



92nd Annual Meeting

Deutsche
Mineralogische Gesellschaft

JENA
21–24 September 2014

Programme



Minerals at Focal Point

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www.dmg2014.de

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Organisation and Imprint

Venue

Friedrich Schiller University Jena
Campus Ernst-Abbe-Platz
Carl-Zeiss-Straße 3
07743 Jena (DE)

Date

21–24 September 2014

Organiser

Deutsche Mineralogische Gesellschaft e.V. (DMG)
www.dmg-home.de

Conference Chair

Prof. Dr. Falko Langenhorst
Friedrich Schiller University Jena
Institute of Geosciences • Department of Mineralogy
Carl-Zeiss-Promenade 10
07745 Jena (DE)

Local Organising Committee

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Klaus-Dieter Grevel
Falko Langenhorst
Juraj Majzlan
Kilian Pollok

Conference Organisation and Industrial exhibition

Conventus Congressmanagement & Marketing GmbH
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dmg2014@conventus.de • www.conventus.de

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Dear colleagues,

This year's annual meeting of the German Mineralogical Society (DMG) will be held for the first time at the University of Jena, Germany. We are pleased that you join this event from 21–24 September 2014.

The congress motto “Minerals at Focal Point” refers on one hand to the object of our discipline and on the other hand to the long tradition of the science center Jena in optical microscopy. Organized under this motto the meeting aims at bringing together researchers from all fields of our multifaceted discipline mineralogy. The meeting program advertises a wide range of topics at the crossroads of crystallography, applied mineralogy, petrology, and geo-/cosmochemistry. We are happy to have received your numerous (almost 300!) contributions to the 17 sessions and look forward to vivid discussions.

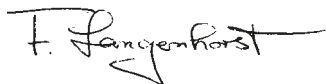
Besides the scientific sessions the conference program offers also an optional half-day excursion to the close-by former Uranium mining district at Ronneburg, a city tour and prolonged hours of opening of the mineralogical collections.

It so happens that the organization of the 2014 DMG meeting coincides with the 100th anniversary of the journal “Chemie der Erde/Geochemistry”, which was originally founded in Jena by one of the fathers of the DMG, Prof. Gottlob Eduard Linck. To celebrate this event a special volume is in press that will be available to the attendees.

The meeting could not happen without the support of sponsors, the engagement of conveners, your contributions and the many helpers of the local team. Thank you all for your efforts! We hope you will enjoy the conference program and look forward to your attendance and contributions. Welcome in the city of light.

With kind regards,

On behalf of the organizing committee,

A handwritten signature in black ink, reading 'F. Langerhorst'. The signature is stylized with a long, horizontal flourish extending to the right.

Falko Langerhorst

General Information

Registration Fees

Member DMG	230 EUR
Non-member	270 EUR
Student member DMG*	120 EUR
Student non-member*	150 EUR

Ice Breaker, 21 Sep.**	included
Social Evening, 23 Sep.	10 EUR
Field trip Ronneburg, 25 Sep.	25 EUR

Accompanying person

Ice Breaker, 21 Sep.	10 EUR
Social Evening, 23 Sep.	40 EUR

* Please send a confirmation of your status either to registration@conventus.de,
Fax +49 3641 31 16-244 or by mail to Conventus GmbH • Carl-Pulfrich-Straße 1 • 07745 Jena (DE)
indicating the keyword: DMG

** Registration required

Payment and Confirmation of Payment

An invoice or confirmation of registration will be sent to you via postal or electronic mail within 14 days. This invoice is a valid invoice which may be submitted to the local tax and revenue office. All fees are due upon receipt of invoice/registration confirmation. Payment transfers must include participant's name and invoice number. Payment is also accepted by credit card (Master-/Eurocard, American Express, VISA). Should you transfer your invoice amount within 10 days of the start of the event, please present your transfer remittance slip onsite.

Accommodation

We reserved a contingent of rooms in different hotels. Please find more information online at www.dmg2014.de.

The registration fee includes

- Admission to all scientific sessions and access to our industrial exhibition
- Welcome reception
- Conference materials (conference bag, programme booklet and abstract book)
- Catering during the coffee breaks
- Special volume of the journal "Chemie der Erde/Geochemistry"
- Booklet to the special exhibition "Die Mineralogische Societät zu Jena" presented in the Mineralogical Collection

General Terms and Conditions

Please find our General Terms and Conditions at www.dmg2014.de.

Travel

DB German Rail Event Ticket

In cooperation with DB German Rail and Conventus you travel safely and conveniently to DMG Conference 2014.



The price for your event ticket of a return trip* to is:

2nd class 99 EUR (for a defined train connection)

1st class 159 EUR (for a defined train connection)

2nd class 139 EUR (for all trains)

1st class 199 EUR (for all trains)



* An advance booking of at least three days is required. Changes and reimbursement before the first day of validity are Euro 15 excluded from the first day of validity onwards. Passengers restrict themselves to a particular train and travel times. For a supplement of Euro 40 full flexible tickets are also available for domestic travels within Germany.

Please find more detailed information on conditions and booking at
www.dmg2014.de/travel-accommodation/travel.

By Train

Jena has two train stations.

From station „West“- 10 min by foot

- After leaving the train station turn left and continue walking to the main road
- “Westbahnhofstraße”
- Turn right and follow the road downhill for 300m
- At the crossroads turn left into Ernst-Häckel-Straße
- After 150 m, walk across the Carl-Zeiss-Platz (right hand side) and turn right into Carl-Zeiss-Straße
- Use the underpass at the right hand side to the Ernst-Abbe-Platz

From station “Paradies” – 10 min by foot

- After leaving the train station, cross the main road in front of the station and walk straight ahead into the street “Am Volksbad”
- Pass the bus station and turn left into “Grietgasse”, follow the street for 150 m
- At the crossroads turn right and walk on “Schillerstraße” for about 120 m
- Then turn left, follow the same route as the tram runs, onto Ernst-Abbe-Platz

General Information

By Car

Venue:

Campus Friedrich-Schiller-Universität
Carl-Zeiss-Straße 3/Ernst-Abbe-Platz
07743 Jena (DE)

The following parking areas near to the venue are available:

- Parking garage of the „Neue Mitte“ (distance to the venue: 160m)
- Parking „Eichplatz“ (distance to the venue: 250m)
- Parking garage of the “Goethe Galerie” (distance to the venue: 400m)

The costs are on average 0.50 EUR/30 min.

Parking without costs is possible in the nearby residential area “Jahnstraße”.

Opening Hours

	Sunday	Monday	Tuesday	Wednesday
Industrial Exhibition		09 ⁴⁵ –18 ⁰⁰ hrs	10 ³⁰ –18 ¹⁵ hrs	10 ³⁰ –15 ¹⁵ hrs
Poster Exhibition		10 ⁰⁰ –18 ⁰⁰ hrs	10 ⁰⁰ –18 ³⁰ hrs	
Check-In	18 ⁰⁰ –19 ³⁰ hrs*	08 ⁰⁰ –19 ³⁰ hrs	08 ⁰⁰ –18 ³⁰ hrs	08 ⁰⁰ –17 ³⁰ hrs
Media Check-In		08 ³⁰ –19 ³⁰ hrs	08 ³⁰ –17 ⁰⁰ hrs	08 ³⁰ –15 ¹⁵ hrs

*The Check-In on Sunday will be in the “Institute of Geosciences”, Burgweg 11.

Internet

WIFI is available for free throughout the whole conference area. Please ask at the check-in desk for the login data.

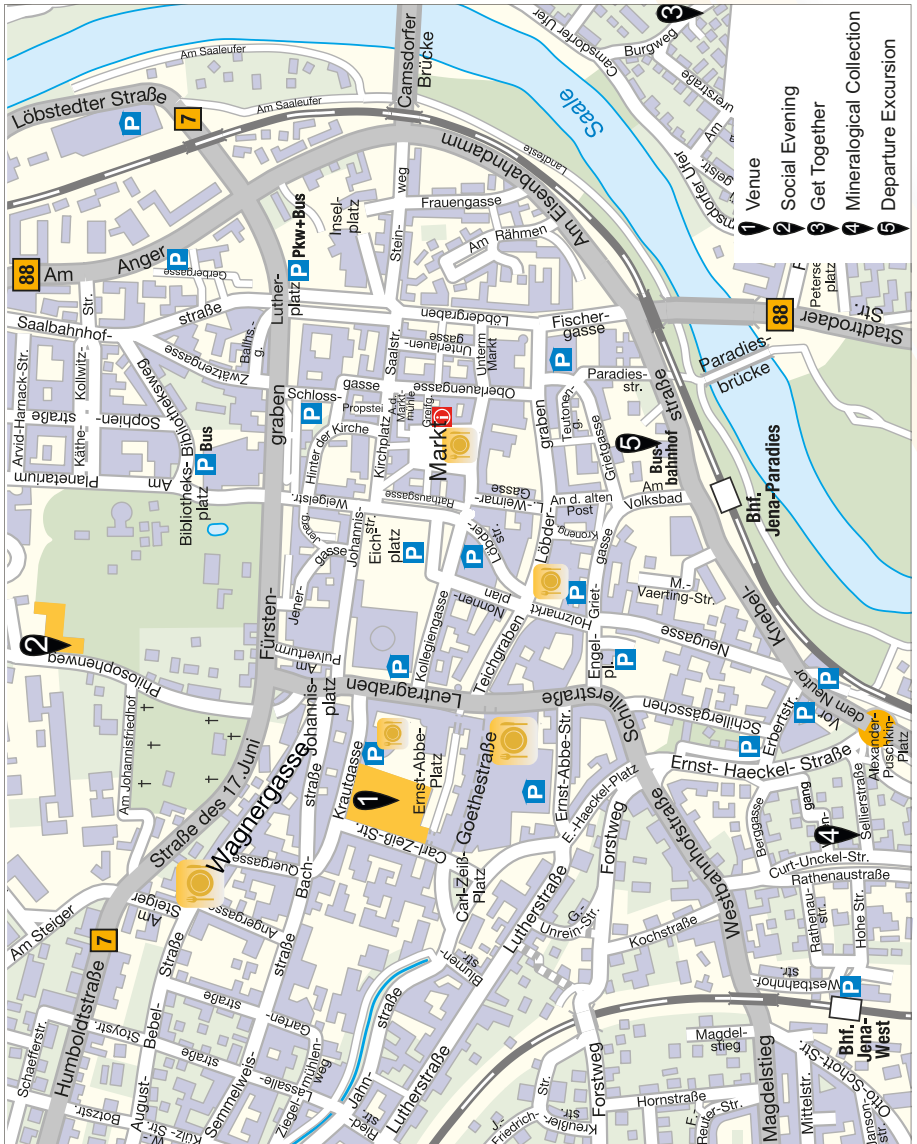
Restaurants and Cafes nearby the Conference Venue can be found on the following places:

- Mensa Ernst-Abbe-Platz
- Goethe Galerie
- Wagnergasse with various Cafes and Restaurants
- Holzmarkt
- Market Place

Service for mobility-impaired People

All rooms are accessible by wheelchair.

City Map



General Guidelines for Authors and Presenters

Submitting your presentation/technical information

Please prepare your presentation in 4:3 aspect ratio. A presentation notebook with a PDF reader and MS Office PowerPoint 2007 will be provided. The use of personal notebooks is possible upon agreement. However, it may interrupt the flow of the programme in the lecture hall. Please provide an adapter for VGA if necessary. A notebook, presenter and laser pointer are available at the speaker's podium in the lecture hall. A technical supervisor will help you.

Speakers preparation

Please submit your presentation at the media check-in (seminar room 121, first floor) no later than 90 minutes before the presentation begins. You may view and/or edit your presentation. For submission, please use a USB flash drive.

Time Allotment

Please prepare your presentation for the allotted amount of time. Oral abstract presentations are 12+3 minutes and keynote lectures 25+5 minutes (talk+discussion). Chairs may interrupt if you overrun your time limit.

Travel grants

Student DMG member who are presenting authors receive a travel grant of 50 EUR at the check-in.

Poster Session

Posters should be no larger than DIN A0 portrait format (84.1 cm x 118.9 cm). Poster boards are 120 cm x 150 cm. They are only to be used with the designated pins. Poster boards will be numbered. You will find your poster number in the programme book on page 54 ff. All posters can be displayed on both days and should be removed at the latest by Tuesday 23 September by 18³⁰ hrs. Posters that have not been removed by that time will be considered as waste.

