Angermünde church, vanadinite was used as a “new” pigment mineral at this time and in this area is confirmed by a second occurrence identified in the same study in the Chorin monastery c. 15 km SW of Angermünde.

The Raman- and REM-EDX-based data help to identify the original pigments used and colours intended for the mural paintings, and thus help to reconstruct a colourful model of the painted vaulted ceiling.

Acknowledgements

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Sulfide compounds in *Niello* experimentally produced from ancient recipes

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Content

Ancient metal objects often are decorated with linear inlays of blackish or brownish metal sulfides creating geometric or zoomorphic patterns. This technique known as niello is widely used since the first century A.D. with an emphasis on the medieval periods. Different metals such as Ag, Cu and Pb have been used by ancient goldsmiths for producing niello by reaction with sulfur [1]. There are basically two technologically divergent ways of applying niello, one by squeezing softened niello “threads” into the incised metal surfaces, the other is to apply the niello in the molten state. The melt-niello involves a special blend of silver, copper and lead sulfides and the discovery of this mixture was regarded advantageous for creating more complex patterns. The earliest example of this type comes from the 9th century [2].

The investigation and experimental replication of niello recipes is part of an interdisciplinary study of a Byzantine-Greek treatise with 69 recipes on gold- and silversmithing that survived as a manuscript written in 1478 assumed to be based on an earlier original probably from the 11th century. Here, for the first time the production of the melt-niello is described. The aim of the experiments (also involving other ancient recipes given by Theophilus Presbyter and Benvenuto Cellini) was to establish which type of metal sulfides would evolve by non-equilibrium technical processes in a goldsmith’s workshop. Furthermore the sulfide compounds that result from different ancient recipes should be identified.

Phase identification was done by X-ray diffraction analysis and micro-chemical methods. According to the systems Pb-S and Ag-Cu-S [3] 11 different sulfide compounds could be expected. Four different melt-niello recipes have been tested and nine sulfide compounds were identified ranging from simple sulfides such as Acanthite/Argentite to more complex phases such as Mckinstryite ($\text{Ag}_5\text{Cu}_3\text{S}_4$). Each recipe produced a characteristic mélange of three to four sulfide compounds. Based on these results it should be possible to relate the sulfide phases on a specific Byzantine jewelry object to a specific recipe used thus revealing new insights into the intercultural transfer of technical and scientific knowledge between Byzantium and the West.

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Session 9.1.: Archaeometry and monument conservation.: Talk

Session 9.1.: Archaeometry and monument conservation.: Talk
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Diffusion-induced copper isotope fractionation in copper metal: Implications for archaeometallurgical research

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Content

Chemical heterogeneity of metals is long known in archaeometallurgy. However the isotopic composition of metals is commonly regarded as homogeneous. While this holds true for lead isotopes, it has not been examined yet for stable metal isotopes like copper or zinc. Investigation in this direction is urged by the application of new isotope systems and laser ablation analysis. This is the more important, as material scientists have reported diffusion-induced metal isotope fractionation, the so called 'isotope effect', since the late sixties. Moreover, potential fractionation of stable metal isotopes is known from other diffusion processes like Soret diffusion. Their effect in archaeometallurgically important metals is poorly understood. For the first time, copper reguli produced in a lab scale smelting experiment were examined and a substantial variation in their copper isotope composition was detected. The observed variation can be explained by the combination of stable isotope fractionation theory and different diffusion processes. They imply an enrichment of the heavier isotope in the colder, earlier crystallised areas of the solidified melt. These observations have important implications for the sampling, analysis, and interpretation of metal objects. If such variation is not homogenised in further metal processing, the link between the isotopic composition of the ore and the metal must be questioned. At least, it is heavily relied on representative sampling or in-situ analyses. Additionally, processing of the metal like casting might induce additional fractionation. This would further complicate the reconstruction of the ore from the object. But at the same time, it opens up possibilities for new applications in archaeometallurgical research.

Magnetic prospecting and magnetic characteristics of semi-terrestrial floodplain sediments

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Content

Magnetometer prospecting is a very quick, non-destructive and efficient method of archaeological prospecting. But often the magnetograms are interpreted without required validation in the lab, which may lead to incorrect assessments of the magnetic field anomalies in (geo-) archaeological contexts [1].

This work is dedicated to the aim of improving upon interpretations of magnetometer measurements and further developing processes that can be applied towards rapid and sufficient clarification of magnetic field anomalies. For this purpose, magnetometric and environmental magnetic measurements, combined with sedimentological findings, are evaluated at the Fossa Carolina site [2].

The magnetometric prospecting is conducted using a vector gradiometer. Magnetic susceptibility is used as a geophysical indicator for the identification of magnetically conspicuous and magnetic field anomaly generating sedimentological layers. Based on the Curie temperature measurements and magnetic domain investigations, the environmental magnetic minerals and their particle sizes are characterized in magnetically conspicuous layers.

In the trench fills or paleochannels of the Fossa Carolina, authigenic SD greigites were discovered in layers exhibiting magnetic field anomalies, thus confirming the supposition by [3] that greigites can be of significance for magnetometer prospecting in semi-terrestrial environments. By contrast, highly-heated, thermoremanent PSD titanomagnetites, causing magnetic field anomalies, were discovered in flanking accompanying structures of the Fossa Carolina. Their origin remains unresolved, yet a natural formation of these magnetic minerals on site is ruled out.

Considering the objective of this research, the methodical approach at the Fossa Carolina proved to be an efficient and relatively economical method for verified clarification of magnetic field anomalies in the magnetograms.

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The mechanical properties of heat-treated silica rocks

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Content

In prehistoric archaeology, heat treatment of stone to produce tools by controlled fracturing (stone knapping) is commonly understood as one of the earliest efforts of humankind to deliberately alter the properties of naturally available materials. Such early heat treatment has important implications for the cultural evolution of anatomically modern humans and it has been interpreted to be a proxy for the archaeological concepts of “modernity” or “complex cognition”. Such inferences must, however, be based on solid interpretations of what stone heat treatment actually implied for past human behaviours such as fire use or tool knapping. Most available archaeometric studies on heat treatment concern mineralogical or crystallographic transformations in the rocks and relatively few detailed data on the thermal evolution of fracture mechanics are actually available to date. In this paper, we present some of the results of a three years lasting research project, shared between the departments of Applied Mineralogy and Prehistory and Quaternary Ecology of the University of Tübingen. We analysed the thermal evolution of four mechanical properties (fracture strength, fracture toughness, elastic modulus and Weibull modulus) of several silica rock samples and compared them to the chemical transformations taking place in these rocks. Our results allow to propose a comprehensive theory of the transformations of tool stone quality upon heat treatment that allows to explain the crystallographic factors and mechanisms that cause them. Apart from the obvious implications for our understanding of the motivations to heat-treat stone in the past, this theory will shed further light on the concepts of tool stone quality and the mechanics associated with stone tool knapping.

XRD on bioapatites concerning archaeometric questions

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Content

Subject of investigation are bones, teeth and ivory of archaeometrical interest. It includes both historical musical instruments and palaeoichthyologic teeth and fishbones. Normally such materials are investigated by geochemical methods. In the case of apatite the concentration of fluorine is often in the focus. Instead, this study approaches the discrimination of bioapatites using X-ray diffractometrical investigations. In this regard lattice constants, reflection shape and crystal perfection (e.g. FWHM) are taken into account. A combination of such parameters enables a remarkable differentiation between prehistoric and recent bioapatites. Thus, the results of the XRD measurements on shark teeth show significant reflection sharpening with time (recent to palaeo). Further, our method provides a discrimination referring to the different animals. For instance, a terpodion key, violin bows and an oboe could be assigned to walrus ivory, mammalian bone and elephant ivory, respectively.

Session 9.1.: Archaeometry and monument conservation.: Keynote speaker

Session 9.1.: Archaeometry and monument conservation.: Keynote speaker

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“Non-invasive” portable laser ablation sampling of art and archaeological materials with subsequent trace element and multi-isotope analyses.

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Content

Chemical fingerprinting of archaeological materials can determine how, when and where objects were made and hence their provenance and potentially authenticity. If public and/or private institutions grant access to study artefacts, generally material cannot be transported, nor is bulk destructive analysis permitted. Portable analytical techniques such as pXRF or pLIBS have poor analytical accuracy and precision and are not capable of determining isotopic compositions. They are generally insufficiently discriminatory for provenancing the source of most materials that comprise archaeological artefacts.

A new integrated trace element and multi-isotope provenancing methodology is presented that uses a portable “non-invasive” pulsed laser ablation sampling technique. Samples are collected on location on teflon filters for return to a clean laboratory for low blank (pg) geochemical procedures. Ablation pits approximately 60 or 120 μm in width and depth remove μg amounts of material. Following dissolution, trace element ratios are determined by ICPMS and combined Sr-Nd isotopes by TIMS. Use of 1013 Ω resistors allows precise analysis of subnanogram amounts of Sr-Nd, which coupled with the trace element data, provides highly effective multi-variant discrimination for material provenance and authenticity verification.

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation).: Poster

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation).: Poster

A-906

Die Förderung wissenschaftlicher Forschungen im Geopark Harz . Braunschweiger Land . Ostfalen

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Content

Der Geopark Harz . Braunschweiger Land . Ostfalen (HBLO) wurde 2002 gegründet und in der Folge als Nationaler, Europäischer und Globaler Geopark anerkannt. Die Aufwertung des Globalen Geoparknetzwerkes zu einer UNESCO-Kategorie im Jahre 2015 hat die Bedeutung der wissenschaftlichen Forschung noch deutlicher in den Fokus gerückt. Der Geopark HBLO ist eine klassische Forschungsregion. Auf dem Gebiet der Geowissenschaften besaß das Harzrandgebiet an der Aufschiebung des variszischen Grundgebirges über die steil aufgestellte mesozoische Schichtenfolge mit seiner „Klassischen Quadratmeile der Geologie“ eine historische „Prime-Position“. Vor allem die Vielzahl von Lagerstätten gaben Anlass für umfangreiche Forschungsaktivitäten. Auch auf archäologischem Feld lieferte die Region zahlreiche bedeutende Forschungsfelder. Heute leidet die Region unter der Schließung bzw. der drohenden Schließung geowissenschaftlicher Institute z.B. in Braunschweig und Clausthal-Zellerfeld. Der Geopark versucht die entstandene Lücke durch die Förderung verbliebener Institute und Museen sowie die Einbindung externer Forschungsinstitute zu unterstützen. Beispiele dafür sind die Grabungen im Posidonienschiefer bei Braunschweig und an der Einhornhöhle bei Scharzfeld. Zudem werden zusammen mit den zuständigen Landesämtern die archäologischen Forschungen in Schöningen, am Harzhorn und der Kaiserpfalz Werla vom Geopark unterstützt und –z.B. in Kooperation mit Senckenberg- auch neue Projekte erarbeitet. Das Potenzial der Geoparkregion ist weiterhin enorm und bietet auch für zukünftige Generationen viele Möglichkeiten. Es ist eine wichtige Aufgabe des Geoparks, dieses Potenzial mit seiner gesellschaftlichen Relevanz immer wieder in Erinnerung zu rufen und in konkrete Planungsprozesse einzubringen.

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation).: Talk

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation).: Talk

A-718

Das Paläogen des Helmstedter Reviers, ein Forschungsthema im Geopark Harz - Braunschweiger Land - Ostfalen

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Content

Das Paläogen des Helmstedter Reviers hat in den letzten Jahrzehnten eine Fülle von Daten zur Sedimentologie und Paläoökologie vom ausgehenden Paleozän bis in das mittlere Eozän im Spannungsfeld zwischen Land und Meer am Südrand der Paläo-Nordsee geliefert. So war z.B. im Tagebau Helmstedt das gesamte Untereozän einschließlich des PETM in einzigartiger Weise erschlossen. Hier konnten über eine Mächtigkeit von mehr als 100m zahlreiche Profile aufgenommen und intensiv beprobt werden. Diese Proben, die bislang nur zu einem geringeren Teil untersucht wurden, können die Grundlage für künftige Forschungen bilden, selbst wenn das Tagebau inzwischen aufgelassen wurde. Einige der wichtigen Sedimentstrukturen konnten über große Lackfilme für Ausstellungszwecke dokumentiert werden.

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation): Talk
A-417

Exhibition MeerErleben – science goes public

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Content

The exhibition MeerErleben (experience the sea), an engaging, interactive exhibition created by MARUM, Center for Marine Environmental Sciences, University of Bremen, was designed for the entire population. Since 2009 it has been displayed in ECE shopping centers in over 30 German cities as well as in Prague. More than eight million visitors have experienced the exhibition. Its aim is to arouse public interest in themes relating to the ocean and marine research. This is achieved through eye-catching open modules that invite the guest to stroll in, have a look, and linger a while. The seven modules present a broad spectrum: Crabs & Co.; Diversity and Evolution; Humans and the Sea; Diving into the Deep Sea; Submersible Technology; Stones, Sand and Sediments; and Dynamics of the Earth. Special exhibits are designed for participation by children. The exhibition is visually enhanced through the use of fascinating videos and photos. It is considered a great success because it presents extensive content for a broad public throughout Germany, and also appeals to visitors who have had little previous contact with science. Public visibility is also significantly enhanced through numerous articles in the press, television programs, and YouTube features.

FID GEO: New services for open access to scientific literature, maps and research data

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Content

The Specialized Information Service for Solid Earth Geosciences (FID GEO) addresses the digital supply of open and reusable research results. The FID GEO offers services for the scientific community, but also the public benefits from open access to scientific literature, maps and research data.

The FID GEO supports the scientific community in the areas of

- 1) open access e-publication of institutional and "grey" literature as well as pre- and postprints of scientific articles,
- 2) digitisation of geoscience literature and maps and
- 3) publication of research data related to scientific articles (data supplements).

Below, recent activities of the FID GEO are described and services are illustrated with examples to point out the benefits for researchers and for science in general.

Currently, the FID GEO is commissioned to digitise older issues of the journal "Zeitschrift für Geophysik" on behalf of the German Geophysical Society. These issues, so far print-only, are to be published electronically and freely available (open access) on the repository of the FID GEO (e-docs.geo-leo.de). While digitisation is funded by the FID GEO, the primary challenge is to clarify the legal situation for publication.

Regarding research data, GFZ Data Services is the partner of the FID GEO, providing the repository for data publication and associated services. The FID GEO presently focuses on raising awareness in the scientific community to the issues of data publishing. The FID GEO promotes the implementation of the standards formulated in the "Statement of commitment" of the "Coalition for publishing data in the Earth and Space Sciences (COPDESS)" and adherence to the "FAIR data principles". The scientific community is approached via existing networks such as learned societies and their umbrella organizations, the DVGeo and the GeoUnion, and also research networks like Geo.X in the Berlin-Brandenburg region. In consultation with the scientific community, model workflows are developed for the publication of research data.

Since 2016 the FID GEO is funded by the German Research Council (Deutsche Forschungsgemeinschaft) and hosted by the SUB Göttingen and the German Research Center for Geosciences GFZ.

Houses of Science – interfaces between science and society

Wefer, G.

MARUM - Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

Content

An awareness of science and research is crucial in our complex and knowledge-based society. Regardless of their age or educational level, it provides citizens with orientation in a rapidly changing environment and the ability to participate effectively in discussions of current events. Many college cities are earnestly considering the question of how and where to promote educational participation and transfer of knowledge for the broadest possible spectrum of the population. Considerations for the physical placement of these increasingly interactive transfer points are often focused on areas in the central city. Existing Houses of Science have proven successful in providing “low-threshold” access to science and in setting new trends in economic and societal development for cities and their surrounding regions.

What are Houses of Science and what do they accomplish?

- They can be an important interface between representatives from science, economics, politics, administration and society.
- As information platforms, they stimulate processes, follow them through and, where appropriate, initiate new formats and implement them.
- They are open venues where scientific knowledge can be passed on to society and discussed with a minimum of effort on the part of the participant, and input from civil society can be acted upon.
- They act as integrating locations of knowledge, because they introduce scientific topics to society and make them accessible.
- Consultation (scientists, students, future students) can be offered in the Houses of Science with suitable facilities.

**Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation): Talk
A-740**

International Outreach within ECORD

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Content

Multinational and multidisciplinary expeditions require international science communication in order to spread word about objectives, research processes, scientific results and achievements. Within ECORD, the European Consortium for Ocean Research Drilling who operates mission-specific platform expedition for IODP (International Ocean Discovery Program), an Outreach and Education Task Force coordinates ECORD's communication. This includes amongst others outreach/public information and educational activities related to IODP in ECORD countries. Target audiences consist of scientists, classrooms and the general public. How is the cooperation organized? How to reach out to the media during an expedition? And what about social media? Using the example of the most recent expeditions (Expedition 364 Chicxulub K-Pg Impact Crater and Expedition 381 Corinth Active Rift Development) these questions are targeted during this talk.

Lehrkoffer Mineralogie für den deutschsprachigen Schulunterricht

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Content

In den letzten Jahren sind mineralogische Lerninhalte zunehmend aus dem Fokus der MINT-Lehrpläne gerückt und kommen häufig nur noch optional oder gar nicht mehr vor. Das Ziel dieses Projektes ist es daher, Lehrkräften eine Möglichkeit zu bieten, sowohl die Bedeutung der Mineralogie als auch mineralogisch-geologische Lerninhalte wieder stärker in den Unterricht zu implementieren.

Nach dem erfolgreichen Abschluss eines Pilotprojektes (<http://www.dmg-home.org/index.php?id=70>) hat sich die Alexander Tutsek-Stiftung bereit erklärt, eine erweiterte Neuauflage des Lehrkofferprojektes finanziell zu unterstützen. Dies ermöglicht die Fertigstellung von 300 weiteren Koffern, welche Schulen kostenfrei zur Verfügung gestellt werden sollen. Im Rahmen dieser Neuauflage ist geplant, basierend auf den Erfahrungen aus dem Pilotprojekt, das bestehende Konzept zu verbessern und neben den derzeit bestehenden (z.B. „Kreislauf der Gesteine“ oder „Kupfergewinnung aus Malachit“) weitere Module zu entwickeln. Dies geschieht in enger Zusammenarbeit zwischen dem AK für Schule und Hochschule der DMG, den Anwendern aus dem Pilotprojekt sowie Lehrenden der MINT-Fächer.

Die mineralogischen Arbeitsmaterialien werden dabei durch Informations- und Übungsmaterialien ergänzt, welche detailliert mineralogische und geologische Inhalte vermitteln und Ideen für Unterrichtseinheiten bieten. Zusätzlich sollen die Begleitmaterialien Anregungen für einen fächerübergreifenden Unterricht enthalten, um die Möglichkeit zu geben, den Koffer ausgehend vom mineralogischen Inhalt in verschiedenen Bereichen einzusetzen. So wäre es möglich, den Lehrkoffer „Symmetrie“ zusätzlich in der Mathematik (geometrische Körper, Volumenberechnung), Physik (Dichtebestimmung), Geographie (Rohstoffe) bis hin zum Deutsch- und Kunstunterricht (Bedeutung von Mineralen und Edelsteinen in Kunst und Literatur) einzusetzen. Im Sinne eines Spiralcurriculums sollen die Koffer weiterhin in mehreren Jahrgängen bereits ab Klassenstufe 5 zum Einsatz kommen und so anhand altersgerecht angepasstem Lehrmaterial mit steigender Komplexität und Differenzierung mineralogische Inhalte und ihre Bedeutung für die Lebenswelt der Schülerinnen und Schüler vermittelt werden.

Die Neuauflage und Erweiterung des Projektes Lehrkoffer Mineralogie hat sich daher zum Ziel gesetzt mittels eines fächerübergreifenden Ansatzes mit Schwerpunkt auf mineralogische Lerninhalte die Bedeutung der Geowissenschaften im naturwissenschaftlichen Schulunterricht zu stärken.

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation): Talk
A-757

Presenting Nature in a hands-on science center exhibition

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Content

Science exhibitions want to raise interest in scientific issues and are aiming to engage their visitors with scientific thinking. But what are the means of exhibitions to try to achieve this goal? While museums focus on presenting real objects from collections, science centers engage visitors interacting with real phenomena and artistic installations. However, during the last decade museums and science centers have been converging in choosing their exhibition means. Examples from Universum Bremen will be shown with respect to geoscience and nature topics in the permanent exhibition. How are different exhibition elements combined in the exhibition design? How are they perceived by the visitors? And how do these elements tell a specific story of „Nature“? The overall story line in the exhibition is a cross-disciplinary approach focusing on basic properties of natural phenomena such as colors, shapes and patterns. It shows, how science exhibitions are able to shed light on specific aspects of nature and how they can open new perspectives for visitors of a general public.

Proben- und Sammlungsbestände aus dem Uranbergbau der SAG/SDAG Wismut

Hiller, A.

Wismut GmbH, Hartenstein, Isle of Man

Content

Der nach dem Ende des Zweiten Weltkrieges aufgekommene Uranbergbau in Sachsen und Thüringen hat eine Vielzahl auflässiger Grubengebäude des historischen Erz-, Spat- und Steinkohlenbergbaus wieder zugänglich gemacht und für weitläufige Neuaufschlüsse gesorgt, eine flächendeckende Prospektion mit intensiver Bohrtätigkeit auf radioaktive Rohstoffe im Südteil der DDR hervorgebracht und die Erschließung einiger neuer Lagerstätten abseits der traditionellen Grubenreviere ermöglicht.

Mit der Entscheidung zur Stilllegung des ostdeutschen Uranbergbaus im Jahr 1990 rückten die ökologisch problematischen Hinterlassenschaften dieses Industriezweiges in den Fokus der Öffentlichkeit und wurden zum Inhalt der europaweit größten Sanierungsprojektes an radioaktiven Altlasten, das bis heute von der bundeseigenen Wismut GmbH realisiert wird. Neben den Herausforderungen der Sanierung sind in den letzten Jahren auch Aspekte der Bewahrung materieller und immaterieller Güter aus der Bergbauära ein Aspekt der Unternehmenstätigkeit.

Bis Mitte der 1960er Jahre wurden große Teile der archivierten Bestände in einer zentralen Sammlung konzentriert, die einen Überblick über das gesamte damalige Arbeitsgebiet der SAG/SDAG Wismut ermöglichte. Diese Sammlung wurde 1967 nach Freiberg überführt und 1997 an die TU Bergakademie Freiberg übereignet. Dort steht sie für wissenschaftliche Bearbeitungen zur Verfügung. In den zuletzt verbliebenen Bergbaubetrieben der SDAG Wismut entstanden Kernlager mit Beständen von ca. 1 Mio. laufender Meter Bohrkern, deren gezielte Archivierung bereits vor 1990 betrieben wurde.

Im Zuge der Konzentration der geologischen Archivbestände erfolgte auch die schrittweise Zusammenführung aller Probensammlungen des Unternehmens am Standort Hartenstein (ehemals Schacht 371). Hier wurde im April 2001 die „Lagerstättensammlung der WISMUT“ eröffnet, in der Schaustufen, Gangprofile und repräsentative Erzstufen, einschließlich radioaktiver Proben, aus den erzgebirgischen Ganglagerstätten zu sehen waren.

Die enge Bindung an das geologische Archiv der WISMUT GmbH ermöglicht die Entwicklung der Ausstellung unter Nutzung geologischer Dokumentationen und sonstiger Archivunterlagen. Mittlerweile hat die Ausstellung in einem unter Denkmalschutz stehenden Gebäudekomplex Platz gefunden und ist Teil konzeptioneller Überlegungen zur langfristigen Präsentation des Wismut-Erbes. Mit jährlich 800-1000 Besuchern ist die Einrichtung fester Bestandteil der Öffentlichkeitsarbeit der Wismut GmbH.

Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation): Talk
A-833

Science Centers – dialogue platforms in science communication

Münder, H.

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Content

For democratic systems evidence based decision making processes are key factors. But how can this be reached in a world with a rapidly growing complexity? One can observe an increasing number of people who don't believe anymore in scientific facts. And these people are not only laymen but also decision makers whose statements can be seen in the news. Of course they want to influence the public opinion. This results in a at least confused general public. But how can this problem be addressed? How can we explain the scientific process to the general public? Can we explain that disagreement between scientists is an inherent part of the scientific process? And what can be the contribution from science centers? These institutions will have a growing societal importance in future. There are classical measures like exhibitions which can be used in this perspective. But this will be not enough facing the future challenges. They have to become dialogue platforms between researchers, stakeholders, decision makers and the general public.

Sprechender Sand als Brücke zu den Geowissenschaften

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Content

Sand ist oft das erste und manchmal auch das einzige Gestein, mit dem sich Kinder, aber auch die meisten Erwachsenen, auseinandersetzen. Sand ist anders als harter und eckiger Fels ein weiches, fließfähiges Gestein. Für viele ist Sand ganz eng assoziiert mit Spielplätzen, Strand, Sonne, Meer und Urlaub, ist also ein mit überaus positiven Attributen besetztes Medium. Gleichzeitig ist Sand für den Geowissenschaftler ein Datenträger, der Informationen unter anderem über Provenanz, Verwitterung- und Sedimentationsprozesse, Klimazonen sowie biologische Aktivität überliefert. Sand ist Rohstoff in vielfältiger Hinsicht. Einige Sande sind als Strandseifen und Paläo-Strandseifen Lagerstätten zur Gewinnung von Elementen wie Titan, Zinn, Zirkonium, Hafnium, Seltenen Erden und weiteren Elementen. Sand als Baumaterial ist der bedeutendste geologische Rohstoff in Deutschland. Sanddünen überstreichen endlose Flächen in Wüsten wie etwa in den Ergs der Sahara oder dem Rub al-Chali auf der Arabischen Halbinsel. Für die Hochhaustürme der Arabischen Emirate wird dennoch Sand aus Australien importiert. Vor den Küsten Indiens tauchen Menschen mit Eimern nach Sand, weil die Sandstrände für die florierende Bautätigkeit schon abgebaggert wurden.

Sand bietet die Möglichkeit, einen scheinbar alltäglichen Stoff mit geologischen Zusammenhängen wie auch mit wirtschaftlichen und gesellschaftspolitischen Implikationen zu verbinden. Mit nicht mehr als einer guten Lupe lassen sich anhand geeigneter Sandproben die Vielfalt der Minerale, die Gesteinsbildung bis zur Existenz geologischer Zyklen auch geowissenschaftlichen Laien nahebringen.

All dies macht Sand zu einem idealen Medium, über das Geowissenschaftler mit Lehrern und Schülern und ganz allgemein mit interessierten Menschen in den Dialog kommen können.

Sand ist ein ideales Medium, um Lehrern, denen die geowissenschaftlichen Hintergründe eigentlich fehlen, eine Brücke zur materialorientierten Geowissenschaft im Unterricht zu bauen. Zu diesem Zweck arbeiten wir im Rahmen des DMG Arbeitskreises „Schule und Hochschule“ an einem Ausbildungskasten für den Schulunterricht zum Thema „Sand“, der naturwissenschaftliche Inhalte vermitteln und gleichzeitig die Verbindung zu politischen und kulturwissenschaftlichen Unterrichtsinhalten ermöglichen soll. Das Vorhaben wird von der Alexander Tutsek-Stiftung gefördert.

**Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation): Talk
A-782**

Start early - harvest later, geoscience at school

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Content

For school classes and teachers, regular courses with a central focus on marine sciences have been offered by the MARUM UNISchool lab since 2001. The courses target classes from grades 3 to 12 and are held three to four days a week. Presently, approximately 3,500 pupils participate annually.

Many pupils visit the lab regular once a year during their whole time in school. The MARUM and six schools are running different models of cooperation.