Poster Session I • Monday, 22 September 2014, 16⁰⁰–18⁰⁰

Economic minerals – formation, characterization, and applications – ECO	54
Magmatic petrology – from melt to rock – MAG	55
Microstructures, textures and interfaces of minerals – MIC	56
Mineral physics and the deep Earth's interior – PHY	57
Mineralogical crystallography – CRY.....	58
Mineralogical museums and collections – MUS	59
Modern techniques for mineralogical research – MOD	60
Stable and radiogenic isotopes – clocks and tracers of rocks – ISO	61
Technical mineralogy – cements, ceramics and glasses – TEC.....	62

Poster Session II • Tuesday, 23 September 2014, 16⁴⁵–18¹⁵

Archeometry and monument conservation – ARC	62
Crystal structures and properties of materials – CSP	63
Functional materials – FUN.....	64
Metamorphic rocks – petrology, geochemistry, geochronology – MOR	65
Meteorites and the early solar system – MET	66
Minerals – fluids – rocks – FLU	67
Minerals in the environment – from geo- to biosphere – ENV	68
The mineral record of impact events – IMP	69

Sponsors and Exhibitors

Sponsors

We would like to thank the following exhibitors and sponsors for their support of the “DMG Conference”.

Main Sponsors

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Springer (Heidelberg/DE)

Systat Software GmbH (Erkrath/DE)

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Ametek GmbH (Wiesbaden/DE)

Bruker AXS GmbH (Karlsruhe/DE)

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JEOL (Germany) GmbH (Eching/DE)

MicroKern (Berlin/DE)

Netzsch-Gerätebau GmbH (Selb/DE)

PANalytical GmbH (Kassel/DE)

Renishaw GmbH (Pliezhausen/DE)

Sphere Optics GmbH (Uhlidingen/DE)

Thermo Fisher Scientific (Dreieich/DE)

Lunch Symposia

The following companies are looking forward to your attendance. Catering will be served during the symposia.

Monday, 22 September 2014, 12¹⁵–13⁰⁰ hrs • Lecture hall 4
Lunchsymposium FEI Deutschland GmbH (Frankfurt a. M./DE)



Advances in SEM and DualBeam technology
Ernst Jan Vesseur, Product Marketing Engineer, FEI Company

Tuesday, 23 September 2014, 12⁴⁵–13³⁰ hrs • Lecture hall 4
Lunchsymposium Carl Zeiss Microscopy GmbH (Jena/DE)



Mineralogical Applications using Scanning Electron Microscopy
Geertje Ganskow, ZEISS Microscopy

Wednesday, 24 September 2014, 12⁴⁵–13³⁰ hrs • Lecture hall 4
Lunchsymposium PANalytical GmbH (Kassel/DE)



Advanced X-ray analysis – Powder Diffraction and beyond
Uwe König, Segment Manager Mining XRD
Thorbjörn Schönbeck, CEO/Sales manager XRD&XRF

Social and Cultural Programme

Get Together

We would like to welcome and invite you to the first evening of the conference. Let's come together to the Barbeque evening in the garden of the "Geowissenschaftlichen Institut". Meet your colleagues and friends and have some interesting conversations while enjoying cool drinks and delicious barbeque food. You can also climb the tower of the institute and enjoy the beautiful view over the city of Jena and the scenic Saale valley.



© Institut für Geowissenschaften

Sunday, 21 September 2014

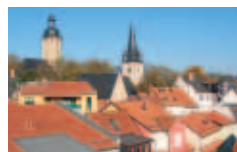
Time 18⁰⁰–21⁰⁰ hrs

Venue Institut für Geowissenschaften, Burgweg 11, 07749 Jena (DE)
Access by foot via Burgweg (no parking possibilities)

Fee 0 EUR, registration required

Guided City Tour: Journey through the history of the city Jena

You have the chance to experience history of Jena in a highly entertaining way. Three dressed up guides tell about their lives in short plays to immerse the audience in past times. This special tour makes history a great experience. Go through Jena's expansion from a town of wine growers with three monasteries to a booming industrial city around 1900.



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Tuesday, 23 September 2014

Time 17³⁰–18⁴⁵ hrs

Meeting point Check-In

Language German

End Mensa am Philosophenweg (Social Evening)

Fee 16 EUR

min. 13 participants, max. 25 participants

Social Evening

Spend the last evening of the conference in the "Mensa am Philosophenweg" while enjoying an excellent dinner with a large buffet and good drinks. Let the conference come to an end and take the opportunity to meet your colleagues and friends in a relaxed atmosphere after a long day.



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Tuesday, 23 September 2014

Time 19⁰⁰–23³⁰ hrs (doors open 18³⁰ hrs)

Venue Mensa am Philosophenweg
Philosophenweg 20, 07743 Jena (DE)

Fee 10 EUR

14

From the third largest uranium production in the world to a challenging remediation operation

Thursday, 25 September 2014

Time 09⁰⁰–14⁰⁰ hrs

Meeting Point bus station (Busbahnhof), 07743 Jena

Fee 25 EUR – Included in the fee are the transfer and handouts (field guide)

Field Trip Guides Georg Büchel, Erika Kothe, Franziska Schäffner (Jena)



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There was extensive uranium mining in the former German Democratic Republic (GDR) in the eastern Thuringia and Saxony during the period of 1946–1990. More than 200 kt of uranium have been mined and the GDR became the third largest uranium producer in the world after USA and Canada. After the political changes in 1990, mining ceased and the company Wismut GmbH was founded for remediation of the areas affected by mining. The remnants of the past activities include a large open pit mine, an underground mining system with 3000 km of underground galleries and shafts, and 260 million m³ of waste rock and tailings piles. The waste piles developed acid mine drainage (AMD) which was mitigated by storing the waste rock in the open pit mine and raising the groundwater level, thus limiting oxygen access and further AMD production. The former uranium mining site is an excellent study site that presents possible mechanisms of the transfer of metals and metal-loids into hydrosphere, pedosphere, and biosphere. The site was selected for the multidisciplinary investigation of geoscientists and biologists within the framework of bio-geo-research and -teaching at the Friedrich Schiller University in Jena. The participants of this field trip will have a chance to see the remnants of the intensive uranium mining and the challenges and opportunities of the following remediation processes.

Points to be visited:

1. Post-mining landscape of the former districts of Ronneburg and Seelingstädt
2. Tailings Culmitzsch: observation deck
3. Creek Gessen: Main discharge area for the leaking mine drainage water
4. Northwestern foot of the former northern dump
5. Test site “Gessenwiese” located at the former heap Gessen (Field work related to Bio-Geo Interactions)

Registration is possible online at www.dmg2014.de.

Mineralogical Collection

The Mineral Collection of the Friedrich Schiller University Jena (founded 1797) is one of the oldest and largest German University Collections. With more than 80.000 objects it is a vital part of research and teaching as well as public relations of the Institute of Geosciences. The permanent collection presents mineral systematics from worldwide localities. It further has a focal point to regional minerals from the Triassic around Jena and on numerous meteorites and tectites.

The current special exhibition shows mineral and rock suites from members of the oldest european geoscientific society, the "Societät für die gesamte Mineralogie zu Jena".

Extended opening hours during the conference:

Sunday, 21 September 2014: 13⁰⁰–18⁰⁰

Monday, 22 September 2014: 13⁰⁰–18⁰⁰

Tuesday, 23 September 2014: 13⁰⁰–19⁰⁰

Wednesday, 24 September 2014: 13⁰⁰–16⁰⁰

Address:

Institut für Geowissenschaften
Mineralogische Sammlung
Sellierstraße 6 • 07745 Jena

Overview Plenary Speakers

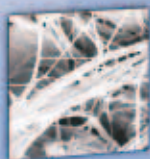
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0133 Milano (IT)
E-Mail: Diego.Gatta@unimi.it

Prof. Klaus Keil
University of Hawaii
Hawaii Institute of Geophysics and
Planetology
Manoa
96822 Honolulu (HI/US)
E-Mail: Keil@hawaii.edu

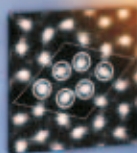
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Programme Overview • Monday, 22 September 2014

Sunday 21 September 2014	
Institute of Geosciences	
13:30-18:00	
DMG Board Meeting	
18:00-21:00	
Ice Breaker	p. 14
	Others
	Social Programme

Monday 22 September 2014		
Lecture Hall 2	Lecture Hall 4	Lecture Hall 5
09:00-09:45		
Opening		
p. 21		
10:15-12:00	10:15-12:00	10:15-12:00
Magmatic petrology – from melt to rock I	Stable and radiogenic isotopes: clocks and tracers of rocks I	Mineralogical crystallography
p. 21	p. 22	p.23
	12:15-13:00	
	Lunchsymposium FEI Deutschland GmbH	
	p. 24	
13:15-14:00		
Plenary Lecture		
Hella Wittmann-Oelze		
p. 24		
14:30-16:00	14:30-15:15	14:30-16:00
Magmatic petrology – from melt to rock II	Stable and radiogenic isotopes: clocks and tracers of rocks II	Economic minerals – formation, characterization, and applications
p. 24	p. 25	
	15:15-16:00	
	Mineralogical museums and collections	
	p. 26	p. 26
	16:00-18:00	
	Poster Session I	
		p. 27
	18:00-19:30	
	Member Meeting	
	p. 28	
19:30-20:30		
Public Lecture		
Klaus Keil		
p. 28		
	Oral Session	
	Plenary Lecture	
	Poster Session	
	Others	
	Lunchsymposium	

The industrial exhibition will be open from 09:45-18:00. Food and beverages will be served during the coffee breaks.

Tuesday, 23 September 2014				
Lecture Hall 2	Lecture Hall 4	Lecture Hall 5	Lecture Hall 7	
09:00–10:30 Magmatic petrology: from melt to rock III p. 30	09:00–10:30 Mineral physics and the deep Earth's interior p. 31	09:00–10:30 Technical mineralogy: cements, ceramics and glasses I p. 32	09:00–10:30 The mineral record of impact events p. 33	
11:00–11:45 Magmatic petrology: from melt to rock IV p. 34	11:00–12:30 Microstructures, textures and interfaces of minerals I p. 35	11:00–11:30 Technical mineralogy: cements, ceramics and glasses II p. 36	11:00–12:30 Modern techniques for mineralogical research I p. 37	
11:45–12:30 Meteorites and the early solar system – HED meteorites p. 34		11:30–12:30 Functional materials p. 36		
	12:45–13:30 Lunchsymposium Carl Zeiss Microscopy GmbH p. 38			
14:00–14:45 Plenary Lecture Diego Gatta p. 38				
15:15–16:45 Meteorites and the early solar system - Chondrites I p. 38	15:15–15:45 Microstructures, textures and interfaces of minerals II p. 39 15:45–16:45 Minerals – fluids – rocks I p. 39	15:15–16:45 Crystal structures and properties of materials p. 40	15:15–15:45 Modern techniques for mineralogical research II p. 41 15:45–16:45 Archeometry and monument conservation p. 42	
16:45–18:15				
Poster Session II p. 42				
				17:30–18:45 Guided City Tour p. 14
19:00–23:30 Social Evening p. 14				
	Oral Session		Poster Session	
	Plenary Lecture		Social Programme	
	Lunchsymposium			

The industrial exhibition will be open from 10:30–18:15. Food and beverages will be served during the coffee breaks.

The industrial exhibition will be open from 10:30–18:15. Food and beverages will be served during the coffee breaks.

Programme Overview • Wednesday, 24 September 2014

Wednesday, 24 September 2014		
Lecture Hall 2	Lecture Hall 4	Lecture Hall 5
09:00–10:30	09:00–10:30	09:00–10:30
Meteorites and the early solar system – Chondrites II p. 43	Minerals – fluids – rocks II p. 44	Metamorphic rocks – petrology, geochemistry, geochronology p. 46
11:00–12:30	11:00–12:30	11:00–12:30
Meteorites and the early solar system – Chondrites III p. 47	Minerals – fluids – rocks III p. 48	Minerals in the environment – from geo- to biosphere I p. 49
	12:45–13:30 Lunchsymposium Panalytical GmbH p. 50	
14:00–14:45		
Plenary Lecture Mihály Pósfai p. 50		
15:15–16:45	15:15–16:45	15:15–16:45
Meteorites and the early solar system – Achondrites and Isotopes p. 50	Minerals – fluids – rocks IV p. 51	Minerals in the environment – from geo- to biosphere II p. 52
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Closing p. 53		
	Oral Session	
	Plenary Lecture	
	Lunchsymposium	
	Others	
The industrial exhibition will be open from 10:30-15:15. Food and beverages will be served during the coffee breaks.		

Thursday, 25 September 2014	
09:00–14:00	
Field trip to Ronneburg p. 15	
	Social Programme

09⁰⁰–09⁴⁵

Room

Opening

Lecture hall 2

Prof. Klaus Dicke (Rector of the Friedrich Schiller University)

Frank Schenker (Mayor of Jena)

Prof. Astrid Holzheid (President of the DMG)

Prof. Falko Langenhorst (Conference Chair DMG 2014)

10¹⁵–12⁰⁰

Room

Chairs

Magmatic petrology – from melt to rock I

Lecture hall 2

Francois Holtz (Hannover/DE), Gregor Markl (Tübingen/DE)

10¹⁵

MAG-T01

Keynote lecture: **From a supercritical fluid to pegmatite**

Rainer Thomas, Paul Davidson (Potsdam/DE)

10⁴⁵

MAG-T02

In-situ observation of crystal growth in a basalt melt and the development of crystal size distribution in igneous rocks

Huaiwei Ni (Bayreuth/DE; Hefei/CN), Hans Keppler

Nicolas Walte (Bayreuth/DE)

Federica Schiavi (Bayreuth/DE; Clermont-Ferrand/FR)

Yang Chen (Ann Arbor, MI/US), Matteo Masotta (Bayreuth/DE)

Zhenjiang Li (Hefei/CN)

11⁰⁰

MAG-T03

Experimental approach to form anorthositic melts – phase relations in the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ – $\text{CaMgSi}_2\text{O}_6$ – Mg_2SiO_4 at 6 wt. % H_2O

Aurelia Zimmer, Chris Ballhaus, Raúl Fonseca (Bonn/DE)

Carsten Münker (Cologne/DE)

11¹⁵

MAG-T04

Petrological and geochemical characterization of abyssal peridotites from the East Pacific Rise and incorporation of OH-Defects in nominally anhydrous orthopyroxene (ODP Leg 147: Hess Deep)

Kirsten Hesse, Esther Schmädicke, Jürgen Gose (Erlangen/DE)

11³⁰

MAG-T05

Crystallization of interstitial liquid and latent heat buffering in solidifying gabbros – Skaergaard Intrusion, Greenland

Olivier Namur (Hannover/DE), Marian Holness (Cambridge/GB)

Madeleine Humphreys (Oxford/GB), Francois Holtz (Hannover/DE)

1145
MAG-T06 **Gabbro glacier or “sheeted sills”? New constraints on the accretion mode of oceanic crust at fast-spreading oceanic ridges**
Jürgen Koepke, Tim Mueller, Stefan Linsler, Eric Paul Wolff
Stephan Schuth (Hannover/DE), Dieter Garbe-Schönberg (Kiel/DE)

1015–1200
Room **Stable and radiogenic isotopes – clocks and tracers of rocks I**
Lecture hall 4
Chairs Carsten Münker (Cologne/DE), Andreas Pack (Göttingen/DE)

1015
ISO-T01 **Cadmium isotope fractionation during evaporation and re-condensation**
Victoria Kremser, Frank Wombacher (Cologne/DE)
Werner Ertel-Ingrisch, Donald Bruce Dingwell (Munich/DE)
Carsten Münker (Cologne/DE)

1030
ISO-T02 **Terrestrial and Lunar Constraints on the Composition of the Earth’s Late Veneer**
Harry Becker, Philipp Gleißner, Zaicong Wang (Berlin/DE)

1045
ISO-T03 **Lunar ^{182}W and the origin of the Moon**
Thomas Kruijer (Münster/DE)

1100
ISO-T04 **Highly siderophile elements in Apollo 16 impact melt rocks: constrains on late accreted material in the earth-moon system**
Philipp Gleißner, Harry Becker (Berlin/DE)

1115
ISO-T05 **A depleted mantle origin for Hadean protoliths of the Acasta Gneisses**
Peter Sprung (Cologne/DE), Erik E. Scherer, Duc T. Nguyen Xuan
Rebecca Bast (Münster/DE), Wouter Bleeker (Ottawa/CA)
Klaus Mezger (Münster/DE; Bern/CH)

1130
ISO-T06 **Geochemistry and petrology of 3.8 Ga archaean peridotites from southern West Greenland**
Julia van de Löcht, Carsten Münker (Cologne/DE)
Jörg Elis Hoffmann (Berlin/DE), Minik Thorleif Rosing (Copenhagen/DK)

1145
ISO-T07 **Tourmaline B-isotopes as tracers of fluid sources in silicified zones of the Barberton Greenstone Belt, South Africa**
Katja Farber, Annika Dziggel, Franz Michael Meyer (Aachen/DE)
Robert Trumbull, Michael Wiedenbeck (Potsdam/DE)

- 10¹⁵–12⁰⁰ **Mineralogical crystallography**
Room Lecture hall 5
Chairs Thomas Malcherek (Hamburg/DE), Ronald Miletich (Vienna/AT)
- 10¹⁵ **P-T-X controls on K and Na incorporation in dravitic tourmaline**
CRY-T01 Eleanor Berryman (Berlin/DE), Bernd Wunder, Dieter Rhede
Richard Wirth, Wilhelm Heinrich (Potsdam/DE)
Gerhard Franz (Berlin/DE)
- 10³⁰ **Al-Mg disorder and tetrahedrally coordinated B in synthetic K- and Mg-rich tourmaline**
CRY-T02 Andreas Ertl (Vienna/AT), Eleanor Berryman (Berlin/DE)
Bernd Wunder (Potsdam/DE), Katharina Scheidl
Gerald Giester (Vienna/AT), Gerhard Franz (Berlin/DE)
- 10⁴⁵ **Temperature-induced P2₁/c to C2/c phase transition in radiation damaged titanite**
CRY-T03 Tobias Beirau, Boriana Mihailova, Thomas Malcherek
Carsten Paulmann (Hamburg/DE), Lee A. Groat (Vancouver/CA)
Ulrich Bismayer (Hamburg/DE)
- 11⁰⁰ **Investigating the annealing dependency of Al/Si distribution in Eifel sanidine**
CRY-T04 Johannes Kähn, Daniel Többens, Jens-Uwe Hoffmann
Manfred Reehuis, Susan Schorr (Berlin/DE)
- 11¹⁵ **Structural processes during zeolite collapse and comparison with melt quenched glass**
CRY-T05 Sindy Fuhrmann, Theresia Palenta, Lothar Wondraczek (Jena/DE)
- 11³⁰ **First crystal-structure descriptions of natural mullite and a related mineral termed “sillimullite”**
CRY-T06 Reinhard X. Fischer, Valeria Tikhonova
Johannes Birkenstock (Bremen/DE)
Lennart Fischer (Hannover/DE), Klaus Herrmann
Kurt Mengel (Clausthal-Zellerfeld/DE), Hartmut Schneider (Cologne/DE)
- 11⁴⁵ **New insights into the crystal structures of uranyl sulfate minerals**
CRY-T07 Jakub Plášil (Prague/CZ)

- 12¹⁵–13⁰⁰ **Lunch Symposium – FEI Deutschland GmbH**
Room Lecture hall 4
- Advances in SEM and DualBeam technology**
Ernst Jan Vesseur, Product Marketing Engineer, FEI Company
- 13¹⁵–14⁰⁰ **Plenary lecture**
Room Lecture hall 2
- 13¹⁵ **The significance of cosmogenic nuclides in large lowland basins**
P01 Hella Wittmann-Oelze (Potsdam/DE)
- 14³⁰–16⁰⁰ **Magmatic petrology – from melt to rock II**
Room Lecture hall 2
Chairs Francois Holtz (Hannover/DE), Gregor Markl (Tübingen/DE)
- 14³⁰ **Rapid hydrothermal cooling above the axial melt lens at fast-spreading mid-ocean ridge**
MAG-T07 Chao Zhang (Freiburg/DE), Jürgen Koepke, Clemens Kirchner
Niko Götze, Harald Behrens (Hannover/DE)
- 14⁴⁵ **First report on PGM inclusions hosted by chromian spinel from high-Cr podiform chromitites, Sabzevar ophiolite, NE Iran**
MAG-T08 Zohreh Moosavinasab (Kiel/DE)
Mohammad Ali Rajabzadeh (Shiraz/IR)
Amir Morteza Azimzadeh (Leoben/AT), Thomas Aiglsperger
J. A. Proenza (Barcelona/ES)
- 15⁰⁰ **Supra-chondritic Nb/Ta ratios and other exotic geochemical signatures in rejuvenated Hawaiian magmas as fingerprints of carbonatitic auto-metasomatism in parts of the Hawaiian mantle plume**
MAG-T09 Alexander Rocholl (Bayreuth/DE)
Klaus Peter Jochum (Mainz/DE), Dieter Rhede (Potsdam/DE)
Brigitte Stoll, Ulrike Weis (Mainz/DE)
- 15¹⁵ **Petrology of Late Miocene calc-alkaline (shoshonitic) lamprophyres from Kos (Greece)**
MAG-T10 Christian Soder (Hannover/DE), Rainer Altherr (Heidelberg/DE)
Rolf L. Romer (Potsdam/DE)

- 15³⁰
MAG-T11 **Tracing crustal assimilation and basement compositions in differentiated volcanic rocks from the Siebengebirge Volcanic Field (SVF) – insights from Sr-Nd-Hf-Pb isotopes**
Kathrin Schneider (Munich/DE), Maria Kirchenbaur, Raúl Fonseca Haino U. Kasper, Nikolaus Froitzheim
Carsten Münker (Cologne/DE)
- 15⁴⁵
MAG-T12 **The origin of sapphire megacrysts in alkaline basalts from the Siebengebirge Volcanic Province, W Germany**
Lisa Baldwin (Liverpool/GB), Chris Ballhaus
Raúl Fonseca (Bonn/DE)
- 14³⁰–15¹⁵
Room **Stable and radiogenic isotopes – clocks and tracers of rocks II**
Lecture hall 4
Chairs Carsten Münker (Cologne/DE), Andreas Pack (Göttingen/DE)
- 14³⁰
ISO-T08 **Triple oxygen isotope analysis of cherts – implications for the temperature and $\delta^{18}\text{O}$ of ancient oceans**
Sukanya Sengupta, Andreas Pack (Göttingen/DE)
Francois Robert (Paris/FR), Joachim Reitner (Göttingen/DE)
Daniel Herwartz (Cologne/DE)
- 14⁴⁵
ISO-T09 **U-Pb Dating of Opaline Silica (Siebengebirge, Rhenish Massif)**
Frank Tomaschek (Bonn/DE), Alexander Nemchin (Stockholm/SE)
Thorsten Geisler-Wierwille, Alexander Heuser (Bonn/DE)
Renaud Merle (Perth/AU)
- 15⁰⁰
ISO-T10 **Isotope (C, O, S, Pb) geochemistry of the Ozbak-Kuh carbonate-hosted Pb-Zn deposit, East Central Iran**
Farhad Ehya (Behbahan/IR)