First model: every class of a school visits the lab once a year.

Second model: only junior high school level classes visit the lab once a year.

Third model: only high school level classes visit the lab regularly.

Fourth level: all classes of a certain school level visit the lab.

All cooperations are part of a long term development where teachers, scientists and pupils work together. Every step is proved in practice and daily routine.

The talk gives an overview of the activities over the years and different schools.

**Session 9.2: New Developments in Science Communication (Neue Initiativen in der Wissenschaftskommunikation): Talk
A-876**

Vitrinen auf - Besucher willkommen

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Content

Universitätssammlungen dienen der Forschung und der Lehre. Gibt es eine räumliche Trennung zwischen Institut und Sammlung, so finden nur wenige Studenten den Weg in die Sammlung, um diese zum individuellen Lernen zu nutzen.

Die Mineralogische Sammlung Jena hatte im Wintersemester 2016/2017 deshalb eine Sonderausstellung konzipiert, die die Studenten trotz räumlicher Trennung etwas locken sollte. „Ich baue Dich auf“ - kein Gemeinschaftsprojekt mit den Psychologen, wie mancher Besucher dachte. Nein, Minerale bauen Gesteine auf. Deshalb wurde ein Querschnitt von etwa 50 Gesteinen unterschiedlichster Art präsentiert und dazu, direkt jeweils drum herum, die Minerale, die diese Gesteine aufbauen. Im Rahmen von öffentlichen Führungen wurden dann die Vitrinen geöffnet und die Besucher konnten Minerale und Gesteine in die Hand nehmen, an die Vitrinen gehen, vergleichen etc. Wie unterscheide ich den Plagioklas vom Orthoklas oder vom Quarz? Wie sieht der Zirkon aus, den wir nur akzessorisch kennen und mit dem Auge selten im Gestein ausmachen können? Ergänzend zu den Objekten gab es Fotos, Dünnschliffabbildungen und die gebräuchlichen Diagramme in die Hand. Auf Bedarf wurde auch - an ausgewählten Exponaten mit Härteskala und Strichtafel gearbeitet.

Das Ausstellungskonzept sah vor, die Übungsgruppen der Ringvorlesung, die den Studienanfängern der Geowissenschaften und Biogeowissenschaften den ersten direkten Kontakt mit Mineralen und Gesteinen liefert, in extra Führungen mit der Ausstellung in Berührung zu bringen.

Wie haben die Studenten und die Übungsleiter darauf reagiert? Was sagte das allgemeine Publikum? Die Ausstellung bot einen anderen Weg der Kommunikation der Objekte mit den Besuchern. Wurde es angenommen? Was sind die Randbedingungen für die Umsetzung eines solchen Projektes? Die Auflösung gibt's im Vortrag!

Session 10.1: Applications in 3D Geological Modelling.: Poster

Session 10.1: Applications in 3D Geological Modelling.: Poster A-628

Creation of a geological high-resolution 3D-model for the city of Frankfurt/Main

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Content

Objective

On the base of high amount of boring data, we created a geological high-resolution 3D model for the near surface underground of Frankfurt/Main. The pressure of the administration of the city to build new apartments of the quick expanding population in Frankfurt calls for new strategies. In this context a profound knowledge of the geological setting is essential. The model aims to be easy to expand and adjust for different geological and hydrogeological questions and thus keep various parameters such as permeability, grain size distribution, porosity, heat conductivity, culminating in quickly available information provided as geological maps, cross sections and virtual drillings.

Results

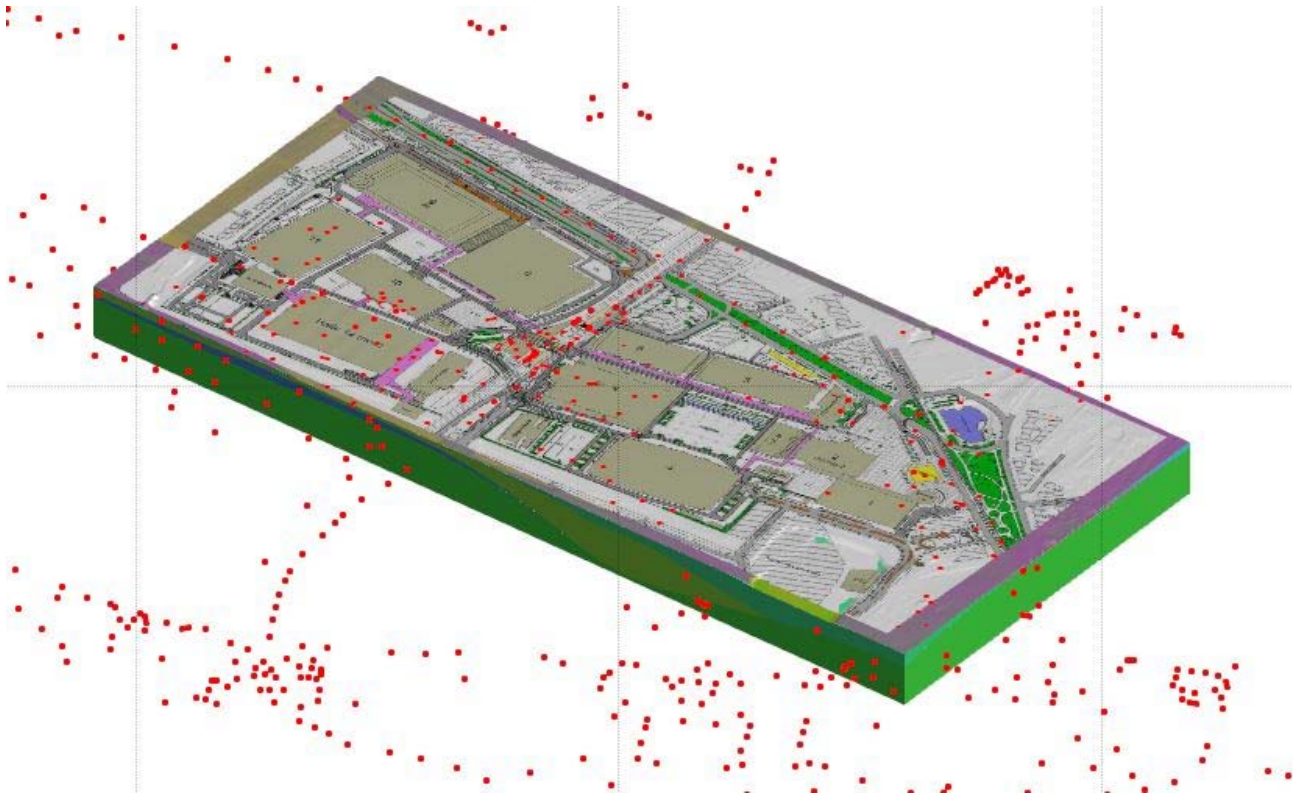
In times of digital evolution, this model is an example of steps necessary to process existing borehole data to evolve a geological high-resolution model in an urban area. The steps already done showed a need for action to improve the handling of existing and new recorded data. In conclusion, existing workflows should be changed to enhance the capabilities of regional authorities to make fitting statements referring to geological parameters and bedding conditions.

Who is interested?

This 3D-model is interesting for work groups specialized in processing data of boreholes, creation of models and visualization of data. All affected (industrial) sectors can take advantages, such as local authorities, building companies, water and sewage management, up to private stakeholders, who are interested in their subsurface.

Working steps

The project is created in close cooperation with the regional environmental authority, the HLNUG, which provided drill-hole data for the area of interest. The data processing was done with spreadsheet and database software. In later steps image editing software were used for an inclusion of existing geological cuts and other data like tectonic faults. For the modelling processes, "Leapfrog Geo" has been chosen due to high demands on the project like simplified handling and an excellent expandability. The application allows to update and expand the model without the detour on other software. Later on, this model should be utilized to simplify the insight in geological composition of this dense populated area through a 3D-database.



Part of a first 3D-model created with drill-hole dat

Development of the 3D geomodel of Brandenburg in the framework of the TUNB-project

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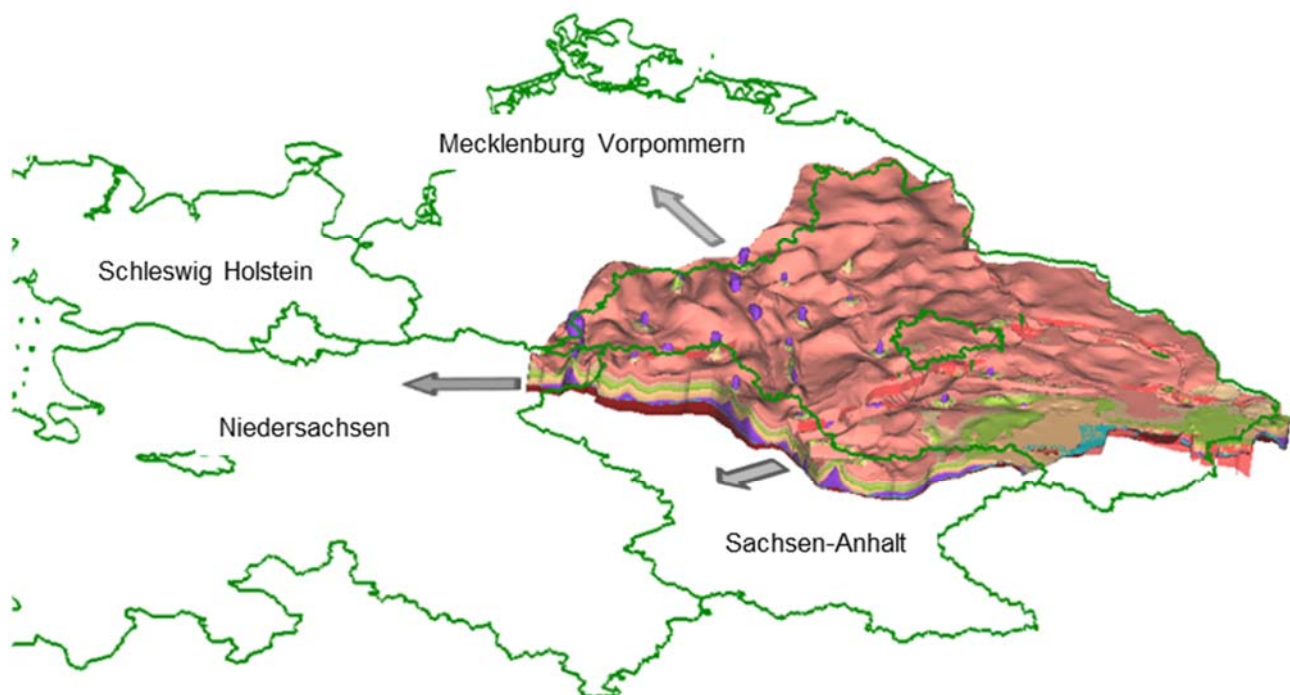
Content

In the framework of the project TUNB "Subsurface potentials for storage and economic use in the North German Basin" a model of the major lithostratigraphic groups and boundaries, the salt structures and the major faults in the Cenozoic, Mesozoic and Upper Permian is developed and harmonized with the neighbouring federal German states to achieve a consistent basin-wide 3D model of the subsurface in the NEGB. The modelling is performed with the software GoCAD® basing on boreholes, depth migrated seismic data of the major investigation periods from the end of the 1950's to the end of the 1980's and interpreted structural maps. This predominantly analogue and unpublished archive inventory was digitized and integrated in an infrastructure within the Spatial Data Infrastructure of Brandenburg. The 3D model and parts of the archive data will be provided to the public through an interactive 2D/3D web application.

The present model of Brandenburg has a working scale of 1:100.000 to 1:50.000 depending on the resolution of the primary data and covers a region of nearly 30.000 km². Challenges are the development of a 3D-model in such scale and resolution, the harmonization of geological and geophysical data from a time period of more than 30 years with different quality and interpretation state and the different and partially not comparable databases of the Federal States of Germany especially the differences between the former Western and Eastern Germany.

To develop strategies and workflows that can handle these challenges a pilot region that covers adjacent parts of all participating Federal States was processed first.

Further developments will be the refining in local focused detail models, the integration of additional stratigraphic layers e.g. detailed tertiary strata, selected storage and barrier complexes of the Mesozoic, harmonization at the international cross-border with the Republic of Poland and the parametrization of regional parts with selected rock properties.



Comprehensive 3D model of Brandenburg (mesozoic and permian strata) and connections to neighbouring states

From 3D modeling to a statewide Fault Database - concepts and first experiences

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Content

Modeling of the underground has become more and more important in the past years. Especially in the course of sustainable and responsible handling with subsurface geo-potentials, the use of three-dimensional models has taken a significant role in the spatial planning of the underground and will continue to do so in the future. With increasing technical and technological possibilities, 3D subsurface models have become much more complex, accurate and diverse. Depending on individual requirements many models of different extent and resolution were created and even Geological Surveys focus on statewide structural models of the subsurface, which may build the framework for future data management, information supply and parameterization approaches. A special challenge of such large-scale models is originated in the discrepancy between a homogeneous level of detail and the heterogeneity, amount and spatial variability of data based on a huge number of research and exploration projects carried out over hundred and forty years. Statewide structural models typically consist of two types of triangulated surfaces (horizons and faults) and are commonly based on reflection seismic data, which is correlated with sparse borehole information. As reflection seismic data is highly influenced by uncertainties inherited from different acquisition efforts and processing steps as well as subjectivity associated with various interpreters a straight documentation system must provide the possibility to notice all available information and metadata.

To unravel the tectonic and structural patterns of Saxony-Anhalt within the scope of the TUNB project (Subsurface Potentials for Storage and Economic Use in the North German Basin) we developed a specific workflow and documentation system for subsurface fault data. All faults derived from seismic data, borehole information and 3D modeling are and will be stored and updated with a systematic nomenclature. Following this nomenclature and hierarchic encoding restrictions the fault database will be complemented with additional information and parameters. In this contribution we will introduce aims, approach and goals focusing on the development of a statewide fault database concept. Concepts of a database-oriented documentation and encoding system as well as first experiences and advantages will be presented. Prospective applications of an object-based fault database information system will be discussed.

Geological 3D modeling of the deep tertiary formations in the southeast of Schleswig-Holstein – A part of the joint project TUNB (Tieferer Untergrund Norddeutsches Becken)

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Geological Survey SH, State Agency for Agriculture, Environment and Rural Areas of Schleswig-Holstein (LLUR), Flintbek, Germany

Content

The joint project TUNB develops a national coherent geological 3D-model of the deep underground of the North German Basin (Federal Institute for Geosciences and Natural Resources and the Geological Surveys of the States of Schleswig-Holstein, Hamburg, Niedersachsen, Bremen, Mecklenburg-Vorpommern, Brandenburg and Sachsen-Anhalt). This large 3D-model will be constructed on the databases of the Tectonic Atlas of Northwest Germany and the German North Sea Sector (GTA) and the Geophysical Map Series of the former GDR (GPK). Co-operating with the project partners, the overall aim is to achieve cross-border consistency of the 3D-model.

Resulting from prior project works, a geological 3D-model showing the base surfaces of the deep subsurface structures of Schleswig-Holstein has already been developed and will now be further improved. One key aspect is a more detailed classification of tertiary strata.

The understanding of deeper horizons is primarily based on data from oil and gas exploration, but the quality of these data is poor for the upper tertiary and quaternary. A much deeper insight into the shallow layering is provided by wells from hydrogeological investigations, which in turn do not cover the deeper horizons. So a combination of data from hydrogeological investigations and oil and gas exploration is used for the analysis of tertiary deposits. Using all these data, the base of Rupelium is modeled within the project TUNB.

The poster will give an overview of the data quality and working steps and will present the current state of work.

How might geological consistency “survive” seismic interpretation, generalization and 3D-modeling? – Conceptual ideas for the German North Sea Sector (TUNB)

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Content

In recent times geological 3D models are topic of major interest, not least because of their increasing importance in communication of scientific/geologic information to the public. In order to provide the user with reliable information, these 3D-models have to reflect a consistent geological evolution in best possible way, i.e. without any contradiction to known regional geological constraints (e.g. tectonic setting). However, geological consistency may be lost in the course of 3D model creation, especially during i) seismic interpretation and its ii) generalization prior to 3D modeling. Although seismic data provide a valuable tool for the interpretation of structural features in the subsurface, numerous reasons may prevent a sufficient seismic resolution of structural elements in the subsurface. Additionally, unequal distributed seismic information about complex structures, left the interpreter with an uncertainty in his interpretation. Moreover, seismic interpretation is often performed in a resolution much higher than it is possible to be represented in a 3D model. Therefore, subsequent to seismic interpretation, a suitable generalization is required, which reduces the structural elements included in the 3D model and, at the same time, maintains the model constraints. However, any generalization applied should be unbiased but must also comply for regional geodynamic constraints.

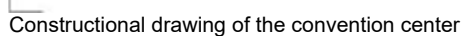
Within the present study, as part of the project TUNB of the BGR, these challenges will be addressed in the final 3D model of the German North Sea sector. Concerning data heterogeneity and gaps in seismic data, we will demonstrate based on exemplary 2D-seismic profiles how we used supra-regional concepts in the southern German North Sea sector allowing us a satisfactory and geological feasible interpretation of seismically “under-determined” areas.

We also will show by a step by step example how we deal with uncertainties of interpretation by a procedure of exclusion. Moreover, we will show “end members” resulting from seismic interpretation without regional constraints and generalization disregarding the regional geodynamic context. Especially around salt structures, where steeply dipping flanks and strong acoustic impedance contrast at the sediment-salt body contact leads to major decrease in seismic resolution. In this context, we will point out the different impact of a presumed salt glacier, salt wedge or salt mini basin in the light of an overall geological concept.

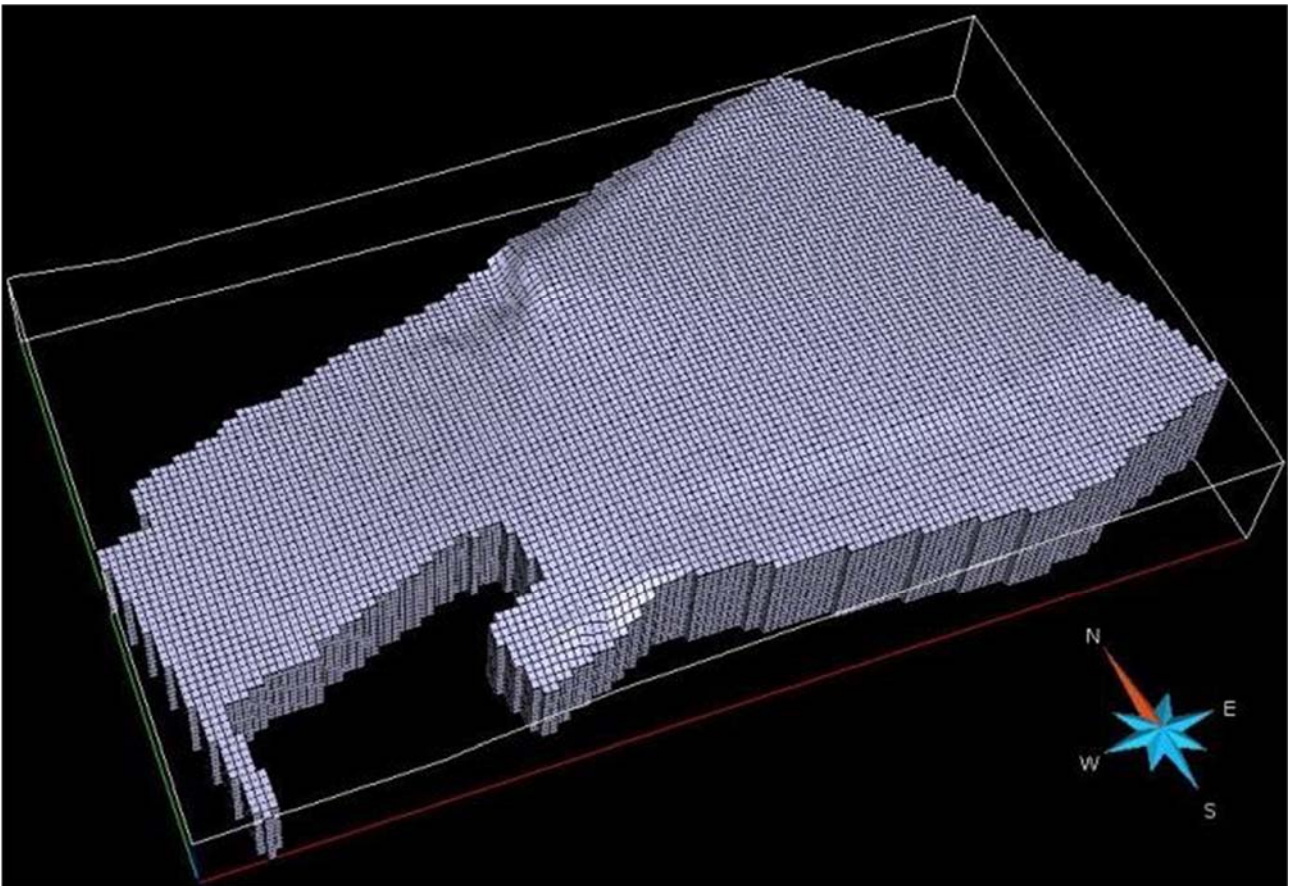
Applied Geosciences, TU Darmstadt, Darmstadt, Germany

Typically geological 3D-models do not include other information such as underground infrastructure. Therefore especially in urban areas respective models do not support needed functionality. To overcome this gap the case study Darmstadt_3D has been initiated.

The majority of the provided data is received as constructional drawings / floor plans. As a first step all existing and available data (from several municipal authorities, engineering or architect's offices, owner) will be gathered and, if necessary, scanned in.



Via CAD software the raw data is drawn and converted into serviceable GIS files (including a consistent spatial reference and assigned height values to all components). Afterwards a 3D modeling software (here GOCAD) is used to generate a single volumetric object, containing all data.



3D foundation / basement floor model of the darmstadtium

In the final stage it's possible to parameterize / attribute the developed object with all relevant specifications (e.g. building materials, surface impoundments / waterproofing, joints, year of construction etc.).

The implementation of underground infrastructure leads to a more precise geological model since respective parameterized objects replace geological objects and thus support more reliable processing downstream. From a hydrological view the building can be assumed as an impervious layer instead of e.g. a near-surface, high permeable weathered layer), which is going to influence a groundwater flow model significantly. Furthermore the comparison with surrounding geology (faults, unconsolidated sediments) and the groundwater settings can be helpful to identify potential risks for the technical infrastructure (e.g. subsidence, exposure to water).

KISS visualization of structural uncertainty in 3D models

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Content

Before the establishment of digital 3D models, geologists had to rely on 2D illustrations (maps, sections, profiles) to visualize their concepts of the deeper subsurface. Maps easily allow a highlighting of uncertain or unknown areas, from the blank space and the writing “hic sunt leones” (still a problem for the mapping geologist) in ancient maps to shaded areas with the description “assumed” and dashed formation boundaries. Contrary, visualizing uncertainties of geological features in a 3D model is much more difficult, since a surface in a digital 3D model (e.g. horizon, fault, salt-structures) is either present or absent. In consequence, this unfortunately gives the impression of an accuracy to the observer that is not provided by the model.

Although many studies deal with the mathematical calculation of uncertainties in 3D models, a suitable and, especially, practical approach for an (empirical) uncertainty visualization as a method to provide information to understand and cope with uncertainties of 3D-models is still missing. Therefore, in the present study we present different easy-to-generate possibilities to visualize these uncertainties within a 3D model.

The scope of them is to “Keep It Simple Stupid” to enable every interpreter to do it on the fly. The simplest way of highlighting uncertain areas is to mark those with a distinctive color-code on the modeled object or to visualize the used data-base (e.g. seismic, wells) together with the model. Another way is to create an “envelope” around structures that are not too well constrained by data. To catch/consider the wide range of interpretation within underdetermined areas (e.g. around salt structures) in the best possible way we suggest a threefold division of the interpretation of salt structures:

- Outer envelope: loss of seismic resolution,
- Inner envelope: onset of chaotic reflection pattern and
- Concept-based interpretation of the salt structure.

Based upon examples from the North German Basin we show the workflow to incorporate the picking of uncertainty in the interpretation of a structure, including the mapping of areas with low seismic resolution.

Modelling and characterization of sandstone reservoirs and fault zones of the Glückstadt Graben for hydrothermal utilization

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Content

Apart from the already explored and currently used hydrothermal reservoirs, a large geothermal potential is expected in deep-seated fault zones. The joint research project, “StörTief”, was carried out between 2013 and 2016 to further investigate deep-reaching faults and the probability for the migration of fluids.

This work, a component of the “StörTief” project, focuses on the 3D geological modelling of the Glückstadt Graben and the lithological characterization of deep-reaching faults and hydrothermal Mesozoic reservoirs. The 3D geological model of the graben visualizes stratigraphic horizons, their contacts to major fault zones and salt structures. Seismic data and well data were used in order to validate and improve the model. We analyzed well reports and interpreted geophysical well log data to obtain lithological and hydraulic parameters of the rock formations and fault zones.

We show depth and thickness maps of the reservoir formations and the geometrical parameters of major fault zones extracted from the 3D model. The faults are mainly N–S to NNE–SSW and NW–SE trending normal faults with average fault throws varying between 100 and 500 m and with vertical lengths up to eight kilometers within the graben. These large values may indicate wide damage zones and a higher potential of permeable pathways for fluids. The distribution of the investigated reservoirs varies vertically and laterally depending on the sedimentation and tectonic history. The interpretation of well data showed that the shape and the character of the well log data imply different facies patterns within a sandstone reservoir indicating regions with reasonable rock parameters for instance areas with high permeability, high porosity and low shale content. Based on the obtained results, we are able to detect regions of Schleswig-Holstein which presumably are suitable for geothermal usability. However, the prediction of permeability and potential migration of fluids within the fault zones connected to these sandstone reservoirs is not yet possible due to the lack of data. We propose fault zones which are worthy of further investigations, e.g. tertiary fault zones near the graben margins. The results of the study may help to improve the planning of future geothermal projects and to minimize the exploration risks.