- 15¹⁵–16⁰⁰ **Mineralogical museums and collections**
Room Lecture hall 4
Chairs Birgit Kreher-Hartmann (Jena/DE), Jochen Schlüter (Hamburg/DE)
- 15¹⁵
MUS-T01 **Digitalisierung der Gesteinsdünnschliffsammlung an der
TU Bergakademie Freiberg**
 Susanne Eberspächer, Christin Kehler
 Gerhard Heide (Freiberg/DE)
- 15³⁰
MUS-T02 **Die Smaragdsammlung Wolfram Schäfer in der Mineralo-
gischen Staatssammlung Munich**
 Rupert Hochleitner, Melanie Kaliwoda (Munich/DE)
- 15⁴⁵
MUS-T03 **The Mineralogical Society of Jena and Count Vargas Bedemar**
 Birgit Kreher-Hartmann (Jena/DE)
- 14³⁰–16⁰⁰ **Economic minerals – formation, characterization, and applications**
Room Lecture hall 5
Chairs Jens Gutzmer (Freiberg/DE), Franz Michael Meyer (Aachen/DE)
- 14³⁰
ECO-T01 **Mineralogy and Geochemistry of PGE-Ni-Cu ore-forming
processes in basic/ultrabasic magmatic complexes – system
and applied approaches**
 Igor Avgustinchik (Moscow/RU)
- 14⁴⁵
ECO-T02 **Cu-Ag-Au-mineralization of the German copper belt – new
results from the Spremberg Kupferschiefer deposit, Lausitz,
Germany**
 Volker Spieth (Tucson, AZ/US), Michael Trinkler (Freiberg/DE)
 Jürgen C. Kopp (Seddiner See/DE), Tillmann Viefhaus
 Hans-Joachim Massonne (Stuttgart/DE)
- 15⁰⁰
ECO-T03 **Automated quantitative mineralogy of sandstones – examples
of QEMSCAN applications for the study of hot water storage
in geothermal aquifers and diagenesis**
 Esther Rosenbrand, Sven Sindern
 Ida Lykke Fabricius (Kongens Lyngby/DK), Lars Gronen
 Franz Michael Meyer (Aachen/DE)

- 15¹⁵
ECO-T04 **Gangue mineralogy and deportment of titanium (Ti) and vanadium (V) in the Kiirunavaara iron ore deposit, Northern Sweden**
Karsten Aupers (Freiberg/DE), Kari Niiranen (Kiruna/SE)
Sandra Birtel, Tobias Höfig, Joachim Krause
Jens Gutzmer (Freiberg/DE)
- 15³⁰
ECO-T05 **Variation in chromite chemistry across the UG2 chromitite layer, Eastern Bushveld Complex**
Felix Kaufmann, Lutz Hecht (Berlin/DE)
Tawanda D. Manyeruke (Sandton/ZA)
- 15⁴⁵
ECO-T06 **Factors of ore-metals concentration during the formation of a large auriferous Bugdaya Mo-porphyry deposit (Eastern Transbaikalia, Russia) – results of thermodynamic modeling**
Vladimir Kovalenker, Akinfiev Nikolai, Kiseleva Galina
Krylova Tat'ana (Moscow/RU)
- 16⁰⁰–18⁰⁰ **Poster Session I**
Room Foyer

Please find all detailed information on page 11.

18⁰⁰–19³⁰ **DMG member meeting**
Room Lecture hall 4

19³⁰–20³⁰ **Public lecture**
Room Lecture hall 2

P02 **Die Frühgeschichte unseres Sonnensystems:
die ersten 10 Millionen Jahre**
Klaus Keil (Honolulu, HI/US)



PFA-Labware



ICP Probenzuführung

Säurereinigung



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- 09⁰⁰–10³⁰ **Magmatic petrology – from melt to rock III**
Room Lecture hall 2
Chairs Francois Holtz (Hannover/DE), Gregor Markl (Tübingen/DE)
- 09⁰⁰ **Partial melting of carbonates – evidence from a diatexite migmatite from Øksfjord, Finnmark, Northern Norway**
MAG-T13 Manuel Menzel, Kurt Bucher (Freiburg/DE)
- 09¹⁵ **Geothermometry in highly evolved peralkaline magmatic systems**
MAG-T14 Christopher Giehl (Kiel/DE), Michael Marks
 Marcus Nowak (Tübingen/DE)
- 09³⁰ **In-situ observations of bubble growth in basaltic, andesitic and rhyodacitic melts**
MAG-T15 Matteo Masotta (Bayreuth/DE)
 Huaiwei Ni (Bayreuth/DE; Hefei/CN), Hans Keppler (Bayreuth/DE)
- 09⁴⁵ **The effect of alkalis and polymerization on the solubility of H₂O and CO₂ in alkali-rich silicate melts**
MAG-T16 Francesco P. Vetere, Francois Holtz, Harald Behrens
 Roman Botcharnikov, Sara Fanara (Hannover/DE)
- 10⁰⁰ **Chaotic Mixing – from lab to nature – revisiting a deep magma chamber**
MAG-T17 Cristina P. De Campos, Daniele Morgavi (Munich/DE)
 Diego Perugini (Perugia/IT), Donald Bruce Dingwell (Munich/DE)

- 09⁰⁰–10³⁰ **Mineral physics and the deep Earth's interior**
Room Lecture hall 4
Chairs Tomoo Katsura (Bayreuth/DE), Monika Koch-Müller (Potsdam/DE)
- 09⁰⁰ **Strength of (Mg, Fe)O ferropericlasite and the fate of**
PHY-T01 **subducting slabs in earth's lower mantle**
 Hauke Marquardt (Bayreuth/DE)
 Lowell Miyagi (Salt Lake City, UT/US)
- 09¹⁵ **Atomistic modelling of dislocations in MgSiO₃ perovskite**
PHY-T02 Antoine Kraych, Pierre Hirel, Philippe Carrez
 Patrick Cordier (Villeneuve d'Ascq/FR)
- 09³⁰ **Modelling of dislocation mobility in transition zone minerals**
PHY-T03 Sebastian Ritterbex, Philippe Carrez, Karine Gouriet
 Patrick Cordier (Villeneuve d'Ascq/FR)
- 09⁴⁵ **Temperature dependence of [100](010) and [001](010)**
PHY-T04 **dislocation mobilities in natural olivine**
 Lin Wang, Szanett Pinter, Stella Chariton, Stephan Blaha
 Robert Farla, Miyajima Nobuyoshi, Tomoo Katsura (Bayreuth/DE)
- 10⁰⁰ **Melting relations in the system CaCO₃-MgCO₃ at 6 GPa**
PHY-T05 Jan Müller, Dieter Rhede, Monika Koch-Müller (Potsdam/DE)
- 10¹⁵ **Nano-inclusions in milky diamonds from Juina, a super deep**
PHY-T06 **source**
 Jennifer Rudloff, Frank Brenker (Frankfurt/DE), Laszlo Vincze
 Bart Vekemans (Ghent/BE), Sylvia Schmitz (Frankfurt/DE)
 Richard Wirth (Potsdam/DE)
 Felix V. Kaminsky (West Vancouver/CA)

- 09⁰⁰–10³⁰ **Technical mineralogy – cements, ceramics and glasses I**
Room Lecture hall 5
Chairs Hans Joachim Kleebe (Darmstadt/DE), Stefan Stöber (Halle/DE)
- 09⁰⁰ **Zirconia in medical application – advantages and drawbacks**
TEC-T01 Melanie Keuper, Christoph Berthold
 Klaus Georg Nickel (Tübingen/DE)
- 09³⁰ **Corrosion of silicate glasses at the nanometer scale – a TXM**
TEC-T02 **and XANES approach**
 Martin Kutzschbach (Berlin/DE), Max Wilke (Potsdam/DE)
 Peter Guttman, Katja Henzler, Stephan Werner (Berlin/DE)
 Katharina Marquardt (Bayreuth/DE)
- 09⁴⁵ **Beitrag zur Festigkeitsentwicklung von Gipsstein und zum**
TEC-T03 **Festigkeitsabfall bei Durchfeuchtung**
 Christian Pritzel, Reinhard Trettin, Yilmaz Sakalli (Siegen/DE)
- 10⁰⁰ **Characterization of a Clay by TG-DSC-MS and Dilatometer-MS**
TEC-T04 **Measurements**
 Ekkehard Post, Gabriele Kaiser, Doreen Rapp (Selb/DE)
- 10¹⁵ **Synthesis and Characterization of the different modification of**
TEC-T05 **doped Dicalcium Silicates (C₂S)**
 Katharina Pöhler, Herbert Pöllmann, Krassimir Garbev
 Peter Stemmermann (Halle/Saale/DE)

- 09⁰⁰–10³⁰ **The mineral record of impact events**
Room Lecture hall 7
Chairs Dennis Harries (Jena/DE), Ralf-Thomas Schmitt (Berlin/DE)
- 09⁰⁰ **The Lake Bosumtwi impact structure – Ivory Coast tektites and microtektites, fall back glass and glass shards in suevites: geochemical distinctions and similarities**
Alexander Deutsch (Münster/DE), Falko Langenhorst (Jena/DE)
Jasper Berndt-Gerdes (Münster/DE)
- 09¹⁵
IMP-T02 **Influence of porosity on shock metamorphism and classification**
Ralf-Thomas Schmitt, Wolf Uwe Reimold, Astrid Kowitz (Berlin/DE)
- 09³⁰
IMP-T03 **New high-pressure phases in the Tissint Martian meteorite indicate small size of Mars impacting body**
Iona Summerson, Ansgar Greshake, Jörg Fritz
Wolf Uwe Reimold (Berlin/DE)
- 09⁴⁵
IMP-T04 **Two stages of liquid immiscibility preserved in young impact glasses**
Lutz Hecht, Christopher Hamann, Matthias Ebert (Berlin/DE)
Richard Wirth (Potsdam/DE)
- 10⁰⁰
IMP-T05 **Element partitioning processes between iron-rich projectiles and silica-rich targets in hypervelocity impact experiments**
Matthias Ebert, Lutz Hecht (Berlin/DE)
Alexander Deutsch (Münster/DE)
Thomas Kenkmann (Freiburg/DE)
- 10¹⁵
IMP-T06 **Nanostructure of Popigai impact diamonds by HRTEM, SEM, and AFM studies**
Tatyana Shumilova (Syktyvkar/RU), Viktoria Kis (Budapest/HU)
Viktor Masaitis (St. Petersburg/RU)
Sergey Tkachev (Argonne, IL/US), Sergey Isaenko
Boris Makeev (Syktyvkar/RU)

- 11⁰⁰–11⁴⁵ **Magmatic petrology – from melt to rock IV**
Room Lecture hall 2
Chairs Francois Holtz (Hannover/DE), Gregor Markl (Tübingen/DE)
- 11⁰⁰ **Ab initio simulation approach to study trace element
MAG-T19 partitioning between metal and silicate melts**
 Daniela Künzel, Sandro Jahn (Potsdam/DE)
- 11¹⁵ **Experimental constraints on REE-based slab thermometry**
MAG-T20 Kevin Klimm, Fabian Schröder (Frankfurt a. M./DE)
 Jon Blundy (Bristol/GB), Axel Gerdes
 Heidi Höfer (Frankfurt a. M./DE)
- 11³⁰ **Big data in geochemistry – a global perspective of REE
MAG-T21 signatures in igneous rocks**
 Dominik Hezel (Cologne/DE)
- 11⁴⁵–12³⁰ **Meteorites and the early solar system – HED meteorites**
Room Lecture hall 2
Chairs Dominik Hezel (Cologne/DE), Marian Horstmann (Münster/DE)
- 11⁴⁵ **Micro investigations of possible fluid-mineral interactions
MET-T01 recorded in eucritic meteorites**
 Christian Vollmer (Münster/DE)
 Adam R Sarafian (Woods Hole, MA/US)
 Arne Janssen (Manchester/GB), Andrew Putnis (Münster/DE)
- 12⁰⁰ **Rare earth element signatures of meteoritic zircon**
MET-T02 Julia Roszjar (Vienna/AT), Martin J. Whitehouse (Stockholm/SE)
 Addi Bischoff (Münster/DE)
- 12¹⁵ **Early dynamic mantle movements in young, semi-crystallized
MET-T03 vesta**
 Beverley J. Tkalcec, Frank Brenker (Frankfurt a. M./DE)