Permeability-based 3D model of the subsurface of the city of Darmstadt, Hesse (Germany)

Habenberger, C.¹, Lehné, R.², Heggemann, H.²

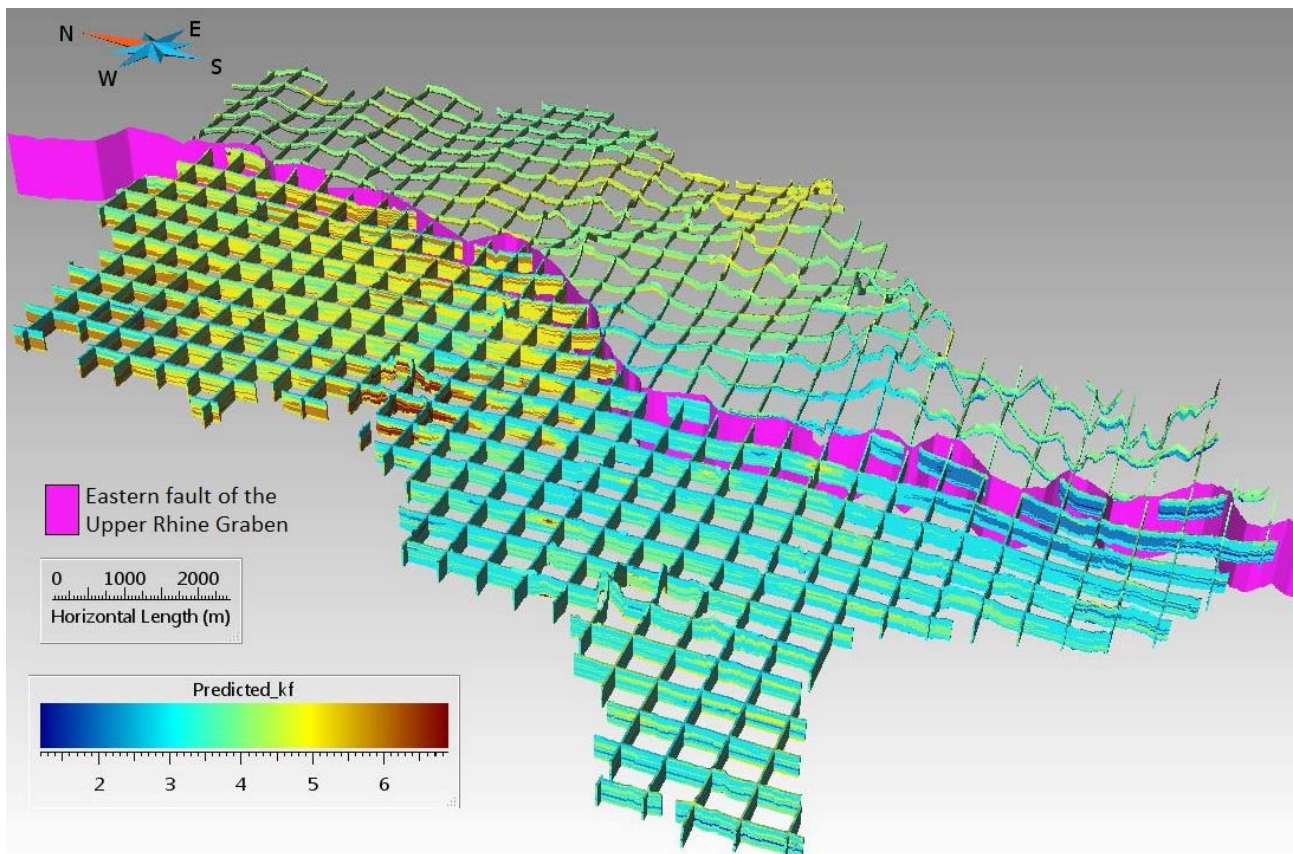
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Content

The project Darmstadt_3D, a cooperation of the Hessian Agency for Nature Conservation, Environment and Geology, the Geoinformation workgroup at Darmstadt University and the city of Darmstadt, targets a high-resolution 3D model of the underground of Darmstadt (Hesse, Germany). Works look for an integrated model that combines geology, hydrogeology as well as underground infrastructure. The model is supposed to help i) answering questions on the subrecent development of the URG and ii) to make geological content part of decision making in urban planning.

The geological setting has its origin in the Alpine Orogenesis and related tectonic stresses, which lead to the development of the URG. The eastern master fault of the URG separates Darmstadt into two parts, i.e. the western near-surface area with Quaternary sediments and the crystalline rocks of the Odenwald as well as the Rotliegend of the Spremlinger Horst in the east.

The 3D-model has been constructed using the softwares ArcGIS and GOCAD and is based on 1,086 quality checked boreholes from the borehole database of Hesse and the civil engineering department of Darmstadt. According to the petrographic description geological layers then have been parameterized by permeability classes and interpolated in ArcGIS. Higher permeability classes symbolize lower permeability and vice versa. The interpolated sections then have been migrated back into the 3D-environment in order to derive depth dependent homogeneous areas.



NE-oriented final 3D model of Darmstadt with the permeability classes (blue = low permeability to red = high permeability).

The 3D model shows transition zones of lower to higher permeability classes in NNW- to SSE-direction (fig. 1). These zones indicate i) a previously unknown Quaternary fault in the eastern part and ii) confirm the existence of the "Gräfenhäuser Bruchzone" in the western part, even if its shape most likely has to be re-described. Both faults fit the orientation of the stress field and the sinistral movement in the area. NW of the "Gräfenhäuser Bruchzone" is an area of very high permeability classes that possibly indicate another fault. Furthermore lateral entries (debris) from the rift shoulders are indicated.

Progress on the way towards a 3D model of Mecklenburg-Vorpommern: Salt structures, faults and lithostratigraphic layers of the Ludwigslust sub-area

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Content

Increasing subsurface uses in northern Germany, e.g. oil and gas exploitation, potash and rock salt mining, underground natural gas storage, brine disposal, usage of geothermal heat, production of drinking water etc., has highlighted the need to develop a strategic planning concept for underground space. Therefore, the Federal Institute for Geosciences and Natural Resources (BGR) and the Geological Surveys of the German federal states (SGD) have started in 2014 the project "Subsurface Potentials for Storage and Economic Use in the North German Basin" (TUNB).

The Geological Survey of Mecklenburg-Vorpommern will develop a 3D model of the northeastern part of the project area. 13 major lithostratigraphic layers between the bases of Zechstein and Rupelian, tectonic faults and salt structures will be visualized to support politicians and decision makers in underground space management. The first steps comprised data acquisition and control. More than 800 deep wells and about 4,250 seismic lines, which were mainly drilled and measured during the last 50 years of oil and gas exploration, are a good basis for modelling of typical reflector horizons that mark lithological surfaces close to stratigraphic boundaries.

The model area of Mecklenburg-Vorpommern is divided into 11 parts. The first model of the sub-area Ludwigslust with a size of 243 square kilometers was finished in 2017. It belongs to the pilot region of the TUNB project at the former inner German border. Besides 13 lithostratigraphic layers, 8 salt diapirs and 31 fault planes both below and above the Zechstein were modelled. All elements that cross the border to the adjacent federal states were harmonized. This was difficult because of different geological data sources, e.g. deep wells were mainly available from research drilling program of the GDR. The number of seismic lines in the border area that could be used for correlation was also limited.

The most challenging task was the identification and correlation of the major faults of the Rehna-Gülze fault zone. These faults cross the state border to Schleswig-Holstein twice due to changes in orientation from NE–SW in the north towards NW–SE in the south. Furthermore, for modelling of salt diapirs in cross border position, e.g. Nostorf and Werle, detailed knowledge of well constraints and interpreted seismic sections was necessary. The experiences gained will help us to continue modelling of the next sub-areas at the border to neighbouring federal states.

**Project TUNB North Sea – An overview of recent R&D work in the German North Sea sector
(part 1: Subsurface potentials)**

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¹Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany, ²Federal Institute for Geosciences and Natural Resources (BGR), Berlin, Germany

Content

Within the project „Subsurface potentials for storage and economic use in the North German Basin“ (German acronym TUNB), the Federal Institute for Geosciences and Natural Resources (BGR) and the geological surveys of the northern German federal states are developing a 3D model of the North German Basin (NGB) harmonised across the state borders.

Embedded in the TUNB project, additional research and development work is performed by BGR in the German North Sea area. Here, we present an overview of the current research topics in regard to the assessment of subsurface potentials for storage and economic use in the German North Sea. Moreover, additional research is carried out concerning more fundamental research topics, e.g. seismic velocity modelling or structural restoration and balancing of Mesozoic rifts (see Bense et al., this volume).

According to the horizons included into the TUNB 3D model, research on subsurface potentials is focused on stratigraphic units and structural phenomena, covering investigation of storage and caprock formations and barrier rock integrity as well as hydrocarbon potential and possible shallow gas deposits.

In more detail, the following topics are covered:

- detailed seismic mapping and seismic stratigraphic analysis of Triassic, Jurassic, Cretaceous and Tertiary sedimentary successions
- seismic mapping of amplitude anomalies in relation to shallow gas
- seismic mapping of source rocks in the NW German North Sea (Entenschnabel)
- development of a 3D basin and petroleum system model for the NW German North Sea
- spatial distribution and variation in the structural style of Tertiary polygonal fault systems, Quaternary tunnel valleys, and crestal faults of salt-structures, their spatial superposition, structural linkage and possible impacts on barrier rock integrity
- assessment of CO₂ storage potentials in the NW German North Sea

**Project TUNB North Sea – An overview of recent R&D work in the German North Sea sector
(part 2: Fundamental research)**

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Content

Within the project „Subsurface potentials for storage and economic use in the North German Basin“ (German acronym TUNB), the Federal Institute for Geosciences and Natural Resources (BGR) and the geological surveys of the northern German federal states are developing a 3D model of the North German Basin (NGB) harmonised across the state borders. Embedded in the TUNB project, additional research and development work is performed by BGR in the German North Sea area, continuing the systematic work of the “Tectonic Atlas of Northwest Germany and the German North Sea Sector” (GTA; e.g. [1]) and the project “Geopotentials German North Sea” (GPDN, www.GPDN.de).

The focus of our work is twofold: first to obtain a more comprehensive and detailed picture of the deeper subsurface and, secondly, to get a thorough understanding of individual structural features in their individual geodynamic context.

The fundamental research topics introduced here include:

- timing, spatial distribution and mechanisms of halotectonic deformation of Late Rotliegend sedimentary successions in the Central and Southern German North Sea
- spatial distribution and evolution of erosional valleys along the Base Cretaceous Unconformity and its possible causes
- detailed seismic mapping and analysis of faults and salt-structures
- structural style, timing, kinematics and subsidence history of Mesozoic rift-raft structures (e.g. southern Central Graben, Horn Graben)
- structural restoration and structural balancing of areas subjected by Mesozoic rifts and/or intense halotectonic overprint
- subsidence analysis and related mechanisms within the NW German North Sea
- seismic velocity modelling
- visualising uncertainties in 3D models
- cross-border harmonisation of seismic interpretation data, stratigraphy and 3D models
- development of data processing and 3D modelling workflows for handling of heterogeneous, multi-age and multi-survey seismic and well interpretation data

References:

[1] Baldschuhn R, Binot F, Fleig S & Kockel F, (2001), Geotektonischer Atlas von Nordwestdeutschland und dem deutschen Nordsee-Sektor. Strukturen, Strukturentwicklung, Paläogeographie, Geologisches Jahrbuch Reihe A, 1-88, 153

Regional scale subsurface model of the Altmark, Saxony-Anhalt

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Content

In the scope of growing attention towards sustainable and economic use of the deep subsurface in Germany the demand for advanced tools like 3D models for underground spatial planning arises. Popular examples of potentials are geothermal energy, the storage of renewable energy, the safe disposal of hazardous substances, hydrocarbon extraction or storage as well as CCS or mining. These applications may get in each other's way when competing for the same or spatially nearby geological features. In the framework of the joint project TUNB (Subsurface Potentials for Storage and Economic Use in the North German Basin) initiated by BGR, the state geological surveys of northern Germany are developing a harmonized 3D structural geological model of the North German Basin with 13 major base horizons between the Upper Permian and the Paleogene.

Here we present the part of the model for the Altmark region in northern Saxony-Anhalt. This regional scale model consists of horizons, faults and salt domes as triangulated surfaces. The construction was done with the SKUA-GOCAD software by Paradigm®. For the area an extensive database was available not least because of its long history of natural gas exploration and geological survey operations. This reflects in approx. 900 boreholes with measured depths greater 300 m, about 2000 interpreted seismic lines and maps for 20 seismostratigraphic horizons with contours and structural features. Utilizing custom database solutions, GIS and SKUA-GOCAD we conducted a comprehensive quality control of the whole dataset and a stratigraphic generalization of the occurring units for the purpose of the regional scale model. The modelling itself was done using the SKUA Platform which is based on geologically constrained volumes, thus improving the consistency of the results. From this 3D model the surfaces relevant for TUNB are extracted. Results display the depth and extent of the base horizons of prominent formations of the North German Basin in coherency to each other. More importantly and for the first time fault zones of regional importance were modelled in a consistent three-dimensional context. The Altmark fault network therefore gives new insights into the structural evolution of the region. For most of the salt domes readily available information about structure and extent was greatly improved. In combination with our database, the model can be used for parametrization but also as a 3D geo-information system.

Storage potentials in the deeper subsurface of the Central German North Sea

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Content

This study assesses the potentials for subsurface storage in the Central German North Sea in a reconnaissance scale, investigating specific stratigraphic units based on standardized criteria for lithology, spatial distribution and thickness. The study aims to 'site screen' the geological subsurface of the Central German North Sea on superregional scale, highlighting the most promising areas for CO₂ storage ("prospective areas"). Additionally, we provide data for future assessment steps, such as site selection and initial characterization as well as storage capacity estimations.

Our procedure in assessing the storage potentials in the study area consists of three consecutive steps: (1) Identification of eligible reservoir and barrier rocks based on lithological, stratigraphical and geophysical data; (2) Mapping of spatial distribution, depth and thickness of identified reservoir and barrier rock units by seismic and well data interpretation as well as implementation of all available data in a consistent, generalized 3D model; (3) Identification of 'prospective areas' by querying the 3D model with minimum criteria for the geological storage of CO₂.

Based on aforementioned criteria, prospective sites with favorable reservoir and barrier rock units have been identified. Results were compiled in map format, combining information on depth, thickness and spatial distribution, complemented by additional reservoir geologic information (e.g. lithological parameters).

Identified reservoir rock units comprise the Upper Rotliegend, the Middle Buntsandstein, the Upper Keuper and the Middle Jurassic. Identified barrier rock units include the Zechstein, the Upper Buntsandstein, the Lower Jurassic and the Lower Cretaceous. The most common combinations of barrier and reservoir rock units were combined to so-called "reservoir-barrier rock units". Generally more than three, locally up to six reservoir-barrier rock units can be observed in the central German North Sea. However, some locations provide no reservoir-barrier rock units, especially due to erosion, facies changes of younger succession and/or halokinesis of Zechstein salt.

Stress variation within stratigraphic sequences – a site selecting factor for nuclear waste repositories

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Content

Understanding of the in-situ stress state in the Earth's crust is important in science and industry likewise. Several methods are used as stress indicators, that provide information on the stress tensor orientations or stress magnitudes. However, no or only few stress data are available for most investigated areas. Interpolation or extrapolation of such data is quite common, but discontinuities and inhomogeneities have locally a strong impact on the orientation and magnitude of stresses. Geomechanical-numerical modelling allows representing these features to estimate the full stress tensor continuously in the 3D space. These physics-based stress predictions allow detailed insight into the present day stress state plus potential future shortening until failure. In particular, the knowledge of these stress state characteristics is important regarding the long-term stability of geological barriers and underground constructions of nuclear waste repositories.

For the deposition of the Swiss high-level radioactive waste, three candidate siting areas are identified in the Alpine foreland. The sedimentary succession overlays the basement, consisting of Variscan crystalline rocks as well as partly preserved Permo-Carboniferous deposits in graben structures. The Mesozoic sequence represents nearly the complete era and is covered by Cenozoic as well as Quaternary deposits. The target horizon (designated host rock) is an >100 m thick argillaceous Jurassic deposit (Opalinus Clay). To enlighten the impact of site-specific features on the state of stress within the sedimentary succession, 3D geomechanical-numerical models with elasto-plastic rock properties are set up.

Model results indicate stress perturbation due to topography and fault geometry and friction properties within a distance of < 1 km. Inside the upper stiff formations (e.g. limestone), stress magnitudes and anisotropies are large. These stiff formations carry the load due to far field tectonic forces, whereas weak formations, like the argillaceous target horizon for the waste disposal, exhibits smaller stress magnitudes. Using the fracture potential as a more unambiguous indicator, the stiff overburden rocks are closer to failure than the target horizon for the repository, whereas stiff formations below the target rocks are far from failure. Stress profiles versus depths indicate, that horizontal stresses vary strongly within only tens of metres by a magnitude of >10 MPa depending on the lithology.

Transformation of printed paper seismic data into SEG-Y files

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Content

Many academic or governmental institutions and commercial organizations have been collecting paper seismic data over the last decades. Especially in frontier regions and areas “abandoned” by newer exploration activities by the E&P industry this “old” seismic data may still be of significant value in academic use. However, the degrading quality of the data due to the progressive deterioration of the aging paper seismic records and the ubiquitous use of seismic interpretation software these days require a technique to save paper seismic data as well as to make the data accessible by modern interpretation software packages.

In the last decade, a number of commercial software packages and services by specialized companies are offered for a vectorization of paper records, i.e. the conversion of a two dimensional bit-map of a paper record into a standard file of traces and time-series values (e.g. SEG-Y). Vectorization services and commercial software solutions are often quite expensive, especially for academic institutions. Available pricier software solutions generally provide limited editing and batch functionality as well as data interoperability.

In this report we provide a manual describing customizable, low-cost workflow procedures for batch processing, georeferencing and transformation of bit-map images of paper records into SEG-Y files using a deft combination of different free software packages (available under the General Public License (GPL)) and/or only one budget commercial software product. Although we introduce an additional no-cost workflow, the use of the commercial software package significantly increase the interoperability, functionality and adaptability of the procedure.

We also illustrate and describe a number of typical pitfalls in vectorization of paper seismic data and give some recommendations for the data preparation prior to batch vectorization.

Session 10.1: Applications in 3D Geological Modelling.: Talk

Session 10.1: Applications in 3D Geological Modelling.: Talk
A-449

"Geologic Toolbox": Three-dimensional GIS Tools for Subsurface Model Visualization and Publishment

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Content

1. Project Aims

Geographic information system (GIS) technology offers a promising means to support spatial decision-making processes or to communicate geo-information to the public. This also applies to geologic application scenarios. Since 3D functionality is available inside GIS environments today, and since platforms to access geospatial information on the Web are utilizable by almost everyone, the provision of geologic models inside 3D GIS seems to be highly desirable.

However, GIS environments rarely support geologic modeling approaches, e.g. topologically interrelated surface layers and volumetric solids or voxels in between, or 3D triangulations (instead of GIS-like "2.5-D" surfaces), what would be needed to represent stratigraphic layers or discontinuities. Moreover, specific software tools such as drillhole data import, cross-section generation, or model consistency checks (e.g. surface/surface intersection) often are missing on the GIS side.

Thus, to overcome the mentioned deficits while opening the application potentials offered by GIS technology to geologists, in the context of the "Geologic Toolbox" project a suitable generic software-architecture will be set up.

2. Solution Approach

As a first prototype implementation, a toolbox extension for ESRI's prominent ArcGIS Pro will be developed and examined with respect to its geology-specific functionality as well as technical aspects such as processing and rendering performance and software abstraction. The software will be provided as open-source Python application via GitHub.

The works are carried out at the Geovisualization Lab at Bochum University of Applied Sciences in cooperation with ESRI Deutschland GmbH. The open project is accompanied by the Ruhrkohle AG and the Hessian Agency for Nature Conservation, Environment and Geology (HLNUG).

3. Results and Conclusions

The prototype implementation offers promising application perspectives. Particularly emphasized are the option of combining geologic data with geo-information from other application areas, Web publishing options (e.g., 3D Web scenes in ArcGIS Online/Portal), and highly-interactive data exploration facilities.

However, there still is a demand for specific model importers and more data exploration tools. From the software engineering perspective, the introduction of an abstract conceptual geologic GIS model (interface classes abstracting from the underlying GIS implementations) will be part of further research and development activities.

3D-Model of the subsurface in the Eastern Altmark, Saxony-Anhalt

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Content

The deep subsurface of the North German Basin (NGB) provides a high potential for sustainable and economic use in the context of Germany's greenhouse gas emission targets. Even though the Eastern Altmark (northeastern Saxony Anhalt, Germany) is only poorly explored, this region plays a major role for the understanding of the structure, parameters and geopotentials of the NGB towards cross-border spatial managing and harmonization efforts in Germany. The investigated area covers ~1600 km² between the Western Altmark and Western Brandenburg. As a part of the Central European Basin System (CEBS) the stratigraphy of the Eastern Altmark is dominated by the up to 1 km thick Late Permian evaporitic Zechstein Group overlain by an up to 4 km thick stratigraphic pile of Mesozoic and Cenozoic sedimentary rocks. The presence of thick salt in the Eastern Altmark has significantly influenced post-salt sedimentation and tectonics due to halokinetic movements and diapirism.

In this contribution we present results from the first three-dimensional modeling and evaluation project in the Eastern Altmark area. A comprehensive database of 2D reflection seismic sections, well data and contour line maps was prepared and used to investigate the tectono-stratigraphic evolution from Late Permian to Cenozoic times. 3D-modeling was conducted using the Paradigm® SKUA platform, which is based on constrained volumes. Five regional fault systems, three salt diapirs and a couple of stratigraphic horizons of regional importance were identified and geometrically modelled. Special emphasis was given to halokinetic and tectonic processes.

Our results show that the structural pattern of the Eastern Altmark is dominated by NNE-SSW and NW-SE trending fault zones and various salt structures. Mild Late Jurassic extension/transtension induced halokinetic movements intensified by differential loading and buoyancy halokinesis. NNE-trending fault zones are dominantly of extensional to transtensional style. Fault zones with a NW-SE strike direction imply extensional and contractional movements during Jurassic and Cretaceous times, which were locally accompanied by halotectonics. At the intersection of main faults salt diapirs intruded into cover sediments. According to our observations, the Eastern Altmark model reflects all characteristics of the large-scale structural and stratigraphic evolution of the NGB and will be applied for further validation and parametrization approaches of the deep subsurface.

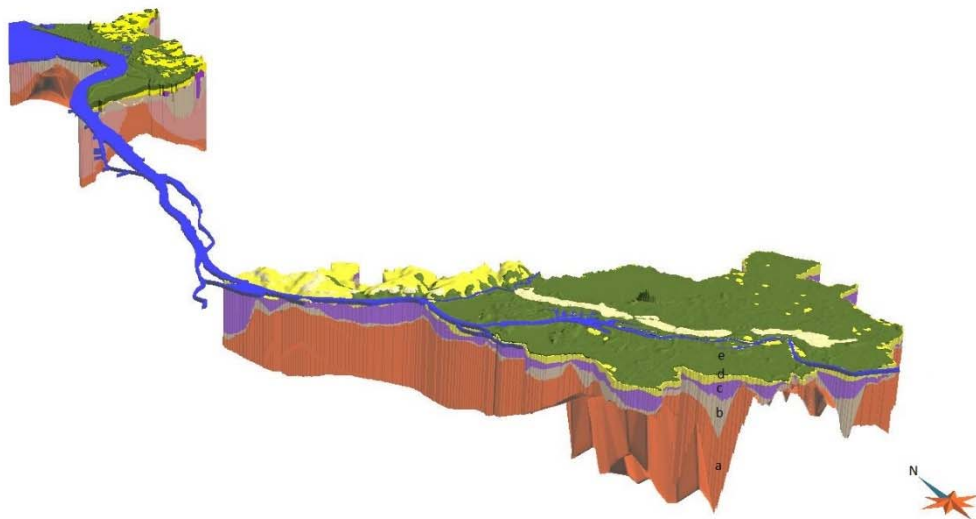
A Parameterized 3D-Structure-Model Of The State Of Bremen (Germany)- An Application For Detailed Groundwater Flow And Transport Studies

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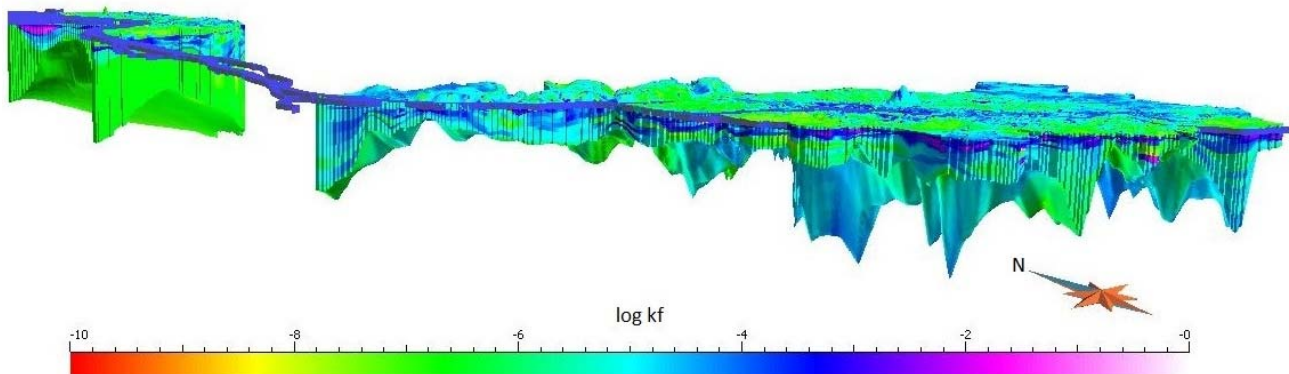
Content

In urban areas the geology is of particular interest for domestic problems. Bremen is situated in the marshy lowlands of the Aller-Weser-glacial valley. Buried valleys, formed during the elsterian glacial stage, act as main groundwater-reservoirs today. The overlying predominantly clayey and muddy sediments protect the groundwater from harmful substances. The complex structure and heterogeneity of porous quaternary sediments affect the direction, the spreading and the velocity of the groundwater flow sustainable. The geological survey of Bremen (GDfB) developed a 3D-structural model of these units by using the software GOCAD (Paradigm®).



3D- structural model of Bremen and Bremerhaven. Units from the bottom to the top: a: tertiary sediments, b: elsterian sandy sediments, c: Lauenburger basin facies, d: saalian sandy sediments and moraine

The model is based on several borehole information derived from our data base. The parameterization of the cell-based model allows the inclusion of more detailed information like the hydraulic conductivity [1]. A groundwater flow model is developed using the parameterized model.



Parameterized structural grid from Bremen and Bremerhaven, cell size 100 x 100 m

High resolution models in restricted areas (e.g. Bremen-Hemelingen), affected by contaminated groundwater bodies, are an example for modelling the spreading of the pollution plume with a transport- and reaction model (MT3D) in areas with less or irregular distributed data. Therefore virtual boreholes were placed by a random process; allow us to construct a virtual heterogeneous aquifer with irregular distributed clay lenses. The model verification is in good accordance with measured data or the observed contamination plume, respectively. This procedure considers macrodispersion effects.

3D- structural and constitutive groundwater flow models represent easily accessible management tools for spatial information, offered to the public, economy and administration as e.g. web-services. They offer a planning aid for construction projects and energetic or substantial use of groundwater resources and support transport- and reaction models to monitor and prognosticate contamination plumes in different time steps.

References:

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An integrated Geoscience approach to de-risk the trap and trapping mechanism of the Oligo-Miocene potential offshore Western Nile delta basin Egypt

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Content

The Exploration in the offshore Nile Delta province has revealed several hydrocarbon plays. The deep marine turbidites is considered one of the most important plays for hydrocarbon exploration in the Nile Delta. These turbidites vary from submarine turbidite channels to submarine basin floor fans.

The Nile Delta is underlain by a Jurassic rift margin formed with the opening of the Neo-Tethys, and was inverted in part by collision-related compression in the Late Cretaceous and Eocene (known Syrian Arc I and II). The southern basin margin has a steep fault-bounded hinge that exerts a fundamental control on the subsequent deposition of slope canyon and turbidite channel reservoir systems of the Cenozoic basin fill. The turbidites play comprises interbedded shales and regional flooding surfaces proven to provide good seals; Miocene-age compressional pulses that reactivated structural fabrics, formed traps and terrestrial-dominated source rocks associated with slope turbidite sediments.

An integrated exploration approach was applied for a selected area within offshore western Nile Delta. Using a variety of geophysical and geological data to assess the prospectivity of the Pre-Messinian sequences. This study depends on integration of several disciplines for a new detailed interpretation and characterization of the sub-Messinian structure and stratigraphy, which was based on regional geological correlation of seismic markers and honored the available well data.

The interpretation focused mainly on the main tectonic events seismic markers top Cretaceous, Oligocene and Miocene sequences. The seismic expression of stratigraphic sequences shows a variety of turbidite channel/canyon systems having examples from West Nile Delta basin discoveries and failures. The approach is focusing on stratigraphic analysis and structural analysis for the area of interest by tying the major regional geological events with its corresponding stratigraphic and structural seismic events.

A detailed structure restoration studies have been carried out to predict each trap timing and style relative to the expulsion time of thermogenic gas.

Tying the variety of tectonic styles, depositional patterns and basin maturation in West Nile Delta basin to the regional geological context provide a favorable understanding of trapping conditions for commercial hydrocarbon generations and accumulations.

High resolution 3D geological modelling of the Prael disposal site (Sprendlingen, Rhineland-Palatinate, Germany)

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Content

The area to be modelled is the former disposal site for industrial waste “Prael”, about 250 m west of Sprendlingen (Rheinhessen). Geologically the disposal site is located in the Mainz Basin. Deposits contaminated groundwater in Sprendlingen.

Three geological units have been modelled as triangulated surfaces: the upper boundaries of the Tertiary, the terraces as well as the deposits in the channels, which are characterized by fine- and coarse-grained compounds.

The 3D model was supposed to help answer the questions about i) the distribution of terraces (the upper aquifer) and whether there are hydraulic contacts between them, ii) the course of the channels, which are very important for the transport of contaminants, and iii) to find out the preferred flow paths of the groundwater. Additionally, groundwater surfaces were created by interpolating the values from measurement campaigns. The present 3D model is the basis for further remediation activities, including the planning of drillings as well as an intended groundwater flow model.

Due to the long history of remediation, bore logs and stratigraphic interpretations of more than 400 wells, covering an area of 1 km², have been provided. In addition 29 cross sections could be considered, based on the bore logs. The input data were completed by the results of hydrochemical analyses and pumping tests. The Tertiary surface is dipping towards the East and shows typical terrace levels (altogether 29 terrace elements). Most of them are hydraulically isolated. Channel structures were modelled north and south of the sealing wall, revealing the highest concentrations of contamination in the southern channels, outside the sealing wall. Most parts of the channel structures are filled with eroded material of Tertiary silt and clay as well as terrace sediments.

The distribution of the terraces, as it is postulated in the 3D model, could be verified by the comparison with pumping tests.

Groundwater surfaces were interpolated separately for the areas inside and outside of the disposal site, because the sealing wall represents a hydraulic barrier. Their flow direction follows the dipping direction of the Tertiary surface, i.e. from West to East. Groundwater mainly is confined to the coarse grain sediments of the terraces and channel fillings. The assumed inverse gradient along the sealing wall (hydraulic gradient from outside to inside) could be verified. Only at the south eastern part the gradient is not inverse.

Results of a 3D facies modelling attempt in the Lower Main Plains (Frankfurt, Germany)

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Content

In the last decades, geological 3D-modelling became a state of the art technology to support planning and decision making in various fields. While surface based models, addressing stratigraphic or genetic boundaries, lead to a better understanding of the geometry and development of the study area, the usability of content derived, especially in unconsolidated rocks or with high facies variations, is limited due to missing parameterizable volumes. To overcome this gap, surface models can be used as a conceptual starting point for defining voxel-based geobodies, which then can be populated with information derived e.g. by geostatistical simulation and prediction of characteristic properties, lifting the usability of respective 3D-content significantly.

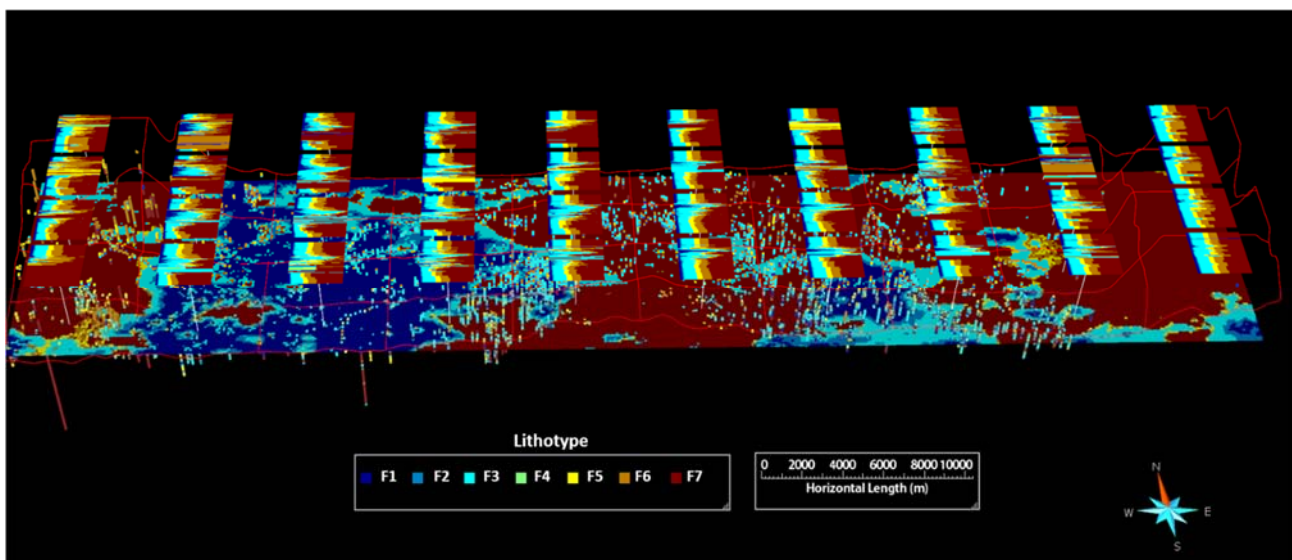


Figure 1: Subset of the 3D model area. Borehole information, facies trend maps and a matrix of the vertical lithotype proportions were used to simulate grain size distribution

In cooperation with the Hessian Geological Survey, this integrated approach has been used to develop a parametrized 3D-model of the unconsolidated sediments for large parts of the Frankfurt/Rhine-Main metropolitan area. From the geological point of view works focus on the Cenozoic subsidence sites of the Lower Main Plains, which host sediments of up to 600 m thickness, being important groundwater aquifers and supplier for raw materials. Based on grain size distributions and resulting permeabilities, seven lithotypes have been defined for parameterization, indicating changes in facies and thus providing a significant benefit for users. Facing problems like categorical values, a heterogeneous distribution of data and varying vertical trends, it turned out that most common interpolation methods do not provide sufficient results for parametrization where facies-depending characteristics need to be considered. Therefore, in this attempt the Truncated Gaussian simulation algorithm was used together with horizontal trend maps and a matrix of vertical lithotype proportion curves [1] as secondary data (Fig. 1). First results show a good accordance between well data and the conceptual model. Facies boundaries clearly can be observed in the parametrized model. Further analyses will reveal whether structures like fluvial channels became visible during parametrization, leading to a refinement of the conceptual model and a better understanding of the depositional environment.

References:

[1] YARUS, J. M., CHAMBERS, R. L., & MAUČEC, M. , (2012), Facies Simulation in Practice: Lithotype proportion mapping and Plurigaussian Simulation, a powerful combination, In Paper P-014 presented at the 9th International Geostatistics Congress, Oslo, 11-15

The first step to a 3D model of the North German Basin – The TUNB “Pilotregion”

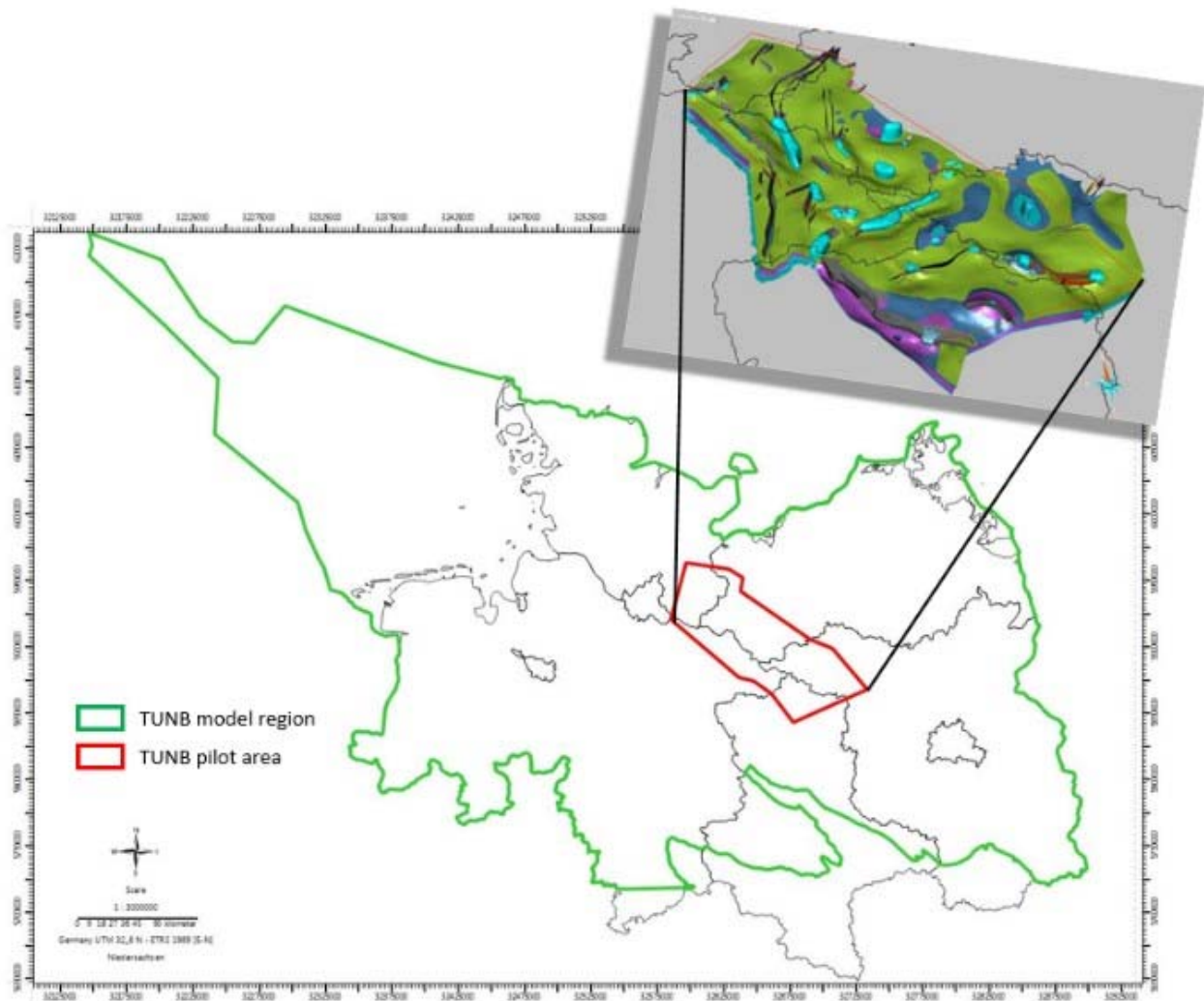
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Content

Utilisation of the deep subsurface in Germany is continuously increasing. Next to the established production of mineral water, thermal water, and hydrocarbons, the deeper subsurface will also be used for the production of hydrothermal energy and the storage of renewable energy such as compressed air and synthetic natural gas, or potentially carbon dioxide. The different demands raise the need for more detailed geological information, e.g. in the form of 3D models of the deep subsurface. The project “Subsurface Potentials for Storage and Economic Use in the North German Basin (TUNB)”, starting back in 2014, aims to create such a model.

The model of the North German Basin will be created by the Federal Institute for Geosciences and Natural Resources (BGR) and the state geological survey organisations (GSO) of the north German federal states Schleswig-Holstein, Niedersachsen, Mecklenburg-Vorpommern, Brandenburg, Sachsen-Anhalt. While every GSO is responsible for its territory, the BGR is responsible for modelling the area of the German North Sea. Due to quite heterogeneous data bases, two different Atlases are in use, one containing structural contour and isopach maps of seismic reflection horizons [1], the second builds on lithostratigraphic units [2], a lot of effort has been taken to harmonise the data and the modelling approaches.



Location of the Model

As a first step a pilot modelling area was chosen to develop and check harmonisation, working and documentation routines. The pilot area covers a small region, where the five federal states lie in close proximity to each other. It stretches over 150 km in NW-SE and 50 km in E-W direction and is located at the former inner-German border SE of Hamburg (see figure).

The model comprises 16 horizons, 24 salt structures and more than 200 faults. It covers about 7,800 km² (~5% of the final model). The model of the "Pilotregion" will also serve as testing area for future work (volume modelling, parametrization, distribution). [1] [2]

References:

[1] Reinhardt, H. G., (1991), Regionales geophysikalisches Kartenwerk der DDR. – Unveröffentlichtes Kartenwerk/Bericht, VEB Geophysik, Leipzig

[2] Baldschuhn, R. Binot, F. Fleig, S & Kockel, F, (2001), Geotektonischer Atlas von Nordwest-Deutschland und dem deutschen Nordsee-Sektor, Geologisches Jahrbuch, Reihe A 153, 1-88

Unraveling structurally-controlled mineralization through multiscale 3D models – An example from the Mount Tom Price iron ore deposit, Hamersley Province, Australia

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Content

The formation of banded iron formation (BIF)-hosted high-grade iron ore deposits of the Hamersley Province (Australia) has been debated for decades. Structural control on their formation is widely accepted whereby infiltration of hypogene and supergene fluids along fluid pathways (e.g., normal faults) resulted in upgrading of BIF to iron ore by metasomatic alteration. However, evidence for the proposed metasomatic reactions is rare, especially along fluid pathways and the nature of the complex 3D geometry of brittle and ductile structures in the Hamersley Province remains poorly understood.

We aim to determine the deformation mechanisms that led to the evolution of the structural frameworks of BIF-hosted iron ore deposits on all scales. Our approach is based on the established principle of self-similarity, whereby small- and meso-scale structures are extrapolated to macro- and deposit-scales and vice-versa. To do this we employ a range of state-of-the-art 3D modelling techniques. Microstructures and mineral textures are visualized by 3D X-ray tomography and scanning electron microscopy. Deformed hand specimens are modelled by serial sectioning, digitization, and explicit and implicit 3D modelling (using Move by Midland Valley, Leapfrog by AranzGeo). A 3D model of the Mount Tom Price iron ore deposit (operated by RioTinto Ltd.) was created using implicit modelling techniques based on 50 years of mining data.

Our study indicates that the style of deformation in Hamersley Province BIF is controlled by differences in rock rheology, contrasting fluid flow properties and layer thickness variations. It also explains the synchronous development of brittle and ductile structures, as well as the variation in the geometry and continuity of faults and folds. Deformation is controlled by fluid-assisted dissolution–precipitation creep of quartz, which leads to the remobilization of silica on all scales. Our analysis also reveals previously undetected strong porosity differences in BIF that may have channeled lateral fluid flow, leading to continuous infilling of iron oxide colloids, which are potential precursors of iron ore minerals. We conclude that iron ore formation was not only passively controlled by deformation structures but that the formation of the structures themselves and the associated physicochemical processes played a fundamental role in the formation of BIF-hosted iron ore deposits.

Session 10.1: Applications in 3D Geological Modelling.: Keynote speaker

Session 10.1: Applications in 3D Geological Modelling.: Keynote speaker
A-577

Challenges and approaches in 3D geological modeling of the Glückstadt-Graben

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Content

In the course of the joint project “StörTief” (LIAG Hannover, LLUR SH Flintbek, KIT Karlsruhe, 2013-2016) the Geological Survey of Schleswig-Holstein studied deep-reaching fault zones and sandstone formations in the Glückstadt-Graben area to provide planning tools for geothermal utilization.

A consistent geological model was constructed to visualize the graben structure with its stratigraphic horizons, major fault zones and salt diapirs. The model is based on the Tectonic Atlas of NW-Germany. Wells and seismic profiles were used to validate and to improve the model. Despite of the remaining uncertainties and challenges in 3D modeling, a first revision and careful correction of the Tectonic Atlas were achieved. The modeling work is currently continued by the TUNB project. We analyzed the lithological composition, the sandstone thickness, the facies and the hydraulic parameters such as porosity and permeability at well locations using geophysical well logs and reports. Different approaches to parameterize model units were investigated to visualize parameters, such as sandstone units and other obtained lithological information. The 3D parameterization is a demanding task and often restricted by the data distribution and provided modeling tools. The 3D interpolation of the lithology in stratigraphic grids leads to reasonable results in small to intermediate regions. In a state-wide scale, this procedure is not yet advisable due to the complexity of the geology and the grid structure. In another approach, thickness values at well locations were calculated and interpolated to integrate top and base horizons of sandstone units into the model. The challenges were the heterogeneity of the data quality and data distribution, the bridging of the data gaps and the prevention of artefacts.

We extracted depth and thickness maps of relevant stratigraphic units and sandstone formations, as well as geometrical parameters of the deep-reaching fault zones. In this project, these results are used to indicate suitable areas for geothermal exploration. However, the 3D model can be used for several applications, for example for evaluating other economic subsurface potentials and usages. It is also an important base for numerical simulations of processes and modeling of physical rock parameters such as temperature, heat flow and hydraulic conductivity.

Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.: Poster

Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.: Poster
A-224

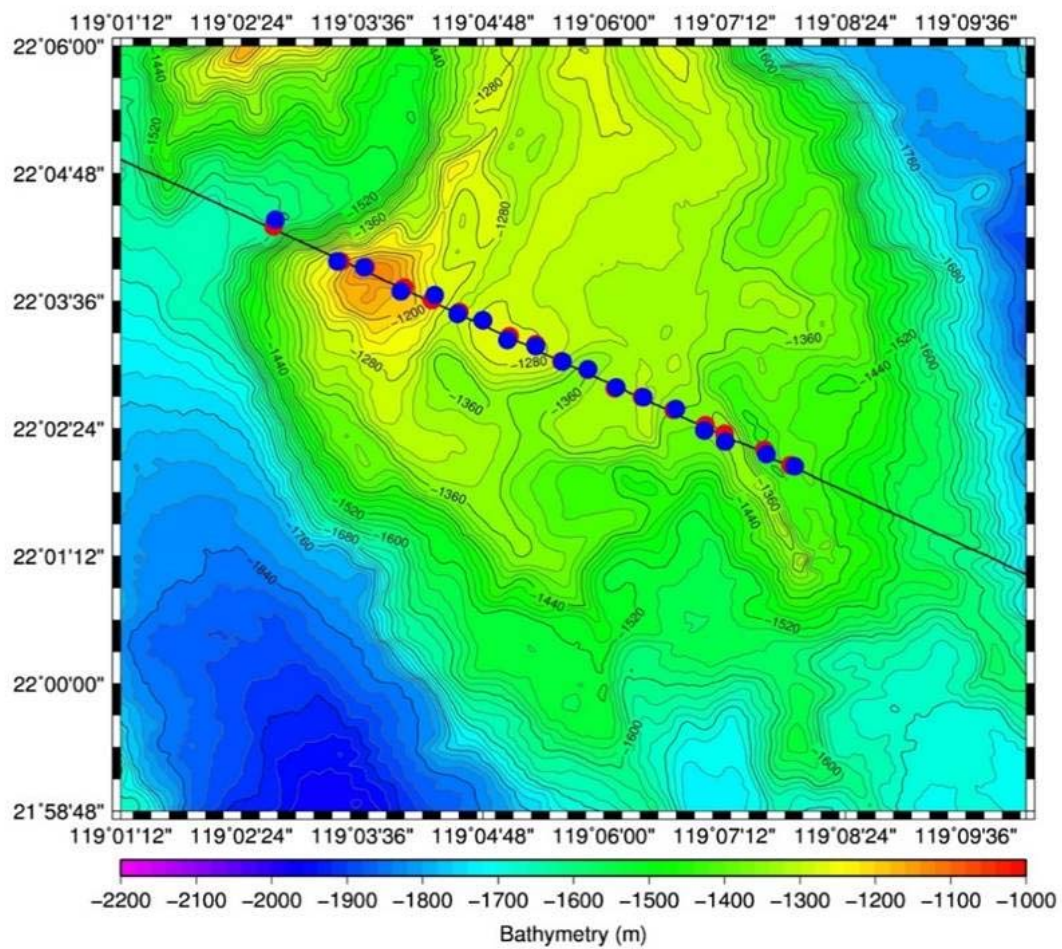
Assessment of Submarine Slope Stability on the Passive Continental Margin

Hsu, H.-H.¹, Dong, J.-J.², Cheng, W.-B.³, Su, C.-C.⁴

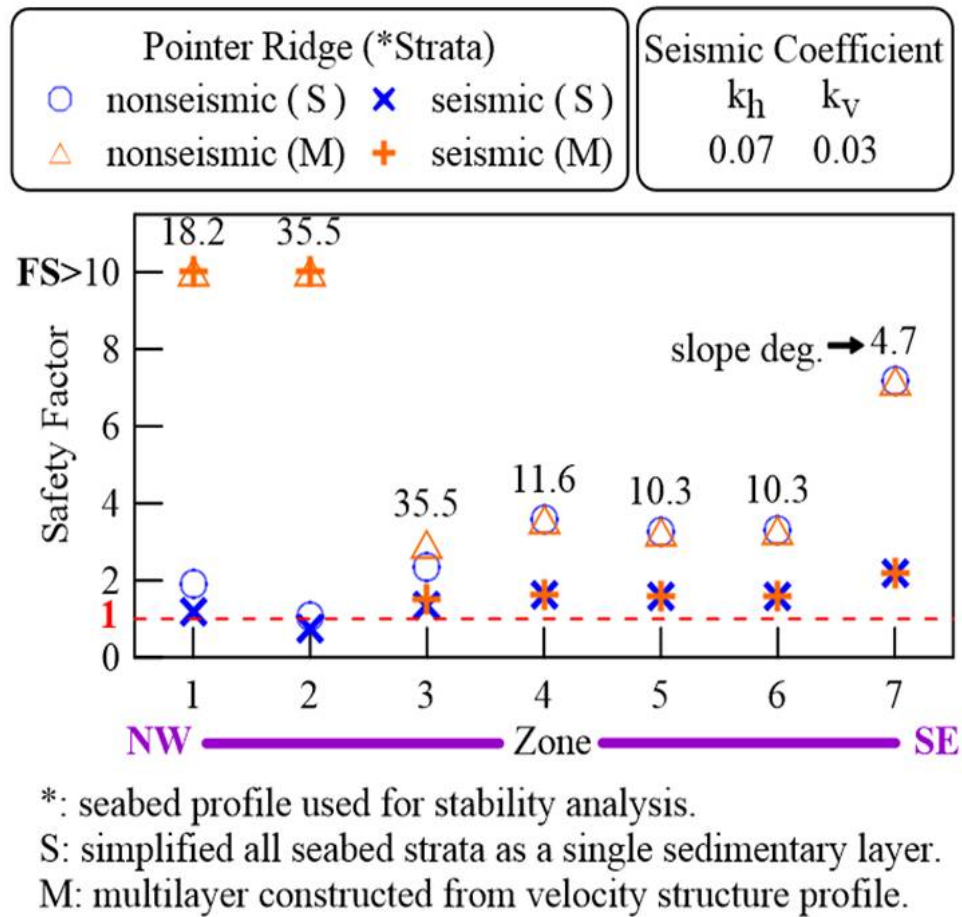
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Content

The abundant gas hydrate reservoirs are distributed in the southwest (SW) off Taiwan. To explore this new energy, geological methods were systematically used and mainly emphasized on the storage potential evaluation. However, the geotechnical characteristics of submarine sediments are not quite clear and are needed to be well studied. In addition, the correlation between gas hydrate dissociation and submarine slope stability is also an important issue. [1] [2] [3] In this study, two submarine profiles on the passive continental margin were selected and assessed their slope stabilities by considering two factors (seismic forces and number of sedimentary layers). The gravity corers obtained from Pointer Ridge and Palm Ridge to conduct soil laboratory tests. The physical property tests and isotropically consolidated undrained (CIU) triaxial tests were carried out to establish reference properties and shear strength parameters. Before the stability analysis is performed, it is necessary to construct the seabed profile. For each submarine profile, data from P-waves and from S-waves generated by P–S conversion on reflection from airgun shots recorded along one line of ocean bottom seismometers were used to construct 2-D velocity sections. The seabed strata could be simplified to be only one sedimentary layer or to be multilayer in accordance with the velocity structure profile. The physical property test results show the soils are high porosity materials and grouped as silt. Results of slope stability analysis show the safety factors (FS) are obviously different in considering the number of sedimentary layers, especially for a very thin surface layer of sediments on a steep slope. The simplified strata condition which treated all seabed strata as only one sedimentary layer might result in the FS lower than 1 and the slope was in an unstable state. For multilayer condition, the FS is higher than 10 and in a stable state.



Detail bathymetry of Pointer Ridge off SW Taiwan. Ocean bottom seismometers (blue dots) are distributed along the black line.



Safety factor (FS) of slope stability analysis under different simulate conditions.

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**Distribution of Natural Marine Methane Emissions along Polar Continental Margins:
Svalbard vs. South Georgia**

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Content

Methane emissions have been found in all oceans along continental margins and those in polar regions have gained special attention as potential source for atmospheric methane in the context of global warming. However, a solid understanding of the distribution, transients and factors controlling the methane release is essential to evaluate their importance in a global context. We compare two polar shelf areas, offshore Svalbard and South Georgia, which are characterized by the occurrence of widespread gas emissions but show contrasting patterns with respect to their distribution, source and migration pathways. Gas emissions offshore Svalbard had previously been documented, and recently we reported on new data collected during two RV Heincke cruises in autumn 2015, which show that seepage is not restricted to a specific area west of Prins Karls Forland but it is widespread along the entire shelf [1] and within the fjords. Our analyses of their distribution indicate a relation to major tectonic structures and sedimentological deposits and possibly indicate a relationship with permafrost captured methane reservoirs. First evidence for active widespread methane emissions at the South Georgian shelf, the second study area, was detected by ship-based hydroacoustic echosounders during RV Polarstern cruise ANT-29/4 in 2013 [2] and further investigated during a recent campaign with RV Meteor in January/February 2017 using a remotely operated vehicle for visual seep documentation, gas quantification and sampling. Their distribution indicates a generic relation to the deeply incised cross-shelf troughs, which are common morphologic features along glacially influenced margins. Processing and interpretation of the huge amount of hydroacoustic data combined with sediment and water samples available from both study areas document differences in the controlling mechanisms that drive the methane discharge, and allow us to assess the gas emission potential of different geological settings in glacially influenced shelf areas.

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Estimates of the gas hydrate stability zone beneath the Yuan-an Ridge offshore southwestern Taiwan based on velocity structure

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Content

The maximum thickness of the gas hydrate stability zone (GHSZ) beneath the YungAn Ridge, a key gas hydrate study sites, offshore southwestern Taiwan was estimated, and a generalized GHSZ profiles across part of this ridge was constructed. Data from P-waves and from S-waves generated by P-S conversion on reflection from airgun shots recorded along profiles of ocean bottom seismometers were collected. Travelttime inversion and forward modeling of multicomponent wide-angle seismic data result in detailed P-wave and S-wave velocities of hydrate-bearing sediment layers. On the assumption that the thickness of the GHSZ is a function of water depth, bottom water temperature, pressure, and thermal gradients in sediments, pore water salinity, gas availability and composition, we calculated the GHSZ along the OBS profile with thermal gradient ranging from 40 to 60 °C/km. Thickness of the GHSZ decreases in the Yungan Ridge profile from about 300 m to 100 m if the regional thermal gradient increases from 40 to 60 °C/km.