- 1100–1230 **Microstructures, textures and interfaces of minerals I**
Room Lecture hall 4
Chairs Rainer Abart (Vienna/AT), Andreas Lüttge (Bremen/DE)
- 1100 **Abandoning rate constants – from rate spectra to overall dissolution rates**
MIC-T01 Cornelius Fischer, Kurganskaya Inna, Rohlfs Ricarda
Lüttge Andreas (Bremen/DE)
- 1115 **Crystallographic controls on the intrinsic rate of aragonite dissolution**
MIC-T02 Rolf Arvidson, Matthias Wagner, Stephan Lenz, Cornelius Fischer
Andreas Lüttge (Bremen/DE)
- 1130 **Kinetic Monte Carlo simulations – Predicting the unpredictable?**
MIC-T03 Kurganskaya Inna, Cornelius Fischer (Houston, TX/US)
Arvidson Rolf (Bremen/DE)
Lüttge Andreas (Bremen/DE; Houston, TX/US)
- 1145 **Architecture of biomaterials – morphologic versus crystallographic hierarchy**
MIC-T04 Bernd Maier, Fitriana Nindiyasari, Erika Grießhaber
Laura Casella (Munich/DE), Harvinder Ubhi (High Wycombe/GB)
Andreas Ziegler (Ulm/DE), Wolfgang Schmahl (Munich/DE)
- 1200 **Kinetics of periclase hydration at 200 MPa and temperatures ranging from 350°C to 620°C**
MIC-T05 Hakan Kuleci, Christian Schmidt, Erik Rybacki
Elena Petrishcheva, Rainer Abart (Vienna/AT)
- 1215 **Interface geometry and topotactic relations of oriented TiO₂ inclusions in a garnet host crystal**
MIC-T06 Gerlinde Habler (Vienna/AT), Alexander Proyer (Gaborone/ZA)
Richard Wirth (Potsdam/DE), Rainer Abart (Vienna/AT)

- 1100–1130 **Technical mineralogy – cements, ceramics and glasses II**
Room Lecture hall 5
Chairs Hans Joachim Kleebe (Darmstadt/DE), Stefan Stöber (Halle/DE)
- 1100 **Phenomenology of the alpha-beta transition of ultra-high**
TEC-T07 **purity cristobalite**
Kai-Uwe Hess, Paul Hrynio, Wolfgang Schmahl
Donald Bruce Dingwell (Munich/DE)
- 1115 **Determination of the bulk heat conductivity of chondritic**
TEC-T08 **material by numerical modelling of the composition**
Stephan Henke, Hans-Peter Gail, Mario Trieloff (Heidelberg/DE)
- 1130–1230 **Functional materials**
Room Lecture hall 5
Chairs Bernd Maier (Munich/DE), Bernd Marler (Bochum/DE)
- 1130 **Garnet-like structured solid solutions $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{M}_x\text{O}_{12}$**
FUN-T01 **(M = Nb⁵⁺, Ta⁵⁺) for all-solid-state-lithium-ion batteries:**
a comparison between solid state reaction and sol-gel synthesis
Maria Maier, Reinhard Wagner, Daniel Rettenwander
Jürgen Schoiber, Georg Amthauer (Salzburg/AT)
- 1145 **Synthesis of coarse-grained garnet-type Li-ion conductor**
FUN-T02 **$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$**
Reinhard Wagner, Daniel Rettenwander, Maria Maier
Georg Amthauer (Salzburg/AT)
- 1200 **Structure-property relationship of transition metal catalysts**
FUN-T03 Claudia Weidenthaler, Valeria Tagliazucca (Mülheim a. d. Ruhr/DE)
- 1215 **Molecular dynamics modeling of irradiation damage in zircon,**
FUN-T04 **monazite, iakargiite and $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore**
Alexey Grechanovsky (Kiev/UA), Nikolai Eremin (Moskow/RU)

- 1100–1230 **Modern techniques for mineralogical research I**
Room Lecture hall 7
Chairs Christoph Berthold (Tübingen/DE), Jörg Göttlicher (Karlsruhe/DE)
- 1100 MOD-T01 **Keynote lecture: X-ray diffraction in the lab – benefits and perspectives using large 2-dimensional detectors and X-ray optics**
Christoph Berthold (Tübingen/DE)
- 1130 MOD-T02 **Coupling a 5kN Bending Jig with a Microdiffractometer: an In Situ Study of Phase Transformations in Zirconia under Tensile Stress**
Tobias Kiemle, Christoph Berthold (Tübingen/DE)
Christian Schröder, Andreas Kailer (Freiburg/DE)
Klaus Georg Nickel (Tübingen/DE)
- 1145 MOD-T03 **High-Speed PIXE – a new tool for automated mineralogy using a Color X-Ray Camera**
Axel D. Renno, Josef Buchriegler, Sandra Dressler, Daniel Hanf
Silke Merchel, Frans Munnik (Dresden/DE), Stanislaw Nowak
Oliver Scharf (Berlin/DE), René Ziegenrucker (Dresden/DE)
- 1200 MOD-T04 **Quantitative chemical analysis of carbon and oxygen in molten Fe-rich alloy by analytical transmission electron microscopy**
Nobuyoshi Miyajima (Bayreuth/DE), Rebecca A. Fischer
Andrew J. Campbell (Chicago, IL/US), Dan Frost (Bayreuth/DE)
Dennis Harries, Falko Langenhorst, Kilian Pollok (Jena/DE)
Sylvain Petitgirard, David C. Rubie (Bayreuth/DE)
- 1215 MOD-T05 **Method development for the LEAP and TEM characterization of (Ba, Ra)SO₄ solid solutions on the atomic level**
Juliane Weber, Uwe Breuer, Aleksei Savenko
Martina Klinkenberg, Felix Brandt, Dirk Bosbach (Jülich/DE)

- 1245–1330 **Lunch Symposium – Carl Zeiss Microscopy GmbH**
Room Lecture hall 4
- Mineralogical Applications using Scanning Electron Microscopy**
Geertje Ganskow (Jena/DE)
- 1400–1445 **Plenary lecture**
Room Lecture hall 2
- P03 **Open-framework silicates at extreme conditions**
G. Diego Gatta (Milano/IT)
- 1515–1645 **Meteorites and the early solar system – chondrites I**
Room Lecture hall 2
Chairs Dominik Hezel (Cologne/DE), Marian Horstmann (Münster/DE)
- 1515
MET-T04 **Keynote lecture: The lithophile trace elements in enstatite meteorites**
Jean-Alix Barrat, C. Bollinger (Plouzané/FR)
- 1545
MET-T05 **Metamorphism in the EH chondrite parent body recorded by minor elements in accessory olivine**
Seann McKibbin (Brussels/BE), Lutz Hecht (Berlin/DE)
Philippe Claeys (Brussels/BE)
- 1600
MET-T06 **Sulfide chemistry of enstatite chondrites – Identification of EH- and EL-subgroups?**
Mona Weyrauch, Marian Horstmann, Addi Bischoff (Münster/DE)
- 1615
MET-T07 **Elemental Complementarities in Rumuruti Chondrite NWA 753**
Pia Friend, Dominik Hezel (Cologne/DE)
Herbert Palme (Frankfurt/DE), Addi Bischoff (Münster/DE)
- 1630
MET-T08 **Almost all chondrules in carbonaceous chondrites are zoned**
Dominik Hezel, Daniel Mucerschi, Pia Friend (Cologne/DE)
Herbert Palme (Frankfurt/DE)

- 15¹⁵–15⁴⁵ **Microstructures, textures and interfaces of minerals II**
Room Lecture hall 4
Chairs Rainer Abart (Vienna/AT), Andreas Lüttge (Bremen/DE)
- 15¹⁵ **Enhanced diffusion rates adjacent to healed cracks – effects on re-equilibration of submicron inclusions in host garnet**
MIC-T07 Thomas Griffiths, Gerlinde Habler, Rainer Abart (Vienna/AT)
Dieter Rhede, Richard Wirth (Potsdam/DE)
- 15³⁰ **Myrmekite formation in the Weinsberg granite (South Bohemian Batholith) – localized interface processes and microstructure evolution**
MIC-T08 Rainer Abart, David Heuser, Gerlinde Habler (Vienna/AT)
- 15⁴⁵–16⁴⁵ **Minerals – fluids – rocks I**
Room Lecture hall 4
Chairs Thorsten Geisler-Wierwille (Bonn/DE), Kilian Pollok (Jena/DE)
- 15⁴⁵ **First-principles study of Zr and Hf speciation in supercritical aqueous fluids**
FLU-T01 Sandro Jahn, Max Wilke (Potsdam/DE)
- 16⁰⁰ **The behaviour of Cl and Br during water-rock interaction and its implications for the halogen budget of basement brines: an experimental study on rocks from the Schwarzwald, SW Germany**
FLU-T02 Mathias Burisch, Michael Marks, Gregor Markl (Tübingen/DE)
- 16¹⁵ **Temporal evolution of mid-ocean ridge vent fluid chemistry: an experimental study**
FLU-T03 Oliver Beermann, Astrid Holzheid
Dieter Garbe-Schönberg (Kiel/DE)
- 16³⁰ **New Insight on Lithium and Boron isotope fractionation during serpentinization derived from batch reaction investigations**
FLU-T04 Christian Hansen, Anette Meixner, Simone Kasemann
Wolfgang Bach (Bremen/DE)

- 15¹⁵–16⁴⁵ **Crystal structures and properties of materials**
Room Lecture hall 5
Chairs Robert Dinnebier (Stuttgart/DE)
 Maria Wierzbicka-Wieczorek (Jena/DE)
- 15¹⁵ **Analyzing in-situ powder diffraction data of minerals and inorganic compounds with symmetry mode approaches**
CSP-T01 Martin Etter, Melanie Müller, Robert Dinnebier (Stuttgart/DE)
- 15³⁰ **Determining verticillated crystals and finding their optical axis with IR-spectroscopy**
CSP-T02 Sonja Höfer, Thomas Mayerhöfer, Jürgen Popp (Jena/DE)
- 15⁴⁵ **Actinide chemistry under extreme conditions – the first example of a mixed valence As(III)/As(V) actinide compound**
CSP-T03 Philip Kegler, Na Yu, Vladislav V. Klepov
 Evgeny V. Alekseev (Jülich/DE)
- 16⁰⁰ **Thermodynamic mixing properties and behavior of grossular-spessartine, $(\text{Ca}_x\text{Mn}_{1-x})_3\text{Al}_2\text{Si}_3\text{O}_{12}$, solid solutions**
CSP-T04 Charles A. Geiger, Edgar Dachs, Artur Benisek (Salzburg/AT)
- 16¹⁵ **Calorimetric studies of boron minerals – danburite $(\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8])$ and olenite $(\text{NaAl}_3\text{Al}_6[(\text{BO}_3)_3\text{Si}_6\text{O}_{18}\text{O}_3(\text{OH})])$**
CSP-T05 Klaus-Dieter Grevel (Jena/DE), Edgar Dachs
 Artur Benisek (Salzburg/AT), Juraj Majzlan (Jena/DE)
- 16³⁰ **Crystal structures and vibrational properties of germanates comprising $[\text{Ge}_4\text{O}_{12}]$ ring units**
CSP-T06 Ivan Leonidov, Ludmila Surat, Vladislav Petrov
 Vladimir Chernyshev, Anatoliy Nikiforov, Emma Vovkotrub
 Alexander Tyutyunnik, Vladimir Zubkov (Ekaterinburg/RU)

1515–1545 **Modern techniques for mineralogical research II**
Room Lecture hall 7
Chairs Christoph Berthold (Tübingen/DE), Jörg Göttlicher (Karlsruhe/DE)

1515 **Phase analysis by optical Cathodoluminescence Microscopy (CLM) in refractory materials**
MOD-T06 Yannick Hemberger, Christoph Berthold
Klaus Georg Nickel (Tübingen/DE)

1530 **Mineral-Water interaction in Callovo-Oxfordian clay rock probed by broadband dielectric spectroscopy**
MOD-T07 Norman Wagner (Weimar/DE), Thierry Bore, Daniel Coelho
Jean-Charles Robinet, Frederic Taillade
Sylvie Delepine-Lesoille (Paris/FR)

23rd ANNUAL MEETING of the German Crystallographic Society (DGK)

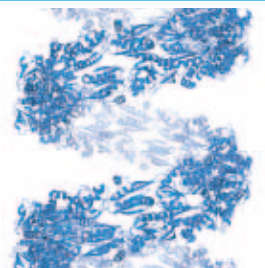


16–19 March 2015



GÖTTINGEN

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15⁴⁵–16⁴⁵ **Archeometry and monument conservation**
Room Lecture hall 7
Chairs Gert Klöß (Leipzig/DE), Frank Schlütter (Bremen/DE)

15⁴⁵ **Ramanspektroskopische Differenzierung von organischen**
ARC-T01 **Pigmenten in biomineralischem Verbund**
 Melanie Keuper, Christoph Berthold, Klaus Bente
 Klaus Georg Nickel (Tübingen/DE)

16⁰⁰ **White coral beads of Latène and Hallstatt age – Original color**
ARC-T02 **or decolorated material?**
 Klaus Bente (Leipzig/DE), Christoph Berthold (Tübingen/DE)
 M. Schrickel (Trier/DE), H. Wendling (Hallein/DE)
 Martin Ende (Vienna/AT)

16¹⁵ **p-ED-XRF analyses including Na and Mg of ancient glasses**
ARC-T03 Hans-Peter Meyer, Alexander Varychev, Johannes Grimm
 Lena Steinmann (Heidelberg/DE)

16³⁰ **Zerstörungsfreie Untersuchungen an weissgrundiger attischer**
ARC-T04 **Keramik mit modernen hoch ortsauflösenden Röntgenana-**
 lyseverfahren und der μ -Ramanspektroskopie
 Christoph Berthold (Tübingen/DE)
 U. Koch-Brinkmann (Frankfurt/DE), K.B. Zimmer (Tübingen/DE)

16⁴⁵–18¹⁵ **Poster Session II**
Room Foyer

Please find all detailed information on page 11.