Structural control on the distribution of gas hydrates in the Vestnesa Ridge

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Content

Gas hydrates, crystalline ice like solids that trap gases mainly methane, are formed under suitable temperature and pressure conditions in continental margins and permafrost settings. Temperature and pressure conditions at shallow depths in the marine sediments (up to 190-195m depth below the seafloor) of the Vestnesa Ridge, western Svalbard margin fulfills the requirements for the formation of gas hydrates. The presence of gas hydrates is widely reported along the Vestnesa Ridge. Many factors like suitable temperature and pressure conditions, availability of methane gas, and availability of pore water affect the formation of gas hydrates at a given site. These factors are strongly influenced by structural and stratigraphic settings of the area. In the present study, effect of structural and stratigraphic settings on these factors and thus the formation of gas hydrates is studied using seismic velocity analysis. We perform seismic velocity analysis using multicomponent seismic data to study the changes in the seismic velocities along the Ridge. We analyze seismic velocities in different azimuths at two ocean bottom seismometers (OBS) sites. These two sites are selected to see the changes in seismic velocities profiles across faults in the region. Seismic velocity analysis show changes in the seismic velocities across the fault thus potentially hinting at the changes in the pore fill across the fault. These anomalies in the seismic velocities are studied and correlated with stratigraphy of the region to study the evolution of gas hydrates. Results from velocity analysis of multicomponent seismic data, especially azimuthal velocity analysis, suggest strong structural and stratigraphic control on the presence of gas hydrates along the ridge.

U-Th geochronology of methane-derived authigenic carbonates reveal the long seepage history of a pockmark on Vestnesa Ridge off W' Svalbard

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Content

Pockmarks, circular depressions on the seabed, are often associated with contemporary seabed methane emissions. However, the timing of pockmark formation and subsequent evolution remain poorly understood. In general, pockmark formation is ascribed to vigorous methane release from the seabed into the water column resulting from relatively rapid gas hydrate dissociation. Most of the released methane is intercepted within the sediment by microbial mediated sulphate-driven anaerobic oxidation of methane (AOM). One consequence of AOM is increased carbonate alkalinity in pore fluids, inducing formation of ¹³C-depleted methane-derived authigenic carbonate (MDAC) rocks. Uranium-thorium chronology of aragonite cement contained in the MDAC rocks provides useful means to reconstruct past methane release and pockmark formation. Here we report U-Th ages of vein filling ¹³C-depleted aragonite of MDAC rocks sampled from the seabed and drill cores up to ~23 m below the seabed, revealing the long history of methane seepage on Vestnesa Ridge off W' Svalbard. This chronology permits assessment of the evolution of this pockmark and potential drivers of methane release.

Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.: Talk

Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.: Talk
A-447

Arctic megaslide at presumed rest

Geissler, W.¹, Gebhardt, C.¹, Gross, F.², Wollenburg, J.¹, Jensen, L.^{1, 3}, Schmidt-Aursch, M.¹, Krastel, S.², Elger, J.⁴, Osti, G.⁵

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Content

Slope failure like in the Hinlopen/Yermak Megaslide is one of the major geohazards in a changing Arctic environment. We analysed hydroacoustic and 2D high-resolution seismic data from the apparently intact continental slope immediately north of the Hinlopen/Yermak Megaslide for signs of past and future instabilities. Our new bathymetry and seismic data show clear evidence for incipient slope instability. Minor slide deposits and an internally-deformed sedimentary layer near the base of the gas hydrate stability zone imply an incomplete failure event, most probably about 30000 years ago, contemporaneous to or shortly after the Hinlopen/Yermak Megaslide. An active gas reservoir at the base of the gas hydrate stability zone demonstrate that over-pressured fluids might have played a key role in the initiation of slope failure at the studied slope, but more importantly also for the giant HYM slope failure. To date, it is not clear, if the studied slope is fully preconditioned to fail completely in future or if it might be slowly deforming and creeping at present. We detected widespread methane seepage on the adjacent shallow shelf areas not sealed by gas hydrates.

CORRELATION BETWEEN TECTONIC STRESS REGIMES AND METHANE SEEPAGE ON THE WEST-SVALBARD MARGIN

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Content

Seafloor methane seepage occurs across the west-Svalbard margin at water depths ranging from the upper shelf at < 300 m to the deep sea at > 1000 m where gas hydrate systems are perennially stable. Along the Vestnesa sedimentary ridge located on oceanic crust, an eastward transition from a zone with clear morphological evidence of past seepage to a zone of active present-day seepage coincides with a change in the faulting pattern of near-surface strata. Tectonic stress modeling of the oblique spreading along the Molloy and Knipovich spreading ridges reveals a zone of tensile stress that extends northward from the Knipovich Ridge and encompasses the active seepage and extensional faulting zone. The westward zone of past seepage is presently located in a strike-slip tectonic regime. We propose a conceptual model that explains seepage periodicity along the sedimentary ridge as controlled by an interplay between regional stresses and pore-fluid pressure at shallow gas accumulations. Periods of active seepage have been coupled to phases of opening of faults and fractures in a tensile regime. Continuous seepage through these open features has led to the formation of seismic chimneys. The extensional regime from the mid-ocean ridges and glacio-isostatic flexural forces are major sources of tensile stresses promoting tensile fracturing and seepage in the past.

Gas sources in shallow sediments of two active pockmarks on Vestnesa Ridge, offshore W-Svalbard: evidence from carbon isotopes of methane, ethane, dissolved inorganic carbon, sedimentary organic matter and methane-derived carbonate nodules

Sauer, S.^{1, 2}, Knies, J.^{2, 3}, Lepland, A.^{2, 3}, Eichinger, F.⁴, Yao, H.², Panieri, G.², Himmler, T.³, Klug, M.³, Schubert, C.⁵

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Content

There is an active methane seepage system on Vestnesa Ridge (offshore W-Svalbard) in a water depths of 1200 m which includes surface expressions like pockmarks and methane-derived carbonates and subseafloor expressions like a bottom-simulating reflector and gas chimneys inferred from seismic data. Previous studies have suggested a predominantly thermogenic methane source in the gas hydrate at Vestnesa Ridge [1], [2], but so far there have been no reports of the isotopic composition of the gas from the actual gas plumes to verify that the seeping gas is thermogenic methane as well.

Here we present headspace gas geochemistry data from ten push cores sampled using the remotely operated vehicle ROV Ægir 6000 at two active pockmarks (Lunde and Lomvi) on Vestnesa Ridge. We observed very heterogeneous seafloor conditions such as huge build-ups of carbonate crusts and patches of bacterial mats within the pockmarks indicating active seepage. The sediments below the bacterial mats are gas-charged, exhibiting a varying but in general very shallow sulphate-methane-transition-zone (SMTZ) depth between 2 and 15 cm below the seafloor. Using XRF-scans of the push cores and methane-derived authigenic carbonate nodules we will investigate the stability/variation of the SMTZ depth over time. The $\delta^{13}\text{C}$ -methane ranges from -77 to -52 ‰ VPDB suggesting a mix of different gas sources and/or different processes influencing the methane in the various push cores, but point towards a predominantly microbial origin of the shallow methane gas. The isotopic composition of the higher hydrocarbons and dissolved inorganic carbon will help to better determine the gas origin. Unfortunately, we did not succeed in sampling gas from the gas plumes.

We will analyze the content and $\delta^{13}\text{C}$ of sedimentary organic matter in the push cores to evaluate if high amounts of methanotrophic biomass could provide the organic matter basis for in-situ production of microbial methane. This will be further investigated using lipid biomarker analyses.

Potentially, gas hydrates found in several meters below the seafloor within the pockmarks could supply thermogenic gas to shallow sediment depths via faults or fractures producing a “mixed gas” signature in shallow depths. A varying mixing ratio of microbial and thermogenic gas could explain the wide range in $\delta^{13}\text{C}$ -methane values which we observed in our push cores.

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Honouring seafloor Seepage as a crucial Key for quantifying leakage of thermogenic gas reservoirs in the Arctic

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Content

Methane seepage at the seafloor is a well-known global phenomenon that can lead to the understanding of deep reservoir dynamics. Mounds and pockmarks are characteristic seepage site features. Seepage is often associated with the occurrence of gas hydrates which are reservoirs vulnerable to pressure and temperature changes. We investigate the interaction between deep thermogenic gas reservoirs across the west-Svalbard margin and the dynamics of gas hydrate and associated seepage systems.

A novel stochastic basin model is presented to reconstruct the seafloor leakage history of the Vestnesa depocenter, coupled to the evolution of fluid migration. We constrain the sources of gas and the spatial-temporal evolution of seepage on the Vestnesa Ridge, a >5 km thick sedimentary drift with active seepage located between the Arctic mid-ocean ridges and the west Svalbard continental shelf.

Our previous 2D leakage-migration model for the ridge's gas hydrate and seepage system indicated a likely sustainment by a Miocene thermogenic methane source, possibly feeding the system for more than 2 million years. We elaborated this concept further into a 3D model by including structural constraints from additional 2D-seismic lines and high resolution P-cable 3D seismic data.

New input parameters from gas isotopic and pore water geochemical data at seep sites are used for model verification. The empirical data provide robust calibration anchors on the modelled timing and rates of gas seepage from the seabed, the hydrocarbon generation regime and fluid migration paths from the deep reservoir to seafloor seepage zones.

By reconstructing a petroleum system that jointly honours leakage history input from high resolution seismic data, gas hydrate mass balances over geological times and rigorously exploited ground truth data from seepage sites, we enforce a new, temporal calibration domain on the model. This approach enables an extensive uncertainty assessment of the hydrocarbon migration leakage pathways from the source rocks via intermediate storage reservoirs to the seabed seep sites.

Conventional petroleum system models are referenced against present day observations and lack history verification. Meaning that a model fit in e.g. hydrocarbon volumes today cannot decipher whether they accumulated 2, 10 or 20 Ma ago. With the first results from the Vestnesa Ridge model, we present a concept that reduces the width of the history validation gap in numerical petroleum systems analysis.

**Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.:
Talk
A-274**

**Influence of tectonic regime on sustaining long-lived gas hydrate systems; an example from
Svyatogor Ridge, Fram Strait**

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Content

The Svyatogor Ridge, located west of the Knipovich Spreading Ridge and south of the Molloy Transform Fault, is hypothesized to have once been the southern tip of Vestnesa Ridge; a large sediment drift that was offset during the last 2 Ma along the MTF. The sedimentary cover across Svyatogor Ridge is limited, compared to Vestnesa Ridge, and basement outcrops are identified ~850 mbsf on the apex of the ridge. Despite the limited sedimentation, and its unique location at the intersection between the Knipovich Ridge and Molloy Transform Fault, Svyatogor Ridge has evidence of shallow gas accumulations; a strong BSR indicating a gas hydrate and underlying free gas system, and fluid flow pathways to the seafloor culminating in pockmarks. Using two high-resolution P-Cable 3D seismic surveys, 2D seismic, and multibeam bathymetry data, we investigate how tectonic and sedimentary regimes have influenced the formation of a well-developed gas hydrate system. Large-scale basement faults identified in the seismic data are interpreted as detachment faults, which have exhumed relatively young ultramafic rocks. These detachment faults act as conduits for fluid flow, allowing circulation of seawater to drive serpentinization and subsequently act as pathways for fluids and abiotic methane to reach the shallow subsurface. The 3D seismic survey at the southern end of Svyatogor Ridge shows evidence for multiple, distinct phases of fluid migration and expulsion, while the northern 3D seismic survey indicates a more sustained seepage system with buried pockmarks observed throughout the sedimentary strata between the BSR and seafloor. Tectonic activity along the Knipovich Ridge and Molloy Transform Fault are hypothesized to be responsible for sustaining this gas hydrate system and associated fluid expulsion over the last ~2 Ma, and we will show first results from stress and paleo-stress analysis.

Modern and past methane emissions recorded by foraminiferal stable isotopes and assemblages and mineralogical data (XRF). Preliminary results from Vestnesa Ridge (Arctic Ocean)

Dessandier, P.-A.¹, Panieri, G.¹, Knies, J.², Lepland, A.², Sauer, S.³, Yao, H.¹, Hong, W.-L.², Bohrmann, G.⁴

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Content

Natural modern and past methane seepage episodes have been identified in Vestnesa Ridge (NW Svalbard). Several active pockmarks related to fluid flow were targeted during the PS1606 cruise with R/V GO Sars and the drilling campaign with R/V MARIA S. MERIA (MSM57/1) in 2016, at about 1200 m water depth within the gas hydrate stability zone.

Our study presents the preliminary results from several push cores collected from ROV-assisted G.O. Sars cruise in the microbial mats related to methane-enriched sediments. These modern day samples are used to reconstruct methane emissions in the past as a calibration step. Paleo-emissions are investigated on drilling MeBo cores up to 62.5 m long, collected with the sea-floor drill rig MARUM-MeBo70 in active pockmark and in a reference station.

We investigated 1) the living and fossil assemblages of benthic foraminifera in the push cores from methane-related microbial mats and 2) the stable isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) signals measured on both living and dead benthic foraminiferal tests. Preliminary results show that benthic foraminifera are living on methane-enriched sediments with less dense and diverse faunas than in the reference core without methane influence. Vital effect on $\delta^{13}\text{C}$ of the different species was constrained by the measurements of $\delta^{13}\text{C}$ on shallow and deep infaunas from the living and dead communities. Secondary overgrowth of carbonate on individuals was also investigated by $\delta^{13}\text{C}$ measurements on planktonic foraminiferal species. The first stable isotope results show anomalously low $\delta^{13}\text{C}$ values of benthic foraminiferal tests, due to methane seeps while standard values characterize the reference site.

We processed X-Ray Fluorescence scanning on drilling MeBo cores from a reference site and from the Lunde pockmark. The reference MeBo core does not indicate any methane influence signal but a classic arctic paleo-record of the last 150 000 years, while the cores from the Lunde pockmark are enriched in sulfur and show evidences of different methane emissions in the past, which are going to be analyzed.

Origin and conversion of light hydrocarbons ascending at an active pockmark on Vestnesa Ridge, Arctic Ocean

Pape, T.¹, Panieri, G.², Hong, W.-L.^{2,3}, Bünz, S.², Lepland, A.^{2,3}, Torres, M.E.⁴, Riedel, M.⁵, Hsu, C.-W.¹, Yao, H.², Freudenthal, T.¹, Wintersteller, P.¹, Bohrmann, G.¹

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Content

Vestnesa Ridge is a ca. 100 km-long sediment drift west of Svalbard. The presence of pockmarks representing seafloor depressions along the summit has been related to focused fluid flow through columnar conduits as well as faults and fractures. In 2016 we performed a drilling campaign with RV MARIA S. MERIA (MSM57/1) and the sea-floor drill rig MARUM-MeBo70 at about 1200 m water depth within the gas hydrate stability zone. Cores were collected with the MeBo and with gravity cores from the active Lunde pockmark and from a reference station. We analyzed light hydrocarbons (C₁/C₂₊) and stable carbon isotopic ratios of methane (δ¹³C-CH₄) in various samples including gas hydrates and MeBo pressure cores as well as δ¹³C of pore water dissolved inorganic carbon (DIC) in order to characterize the origin of the hydrocarbons and their behavior during migration.

At the reference station, where a lack of fluid advection is inferred from an absence of seafloor gas emissions and hydrates, gas in the deepest MeBo core section (62 m below sea floor, mbsf) was characterized by C₁/C₂₊ of ~250 and δ¹³C-CH₄ values of ~-60‰ V-PDB. Using conventional classifications, light hydrocarbons at this depth plot close to the field of thermogenic hydrocarbons. Between 62 and 48 mbsf there is a gradual increase in C₁/C₂₊ with decreasing depth (up to ~2,730) and a decrease in δ¹³C-CH₄ to values as low as ~-94‰ at 9 mbsf, which suggest admixture of microbial methane. Coupling of carbon cycling is indicated by similar trends in the δ¹³C profiles of both DIC and dissolved methane pools.

At the gas emission site within the Lunde pockmark high upward fluid flux sustains gas hydrate formation. Gas in hydrates buried between 0.5 and 6.5 mbsf was characterized by C₁/C₂₊ ranging between 170 and 420 and δ¹³C-CH₄ values between -49 and -54‰, i.e., plotting in the field of thermogenic hydrocarbons. Similar compositions were measured in gas extracted from sediments as deep as 15 mbsf. This demonstrates that within the pockmark a greater portion of deep-sourced hydrocarbons reaches uppermost sediments. Stable δ¹³C-CH₄ values observed throughout the recovered section contrasts with a strong depletion in the δ¹³C-DIC values (~-39‰ at 1 mbsf). This decoupling shows that at this site a small fraction of the upward migrating CH₄ enters the DIC pool. We conclude that intense upward migration of almost unfractionated thermogenic hydrocarbons fuels shallow hydrates and seafloor gas emissions at Lunde pockmark.

Widespread methane seepage along the continental margin off Svalbard - from Bjørnøya to Kongsfjorden

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Content

Numerous articles have recently reported on gas seepage offshore Svalbard, because of gas emission that may be due to gas hydrate dissociation, possibly triggered by anthropogenic ocean warming. Here we report on findings for a much broader extent of seepage in water depths at and shallower than the gas hydrate stability zone. More than a thousand gas seepage sites imaged as acoustic flares generate a 600 kilometer-long plume. Most flares were detected in the vicinity of the Hornsund Fracture Zone. We postulate that the gas ascends from depth along the fracture zone; its discharge is focused on bathymetric highs and is constrained by glaciomarine and Holocene sediments in the troughs. A fraction of this dissolved methane (~1.8%) was oxidized whereas a minor but measureable fraction (0.05%) was transferred into the atmosphere in August 2015. The large scale seepage reported here is not linked to anthropogenic warming.

Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.: Keynote speaker

Session 10.2: Methane- and methane-hydrate-related processes at margins around the Arctic Ocean.: Keynote speaker
A-496

Gas Hydrate Dissociation at the Continental Margin off Svalbard Induced by Glacial Rebound rather than Global Warming

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Content

Focused gas seepage at the upper continental slope of Western Svalbard at around 400 m water depth has been attributed to gas hydrate dissociation induced by warming of ambient bottom waters. Numerical studies support this hypothesis since the seepage sites are located at the up-dip limit of the gas hydrate stability zone where a moderate rise in bottom water temperature may induce hydrate melting. However, gas hydrates have never been sampled in the area while the dating of authigenic carbonates reveals that seepage has been active for at least three thousand years.

During a recent research cruise with RV MERIAN (MSM57, July – September 2016) up to 35 m deep boreholes were drilled in the area employing the MeBo drilling system operated by MARUM. No gas hydrates were found in the vicinity of the seep sites. Additional MeBo boreholes drilled at water depths of 350 to 450 m also did not to recover gas hydrate. However, pore waters were significantly depleted in dissolved chloride at water depths of 391 – 405 m and sediment depths of 17 – 23 m below seafloor.

The model-based evaluation of down-core dissolved chloride profiles indicates that the freshening of pore fluids already started several thousand years ago, that is before the onset of anthropogenic warming. Published records of bottom water temperature at the upper slope suggest a stable temperature baseline over the Holocene while sea-level reconstructions from the northwestern coast of Svalbard indicate a significant drop in relative sea-level over the Holocene that was induced by postglacial rebound reflecting the withdrawal of the Barents Sea Ice Sheet over this area. Model runs incorporating these geophysical constraints show that the resulting decline in hydrostatic pressure at the seabed over the Holocene induced gas hydrate dissociation and dissolved chloride depletions that are consistent with those measured at 394 and 404 m water depth. Dissolved sulfate profiles calculated by the model also comply with the data. Based on these model results, we propose that the observed freshening is due to hydrate dissociation that was induced by the post-glacial rebound of the seabed over the Holocene when the rate of seabed uplift outpaced the rate of eustatic sea-level rise. Hence, it seems that gas hydrate dissociation was induced by a natural decline in seabed pressure rather than anthropogenic temperature rise.

Session 10.3: Tectonic Systems (TSK open session).: Poster

Session 10.3: Tectonic Systems (TSK open session).: Poster
A-621

Mapping and microscopic investigation of a retro- and again prograde overprinted nappe, sheared into the Elbtalschiefergebirge near Berggiesshuebel (Saxony, Germany)

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Content

Within the scope of a Bachelor Thesis a nappe of highly metamorphic overprinted and mylonitised granodiorite was mapped. It occurs as a slice sheared into the Paleozoic units of the Elbtalschiefergebirge (Elbezone). To determine its regional extension, its origin and its paleotectonic history an area next to Berggiesshuebel was mapped and the occurring rock types have been investigated macroscopically as well as microscopically. Furthermore a sample of the "Unterer Graugneis", a biotite rich metagranodiorite of the Freiberg Formation was included in the study and which is thought to be the original rock unit of the sheared slice.

Microscopic analyses of the slice reveal a metamorphized and mylonitised granodiorite. An initial greenschist facies metamorphic overprint is recognized by chloritization of the contained biotites, which still can be observed in the western part of the nappe. Thereby this chloritization was caused by the shearing process in combination with fluid interaction. In contrast, biotites in the eastern part show no characteristics of chloritization. They rather show a prograde overprint caused by the intrusion of the Markersbach Granite. Similar effects can be recognized by the surrounding rock units of the Elbezone (Paleozoic phyllitic metasediments). Thus, shearing of the metagranodiorite slice must have occurred before the intrusion of the Markersbach Granite, which took place around 330 million years ago. Furthermore the intrusion of the granite caused an uplift as well as a bending of the eastern part of the metagranodiorite nappe. In this process, the phyllitic metasedimentary rocks of the Elbezone have been included.

Macroscopic comparison of the metagranodiorite nappe and the "Unterer Graugneis" of the Freiberg Formation reveal clear differences in color, texture and the sizes of the contained components. In contrast, microscopic studies show a similar mineral composition. Despite, textural differences could also been identified microscopically as in the metagranodiorite nappe a reduction of crystal sizes and the formation of some kind of matrix was recognized as well as characterization of a recrystallization process both resulting in a ductile deformation, namely the mylonitization of the rock. This deformation can be attributed to the shearing which occurred most likely in Variscan times and caused the location of the metagranodiorite nappe inside the metasedimentary units of the Elbezone.

New views on the crustal-scale geometries of the Taiwan fold-thrust belt

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Content

Taiwan is located along an active plate boundary between the Eurasian and Philippine Sea Plates, with convergence rates amounting to c. 8 cm/yr. The island has since long served as a cradle for many tectonic concepts (e.g., fault-related folding, critically tapered thrust wedges, or climatic forcing on orogen growth). Yet, the internal parts of the Taiwan fold-thrust belt (FTB) are still improperly understood in terms of fault kinematics, internal geometries and the amount of shortening they underwent since the onset of arc-continent collision in the Mio- to Pliocene. As a consequence, geometrical restorations of the Eurasian passive margin prior to continental subduction are often guesses rather than quantitative estimates. We constructed three new crustal-scale geological cross-sections at various latitudes of the Taiwan FTB, with crust-mantle interfaces constrained from a recent 3D-model employing seismological data. We consider the pre-Cenozoic basement exposed in the Tananao Schist Complex to comprise two imbricates of largely Eurasian basement (Tailuko and Yuli Belts), which overthrust the Cenozoic passive margin series and which are, in turn, tectonically overlain by the upper-plate-derived Coastal Range series. A tentative restoration of one of our sections (modified after [1]) yields a minimum shortening of 120 km in the Eurasian passive margin series, with about 50% of the basement, on top of which the accreted material was initially sitting, already subducted below the Philippine Sea Plate (Fig. 1).

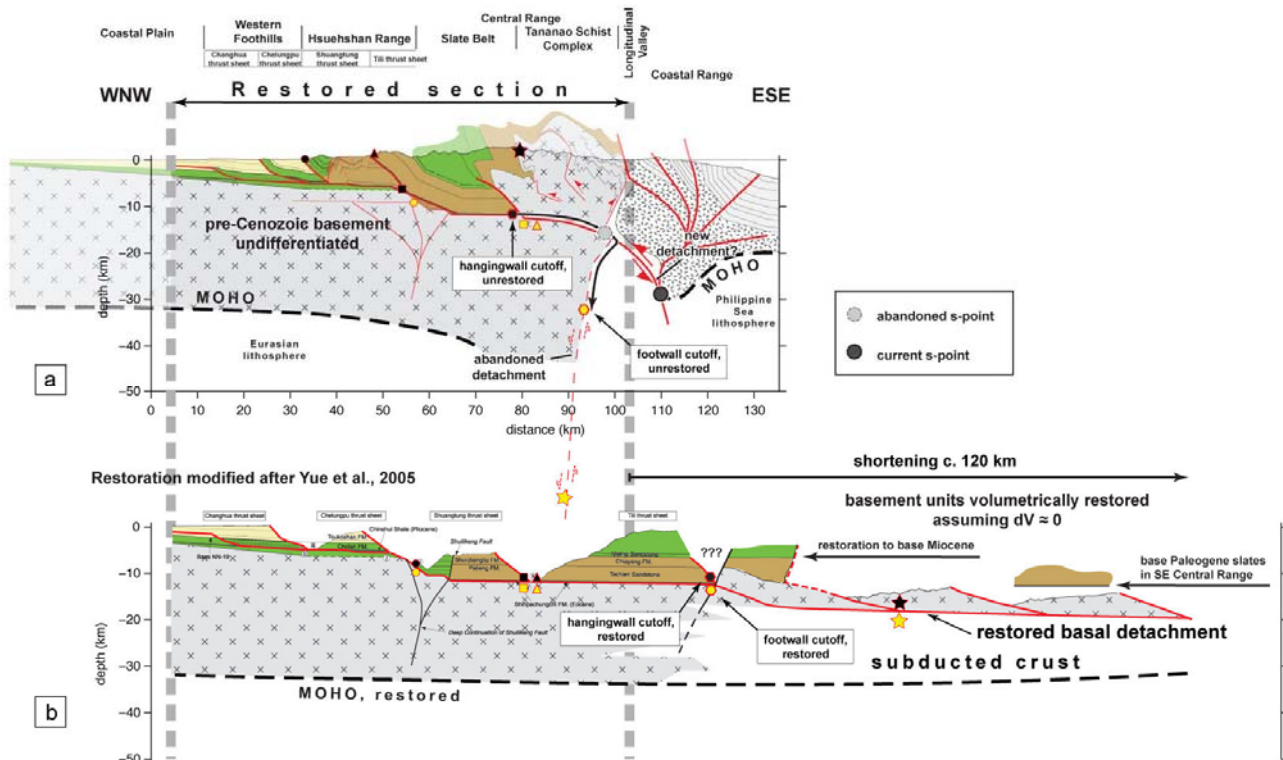


Fig. 1: a) crustal scale transect across central Taiwan, (b) tentative restoration of (a), modified after Yue et al. 2005).

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Quaternary tectonic activity in the intermontane Calchaquí Valley, Eastern Cordillera (Cachi-Payogasta area), NW Argentina

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Content

The E Cordillera of the southern Central Andes in NW Argentina is characterized by intermontane basins flanked by reverse-fault bounded ranges. The basins are located in the interior parts of the orogen and straddle the eastern boundary of the high-elevation intra-orogenic Andean Plateau. One of the largest intermontane basins is the N-S oriented Calchaquí Valley. In its northernmost sector the valley is bounded by E and W-dipping reverse faults (Calchaquí Fault and Toro Muerto Fault), respectively. The basin exposes deformed Tertiary strata that are unconformably overlain by Quaternary conglomerates that are part of coalesced alluvial fans. This sector of the valley narrows considerably and neotectonic activity in this area has been thought to be associated with the range-bounding faults. In addition, it has been proposed that the main Quaternary faults reflect the reactivation of Tertiary structures.

The effects of Quaternary deformation in this area are recorded by faults, folds, unconformities, and cataclasized and tilted conglomerates. In addition, changes in paleocurrents and provenance, anomalies in the drainage network, and convex longitudinal stream profiles unambiguously demonstrate the impact of Quaternary tectonic activity in the Calchaquí Valley. Importantly, this region broadly coincides with areas frequently affected by destructive historical seismicity.

Taken together, available sedimentological, geomorphological, and structural information as well as historical and instrumental seismicity data show that the northern sector of the Calchaquíes Valley has been actively deforming during the Quaternary. This emphasizes the need to perform additional systematic investigations of the characteristics of the Quaternary deposits and their tectonic overprint at regional scale to help understand the spatiotemporal evolution of tectonic processes in light of ongoing contraction and potential hazards.

The study was supported by the StRATEGy program (DFG), CUA-DAHZ, and CIUNSa 2636.

Scaled analogue modelling of transpression using the MultiBox

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Content

Scaled analogue modelling has advanced as an important tool in geodynamics to better understand aspects of deformation. We developed a new analogue box, the MultiBox, capable of deforming granular and viscous materials under any deformation regime including pure shear, simple shear and any components of transpression and transtension. The large box size (1 m x 1 m x 30 cm) guarantees high accuracy of length scaling. The box consists of two halves, each of which contains a piston, whereby one half is mobile and moves relative to the fixed one, thus generating a velocity discontinuity. Powerful Trinamic step motors drive all moving box parts and are controlled independently by a NI cRIO-9030 system via an Intel CPU and FPGA. The FPGA enables accurate signal processing and hardware level safety features. Using the programming language LabVIEW, this allows us to record and synchronize surface deformation of analogue materials with an 8 Megapixel video camera and a Kinect 2 512 x 424 Pixel infrared depth camera. Our facility permits cross-correlation of sequential pixel images using Particle Imaging Velocimetry (PIV) technology, executed in Matlab and PIVLab, and computation of 2D surface displacement vector fields.

Based on simple two-layer models using silicone (PDMS), representing the viscous lower crust, and a 2:1 flour-sand mixture modelling Mohr-Coulomb upper crust, we examined fault patterns formed under transpression. Piston velocities and shear rates were kept constant, whereas thicknesses of the two layers were systematically changed in a set of seven experiments. This allowed us to assess the influence of layer thicknesses on evolving fault patterns in model upper crust. Experiments were scaled to length, density, viscosity, and time, and were conducted over a period of 4 hours.

In order to visualize the evolution of fault patterns, we generated cumulative fault maps, each of which displays all faults imaged by PIV and formed in 30 minute-intervals. A remarkable result of all experiment is distributed deformation during the first 1.5 hours, which then changed to strongly localized deformation resolved at a few faults. The initial thickness of the viscous layer seems to have had little influence on the evolution of model upper crustal fault patterns. The patterns seem to be controlled chiefly by the thickness of the brittle crust. More specifically, localized faulting occurred only after attainment of a threshold in upper crustal thickness.

Structural analysis and petrographic description of the Upper Allochthon of the western Fjällfjäll-window (northern Sweden)

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Content

The working area is part of the Scandinavian Caledonides, which were formed in the Paleozoic era due to the collision of Laurentia and Baltica. The resulting orogenic wedge was pushed onto the Baltic shield in the form of an allochthonous nappe stack consisting of different nappes, namely the Lower, Middle, Upper and Uppermost Allochthon. The Middle Allochthon consists of turbidites, deposited on the western edge of Baltica, and the Upper and Uppermost Allochthon are formed of island-arc-material and deep sea sediments. The lower nappes crop out in tectonic windows in the region of Västerbotten. The working area is situated in the north-western part of the Fjällfjäll-window, which consists of units of the Middle and Upper Allochthon in an antiform duplex structure. The Upper Allochthon can be further subdivided into the Seve- and Köli-Nappe. The Köli-Nappe and the Middle Allochthon are the dominant geological units of the working area. All units were exposed to a regional metamorphic overprint. The petrographic analysis of thin-sections allows a subdivision of the nappe-structures. The Middle Allochthon, which is present in the form of Meta-Arkose, shows temperature-/pressure-conditions fitting the greenschist facies. The Köli-Nappe consists of Meta-Gabbro, Meta-Greywacke and Serpentinite. It underwent higher metamorphic conditions of the amphibolite facies.

This Bachelor thesis focused on the northern part of the Fjällfjäll-window and its geological units, with detailed investigations of the serpentinite lenses. Results show a bending of the western serpentinite lens as well as a fragmentation of the eastern lens into different smaller lenses. The Middle Allochthon does not show a smooth bend, but forms a wave-like structure with intercalations of the Meta-Greywacke of the Upper Allochthon.

Two penetrative foliations, S_n und S_{n+1} , could be observed in the working area. The younger foliation (S_{n+1}) is mainly present in the layers of the Meta-Greywacke of the Upper Allochthon and in the Meta-Arkose of the Middle Allochthon.

In conclusion, the results of this thesis depict a more detailed look on the units of the Northern part of the Fjällfjäll-window and the sequence of events that led to their formation.

Study of the gravity data of south of Talafar and Mosul city – NW Iraq

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Content

The study area is located in the northwestern part of Iraq bounded by latitude ($36^{\circ} 52' - 35^{\circ} 78'$) and longitude ($42^{\circ} 27' - 43^{\circ} 24'$).

Several important anomalies appear on the regional anomalies map: Positive anomalies H1 and H2 may be reflecting the effects of high blocks within the basement rocks and extended to sedimentary cover. Negative anomaly L1 is a wide low anomaly having E-W direction. Negative anomaly L2 elongated, trending NW-SE. These low anomalies may be reflecting the effect of low block within the sedimentary cover and extended to basement too.

Several faults recognized within the regional maps of the studied area. Four of them having NW-SE directions and others of NE-SW directions. These faults may be not extended to basement rocks.

Residual anomaly maps show several small-scale high and low anomalies most of them having NW-SE and E-W direction. Positive anomaly H1 is elongated anomaly having a direction of NW-SE. The length of the anomaly is exceeding 10km and while it is width at central part of it reaches to 5km. Positive anomaly H2 is elongated anomaly having a direction of NW-SE. The length of the anomaly is exceeding 15km and it is width reaches to 5km. Anomaly H3 is elongated anomaly having a direction of NW-SE. The length of the anomaly is exceeding 15km and it is width reaches to 6km. Positive anomaly H4 having a length exceeding 12km and it is width reaches to 3km and may be reflecting an elongated. Positive anomaly H5 is elongated anomaly. Anomaly H6 is an NW-SE elongated positive anomaly consists of more than two domes. The length of the anomaly is exceeding 40km and it is width reaches to 10km. Anomaly H7 trending E-W. Negative anomaly L1 trending E-W. Negative anomaly L2 having a length reaches to more than 50km and it is width exceeds 12km. this anomaly consist of two domes. Anomaly L3 is negative anomaly is NW-SE having a length of more than 20km and the width is about 10km. all these anomalies may be reflecting the effect of anticline and syncline structures within the sedimentary cover.

Several fault dedicate on the maps having different length and directions. Most of these assumed fault locations trending NW-SW of Zagros trend formed during the alpine orogeny and some of them trending E-W (Torus trend) or trending NE-SW formed during the Najd orogeny. All these faults occurred within sedimentary rocks.

Wollard (1962) equation used to determine the depth of Moho discontinuity.

Tectonic and metamorphic frameworks of the Balkan and Asia Minor: a preliminary work

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Content

Based on the experience of the making of the maps of Mesozoic to Tertiary metamorphism in the Alps “Metamorphic Structure of the Alps” (Oberhänsli, et al. 2004, Bousquet, et al. 2012a) and “Tectonic Framework of the Alps” (Schmid et al., 2004, Bousquet, et al. 2012b), where an interplay of data from structural geology and tectonics with metamorphism as well as age data and geophysical information was used to visualize the spacio-temporal geodynamic evolution of this complex orogenic system, we present a new tectonic frame for the continuation from the Alps to the Asia Minor. This map includes the Balkan, Aegean and Turkish realm in Asia Minor including the Carpathians, Dinarides, Rhodopes, Peloponnese, Aegean as well as Pontides and Taurides. The motivation for the compilation of this map is based on new metamorphic and age data especially for the Carpathians, Rhodopes, Aegean and Turkey. A tectonic map of the Carpatho-Dinaride realm that is consistent with a basic scheme of continental and oceanic realms and their structural relation as developed for the Alps was published by Schmid et al (2008 and in prep.): However, the east ward continuation across Asia Minor is missing. With this new general map, we try to solve the problem of the continuation of the different continental and oceanic units from the Balkan over the Peloponnese and Aegean into Turkey and further to Iran. Due to intense neotectonic effects and movements and the Miocene to Neogene basins and volcanics that cover major parts of Turkey this is still speculative. Several small continental units (Menderes, Kirsehir) of Pan African origin, carrying along old metamorphism, are amalgamated along several Tethyan oceanic units and cannot simply be correlated with the Balkan setting. Our interpretation is based on work done in the realm of MEBE and DARIUS, two international joint ventures of academia and industry as well as many TÜBİTAK projects in Turkey.

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The lowermost tectonic units of the Cretan nappe pile in the Talea Ori

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Content

The lowermost tectonic units of the Cretan nappe pile are exposed in the Talea Ori mountains at the central northern coast of Crete. There, high-pressure low-temperature metamorphic, mostly siliciclastic rocks of the Bali formation and the Phyllite-Quartzite (PQ) unit occur to the north of the Talea Ori group, which forms an overturned large-scale anticline structure. The structural position of the siliciclastic units has been discussed controversially. Here, we present a new structural mapping and a meso- and microstructural characterization of these rocks.

Rocks of the Bali formation and the PQ occur likewise to the north of the Talea Ori group and within the center of the anticline. The contact of the Bali formation to the formations of the Talea Ori group is mostly characterized by normal faults but also concordant contacts are found. The contact of the Bali formation to the PQ is not well exposed and difficult to interpret given a rather gradual change in lithology and increasing strain towards the contact. In both formations, shear zones are abundant that are characterized by a prevalent slaty cleavage, extensional shear bands, crenulation cleavage, kink bands and abundant quartz veins that are associated to the ductile deformation of the rocks. The vein quartz microstructures from both units give evidence of crystal-plastic deformation, recovery and grain-boundary migration, suggesting temperatures of about 300-350°C. Clastic components in coarse conglomerates of the Bali formation are derived from an external source, not exposed in the Talea Ori (well-rounded black vein quartz pebbles), few from not exposed metarhyolites and gneisses, and others from a very local source (cherts, metasediments) exposed next to the conglomerates. Even detrital albite clasts with inclusions forming an internal foliation, very similar to metamorphic albite blasts in schists of the PQ occur, suggesting that few components might have been derived from the PQ.

Our observations confirm that the Bali formation is the lowermost unit of the Talea Ori group. The PQ is at least also structurally occurring below the Talea Ori group in the core of the anticline. New geochronological data constrain the age relations of the formations. Our findings on the base of the Talea Ori group are important, as it represents the lowermost level of the Cretan nappe pile and the basement is unknown so far.

Thin-skinned thrusting and associated triangle zone formation in the North German Basin - an example from the southern Altmark area, Central Germany

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Content

The thick-skinned Central European Belt comprises a pattern of NW-SE-trending fault zones and large basement uplifts (e.g. the Harz and Flechtingen High), which were formed and activated during distributed intraplate contraction in the Late Cretaceous. These fault zones are typically interpreted to be of thick-skinned style. Fault zones in the Mesozoic cover sequence are suspected to be associated with partially reactivated or newly formed basement faults or culminate at zones of structural inheritance. Although a potential detachment horizon - the approx. 1 km thick Late Paleozoic Zechstein evaporites - exists, thin-skinned thrusts are often disregarded, even though they are more typical for contractionally overprinted foreland basins of orogens.

Here we present the results of a case study from the WNW-ESE-trending Ristedt fault zone (Southern Altmark area). The fault zone is located approx. 7 km north of the Gardelegen basement thrust and deformed a 1.5 km thick stratigraphic sequence of Triassic to Early Late Cretaceous age. Considering few 2D seismic data and dense-distributed borehole information, the central part of this fault zone was analyzed using cross-section construction and balancing techniques to unravel the highly complex internal structure. Our results show that the Ristedt thrust forms a narrow anticline, which is surrounded by up to 2 km thick syntectonic sediments of Santonian to Campanian age. The underlying, nearly horizontal basement (base of Zechstein evaporites) does not show indications for contraction. The fault zone in the core of the anticline is characterized by a lower foreland-vergent thrust fault and three hinterland-vergent thrusts in strata overlying a potential secondary detachment, the Upper Buntsandstein salt. The entire fold core forms a complex triangle zone, a typical structural element commonly interpreted in thin-skinned fold-and-thrust belts. Restoration shows that backthrusts evolved at the upper ramp edge of the foreland vergent thrust contemporaneous to sedimentation in the adjacent basins. This fits well with various kinematic and mechanic models of triangle zones worldwide. Shortening estimates from section restoration (2.25 km) fit well with the measured amount of uplift at the Gardelegen basement thrust to the south, confirming the transition from thick-skinned to thin-skinned deformation during Late Cretaceous intraplate contraction in the North German Basin.

Session 10.3: Tectonic Systems (TSK open session).: Talk

Session 10.3: Tectonic Systems (TSK open session).: Talk
A-829

Basin formation: what can we learn from the North Pyrenean Zone?

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Content

While several tectonic models are proposed to explain the formation of extensive basins and passive margins, only one single thermal model (McKenzie), as a dogma, is used to understanding and modeling the formation and evolution of sedimentary basins. This model is based on the assumption that the extension is only by pure shear and it is instantaneous. Under this approach, the sedimentary deposits occur in two stages, a short step controlled by tectonics and a longer one resulting of the cooling of the lithosphere. However, most stratigraphic data indicate that less thermal model can account for documented vertical movements. The study of the thermal evolution, coupled with other tectonic models, and its consequences have never been studied in detail, although the differences may be significant and it is clear that the petrological changes associated with changes in temperature conditions, influence changes reliefs. Recent studies of continental passive margins collectively describe a great variety of processes accounting for the extreme thinning of the continental crust. Among all the parameters that may act during crustal stretching, the thermal state of the system and the temporal evolution of the heat distribution during thinning appear of major importance.

We propose a study of the northern Pyrenean zone, part of the Pyrenean belt. It is resulting in the inversion of several lower Cretaceous basins, separated by small crustal blocks.

We focussed our study on the basin formation and its relation to the thermal evolution of the lithosphere. Sediments at the base of the basin and the underlying crust are displaying a similar thermal evolution, by reaching temperatures up to 800°C at low pressure, different to the lithospheric mantle, in which rocks show a clear isothermal decompression.

The high temperature event is coeval of tectonic sliding inside the basin.

The Cretaceous basins of the North Pyrenean Zone are a case study of synchronous sedimentation, HT-LP metamorphism and crustal melting.

In conclusion the formation of a Pyrenean type basin is leading to a crustal boudinage and to the formation of a "anomalous" geophysical layer as observed in many OCT

Cretaceous tectonic evolution of the Sava-Klepa-Massif, Former Yugoslav Republic of Macedonia, based on automated paleostress analysis using calcite twins (new PACT-software)

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Content

The determination of paleostress orientation leads to a better understanding of past and recent plate motion, and are of particular interest for oil, gas and mining industries. PACT (Paleostress Analysis with Calcite Twins) is a new MATLAB®-based software package for automated reconstruction of paleostress orientations based on calcite twins after Turner [1]. Both, calcite c-axes and deformation twin plane orientation are measured with an automated fabric analyser microscope (Fabric Analyser G60; Russel-Head Instruments, Templestowe, Australia) and P-B-T stress axes are calculated. Further features of PACT are the conversion of universal stage measurements into the correct PACT-input-syntax, the rotation of measured data from thin section into field orientation, and the data separation in case of heterogeneous stress regimes. PACT will be implemented to the FAME (Fabric Analyser based Microstructure Evaluation) software [2] [3] which can be downloaded and used for free, as a Windows® stand-alone executable on <http://peternell.org/archive.html>. We apply PACT to Palaeozoic marble samples located near the Klepa-Massif (Former Yugoslav Republic of Macedonia) within the Sava-zone. Our aim is to test the controversially discussed hypothesis that the Klepa block (constituted of a basaltic sequence including pillows, sheet flows, dikes, and cumulates) represents a new oceanic tract that rifted during the Early Cretaceous until the Late Cretaceous, after the collision of the European and the Adriatic continental plate [4]. Concerning this, a first, simplified tectonic model is introduced, indicating that the rifting was controlled by a pull-apart tectonic setting.

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Dating Multiple Brittle Structure Generations by U-Pb SSI ages on Calcite Fibres

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Content

Tectonic forces shape the surface of our continents by ductile to brittle deformations. While relative relationships can be inferred from the geology, the absolute timing of the multiphase tectonic processes is commonly less clear. Brittle deformation is often recorded by calcite fibres and until now, most attempts to directly date these events have failed, because formation temperatures are too low for classical thermo-chronometers.

The aim of this work is to directly date brittle deformational events in carbonate rocks of the Al Hajar Mountains in Oman using the U-Pb small scale isochron (SSI) method recently developed at GUF. The study area is a perfect target as it is known to be affected by multiple deformation events during Cretaceous to recent time.

The method is applied on samples from cross-cutting calcite veins and fibres (orientated thin/thick sections) by *in situ* analyses using an Excimer laser coupled to an Element2 SF-ICPMS. It is based on the fact that carbonates, (re-)crystallised and equilibrated during an event, contain low but variable amounts of U and μ ($^{238}\text{U}/^{204}\text{Pb}$). Therefore, multiple spot analyses at the mm- to cm-scale will yield variable U/Pb ratios and thus form a linear array in the $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{238}\text{U}/^{206}\text{Pb}$ space; the lower intercept with the Concordia is interpreted as crystallisation age and the intercept at the y-axis as the initial Pb isotope composition.

The studied deformational events span from a late Cretaceous ophiolite obduction, followed by extension, to late Eocene to Miocene shortening and mountain uplift in the Al Hajar Mountains. The results show that top-south, layer-parallel shearing due to ophiolite obduction occurred in the Coniacian to early Campanian. Following this are top-NE, early Paleocene layer-parallel veins which developed during post-obduction exhumation, after which a series of strike-slip structures cross-cut and reactivated older faults due to Eocene to early Miocene horizontal shortening, which mainly causes the current high topography of the Al Hajar Mountains. The youngest structures are crack-seal fibres in hairline veins dated as late Miocene to middle Pleistocene [1].

The results show that the SSI technique successfully constrains complicated successions of brittle deformational structures.

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Extensional veins are no reliable indicator for hydraulic fracturing at near-lithostatic pore fluid pressures and low differential stresses

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Content

Since decades, the Mohr-Coulomb criterion is used to interpret extensional veins to originate from hydraulic fractures that propagated driven by high pore fluid pressure P_f at low differential stress $\sigma_d < 4T_0$ (T_0 : tensile strength). The paramount validity of this assumption is disproved by results of triaxial extension tests. For instance, Ramsey und Chester (2004), using dogbone-shaped samples, find a gradual increase in fracture angles with respect to the σ_1 - σ_2 plane with increasing mean stress, but failure stresses and fracture angles mismatch a continuous parabolic failure envelope. Triaxial extension tests on cylindrical samples systematically result in extensional fractures at $\sigma_d \leq 4T_0$, even under fully compressive external loads. For instance, Bauch (2005) reports fracture angle $< 5^\circ$ at $\sigma_1 = \sigma_2 = 96$ MPa and $\sigma_3 = 7$ MPa in a rock sample with $T_0 = 3.9$ MPa (Bauch and Lempp, 2004), i.e. $\sigma_d \approx 23T_0$. Takahashi et al. (2010) report tensile fracturing at conditions up to $\sigma_1 = \sigma_2 = 100$ MPa and $\sigma_3 \approx 18$ MPa for Kimachi sandstone (T_0 not reported). Mechanical models for extensional fracturing under compression have been proposed by e.g. Stacey (1981) and by Horii and Nemat-Nasser (1985). Published fluid inclusion (FI) datasets derived from extensional veins record fracture aperture growth at conditions incompatible with low σ_d . For example, FI data provided by Nüchter und Stöckhert (2008) and by de Ronde et al. (2001) indicate aperture growth of metamorphic veins at almost hydrostatic or slightly elevated P_f , respectively, for which σ_d must have been high. From this, I conclude (1) that extensional veins may form at $\sigma_d \leq 4T_0$, and (2) that the Mohr-Coulomb criterion fails to predict failure stresses and fracture angles when $\sigma_2 > \sigma_3$, thus cannot predict the conditions required for growth of extensional veins.

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Feldspar microstructures in greenschist facies granitoid mylonites. A case study of pegmatites from the Austroalpine basement.

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Content

The aim of this study is to correlate feldspar microstructures to specific deformation mechanisms, which is crucial for a better understanding of the rheology of the feldspar-rich continental crust. Experiments and natural studies have shown that the interaction of brittle, dissolution-precipitation and crystal-plastic mechanisms, as well as mineral reactions, are very important for the feldspar deformation behaviour over a large temperature range.

In this study we present microstructures from pegmatites from the Austroalpine basement south of the western Tauern Window. These Permian pegmatites constitute a Ca-poor system. They mainly contain albitic plagioclase, K-feldspar, quartz and muscovite. Growth of garnet, phengite and epidote indicates that the pegmatites experienced middle greenschist facies conditions during Alpine tectonometamorphism. Deformed pegmatites show feldspar and mica clasts suspended in a finer grained matrix. We distinguish 3 microstructures that record grain size reduction of magmatic feldspar, forming a fine-grained feldspar matrix.

1. Polyphase aggregates of feldspar and quartz occur at sites of dilation, i.e. strain shadows and fractures. This indicates that material precipitated from the pore fluid during deformation.
2. Albite replaces K-feldspar clasts along the rim, resulting in a sawtooth-shaped boundary. There is no specific orientation relationship between old and new grains. This replacement of K-feldspar by albite is interpreted to be driven by chemical gradients.
3. Polycrystalline plagioclase aggregates replace plagioclase clasts at sites of shortening and along fractures parallel to the foliation. There is a weak, but clear host-control on the crystallographic orientation of new grains. New grains have the same or slightly lower An-content than the clast. This indicates that replacement is mainly driven by the reduction in strain energy.

These three processes can result in a feldspar matrix of isometric albite grains with grain diameters of 20-70µm. The grains have no internal deformation features and a weak, if any, CPO, indicating that after grain size reduction no further deformation took place. This is consistent with coarse quartz ribbons. In contrast, in samples with fine-grained recrystallized quartz ribbons, matrix feldspar grains are elongate and lens-shaped with a long axis of 50-200 µm. This albite matrix is suggesting preferred growth of grains parallel to the stretching lineation during ongoing deformation.

Microcontinent Alkapeca and the tectonics of the Western Alps

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Content

A retrodeformation of oceanic and continental thrust sheets in the Penninic Zone of the Western Alps is proposed which takes out-of-sequence thrusting of the Dent Blanche-Sesia continental basement nappes into account. It results in a Jurassic paleogeography with two oceanic basins, Piemonte Basin (represented by Zermatt-Saas ophiolites) and Liguria Basin (represented by Tsaté ophiolites), separated by a Dent Blanche-Sesia microcontinent. The Prépiémontais nappes at least partly represent detached sediment cover of the microcontinent. Analogous tectonic units in Liguria (Gazzo-Isoverde) and Alpine Corsica (Nebbio) form a link between this Western Alpine microcontinent and Alkapeca, the Western Mediterranean microcontinent whose remnants are found in Calabria, Sicily, Rif, and Betic Cordillera. In Late Cretaceous, the northern part of the Liguria Basin located in the Alps was consumed by down-to-the-Southeast subduction, leading to collision between northern Alkapeca (Dent Blanche-Sesia) and Adria at the end of the Cretaceous. In contrast, the southern, Apenninic part of the Liguria Basin, in the hanging wall of the subduction zone, stayed open. During Paleocene and Eocene, the floor of the Piemonte Basin was subducted down to the Southeast, leading to the collision between Alcapeca and Iberia/Briançonnais all the way from the Western Alps to southern Spain. Whereas in the Alps, both basins had been closed by the end of the Eocene and thrusting shifted to more external zones, in the western Mediterranean a new, northwest-dipping subduction zone formed in the Oligocene, consumed the remaining parts of the Liguria basin, and developed through roll-back and back-arc spreading into the strongly arcuate Apennine / Calabrian / Rif / Betic mountain belt.

Modeling the Influence of Slab Advance on Upper Plate Deformation at Plate Corners

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Content

Plate corners are the characteristic kinks in plate boundaries that separate long stretches of straight or slightly concave plate boundaries. At these corners, also called syntaxes, the subduction orientation changes and causes a buckling and flexural stiffening of the downgoing plate. The resulting 3D curvature is suspected to exert major control on subduction and exhumation dynamics. Particularly, the exceptionally high rock exhumation rates localized in a small region recorded at the plate corners of St. Elias, Alaska, and both Himalayan syntaxes, Namche Barwa and Nanga Parbat, excite scientific interest. In contrast, the well-defined Andean syntaxis exhibits no observable increase in rock uplift rates.

In this study, we use a fully coupled, transient 3D thermomechanical numerical model to investigate the rock uplift and predicted thermochronometric ages in a simplified plate corner setting. By varying velocity boundary condition, we identify key mechanics that contribute to rapid and focused uplift.

In all models, a band of uplift following the outline of the subducting slab, as well as a smaller region of focused uplift situated closer to the trench and above the indenter. As time progresses, this region shifts closer towards the trench with larger slab advance velocities, whereas in models with a more stationary slab, this region moves away from the trench. The predicted thermochronometric ages continuously decrease during the model run towards a steady state that resembles the pattern set by the exhumation rates.

From our models, we conclude that at plate corners, the indenter acts in two ways to create a region of focused uplift above its apex. Firstly, the lower dip angle of the megathrust exerts stronger traction on the material accreted at the megathrust and thus favors localized failure. Secondly, the flexurally stiffened bulge presents a stronger barrier for the overriding plate if the slab advances. Both effects concur, depending on the velocity boundary conditions, to set the conditions required for localized rock uplift to occur.

For plate corners around the world, this implies that the potential for rapid and focused exhumation is set by the indenter shape of subducting slabs at plate corners. Nevertheless, additional parameters like the strength of subducting and overriding plate material or erosion potential are required to explain the variation in exhumation rates observed in syntaxes around the world.