19⁰⁰–23³⁰ **Social evening at Mensa am Philosophenweg**
 Address: Philosophenweg 20 • 07743 Jena (see. Page 14)

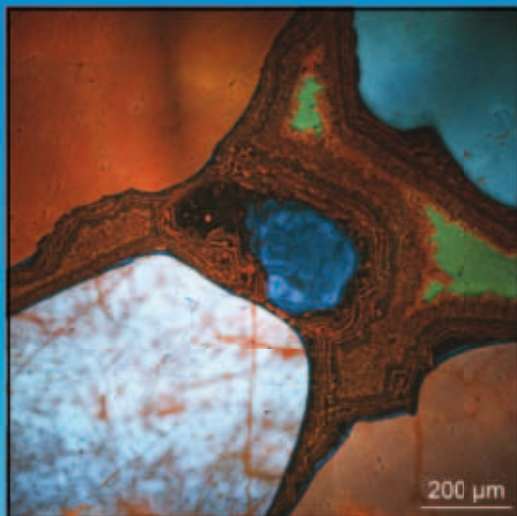
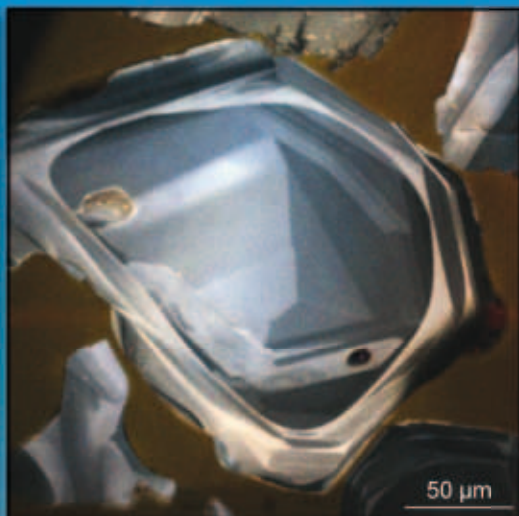
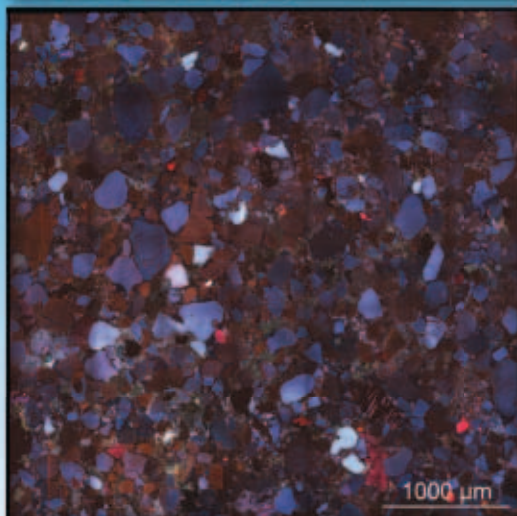
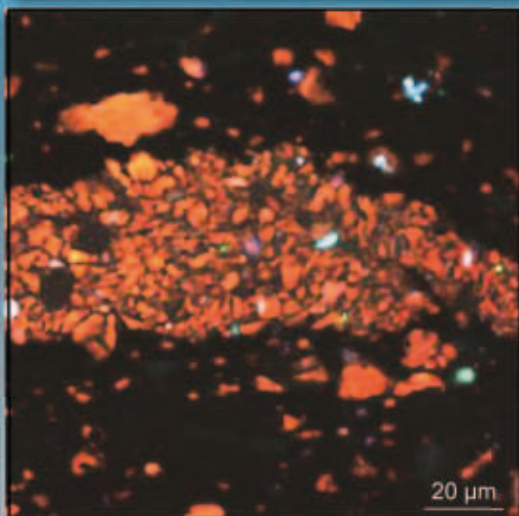
- 09⁰⁰–10³⁰ **Meteorites and the early solar system – Chondrites II**
Room Lecture hall 2
Chairs Thomas Kruijer, Knut Metzler (Münster/DE)
 Julia Roszjar-Walter (Vienna/AT)
- 09⁰⁰ **Experimental study of oxygen isotope exchange between**
MET-T09 **chondrule melt and water vapor**
 Tommaso Di Rocco, Andreas Pack (Göttingen/DE)
- 09¹⁵ **Abundances of highly siderophile and chalcogen elements in**
MET-T10 **the components of unequilibrated L chondrites**
 Yogita Kadlag, Harry Becker, Franziska Schubring
 Tanja Giebner (Berlin/DE)
- 09³⁰ **The mineralogy and metallography of a regolith particle**
MET-T11 **returned from asteroid 25143 Itokawa**
 Dennis Harries, Falko Langenhorst (Jena/DE)
- 09⁴⁵ **Evidence for microimpacts in an olivine-dominated asteroidal**
MET-T12 **dust particle returned by the Hayabusa space mission**
 Falko Langenhorst, Dennis Harries, Kilian Pollok (Jena/DE)
 Peter A. van Aken (Stuttgart/DE)
- 10⁰⁰ **Early formed chondrules in the Krymka (LL3.2) chondrite**
MET-T13 **Knut Metzler (Münster/DE), Marc Chaussidon (Paris/FR)**
- 10¹⁵ **Oxygen isotope systematics of CM chondrite calcite:**
MET-T14 **constraints on aqueous alteration**
 Marian Horstmann, Christian Vollmer
 Moritz I. F. Barth (Münster/DE), Marc Chaussidon
 Andrey Gurenko (Nancy/FR), Addi Bischoff (Münster/DE)

- 09⁰⁰–10³⁰ **Minerals – fluids – rocks II**
Room Lecture hall 4
Chairs Thorsten Geisler-Wierwille (Bonn/DE), Kilian Pollok (Jena/DE)
- 09⁰⁰ **The behavior of H₂ and CO₂ in siliciclastic reservoirs during energy/hydrogen storage**
FLU-T05 Steven Henkel, Dieter Pudlo (Jena/DE), Frieder Enzmann (Mainz/DE)
Karin Eusterhues, Michael Abratis (Jena/DE), Jörg Nissen (Berlin/DE)
Daniel Albrecht, Viktor Reitenbach, Reinhard Gaupp (Jena/DE)
Leonhard Ganzer (Clausthal-Zellerfeld/DE)
- 09¹⁵ **Multi-phase carbonate precipitates in the CO₂ reservoir at the Ketzin pilot site – CO₂-induced trapping mechanism or drilling artefact?**
FLU-T06 Susanne Bock (Jena/DE), Carmen Höschen (Freising/DE)
Martin Nowak (Jena/DE), Hans-Jürgen Förster (Potsdam/DE)
Reinhard Gaupp (Jena/DE)
- 09³⁰ **Vein mineralizations in Mesozoic sediments – archives of fluid-evolution in the Thuringian basin (Germany)**
FLU-T07 Petra Lepetit, Lothar Viereck, Michael Abratis (Jena/DE)
Axel Gerdes (Frankfurt a. M./DE)
Stefanie Fritsch (Saarbrücken/DE)
- 09⁴⁵ **Incorporation of quartz into corundum via aqueous fluids: experimental and natural examples**
FLU-T08 Dina Schultze, Gerhard Franz (Berlin/DE)
- 10⁰⁰ **Changes in tourmaline trace element geochemistry during magmatic fractionation and hydrothermal ore deposition**
FLU-T09 Marguerita Duchoslav, Michael Marks, Thomas Wenzel
Gregor Markl (Tübingen/DE)
- 10¹⁵ **Structural incorporation of W⁶⁺ into hematite and goethite and its bearing on hydrothermal and supergene Fe ores**
FLU-T10 Stefan Kreißl (Tübingen/DE), Ralph Bolanz (Jena/DE)
Jörg Göttlicher, Ralph Steininger (Karlsruhe/DE)
Gregor Markl (Tübingen/DE)

Reveal *ppm* differences

Color CL imaging showing ppm level differences in mineralogy

Assists interpretation of mineral provenance Geological and materials science applications



Images, clockwise from top left: (Top Left) Quartz areole, garnet and metamorphic source. Image shows well developed overgrowth cement with multiple zoning. Sample prepared using the Gatan flux™ II and imaged with Gatan ChromaCL2™ imaging system. Image courtesy of Dr. J. Schieber, Indiana University. (Top Right) Growth zoning in an individual zircon grain. Sample imaged with Gatan ChromaCL2 imaging system. (Bottom Right) Provenance identification in shale. Single-source dominated provenance Barrett shale (Miss.) Texas, low grade metamorphic Chertite outcrop. Sample prepared using the Gatan flux II and imaged with Gatan ChromaCL2 imaging system. Image courtesy of Dr. J. Schieber, Indiana University. (Bottom Left) Reservoir quartz of mixed provenance displaying healed fractures and chemical overgrowths. Super-image acquired using Gatan ChromaCL2 imaging system and CHY532 field stitching software package.



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- 09⁰⁰–10³⁰ **Metamorphic rocks – petrology, geochemistry, geochronology**
Room Lecture hall 5
Chairs Reiner Klemm (Erlangen/DE), Hans-Peter Schertl (Bochum/DE)
- 09³⁰ Keynote lecture: **Eclogite-facies metasomatism in the Monviso**
MOR-T01 **ophiolite (Italy) records long-range, channelized transport of fluids along the subduction shear zone**
Samuel Angiboust (Potsdam/DE), Thomas Pettke (Bern/CH)
Cees Jan De Hoog (Edinburgh/GB), Onno Oncken (Potsdam/DE)
- 09³⁰ **Jadeitite and jadeite-bearing rocks from the Rio San Juan**
MOR-T02 **Complex (RSJC), Dominican Republic – the impact of zircon**
Andreas Hertwig (Bochum/DE)
William C. McClelland (Iowa City, IA/US)
Kouki Kitajima (Madison, WI/US), Hans-Peter Schertl
Walter V. Maresch (Bochum/DE), John W. Valley (Madison, WI/US)
- 09⁴⁵ **New age constraints for the development of the Münchberg**
MOR-T03 **Massif**
Franz Gerhard (Berlin/DE), Johannes Glodny (Potsdam/DE)
Axel Gerdes (Frankfurt a. M./DE)
- 10⁰⁰ **Evidence from the Acasta Gneisses for strongly depleted**
MOR-T04 **Hadean mantle components**
Maltese Alessandro (Münster/DE), Peter Sprung (Cologne/DE)
Erik E. Scherer (Münster/DE), Klaus Mezger (Bern/CH)
Wouter Bleeker (Ottawa/CA)
- 10¹⁵ **Ardennite-(V) within a high-P/T metamorphic conglomerate**
MOR-T05 **near Vitolište in the westernmost Vardar zone, Republic of Macedonia (FYROM)**
Rainer Altherr, Christian Soder, Marcel Böhm, Patrick Frühauf
Alexander Mitev, Thomas Ludwig
Hans-Peter Meyer (Heidelberg/DE)