Petrogenesis and tectonic significance of A-type granites from the Europe-Adria collision zone in Eastern Croatia

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Content

The aim of this study is to investigate the petrogenesis of alkali feldspar (AF) granites and syenites of the Sava zone, located within the basement of the Pannonian basin (Privlaka, Eastern Croatia). Cretaceous bimodal magmatism of the Sava zone is key for understanding the suture zone between Europe and the Adria. This magmatism is ambiguously interpreted and attributed to various tectonic settings [1,2,3]. Petrographic analysis, mineral chemistry and whole rock analysis of Privlaka AF granites and syenites point to an A₂-type affinity. The granites display a variety of textures, including granular, porphyritic and granophyric. These are mainly hypersolvus granites composed of perthitic orthoclase, quartz and subordinate albite, along with interstitial Fe-rich biotite, subhedral to euhedral ferro-edinite and accessory magnetite, zircon and apatite. AF syenite has similar mineral compositions, with perthitic orthoclase, albite, minor quartz, biotite, ferro-edinite and accessory magnetite, zircon and apatite. Al-in-hornblende barometry [4] yields pressures of 2.0 to 2.7 kbar for coarse-grained granite. Privlaka AF granites are metaluminous to peraluminous, with high SiO₂ contents (72.59-77.89%). They are characterized by Rb, Th, U, K, Zr and LREE enrichment and depletion in Ba, Ti, Sr and slight depletion of Nb and Ta, relative to chondrite. Pronounced negative Eu anomalies are found in these rocks. AF syenite is metaluminous with moderate SiO₂ content (61.15%). Compared to chondrite, it is characterized by enrichment in Rb, U, K and LREE, depletion in Sr and Ti and no Eu anomaly. Similarities in the mineralogical and geochemical characteristics of the granites and syenite point to derivation from the same source. The absence of a negative Eu anomaly in the syenite excludes derivation by fractionation from a basic magma. The geochemical characteristics suggest that they are post-orogenic, A₂-type granites, indicating an Upper-Cretaceous-age extensional event in this area.

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Quartz texture development of an exhumation shear zone in the Erzgebirge, N-Bohemian Massif: constraints from microstructures and EBSD data

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Content

The overthrusting of isothermally exhumed (ultra-)high pressure ((U)HP) units onto medium pressure (MP) gneiss complexes is a striking feature of the Variscan Erzgebirge (N-Bohemian Massif). In terms of shear mode, strain geometry and the relation of the different rock fabrics the complexity of this high strain zone is poorly understood. Here we present first results from detailed studies of the (U)HP / MP shear zone suite in the roof of the MP gneiss dome of Catherine-Reitzenhain including microtectonics, PT-analysis and EBSD texture analysis.

Generally, the entire zone is characterized by a flat lying main foliation. The complex particle path in the shear zone is indicated by a large scatter of the x axis of the finite strain ellipsoid. In the MP units an initially NE-SW oriented stretching lineation is obliterated by a second elongation with W-E azimuth. In contrast, the (U)HP unit only preserve a W-E oriented stretching lineation. Furthermore, the overthrusting of the UHP onto the MP units is revealed due to microkinematic indicators with top to WSW-WNW shearing. PT-analysis of paragneisses and PT-data of eclogites (1) indicates a constant temperature increase from 650°C in the MP units up to 1100°C in the (U)HP units.

In terms of the quartz crystallographic preferred orientation (CPO) we distinguish two characteristic endmembers. In central parts of the shear zone suite [0001] pole figures exhibit small girdle distributions around z and point to a {10-11}, i.e. the positive rhombs maxima in z (group 1). The grain shape is characterized by a low grainsize distribution and hence displays dynamic subgrain rotation recrystallization. In contrast, in the hanging (Tmax: 1100°C) as well as in the footwall (Tmax: 650°C), i.e. the peripheral parts of the shear zone suite the CPO is characterized by a pronounced point [0001] maxima in y, a pronounced {10-11} maxima is lacking (group 2). The particular quartz grains show all features of dynamic recrystallization by pervasive grain boundary migration. In conclusion, our observations can be explained by different recrystallization modes in different parts of a ductile shear zone, and corroborates the results of HT deformation experiments on quartzite (2), that shows that the CPO of quartz depends more on parameters like stress and strain than temperature.

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Strong temporal variation in exhumation in the Olympic Mountains (USA): New results from thermochronometer data and thermo-kinematic modeling

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Content

The competing influence of climate and tectonics on mountain building, and whether mountain ranges reach a steady-state in their evolution, is still widely discussed. Here, we investigate the evolution of the Olympic Mountains (Washington, USA) by means of thermochronology and thermo-kinematic modelling and discuss, how both tectonics and climate can influence the development of a mountain range independently from each other. The Olympic Mountains are an exhumed portion of the accretionary wedge of the Cascadia Subduction Zone, where the Juan de Fuca Plate is subducted beneath the North American Plate. The range began exhuming ~18 Ma, and may have achieved flux steady-state by 14 Ma. However, the present-day topography is clearly the result of intense Pleistocene glaciation.

In order to evaluate the long-term exhumation history of the orogen, we present new apatite (U-Th)/He (AHe), apatite fission track (AFT), and zircon (U-Th)/He (ZHe) ages for five sedimentary bedrock samples. All thermochronometer systems yield reset cooling ages for all samples. AHe ages are generally young (1.5 – 3.7 Ma), and AFT ages (5.0 – 7.1 Ma) overlap within errors with ZHe ages (4.8 – 10.2 Ma) for some of the samples. We performed 1D thermo-kinematic modelling to find plausible exhumation histories, which accurately explain our observed cooling ages. Three samples record high exhumation rates (>3 km/Ma) starting at 7–8 Ma. These high exhumation rates created equally high cooling rates, which led to the observed overlap of AFT and ZHe ages. After this exhumation pulse, rates decrease to ~0.1 km/Ma around 5–6 Ma. A suite of samples show a later increase in rates during the Pleistocene to 1.0–1.5 km/Ma. We interpret the reduction of exhumation rates ~5–6 Ma as a response to tectonic forcing, as there was a significant reduction in plate subduction velocities around this time. The increase in exhumation rates during the Pleistocene is best explained as a response to significant glacial erosion, i.e. a response to climatic changes. We suggest the spatial variation in exhumation histories between samples to be the upper plate response to the shape of the subducting slab, i.e., the location of this orogen within an orogenic syntaxis. Concluding, the Olympic Mountains indicate both the influence of tectonics as well as climate on their evolution and that this mountain range has not been in steady-state during its entire evolution.

Structural evolution of shear zones along the Combin zone (Switzerland, Italy) and implications for the dynamics of the orogenic wedge in the Internal Western Alps

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Content

The Western Alps consist of a stack of continental and oceanic units that assembled along the Adriatic continental margin during Late Cretaceous - Paleogene subduction, exhumation, and accretion. The Combin zone comprises oceanic material (Tsaté nappe) and thin sheets of continental metasediments (Cimes Blanches and Frilhorn nappes). The Tsaté nappe represents a former accretionary wedge and mainly consists of calcschists with bodies and lenses of greenschist and serpentinite. The Combin zone is bounded by two major Alpine tectonic contacts, the Dent Blanche Basal Thrust at the top and the Combin Fault at the base. It is overlain by the continental Dent Blanche nappe and underlain by the continental St. Bernhard nappe system in the NW and the oceanic Zermatt-Saas zone in the SE. Structural analyses of greenschist-facies shear zones along the Combin zone in the area between the Rhône valley in the north and the Aosta valley in the south revealed a polyphase deformation history:

D1) After initial accretion, the Combin zone experienced top-NW shearing due to foreland-directed overthrusting and associated exhumation of the Dent Blanche nappe.

D2) A subsequent phase of normal-sense top-SE shearing localized within the Combin zone due to ascent of units in its footwall.

D3) During a phase of dominant pure shear deformation at mid-crustal levels, earlier top-NW/SE shear zones were reactivated and partly obliterated. This phase resulted from underthrusting and accretion of European continental margin units and associated updoming of the nappe stack.

D4) Due to increasing collisional tectonics, the Combin zone and adjacent units were subject to compression leading to the formation of folds and crenulations deforming preexisting fabrics. In the hanging wall of the northwestern Combin Fault, this phase also led to the formation of low-grade top-(S)W shear zones.

D5) Semi-ductile to brittle orogen-perpendicular (NW-SE) extensional deformation partly overprinted structures related to ductile deformation.

We conclude that large amounts of strain localized along the two tectonic contacts, i.e. within mylonites along the Dent Blanche Basal Thrust and Combin Fault. Structural observations also indicate that D1 and D2 shear zones along and within the Combin zone developed in response to ascent of units in its hanging wall and footwall and therefore facilitated their exhumation by extrusion tectonics.

Structure and composition of fault zones in claystone – Constraints from microstructural and geochemical investigations

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Content

The sealing capability of clay rich sediments used as a geologic barrier for the storage of hydrocarbons or carbon dioxide or for the storage of heat generating radioactive waste can be significantly reduced if the claystones are cut by brittle faults. The objective of our studies are (1) to assess and quantify lithological variations of various clay rock formations on multiple scales and (2) to constrain the structure of artificial and tectonic fault zones and their relevant deformation mechanisms.

Our approach is a combination of microstructural observations using SEM, CT imaging and optical microscopy with a set of geochemical and phase analyses, like XRD, XRF and ICP-MS. In addition, organic (TOC) and inorganic carbon (TIC), total sulphur (TS) as well as the cation exchange capacity (CEC) were determined.

From our first investigations in Mont Terri and in German Lower Cretaceous claystones it is concluded that fractures in claystones occur locally in brittle shear zones, and often evolve around heterogeneities. Under the microscope, the fine grained fault core is cataclastically reworked and often accompanied or bordered by a more or less developed calcite rich damaged zone, including veins and folds. Discrete microscales are separating the faulted claystone into small, duplex like bodies. 2D grain shape analyses prove a reorientation of elongated porphyroclasts and clay particles towards the strongly sheared domain with an angle of 30-70° relative to the main slip plane.

The geochemical composition of undeformed wall rock and fault rock is different concerning the amount of Ca, Mn, Sr and TIC. Isocon diagrams of the fine grained fault core suggest only minor fluid-rock ratios during deformation. However, volume loss in this domain is related to pressure-solution, which is indicated by stylolites. In contrast, the surrounding damaged zone shows an enrichment of Sr, CaO and MnO, the corresponding volume gain can be related to opening of fractures and pores, now filled with calcite. Based on our preliminary results we conclude that fault zones in claystones can form a complex network of discrete microscales, which result from cataclasis and solution-precipitation creep as well as local microfolding. As the phyllosilicates show a strong shape-preferred orientation in the fault zones, the latter are prone to be reactivated in cases of rising pore fluid pressure, increasing differential stress, or during gallery excavation.

Subduction zone processes: Microstructural record from the exhumation of the high-pressure Adula Nappe (Switzerland)

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Content

The Adula Nappe of the Central Alps was originally part of the distal European continental margin and entered a south-dipping subduction zone experiencing high- to ultrahigh pressure peak conditions at about 38 Ma. During exhumation, the unit underwent polyphase deformation associated with a pressure drop of 13–9 kbars in the Northern Adula Nappe and 20–10 kbars in the central part. Despite extensive research during the last decades, the internal deformation of the Adula Nappe during exhumation is not completely understood. Especially the large pressure-temperature gradient from 12–17 kbar/500–600 C° in the north to at least 3 GPa/800–850 C° in the south is a topic of debate. It was either caused by internal, heterogeneous deformation of the during exhumation, or by tectonic overpressure, which would indicate that the Adula Nappe was not as deeply subducted as previously assumed.

In this study, we sampled metasediments and orthogneisses in a close-meshed net throughout the entire Adula Nappe. Crystallographic preferred orientations (CPOs) were measured with time-of-flight neutron diffraction at the SKAT diffractometer at JINR, Dubna, Russia.

Quartz CPOs show a great variability, but generally yield a top-to-the-north sense of shear. Most c-axes patterns exhibit peripheral maxima at an angle to the foliation normal pointing to dominant basal < a > slip, especially in the northern nappe. The samples from the central nappe show also maxima between Z and Y of the c-axis pole figure indicative of rhomb-, π - and prism < a > slip, combined with asymmetric crossed or single girdles. A few samples yield small circle distributions suggesting a flattening component. Mica exhibits a pronounced alignment of its basal plane within the foliation and high m.r.d. in all samples. In some of the gneiss samples even plagioclase shows a weak CPO with an alignment of its (010) plane within the foliation. Despite the variability of the quartz c-axis patterns, we can infer dominant top-to-the-north directed shear at the exhumational front of the northern Adula Nappe during Zappone deformation, which corresponds to previous investigations. The patterns of the central Adula Nappe are more complex with a multiple slip system activity. The high strain and complex geometry, as well as remnant indicators of flattening strain point to vertical flattening and intense shearing during exhumation without a need for tectonic overpressure. However, further investigations are required.

The eclogites of the Schober Group: An example for Variscan and Eoalpine eclogite-facies metamorphism of the Austroalpine basement rocks

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Content

The Schober Group is located in the Lower Central Austroalpine, which comprises pre-Permian basement rocks with Variscan metamorphism, partly overprinted by Cretaceous metamorphism.

At the Prijakt Mountain in the western part of the Schober Group, a several hundred meters thick eclogite body occurs. The protolith age is 590 ± 4 Ma obtained by Pb-Pb zircon dating [1]. The age of the high-pressure metamorphism, Variscan vs. Alpine, is controversial. Based on petrology and structure, Schulz [2] proposed early-Variscan high-pressure metamorphism for the eclogites with P/T conditions of 1.4-1.6 GPa and 550-650°C. Linner [3] obtained a garnet-whole rock Sm-Nd age of 115 ± 33 Ma for the Prijakt eclogites and therefore proposed Eoalpine metamorphism at 1.6-1.8 GPa and 660 ± 30 °C.

We performed Lu-Hf geochronology on two eclogite samples from Prijakt. In both samples, two garnet generations occur. In one sample (PRI 4), the older generation (grt 1) is predominant with thin rims of grt 2, whereas in the other sample (PRI 3), grt 1 is only present as relics and grt 2 dominates. Lu-Hf ages are Late Carboniferous for PRI 4 (also confirmed by Sm-Nd) and Late Cretaceous for PRI 3. We interpret that these rocks experienced eclogite-facies metamorphism twice, in the Variscan and in the Eoalpine orogeny. While the Variscan eclogite paragenesis of PRI 3 was almost completely retrograded before the Eoalpine eclogite-facies metamorphism, PRI 4 preserved its Variscan high-pressure assemblage and therefore yielded a Variscan age. Thus our study confirms that the basement of the Schober Group was subducted twice, in the Variscan and in the Eoalpine orogeny.

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The influence of eclogitization of lower crustal rocks on receiver functions

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Content

Geophysical methods are used to image the earth's interior and help to understand processes taking place at depth (e.g., subduction zone processes). However, interpretation of signals retrieved from such methods is often difficult. With the receiver function method the shallow part of subducting crust can often be imaged clearly. At greater depths, the subducted material eludes detection, which is commonly attributed to the insufficient seismic velocity contrast of the subducted and eclogitized crust to the surrounding mantle. However, the descending material does not disappear from seismic images abruptly. In fact, a zone of "blurring" can be observed in most receiver function images likely representing the transition to high pressure rocks. A natural analogue is found in the Caledonian Lindås nappe of western Norway, where former lower continental crust that has been subducted to depths of approximately 60 km and hence partially eclogitized, is exposed at the surface today. Here, we combine structural mapping, petrological analysis, and seismic modelling to study how eclogitization and associated structures affect receiver function signals. In the study area, eclogitization is fluid induced and eclogites are dominantly present in shear zones of variable scale (cm to 100s of meters). In order to constrain seismic properties of these rocks we performed seismic velocity measurements with a true triaxial multi-anvil press and compared these results to velocities derived from thermodynamic modelling. Both methods produce consistent results for p- and s-wave velocities of eclogites and granulites. Additionally, seismic anisotropy in eclogites is significantly higher than in granulites. These results were in turn used to derive simplified receiver function models to deduce the influence of structural and petrological changes on seismic signals during subduction. With these seismic models we can reproduce the "blurry" zone observed in receiver function studies from many subduction zones. This indicates that partial eclogitization indeed is the major controlling factor of this zone. Further, the simplified seismic models show that eclogite-facies shear zones constitute seismic reflectors and different geometries produce distinctly different receiver function signals. The structures and petrophysical properties of the shear zones found in the Lindås nappe can thus be used to aid the interpretation of receiver functions obtained from subduction zones active today.

Triangle Zones

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Content

Triangle zones are important structures found in foreland fold-and-thrust belts all over the world and are commonly associated with tectonic wedging. However, tectonic wedging and consequently the formation of passive hinterland verging roof thrusts requires particular mechanic conditions such as pre-fractured rocks, syntectonic sedimentation, or a specific stratigraphic layering with variable mechanically weak and rigid formations. In this contribution models of triangle zones and hypotheses regarding their formation are reviewed. We present selected geometric and kinematic models of triangle zones and discuss their mechanical implications.

Our results show that the term “triangle zone” is often used in a contradictory sense and interpretations are affected by large uncertainties. Passive roof thrusts are not necessarily required in all cases and suggested models of triangle zones, even if they are geometrically and kinematically viable, are hampered by their mechanical implications. With respect to a large number of published triangle zones and associated kinematic as well as mechanic models we present a new definition and classification scheme, which is applied to natural examples worldwide. We show that triangle zones can be separated into two types: (1) detachment dominated and (2) ramp dominated triangle zones. Both types imply particular mechanic conditions of involved detachments and regional dynamics. Regarding the large uncertainties associated with triangle zone interpretation we suggest to only use the term “triangle zone” in a very stringent manner and only if irrefutable evidences for stratigraphic repetitions within a duplex are given. The results should then be validated with additional kinematic and mechanic considerations. Geometric and kinematic uncertainties as well as implications of the proposed model explaining observed triangular structures should be reflected in the nomenclature used.

Session 10.4: Advances in Scientific Drilling in the Oceans and on the Continents.: Poster

Session 10.4: Advances in Scientific Drilling in the Oceans and on the Continents.: Poster
A-531

Agricultural activity in the Baltic region and coeval terrestrial and marine ecosystem changes – palynological pilot studies (IODP Exp. 347 Sites M0059, M0063)

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Content

The Baltic Sea region is an interesting research area for the reconstruction of past changes in terrestrial ecosystems, since it is adjacent to different vegetation zones. Anthropogenic impact influenced the terrestrial ecosystem development in the Baltic region, particularly during the past 2000 yr. This impact can be identified via palynological studies, e.g. via increasing presence of cultivated taxa in the pollen data.

Terrestrial pollen records do not allow to assess coeval changes in the marine realm, though these would be of particular interest to see if agricultural activity might have had an impact on the marine ecosystems of the Baltic Sea. A direct correlation with marine proxies, e.g. dinoflagellate cysts, can however be achieved via the examination of pollen grains in marine cores, like those gained during IODP Exp. 347.

We present reconstructions of the evolution of terrestrial and marine ecosystems in the central (Site M0063) and southwestern Baltic region (Site M0059) during the Late Holocene. Our results show that increasing percentages of pollen grains of cultivated *Poacea* occur around 1500 yr BP at both sites, coevally with a relative decrease in broad-leaved tree pollen. At Site M0063, the increase of agricultural activity is coeval with high occurrences of *Radiosperma corbiferum* and decreasing salinity (as indicated by dinocyst process lengths and low dinocyst occurrences). At Site M0059, increased presence of rye pollen is also coeval with a decrease in organic-walled dinocysts, with exception of the Genus *Gymnodinium*, which shows a rapid increase (Kotthoff et al. 2017). In the framework of an ongoing project, it shall be analyzed if these marine signals are connected to factors such as nutrient input.

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Assessing microbial, mineralogical, and hydrothermal processes in the ICDP borehole on Surtsey: a combined observatory and experimental approach

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Content

ICDP supports the SUSTAIN drilling project, which is aimed at investigating the formation and hydrothermal alteration of Surtsey volcano in the Vestmannaeyjar archipelago, Iceland. Rapid and intense alteration of tephra has been key to the post-eruption evolution of Surtsey. We here report on the goals and plans of SUSTAIN and our individual research project, which is one of 17 within SUSTAIN.

SUSTAIN aims to sample the complete succession of a neo-volcanic island from the surface to the underlying oceanic crust. Recovered drill core and post-drilling borehole experiments will allow us to examine the coupled changes of porosity and permeability by mineral dissolution and precipitation and the consequences for changes in rock physics properties. For reaching these aims, an inclined >200-meter deep hole is planned to sample the conduit system of the 1963 eruption. A second vertical hole will be 200 meters deep and sample hydrothermally altered tephra down to the underlying oceanic basement next to the 1979 drill hole. More details about SUSTAIN are provided by [1] Jackson et al. (2015).

The Surtsey Subsurface Observatory will be installed for long-term monitoring and in situ experiments. The installment is to be placed in the vertical hole, which will be cased with anodized aluminum to facilitate exploring basement water chemistry and water-rock-microbe interactions over time. The observatory consists of miniature temperature loggers and perforated PEEK-incubators that contain hyaloclastite from Surtsey as well as forsteritic olivine. The incubation devices will be hung down the hole on a Vectran rope and placed in areas where the casing is perforated to allow for flow of basement fluid. The incubators and autonomous temperature loggers will be left in the hole for two years.

In the meantime, work on ICDP drill core will be conducted to examine the distribution of primary versus secondary phases versus pore space to derive empirical relations between porosity, permeability, the extent of replacement of primary phases, and nature and distribution of secondary phases. The combined results will allow us to relate mineral chemical and textural information in order to gain specific insights into the relations between pore space evolution and mass transfer reactions.

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Drilling overdeepened Alpine Valleys (DOVE)

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Content

A recently approved ICDP proposal targets formerly-glaciated areas, which are often characterised by deeply incised structures filled by Quaternary deposits. These buried troughs were formed by glacial overdeepening, likely caused by pressurized subglacial meltwater below glaciers. The drilling initiative consists of several drill sites in six different countries. Being the best studied mountain range, the Alps will serve as textbook example allowing application of drilling results to other glaciated areas around the world. The drill holes, to be cored all the way to bedrock, will explore the type and age of the infillings of these overdeepened troughs. Such drill-cores hold the keys to understand the rates and nature how mountain ranges and their foreland have been shaped by repetitive glaciations. The overarching goal will be to date the age and extent of past glaciations and their connection to palaeoclimate, palaeoecology and landscape history. As of today, it is not known how these glaciations varied along and across the Alps through the past, as ice build-up along and across the Alps depends on atmospheric circulation patterns.

First results of drill holes in similar settings have produced local knowledge of the timing of glacial activity. Only an alpine-wide initiative, however, will be able to reconstruct the spatial and temporal variation of glacier advances and erosion and will yield an image sufficient to reconstruct the pattern of ice dynamics and related landscape forming processes over several glacial-interglacial cycles.

Next to these past environmental aspects, the valley fills are of large interest for groundwater aquifers, as water resources may become scarce in the context of the projected climate change. Related to this role, they may be used for shallow geothermal applications, which, however, rely on to date not well-constrained physical properties of the infilling sections.

All these goals will be first addressed by high-quality geophysical surveys that quantify the geometry of overdeepenings. Drill holes will be analysed through downhole logging, groundwater sampling and subsurface biosphere testing. Sedimentological, geochemical and biological analyses will characterise the sediment cores, and a combination of different techniques will establish the chronological framework. Eventually, the results will be cross-checked by modelling both glacial erosion and past climate circulation patterns.

**First deployment of a multi-barrel sea floor drill rig on the Antarctic continental shelf:
experiences from the MARUM-MeBo70 on Polarstern-Expedition PS104**

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Content

The MARUM-MeBo (abbreviation for Meeresboden-Bohrgerät, the German expression for seafloor drill rig) is a robotic drilling system that is developed since 2004 at the MARUM Center for Marine Environmental Sciences at the University of Bremen in close cooperation with Bauer Maschinen GmbH and other industry partners. The MARUM-MeBo drill rigs can be deployed from multipurpose research vessel like, RV MARIA S. MERIAN, RV METEOR, RV SONNE and RV POLARSTERN and are used for getting long cores both in soft sediments as well as hard rocks in the deep sea.

The first generation drill rig, the MARUM-MeBo70 is dedicated for drilling depths of more than 70 m (Freudenthal and Wefer, 2013). Between 2005 and 2017 it was deployed on 18 research expeditions and drilled more than 3 km into different types of lithologies including carbonate and crystalline rocks, gas hydrates, sands and gravel, glacial till and hemipelagic mud with an average recovery rate of 67 %. In February and March 2017 the MeBo70 was used on the West Antarctic continental shelf in the Amundsen Sea Embayment for the first time. The goal of the deployment on RV Polarstern expedition PS104 was to recover a series of sediment cores from different ages that will provide material for investigating the glaciation history of this area known as the most dynamic drainage area of the West Antarctic Ice Sheet. In this presentation we will focus on the operational experiences of this first deployment of a multi-barrel sea floor drill rig on the Antarctic continental shelf.

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KTB Deep Lab - A World Site for Ultra Deep Experiments and Investigations

Kück, J., Harms, U.

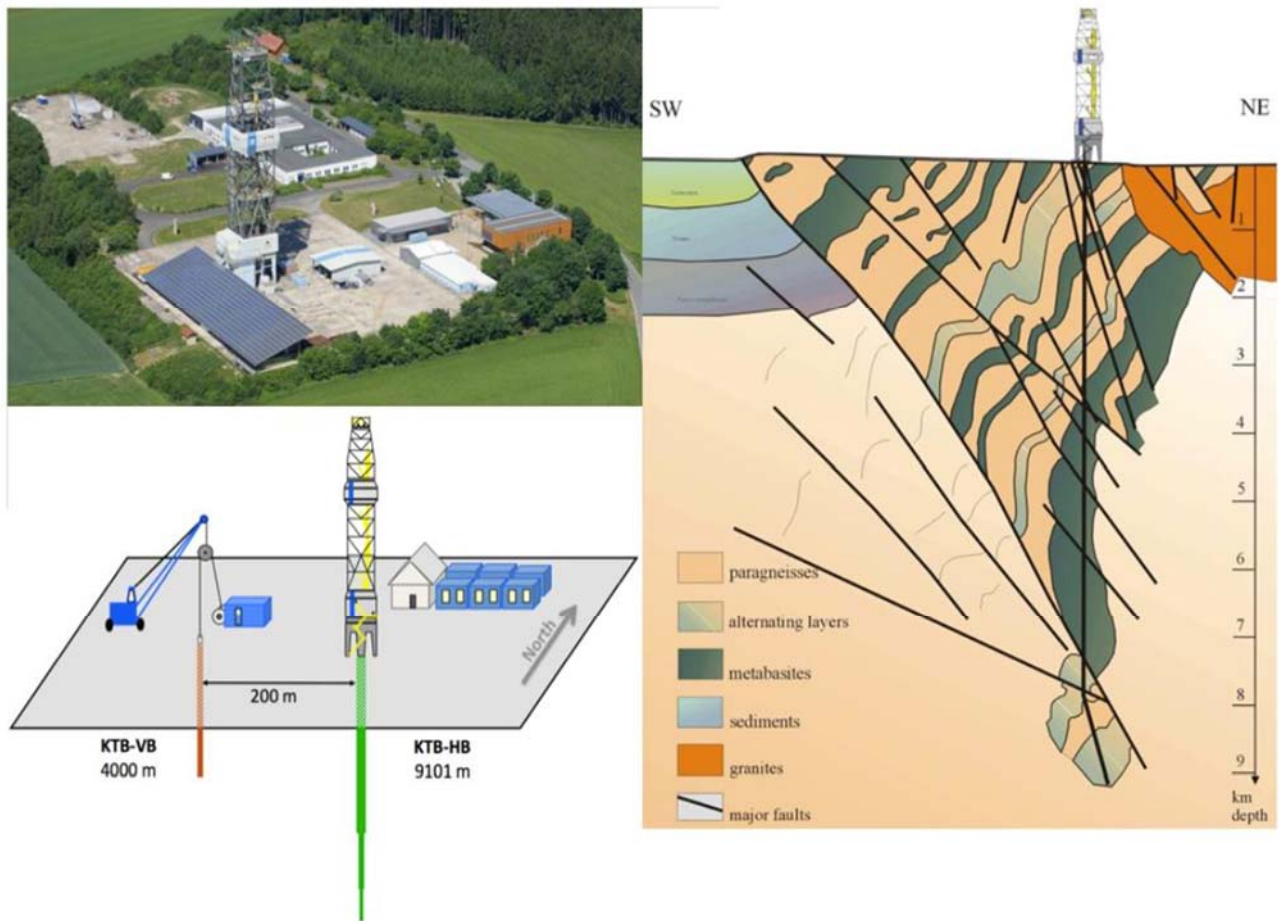
GFZ Potsdam, Potsdam, Germany

Content

Are you looking for an easy and probably long-term access to deep, extensive fluid systems, the deep biosphere at high temperature & pressure, a place underground to study temporal variations over long times? Or for a big sized and deep borehole to test a new method and instruments? Or for a location to try cross-hole experiments without time pressure? All this at low costs and at a convenient location?

These and even more options are at hand at the KTB Deep Lab in Windischeschenbach, Bavaria, Southern Germany, less than 2 hours away from Munich international airport. The unique setting of two adjacent deep boreholes of the former German KTB ultra deep drilling program (4 km & 9.1 km) in crystalline basement rocks just 200 meters apart from each other are available to the scientific community for exceptional experiments and investigations under in-situ conditions. Both boreholes were described and characterized geoscientifically in detail in the course of the KTB program. They are steel-cased almost entirely except for the bottommost sections (≈ 100 m).

The KTB Deep Lab is run since 1996 by the GFZ German Research Centre for Geosciences, Potsdam. The extensive KTB Deep Lab wireline infrastructure of logging winches, cables, borehole logging sondes and a workshop allows for a variety of downhole applications, in-situ tests and experiments in a wide range of pressure and temperature conditions. The experienced GFZ engineers and scientists will help you to make your ideas or scientific task a successful experiment. Access to the boreholes is free of charge for all non-commercial scientific purposes. A fee might apply for use of the KTB infrastructure, participation of GFZ personnel, depending on the extent of use.



Overview KTB Deep Lab

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Session 10.4: Advances in Scientific Drilling in the Oceans and on the Continents.: Talk

Keynote speaker
A-821

Greenhouse to Icehouse Antarctic paleoclimate and ice history from George V Land and Adélie Land shelf sediments

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Content

Along the George V and Adélie Land (GVAL) shelf of Antarctica, shallowly-buried strata contain a record of Antarctica's climate and ice history from the lush forests of the Eocene greenhouse to the dynamic ice sheet margins of the Neogene. Over these times, Antarctica and the Southern Ocean have played a central role in controlling sea level, deep-water formation, ocean circulation, and exchange of carbon dioxide with the atmosphere. Yet currently there are very few direct records of Antarctic climate and ice conditions from close to the continent. On the GVAL shelf, short piston cores and dredges have recovered Cretaceous and Eocene sediment at the seabed. In 2010, IODP Expedition 318 recovered earliest Oligocene and early Pliocene subglacial and proglacial diamicts, providing direct records of ice advances across the shelf at these times, and confirming that target sediments are accessible at shallow burial depths. However, challenging ice and drilling conditions from the JOIDES Resolution resulted in poor core recovery and abandoning sites before the stratigraphic targets were reached. Here we propose to use the MeBo sea bed drill for improved core recovery and easier access to the shelf. We propose to drill two stratigraphic transects of shallow (~80m) holes to investigate Antarctica's role in icehouse and greenhouse climates, and the transitions between the two.

To investigate Oligocene to Pliocene ice sheet dynamics, we target strata above and below regional erosional and downlap surfaces to date and characterize major episodes of ice sheet advance and retreat. These direct records of ice extent on the shelf can be set in the context of Southern Ocean records of temperature, ice-rafted debris (IRD) and latitudinal fluctuations of the opal belt, and hence we can relate ice behavior to paleoclimate conditions. The ice and climate history of the GVAL margin can provide warm-world scenarios to help understand ice sheet instability in analogous future warm climates.

In the Cretaceous and Eocene greenhouse target intervals: temperature and vegetation records will provide high-latitude constraints on pole-equator temperature gradients and their evolution; the proximity of the sites to the coastal lowlands will enable us to assess the hypothesized role of thawing permafrost in Eocene hyperthermal events; and late Eocene cooling and possible pre-cursor glaciations can also be documented by drilling.

A new seismic stratigraphy for the Plio-/Pleistocene at the Agulhas Plateau related to the variability of sediment provenance in the Indian-Atlantic Ocean gateway

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Content

The exchange of shallow and deep water masses between the Indian Ocean and the Atlantic constitutes an integral inter-ocean link in the global thermohaline circulation. In the gateway south of South Africa long-term changes in deep water flow during the Cenozoic have been initially studied using reflection seismic profiles. But the seismic stratigraphy was poorly constrained and not further resolved within the time period from the late Miocene to present. In particular, there were limited Pliocene records that could be used to investigate the influence of climatic (e.g. Antarctic ice volume) and tectonic (e.g. closure of the central American seaway) on the deep-water variability. In 2016 the International Ocean Discovery Program (IODP) Expedition 361 ("SAFARI") drilled on the southeast African margin and in the Indian-Atlantic ocean gateway [1]. The expedition was mainly targeted to reconstruct the history of the greater Agulhas Current system and recovered complete high-resolution Plio-/Pleistocene sediment sections at six drilling locations. Here we present preliminary results from Site U1475 (Agulhas Plateau), a location proximal to the entrance of North Atlantic Deep Water (NADW) to the Southern Ocean and South Indian Ocean. The site is located over a sediment drift in 2669 m water depth and comprises a complete stratigraphic section of the last ~7 Ma. We show cleaned, edited, and spliced high-resolution data sets of sediment physical properties measured at Site U1475. While the velocity and density records are used to calculate synthetic seismograms for a detailed correlation of the drilling results with the site survey seismic reflection profiles, colour reflectance and natural gamma radiation are interpreted as indicators of biogenic vs. terrigenous sediment input. Preliminary age assignments based on the shipboard bio- and magnetostratigraphy for the most prominent reflectors are ~2.0, ~3.8, and ~5.1 Ma. Furthermore rhythmic bedding within a Pliocene mudwave sequence likely reflects the 100-kyr orbital cycle. While the acoustic parameters are dominated by this 100-kyr eccentricity cycle, colour reflectance and natural gamma radiation show highest variability in the precession band. This very regular response to orbital forcing suggests that the shipboard age model can be significantly improved by cyclostratigraphy.

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Fractionation of Ca isotopes during transport and recrystallization processes in marine deep sea sediments of the Eastern Pacific

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Content

We studied diagenetic reactions in deep sea sediments from the Equatorial Eastern Pacific by analysing Ca isotope ratios of porewater and sediment on eight sediment cores from IODP Exp. 320/321. The Ca isotope ratio ($\delta^{44/40}\text{Ca}$) is a powerful tool to investigate diagenetic reactions in marine sedimentary porewater systems, as it is sensitive to processes such as carbonate dissolution, precipitation and recrystallization, due to the isotopic difference between dissolved Ca and solid carbonate minerals, and is also affected by ion exchange as well as deep fluid sources (e.g. [1] [2]). Two sediment cores show Ca isotope profiles that start at the sediment/water interface with seawater-like values, then decrease to sediment-like values due to recrystallization and then increase in the bottom part again to seawater-like values. The other studied cores show different degrees of flattening of this middle bulge. We interpret this systematic either as an effect of sediment thickness, decreasing recrystallization rates and/or fluid advection at the respective sampling sites. Element concentration profiles and Sr-isotope variations on some of these sediment cores show a similar behavior, supporting our findings ([3] [4]). The seawater-like values at the bottom of the sediment pile are supposed to be caused by fluids migrating through the oceanic basement, fed by seawater influx at (inactive) seamounts (e.g. [5]). There are two hypotheses for such a fluid flow: a) two seamounts or bathymetric pits are connected, with a recharge and a discharge site ([6]), or b) uptaken fluids could be released through the surrounding seafloor as well due to diffusive exchange with the underlying oceanic crust (e.g. [7]). Our Ca isotope results combined with a transport reaction model approach support the latter hypothesis.

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High-resolution seismic imaging of the internal structure of the Tannwald Basin: a distal branch basin of the Rhine Glacier

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Content

Sedimentary infills of glacially-overdeepened valleys are, together with glacial geomorphology, the best-preserved archives of the past glaciations, both in and around mountain ranges. The ICDP project DOVE – Drilling Overdeepened Alpine Valleys – intends to recover a number of sediment cores from the glacially-overdeepened structures at several complementing locations within the European Alps and their foreland. The overall scientific object is to improve the understanding of the timing of the onset, the number, and the extent of Quaternary glaciations in the Alps.

One of the three locations to be drilled in the first phase of DOVE is the Tannwald Basin (Baden-Württemberg), approximately 60 km north of the Alps. Defined as a geophysical test site, we intensively investigated this site using reflection seismics, with the aim to integrate high-resolution three-dimensional (3-D) and multi-component seismics to produce an improved structural and process-related characterization of the facies within the valley infill.

The elements of the SH-wave and 6-C seismic images correlate well with major structures in the P-wave image. However, in detail, significant differences exist that provide important, complementing information about the sediment characteristics.

The Tannwald Basin was incised into Tertiary molasse sediments by the Rhine glacier system, which also filled the valley with sediments. The basin was subglacially eroded during the Hosskirchian stage; our data show that its base is up to 250 m below the surface, with the axis of the deepest part running north-south. The seismic image enables us to differentiate the various seismic facies of sediments that fill the basin. It is filled with lacustrine fines of the Dietmann Formation (chrono- and lithostratigraphy cf. Ellwanger et al. 2011). At a depth of 56 m, the valley is overlain by till and meltwater sequences of Rissian and Würmian ice advances. A nearby well substantiates these findings and our interpretation that a 15 m-thick, allochthonous block of Molasse was glacially emplaced at the base of the basin.

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**Impact melt dynamics during cooling and peak ring formation of the Chicxulub crater,
Mexico**

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Content

Processes occurring during cooling of impact melt of large impact craters are not well understood. IODP-ICDP Expedition 364 “Drilling the K-Pg impact crater” drilled through 36 m of impact melt rock that covers the peak ring of the Chicxulub crater. From bottom to top, the core consists of (1) 587 m of shocked, mostly granitoid target rock, (2) 130 m thick impact melt rock and suevite, and (3) 112 m of post-impact platform carbonate rocks. Based on visual inspection, microstructural and electron microprobe analysis, we examined the structural and some chemical characteristics of impact melt rock overlying the peak ring in an attempt to elucidate its dynamics during solidification.

The impact melt rock is layered and consist of four subunits: (1) A 9 m thick basal subunit covers and intruded fragmented granitoid target rock, and consists of, at least, two pitch-black, silicate melt rock phases, evident by different compositions of plagioclase. The melt rocks contain few fragments, derived chiefly from gneissic basement rock. The glassy appearance and mottled texture of the melt rocks points to quenching and (auto)-brecciation of solidifying melt. (2) A 16 m thick subunit is characterized by, at least, two interlayered, i.e., immiscible, melt rock phases displaying convoluted, centimeter-scale folds. One phase consist of the pitch-black silicate phase. The other melt rock phase is bright green and derived from carbonate rock. The cusp-and-lobe geometry of the two phases suggests that the silicate was the more viscous one during folding and solidification of both phases. (3) A 6 m thick melt breccia unit is made up by the same melt rock phases, but displaying an enhanced contrast in mechanical competency. Specifically, angular to sub-rounded fragments of dark melt rock are enveloped by the flow-textured, carbonate melt rock. (4) The uppermost subunit is 5 m thick and is composed of carbonate fragments set in a brown matrix, the composition of which remains to be determined.

The structural and chemical characteristics of the lower portion of the melt rock point to deformation and incomplete separation of a silicate and a carbonate melt during solidification. Moreover, two oppositely directed temperature gradients quenched the top and the base of the melt and led to variable fragmentation of the melt phases during ongoing deformation, i.e., peak-ring formation.

IODP Exp. 366 to the Mariana forearc: blue mud from serpentinite mud volcanoes

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Content

Geochemical cycling, seismicity, and deep biosphere activity in subduction zones are affected by water–rock interactions. International Ocean Discovery Program Expedition 366 addressed the nature of these processes in shallow to intermediate depth of the Mariana subduction channel.

In the Mariana forearc, slab-derived fluids and solids form serpentinite mud volcanoes, which provide otherwise inaccessible samples from the subduction channel at depths to 19 km. Materials derived from the subducting Pacific plate thereby ascend via conduits in the deeply fractured upper Philippine Sea plate, and form vast serpentinite mud volcanoes at the seafloor. Mudflows include materials from the upper as well as from the subducted plate, all embedded in a serpentinite mud matrix. The mud volcanoes occur in varying distance from the deep-sea trench, thus representing a range of depths and temperatures to the downgoing plate and the subduction channel.

IODP Exp. 366 cored three serpentinite mud volcanoes (Yinazao, Fantangisña, and Asùt Tesoro) located 13 to 19 km above the slab ([1]) with estimated slab temperatures of 80 to 250°C ([2]). Cores were recovered from summits and flanks of the mud volcanoes. Recovered materials are mostly serpentinite mud containing millimetre- to metre-sized clasts of forearc crust (mafic) and mantle (ultramafic, strongly serpentinitised by rising fluids) material but also recycled clasts of the subducted plate (lithified sediments, alkali basalts, limestones) and forearc sediments (pelagic, volcanic ash deposits).

The serpentinitised ultramafic rock and mud materials are largely uniform in major element composition but vary in trace element composition. These variations may reflect different *T* and *P* conditions in the underlying subduction channel. Fluid discharge rates and dissolved gases (H₂, CH₄, C₂H₆) are currently highest at the mud volcano farthest away from the trench, presumably supporting active microbial communities; extensive sampling for shore-based work was conducted during the expedition.

Physical property (e.g., porosity, GRA density) and heat flow data from summit and flank sites vary significantly, and are consistent with active fluid discharge at the summits.

During Exp. 366, we also installed screened borehole casings at each of the summit sites for future *in situ* experimentation with CORK-Lite observatories.

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Processes recorded in the K-Pg boundary deposit within the Chicxulub impact from IODP-ICDP Expedition 364

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Content

The International Ocean Discovery Program (IODP) Expedition 364 with co-funding from the International Continental Scientific Drilling Program (ICDP) drilled into the offshore portion of the Chicxulub impact crater in April-May, 2016. Site M0077 recovered core from 505.7-1334.73 m below seafloor and was located near the top of Chicxulub's topographic peak ring providing a unique setting for examining the Cretaceous-Paleogene (K-Pg) boundary deposit within the crater. The bulk of the cored interval of the peak ring at Chicxulub consists of granitoids originating from mid-crustal depths and emplaced through collapse of a central uplift in the first 10 minutes after impact.

These uplifted target rocks are overlain by ~130 m thick sequence of impact melt rock and breccias (suevite). The contact between impact melt rock (Unit 3) and suevite (Unit 2) is gradational as indicated by partially digested clasts within an impact melt rock matrix overlain by 10 m thick sequence with large clasts (Unit 2C). These are impactites that initially stayed within the transient crater cavity and were dynamically emplaced onto the peak ring immediately after its formation and prior to reentry of ocean waters. Upsection Unit 2B includes a 30 m thick section with similar clast sizes followed by a 15 m thick upward fining section. This sequence is consistent with first emplacement without settling through water followed by emplacement through the ocean waters that re-entered the Chicxulub basin within 10s of minutes. Across an erosional surface, the suevite of Unit 2A (~45 m thick) includes a reverse graded section (mass wasting?) followed by a fining upwards section overlain by sand-sized suevite with successive zones upsection of faint layering, possible cross bedding, and then clear dipping layers and cross-cutting beds. These observations suggest a complex series of resurge events (tsunami and/or seiches) took place could have occurred for hours after the impact. Overlying the suevite sequence is an 80 cm thick transitional layer that is being examined for its fossil content and impactor signature as a possible 80 cm equivalent to the <1 cm K-Pg deposit that in distal sites. This layer has the potential to record the greatest changes in accumulation rate as it may have deposited in as little as weeks based on Stokes Law or as long at 30 kyr based on the presence of Danian foraminifera in the limestone overlying this transitional layer.

Progress in the ICDP Oman Drilling Project

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Content

The Samail Ophiolite, in Oman and the United Arab Emirates, is the largest, best-exposed section of oceanic lithosphere in the World. The Oman Drilling Project is a comprehensive drilling program that will sample the whole ophiolite sequence, from crust through to upper mantle, in a series of diamond- and rotary-drilled boreholes. Data collection will include analysis of rock core, geophysical logging, fluid sampling, hydrological measurements and microbiological sampling.

The active drilling phase one took place from December 2016 to March 2017. Wireline diamond coring took place in the following sequence: Site GT2 (Wadi Gideah, mid-level gabbros), Site GT1 (Wadi Gideah, lower gabbros), Site GT3 (Wadi Abdah, dyke-gabbro transition), Site BT1 (Wadi Mansah, listvenites and basal thrust). Simultaneously to the diamond coring, rotary drilling was performed at Site BA1 (Active alteration). At the end of active phase one, four cores, each 400 meters long, were obtained.

The basic core curation, initial description, core scanning, piece labelling, data logging into the ICDP DIS system, and the packing into transport boxes for shipping was established by on site science teams of 3 to 6 persons who had to manage a core flow up to 33 meters core per day. The core conditions are excellent, with smooth cut surfaces enabling good conditions for macroscopic core description, and high recovery rates near 100%. Detailed description of cores drilled in phase one were performed over 60 days (two science parties, lasting 30 days each) in summer 2017 on board the IODP drilling ship Chikyu, in Japan, during a non-IODP period while this ship was in the port. Here, detailed core descriptions, instrumental scanning, measurements of physical properties, and individual sampling have been undertaken according to the "IODP standard" within small science groups related to igneous petrology, metamorphic petrology, structural geology, geochemistry, microbiology, paleomagnetism, and petrophysics. For each core, visual core descriptions (VCD) were produced, and detailed thin section work was also included. Preliminary results will be shown.

Phase two, the coring at sites BA1 (Active alteration) and MD1 (Crust-mantle boundary), as well as further rotary drilling, will take place in October 2017. Detailed description of cores drilled in phase two is planned to take place on board of the US drill ship JOIDES Resolution in summer 2018 during its non-IODP period.

Sedimentary sequences below the Ekström Ice Shelf, Dronning Maud Land, Antarctica: A pre-site survey for deep drilling (Sub-EIS-Obs)

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Content

During the last season and ongoing planning, pre-site surveys are operated at the Ekströmen, Dronning Maud Land, close to the Neumayer-Station III, with the primary target to build a stratigraphic age framework of the under-shelf-ice-sediments. These sediments are overlying the Explora Wedge [1], [2], a syn- or post-rift volcanic deposit, and dipping north- to north-eastward. Expected ages could range from Late Mesozoic to Quaternary. From new vibroseismic profiles we will select sites for short core seafloor sampling of the oldest and of the youngest sediment sequences to confine their age time span.

After that, we could select one or several sites for potential deep drillings (several hundred-meter-deep) with the support of international partner, if we could rise interest. The deep drillings should recover the sediments overlying the Explora Escarpment, and should discover the nature of the Explora Wedge as well. We expect that the overlying sediment sequences could reveal the history of polar amplification and climate changes in this part of Antarctica, the build-up of the East Antarctic Ice Sheet during past warmer climates and its Cenozoic and future dynamic and variability.

The plan for seasons 2017/18 and 2018/19 are the testing of different sea floor sampling techniques through Hot Water Drill (HWD) holes. To select the drill sites for this shallow coring additional high resolution seismic will be acquired as well.

Having holes through the shelf ice and sampling the sea floor will provide the unique opportunity for further piggy bag experiments consisting of multi-disciplinary nature. Experiments and measuring setup for oceanography, sea and shelf ice physics, geophysics, geology, hydrography, and biogeochemistry could be planned to characterize the sea-ice and shelf ice system, underlying water column, and the sediments. Video characterization underneath the shelf ice and at the seafloor, sediment trap deployment, seafloor mapping with an AUV (Leng, DFKI, ROBEX) could lead as well to innovative new interdisciplinary observations and discoveries of the sub-ice environment and ecosystem [3].

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Target-rock weakening during peak-ring formation of the Chicxulub crater inferred from Expedition 364 drill core

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Content

The floors of large impact structures are largely flat and contain one or more morphological rings. The formation of the innermost topographic ring, the so-called peak ring, and the causes of target rock weakening leading to the observed flat crater floors are not well understood. Constraining these mechanisms is the prime structural geological objective of Expedition 364 “Drilling the K-Pg Impact Crater”, using the Chicxulub impact structure, Mexico, as a terrestrial analogue for the formation of planetary impact basins.

A total of 829 meters of core was recovered from borehole M0077A drilled into the peak ring of the Chicxulub crater. From bottom to top, the core is crudely composed of: (1) pervasively shocked granitoid target rock hosting meter- to decameter-thick impact melt rock and suevite dike-like bodies, (2) a 130 m thick impact melt rock and suevite unit overlying the target rocks, and (3) a 112 m thick section of post-impact pelagic carbonate rocks. Based on visual appraisal of the drill core, we determined prominent impact-induced deformation structures in target rock.

In addition to microscopic planar structures formed by shock metamorphism, the target rocks are replete with impact-induced, mesoscopic planar deformation structures. These structures include: (1) cataclastic deformation zones, (2) striated shear faults, (3) crenulated mineral foliations, (4) ductile shear band structures, and (5) open fractures. Structural overprinting criteria point to a relative age for these structures. Zones of cataclasite are consistently displaced or used by shear faults. Cataclasite bands in target rock fragments included in suevite are cut by the latter and a striated target rock fragment was found in impact melt rock. Suevite and impact melt were emplaced in zones of dilation, often localized by shear faults. Collectively, these observations suggest that cataclastic deformation was followed by shear faulting, followed in turn by emplacement of suevite and melt into dilation zones. This succession of deformation mechanisms is corroborated by the observation that suevite and impact melt bodies are devoid of cataclasite and shear faults. These lithological units were still viscous when they were deformed by ductile band structures. Thus, the shear band structures formed after the shear faults. Based on the structural overprinting relationships, we attempt to relate the mesoscopic planar structures to cratering stages known from impact mechanics.

The ICDP drilling project on Lake Towuti, Indonesia: preliminary sedimentological, mineralogical, and geochemical results from surface sediments and drill cores

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Content

More than 1000 m of sediment core were recovered from three different drill sites in tropical Lake Towuti (2.5°S, 121°E; Fig. 1), Indonesia, during the Towuti Drilling Project (TDP) in spring 2015. Furthermore, a set of 84 lake surface sediment samples, distributed over the entire lake, were collected in order to better understand modern sedimentary processes.

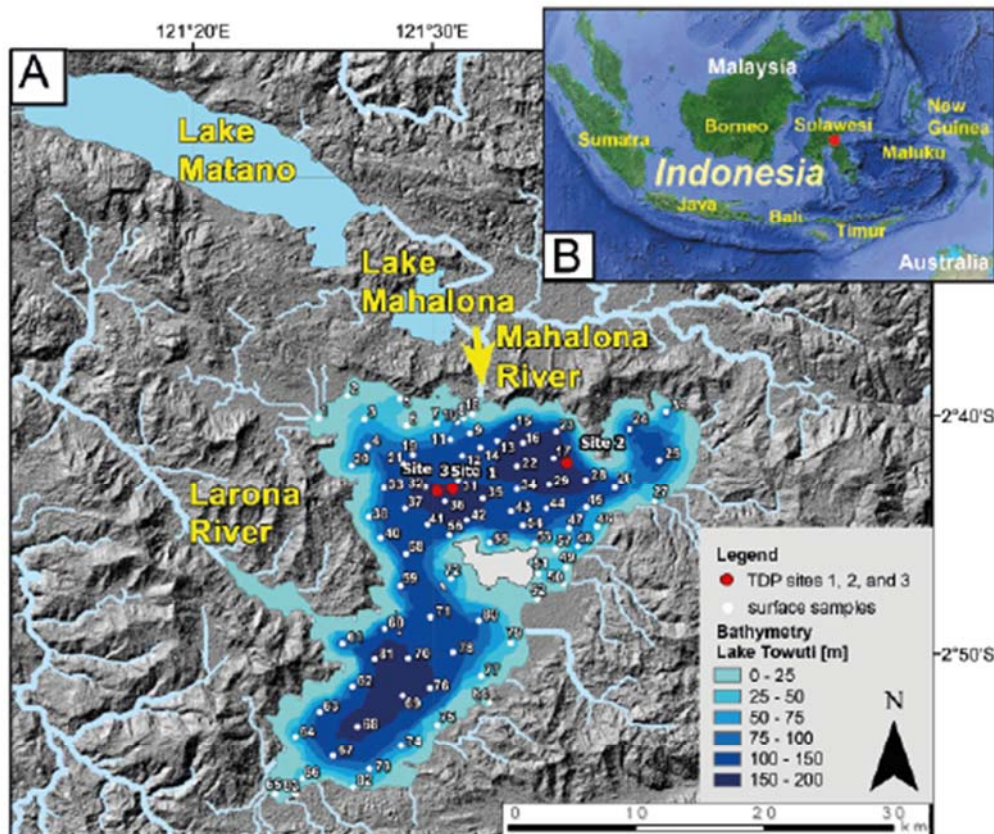


Figure 1: (A) Digital Elevation Model (DEM) of the Lake Towuti area showing the lakes Matano and Mahalona further upstream, the major inlets, the outlet Larona River, the lake bathymetry, and the sampling sites. (B) Location of Lake Towuti (red dot) on Sulawesi Island, southeastern Asia.

The surface samples were investigated for physical, chemical, mineralogical, and biological properties at the University of Cologne (UoC), Germany. The sediment cores underwent initial core description including: macro- and microscopical lithological descriptions, line-scan imaging, logging of physical properties (MSCL), and subsampling at the National Lacustrine Core Facility of the University of Minnesota, USA, in November 2015 and January 2016. Afterwards, the subsamples and archive core halves of TDP Site 2 were shipped to the UoC for X-Ray Fluorescence (XRF) scanning. From this core, 672 subsamples were investigated for sedimentological, geochemical, and mineralogical properties, supplemented by visible to near-infrared infrared spectroscopy (VNIR) at Brown University, USA.

The data from the surface samples show evidence that allochthonous sedimentation in Lake Towuti today is dominated by fluvial supply from five distinguishable source areas: (i) the Mahalona River to the north, which drains lakes Mahalona and Matano, (ii) inlets around the village of Timampu to the northwest, (iii) the Loeha River to the east, (iv) the Lengke River to the south, and (v) the Lemo-Lemo River to the northeast of Lake Towuti. Of these, source areas (ii) and (iii) as well as (iv) and (v) have similar geochemical compositions, respectively. In addition, the lake sedimentation is significantly influenced by gravitational sediment supply or erosion and transport from steep slopes as well as lake-internal gravitational and density-driven processes. The uppermost ~41 m of sediment core 2A consist of pelagic sediments (totaling ~11 m) and event layers from mass movement (~30 m) that were formed during the past ~50 cal kyr. In this period, the data reflect significant climatic and environmental changes, in particular in precipitation and lake level. These changes seem to be coupled to prominent paleoclimatic events.