- 11⁰⁰–12³⁰ **Meteorites and the early solar system – Chondrites III**
Room Lecture hall 2
Chairs Thomas Kruijer, Knut Metzler (Münster/DE)
 Julia Roszjar-Walter (Vienna/AT)
- 11⁰⁰ Keynote lecture: **Noble gases in meteorites – What do they tell**
MET-T15 **us about the (early) solar system?**
 Rainer Wieler (Zurich/CH)
- 11³⁰ **Clues to the formation of nanoscale alteration textures in the**
MET-T16 **CM chondrites Murchison and Maribo**
 Moritz I. F. Barth, Christian Vollmer, Addi Bischoff
 Marian Horstmann (Münster/DE)
- 11⁴⁵ **Reconstructing the thermal history of type II chondrules in the**
MET-T17 **CO chondrite Kainsaz from chemical zoning in olivine and**
 chromite
 Sabrina Schwinger, Ralf Dohmen
 Hans-Peter Schertl (Bochum/DE)
- 12⁰⁰ **Impact induced compaction of chondritic parent bodies and**
MET-T18 **the initial porosity distribution of chondrites**
 Eike Beitz, Jürgen Blum (Braunschweig/DE)
 Gabriela Parisi (La Plata/AR)
- 12¹⁵ **Modelling the thermal history of the parent body of Acapulco-**
MET-T19 **and Lodran-like achondrites**
 Stephan Henke, Hans-Peter Gail, Mario Trierloff
 Winfried H. Schwarz, Jens Hopp (Heidelberg/DE)

- 11⁰⁰–12³⁰ **Minerals – fluids – rocks III**
Room Lecture hall 4
Chairs Thorsten Geisler-Wierwille (Bonn/DE), Kilian Pollok (Jena/DE)
- 11⁰⁰ **Ferrous minerals in banded iron formation from Hamersley Range, Australia – Are they primary or diagenetic?**
FLU-T11 Martin Schumann, Kilian Pollok, Falko Langenhorst (Jena/DE)
- 11¹⁵ **Zoned supergene mineral associations formed during weathering of galena – mineralogical description and hydrogeochemical modeling**
FLU-T12 Maximilian Keim, Gregor Markl (Tübingen/DE)
- 11³⁰ **Formation of colloidal multilayers on nanostructured crystal surfaces-an experimental approach**
FLU-T13 Philipe Kiefer, Cornelius Fischer, Andreas Lüttge (Bremen/DE)
- 11⁴⁵ **Dissolution of polycrystalline material analyzed by the rate spectra concept**
FLU-T14 Stephan Lenz, Cornelius Fischer, Rolf Arvidson
 Andreas Lüttge (Bremen/DE)
- 12⁰⁰ **Fluid infiltration and pseudomorphs formation during the replacement of garnet and pyroxene in the Caledonides of western Norway**
FLU-T15 Centrella Stephen, Putnis Andrew (Münster/DE)
 Austrheim Hakon (Oslo/NO)
- 12¹⁵ **The replacement of Celestine (SrSO₄) by Strontianite (SrCO₃) studied in situ by Raman spectroscopy**
FLU-T16 Michael Sulzbach, Thorsten Geisler-Wierwille (Bonn/DE)

- 1100–1230 **Minerals in the environment – from geo- to biosphere I**
Room Lecture hall 5
Chairs Giovanni De Giudici (Cagliari/IT), Erika Kothe
Juraj Majzlan (Jena/DE)
- 1100 **Unique algae bacteria mineral assemblages in a highly
ENV-T01 metalcontaminated stream**
Jiro Mori (Jena/DE), Thomas R. Neu (Magdeburg/DE)
Matthias Händel, Kai Uwe Totsche, Kirsten Küsel (Jena/DE)
- 1115 **Mesorhizobium australicum mediates low pH Mn(II) oxidation
ENV-T02 leading to the formation of bixbyite**
Tsing Bohu (Jena/DE), Cara Santelli (Washington, DC/US)
Denise Akob (Reston, VA/US), Kirsten Küsel (Jena/DE)
- 1130 **Characterization of biogenic Mn oxides produced by
ENV-T03 Mn(II)-oxidizing bacilli isolated from a Mn oxide-rich soil layer**
Sathish Mayanna (Jena/DE), Caroline L. Peacock (Leeds/GB)
Erika Kothe, Georg Büchel (Jena/DE)
- 1145 **Mineralogical investigation of a geogenic TI-As contamination
ENV-T04 near Buus (Switzerland)**
Julia Petrikis (Jena/DE), Andreas Voegelin (Dübendorf/CH)
Lukáš Palatinus (Prague/CZ), Juraj Majzlan (Jena/DE)
- 1200 **Rare earth element patterns – process indicators in the
ENV-T05 biogeosphere**
Anja Grawunder, Francesca Langella, Matthias Händel (Jena/DE)
Matthias Gube (Jena, Göttingen/DE), Dirk Merten, Erika Kothe
Georg Büchel (Jena/DE)
- 1215 **Mineralogy and microbial diversity in As-rich waste dumps
ENV-T06**
Felix Yebo Amoako, Juraj Majzlan, Erika Kothe (Jena/DE)

1245–1330 **Lunch Symposium – PANalytical GmbH (Kassel/DE)**
Room Lecture hall 4

Advanced X-ray analysis – powder diffraction and beyond
Uwe König (Kassel/DE), Thorbjörn Schönbeck (Kassel/DE)

1400–1445 **Plenary lecture**
Room Lecture hall 2

P04 **Biomieralization in magnetotactic bacteria and biomimetic synthesis of magnetic nanoparticles**
Mihály Pósfai, Eva Tompa, Ilona Nyirő-Kósa (Veszprém/HU)
András Kovács, Rafal E. Dunin-Borkowski (Jülich/DE)
Balázs Tóth, Ferenc Vonderviszt (Veszprém/HU), Rene Uebe
Dirk Schüler (Bayreuth/DE)

1515–1645 **Meteorites and the early solar system – achondrites and isotopes**
Room Lecture hall 2
Chairs Thomas Kruijer, Knut Metzler (Münster/DE)
Julia Roszjar-Walter (Vienna/AT)

1515 **Disturbed Lu-Hf isotope systematics of achondrites:**
MET-T20 **Testing a new hypothesis**
Rebecca Bast, Erik E. Scherer (Münster/DE)
Peter Sprung (Cologne, Münster/DE), Mario Fischer-Gödde
Christian Vollmer, Addi Bischoff (Münster/DE)
Klaus Mezger (Bern/CH)

1530 **Isotopic variability of tantalum isotopes in early solar system materials**
MET-T21 Markus Pfeifer (Cologne/DE)
Bo-Magnus Elfers (Cologne, Bonn/DE)
S.T.M. Stefan (Cologne, Bonn, Göttingen/DE)
Carsten Münker (Cologne, Bonn/DE)

1545 **Isotope anomalies of Hf and W in chondrite leachates and residues**
MET-T22 Bo-Magnus Elfers, Stefan Peters, Frank Wombacher
Carsten Münker (Cologne/DE)

- 16⁰⁰
MET-T23 **High-precision measurements of p-process ¹⁹⁰Pt in weakly irradiated irons**
Stefan Peters (Göttingen/DE)
Carsten Münker (Bonn, Cologne/DE)
- 16¹⁵
MET-T24 **The importance of sulfur for the partitioning behaviour of the HSEs during Earth's accretion and differentiation**
Vera Laurenz, David C. Rubie, Dan Frost (Bayreuth/DE)
- 16³⁰
MET-T25 **Geochemical constraints on the evolution of the Earth-Moon system**
Carsten Münker (Cologne/DE), Chris Ballhaus
Raúl Fonseca (Bonn/DE), Toni Schulz (Vienna/DE)
- 15¹⁵–16⁴⁵
Room **Minerals – fluids – rocks IV**
Chairs Lecture hall 4
 Thorsten Geisler-Wierwille (Bonn/DE), Kilian Pollok (Jena/DE)
- 15¹⁵
FLU-T17 **Behavior of Sr and Y during apatite replacement – insights from Hydrothermal Diamond Anvil Cell experiments**
Christof Kusebauch, Stephan Klemme, Ineke Wijbrans
Jasper Berndt-Gerdes (Münster/DE), Manuela Borchert
Karen Appel (Hamburg/DE), Timm John (Berlin/DE)
- 15³⁰
FLU-T18 **Fluid composition effects on the experimental replacement of Carrara marble by apatite**
Elisabete Trindade Pedrosa, Andrew Putnis (Münster/DE)
- 15⁴⁵
FLU-T19 **Experimental alteration of bone in acidic solutions**
Franziska Maria Stamm (Bonn/DE), Thomas Tütken (Mainz/DE)
Alexander Heuser (Bonn/DE), Aurélien Bernard (Nantes/FR)
Thorsten Nagel, Thorsten Geisler-Wierwille (Bonn/DE)
- 16⁰⁰
FLU-T20 **New Insight in the coupled dissolution and precipitation of aragonite and calcite**
Matthias Wagner, Stephan Lenz, Rolf Arvidson
Andreas Lüttge (Bremen/DE)

- 16¹⁵
FLU-T21 **A real-time, in situ Raman spectroscopic study on borosilicate glass corrosion**
Christoph Lenting, Thorsten Geisler-Wierwille (Bonn/DE)
- 16³⁰
FLU-T22 **Pattern formation during the alteration of glasses – insights from experimental studies and modelling**
Lars Dohmen, Christoph Lenting, Thorsten Nagel
Thorsten Geisler-Wierwille (Bonn/DE)
- 15¹⁵–16⁴⁵
Room **Minerals in the environment – from geo- to biosphere II**
Chairs Lecture hall 5
Giovanni De Giudici (Cagliari/IT), Erika Kothe
Juraj Majzlan (Jena/DE)
- 15¹⁵
ENV-T07 **Former U mining provides an excellent study site for supergene Mn mineralization under acidic conditions**
Franziska Schöffner, Dirk Merten (Jena/DE)
Giovanni De Giudici (Cagliari/IT), Georg Büchel (Jena/DE)
- 15³⁰
ENV-T08 **Extracellular Biomineralization processes in carbonate benthic foraminifera and cyanobacteria**
Giovanni De Giudici, Daniela Medas, Francesca Podda
Antonietta Cherchi, Carla Buosi (Cagliari/IT)
Pierpaolo Zuddas (Paris/FR), Carlo Meneghini (Rome/IT)
- 15⁴⁵
ENV-T09 **Mineralogical changes of asbestos fibers in human lungs**
Ruggero Vigliaturo (Torino/IT; Jena/DE), Dennis Harries
Kilian Pollok, Falko Langenhorst (Jena/DE), Silvana Capella
Elena Belluso (Torino/IT)
- 16⁰⁰
ENV-T10 **Kinetics of olivine dissolution in the presence of Synechococcus sp. cyanobacteria biomass in partially closed batch reactors**
Sebastian Weber, Raul Martinez (Freiburg/DE)

- 16¹⁵
ENV-T11 **Akaganéite and schwertmannite – spectral properties and geochemical implications of their presence on Mars**
Janice Bishop (Mountain View, CA/US)
Enver Murad (Marktredwitz/DE), M. Darby Dyar (South Hadley, MA/US)
- 16³⁰
ENV-T12 **Air pollution on the eve of Chinese Spring Festival 2008 in Beijing**
Hejing Wang, Nan Zheng (Beijing/CN), Ang Ji (Shanghai/CN)
Erping Fan, Ting Li, Ling Wang, Zhao Zhou, Lei Yuan (Beijing/CN)
- 16⁴⁵–17¹⁵
Room **Closing**
Lecture hall 2

Economic minerals – formation, characterization, and applications

- ECO-P01 **Minerals of hydrothermal copper-deposits from northern Chile**
Niels-Jonas Krekeler, Birgit Kreher-Hartmann (Jena/DE)
- ECO-P02 **Mineralogy, formation conditions and hydrothermal alteration at the Ag-Au epithermal deposit Nová Baňa (Slovakia)**
Khulan Berkh, Juraj Majzlan (Jena/DE), Peter Koděra
Martin Chovan (Bratislava/SK)
František Bakos (Banská Štiavnica/SK)
Adrián Biroň (Banská Bystrica/SK)
- ECO-P03 **Influence of submarine and subaerial alteration on trace element distribution in VMS ores from the Oman Ophiolite**
Martin Koppelberg, Sven Sintern
Franz Michael Meyer (Aachen/DE)
- ECO-P04 **The Rietveld refinement applied to the bauxite and its clayey cover at Juruti, Pará, Brazil**
Leonardo Boiadeiro Ayres Negrao (Brasilia-DF/BR)
Herbert Pöllmann (Halle/Saale/DE)
Marcondes Lima da Costa (Belém-PA/BR)
- ECO-P05 **Fluid mixing processes involving red bed- and basement-interacted fluids recorded in fluid inclusions from a hydrothermal Mn-Fe vein system at Sailauf (Germany)**
Tobias Fusswinkel, Thomas Wagner (Helsinki/FI)
Thomas Wenzel (Tübingen/DE), Markus Wälle (Zurich/CH)
- ECO-P06 **Arsenic in pyrite – commonalities and disparities: an overview**
Stefan Kiefer, Juraj Majzlan, Ralph Bolanz (Jena/DE)
Jörg Göttlicher (Karlsruhe/DE), Jiří Zachariáš (Prague/CZ)
- ECO-P07 **Formation of REE-rich veins in ferrocarbonatite, NW Namibia**
Dominique Leible, Kirsten Drüppel (Karlsruhe/DE)
- ECO-P08 **Occurrence of Ilmenite on the Ti-bearing Ore deposit in Jikjeon-Ri, Hadong, Korea**
Jiyoung Kwak, Jinbeom Choi, Dongho Kim (Jinju-si/KR)

- ECO-P09 **Resource potential of REE as by-product of an existing mining operation – a geometallurgical assessment**
Sandra Birtel, Marius Kern, Tobias Höfig, Joachim Krause
 Jens Gutzmer (Freiberg/DE)

Magmatic petrology – from melt to rock

- MAG-P01 **Mineral chemistry of chromian spinel in high-Cr podiform chromitites from Sabzevar ophiolite, NE Iran – implications for parental melt composition and geodynamic setting**
Zohreh Moosavinasab, Mohammad Ali Rajabzadeh (Shiraz/IR)
 Amir Morteza Azimzadeh (Leoben/AT), Thomas Aiglsperger
 J. A. Proenza (Barcelona/ES)
- MAG-P02 **Mineral Paragenese und Mineralchemie der Büyük Yayla Obsidiane, İkizdere-Rize/NE-Türkei**
 Münür Burhan Sadıklar (Trabzon/TR)
- MAG-P04 **Major, trace and rare earth elements distribution in magmatic rocks of the Bystrinskoe Au-Cu skarn-porphyry deposit (Eastern Transbaikalia, Russia) – metallogenic consequences**
 Abramov Sergei, Vladimir Kovalenker
 Yazykova Yulia (Moscow/RU)
- MAG-P05 **Partial melting effects and melt-peridotite interactions in the Pozanti-Karsanti ophiolite (eastern Taurides, Turkey)**
 Samet Saka (Trabzon/TR), Melanie Kaliwoda (Munich/DE)
 Ibrahim Uysal (Trabzon/TR), Recep Melih Akmaz (Zonguldak/TR)
 Rupert Hochleitner (Munich/DE)
- MAG-P06 **Basalts and basanites of the Heldburger Gangschar, Thuringia**
Anne Dreißigacker, Bahadur Zeynalov, Ralf Milke (Berlin/DE)
- MAG-P07 **Niobium minerals in the Heldburg phonolite, Thuringia**
Beate Begerock, Julian Haas, Ralf Milke (Berlin/DE)
- MAG-P08 **Phonolites in the mantle?**
 Thomas B. Grant, Ralf Milke (Berlin/DE)
- MAG-P09 **The influence of Iron on Sulfur speciation in slab melts**
Anne Kaufmann, Kevin Klimm (Frankfurt/DE)

- MAG-P10 **Trace element partitioning between spinel and silicate melt: the effect of oxygen fugacity and spinel composition**
Ineke Wijbrans, Stephan Klemme, Jasper Berndt-Gerdes
Christian Vollmer (Münster/DE)
- MAG-P11 **The haplogranite system as a geobarometer for highly evolved melts – experimental investigations on the effect of Anorthite**
Sören Wilke, Carolin Klahn, Dominik Mock, Francois Holtz
Renat Almeev (Hannover/DE)
- MAG-P12 **The late-stage evolution of basalts in the Bushveld Complex**
Saskia Hövelmann (Hannover/DE)
Bernard Charlier (Hannover/DE; Liège/BE), Olivier Namur
André Stechern, Lennart Fischer, Francois Holtz (Hannover/DE)
- MAG-P13 **Basic-granitic magma interaction in the dike complex (Western Sangilen)**
Elena Vasyukova (Novosibirsk/RU)
- MAG-P14 **From rock to magma frictional melting in the conduit**
Jackie Kendrick, Yan Lavallee, Donald Bruce Dingwell (Liverpool/GB)

Microstructures, textures and interfaces of minerals

- MIC-P01 **Almandine – synthesis, crystal chemistry, defects and physical properties**
Charles A. Geiger (Salzburg/AT)
Adrian Brearley (Albuquerque, NM/US), Edgar Dachs
Gerold Tippelt (Salzburg/AT)
- MIC-P02 **Element partitioning at a propagating reaction interface: growth of spinel in the MgO-Al₂O₃ system, experiment and thermodynamic model**
Rainer Abart, Petr Jerabek, Jiri Svoboda, Erik Rybacki
Dieter Rhede (Vienna/AT)
- MIC-P03 **Internal Microstructures and Breakdown of Garnet from Moldanubian Granulites (Gföhl Unit, Dunkelsteinerwald, Lower Austria)**
Nathalie Bourgin, Rainer Abart, Konstantin Petrakakis (Vienna/AT)

- MIC-P04 **The most frequent interfaces between olivine crystals**
Katharina Marquardt (Bayreuth/DE)
 Gregory S. Rohrer (Pittsburgh, PA/US), Luiz Morales
 Erik Rybacki (Potsdam/DE)
- MIC-P05 **Behavior of Fe during dissolution-precipitation reactions**
Gerhard Franz, Dina Schultze (Berlin/DE)
 Friedrich Lucassen (Berlin, Bremen/DE), Richard Wirth (Potsdam/DE)
 Jörg Nissen (Berlin/DE), Dieter Rhede (Potsdam/DE)
- MIC-P06 **Computertomografische Vergleichsstudien rezenter Korallen
 und eisenzeitlicher Korallenzieher**
A. König, Frank Dehn, Klaus Bente (Leipzig/DE)
 Peter Krüger (Dresden/DE)
- MIC-P07 **Deformation fabrics at the transition from spinel to garnet
 Iherzolite in the CMAS system**
 Florian Heidelberg (Bayreuth/DE)
- Mineral physics and the deep Earth's interior**
- PHY-P01 **Theoretical prediction of new CaAl_2O_4 high-pressure super
 dense phase**
Nikolai Eremin (Moscow/RU), Alexey Grechanovsky (Kiev/UA)
 Vadim Urusov, Ekaterina Marchenko (Moscow/RU)
- PHY-P02 **Atomistic modeling of dislocations with [100] Burgers vector
 in MgSiO_3 post-perovskite**
Alexandra Goryaeva, Philippe Carrez
 Patrick Cordier (Villeneuve d'Ascq/FR)
- PHY-P03 **Stability and structure of $\text{Mg}_2\text{Fe}_2\text{O}_5$ at high P-T conditions**
Laura Uenver-Thiele, Alan Woodland (Frankfurt a. M./DE)
 Tiziana Boffa Ballaran, Dan Frost (Bayreuth/DE)
- PHY-P04 **Structural properties of carbonate-silicate melts in the system
 $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$: Incorporation of trace elements
 investigated by Extended X-ray Absorption Fine Structure
 Spectroscopy**
Julia Pohlentz (Potsdam/DE), Olivier Mathon
 Sakura Pascarelli (Grenoble/FR), Stéphanie Belin (Saint Aubin/FR)
 Andrei Shiryaev, O. G. Safonov, Vadim Murzin
 Ksenia Shablinskaya (Moscow/RU), Max Wilke (Potsdam/DE)

PHY-P05 **Pressure-induced structural phase transition of Pb-lawsonite**
Martin Ende (Vienna/AT), Monika Koch-Müller
Bernd Wunder (Potsdam/DE)

PHY-P06 **In situ X-ray diffraction investigations of goethite (FeO (OH)) and groutite (MnO (OH)) at high pressures and temperatures**
Klaus-Dieter Grevel (Jena/DE), Felix Wiethoff (Bochum/DE)
Julia Petrikis, Juraj Majzlan (Jena/DE), Jens Kirste (Leipzig/DE)
Christian Lathe (Potsdam/DE)

Mineralogical crystallography

CRY-P01 **Synthesis and structure of a new crystalline silicic acid: hydrated H-Apophyllite, $H_{16}Si_{16}O_{40} \cdot 8 H_2O$**
Bernd Marler (Bochum/DE)

CRY-P02 **The vibrational entropy of solid solutions**
Artur Benisek, Edgar Dachs (Salzburg/AT)

CRY-P03 **Crystal structures and isotypism of the iron arsenate kumarizaitite and the iron phosphate tincite**
Uwe Kolitsch, Christian L. Lengauer, Gerald Giester (Vienna/AT)

CRY-P04 **Crystal structure of $Cu_{10}(AsO_4)_4(SO_4)(OH)_6 \cdot 12H_2O$, a new copper arsenate-sulphate mineral closely related to leogangite**
Uwe Kolitsch, Christian L. Lengauer (Vienna/AT)

CRY-P05 **Al-Mg and Al-Fe disorder in metamorphic tourmaline**
Andreas Ertl, Ekkehart Tillmanns, Ralf Schuster
Franz Brandstätter (Vienna/AT)

CRY-P06 **Recrystallisation study of radiation damaged titanite and pyrochlore**
Peter Zietlow, Tobias Beirau (Hamburg/DE)
Lee A. Groat (Vancouver/CA), Carsten Paulmann
Ulrich Bismayer (Hamburg/DE)

CRY-P07 **The correction of beam-shadowing effects due to partially filled sample holders in Bragg-Brentano experiments**
Hanna Lührs, Johannes Birkenstock
Reinhard X. Fischer (Bremen/DE)

- CRY-P08 **Crystal-chemical characterization of ammonium exchanged zeolites**
 Iris Spieß, Li Wang, Hauke Hölzen
 Johannes Birkenstock (Bremen/DE)
 Werner H. Baur (Western Springs, IL/US)
Reinhard X. Fischer (Bremen/DE)
- CRY-P09 **Structural phase transitions of $\text{Cu}_2(\text{OH})_3\text{Cl}$**
Thomas Malcherek (Hamburg/DE), Mark D. Welch (London/GB)
 Matthew J. Sciberras (Sidney/AU), Jochen Schlüter (Hamburg/DE)
 Peter A. Williams (Sidney/AU)
- CRY-P10 **A new calcium arsenate mineral, $\text{Ca}_3(\text{AsO}_4)_2 \cdot 5.9\text{H}_2\text{O}$, and its crystal structure**
Uwe Kolitsch, Gerald Giester (Vienna/AT)
- Mineralogical museums and collections**
- MUS-P01 **Collections of Crystal Models at TU Berlin**
 Susanne Franziska Herting-Agthe (Berlin/DE)
- MUS-P02 **A remarkable paragenesis of antimony-sulfosalts from Southern Spain**
Christian Rewitzer, Rupert Hochleitner
 Karl Thomas Fehr (Munich/DE)
- MUS-P03 **„Natur und Kunst, sie scheinen sich zu fliehen und haben sich, eh man es denkt, gefunden“ Gemeinsame Veranstaltungen des Museums Reich der Kristalle mit Münchner Kunstmuseen**
Melanie Kaliwoda, Rupert Hochleitner (Munich/DE)
- MUS-P04 **Die Minerale in der Äußeren-Kennzeichen-Sammlung von Abraham Gottlob Werner**
Beata Heide, Susanne Paskoff, Andreas Massanek
 Gerhard Heide (Freiberg/DE)
- MUS-P05 **Pilot project – further development of SeSam_neo providing a new collection management system for the Geoscientific Collections at the TU Bergakademie Freiberg**
Nadine Janetschke, Jan-Michael Lange
 Martin Kaden (Dresden/DE), Andreas Massanek, Birgit Gaitzsch
 Gerhard Heide (Freiberg/DE)

Modern techniques for mineralogical research

- MOD-P01 **Roughness parameter distributions as tool to monitor topography changes at mineral surfaces**
Kilian Pollok (Jena/DE)
- MOD-P02 **Quantification and verification of mineral phase content of iron – rich brown coal fly ash by Rietveld-method**
Axel Horn, Herbert Pöllmann (Halle (Saale)/DE)
- MOD-P03 **Challenges in the fully automated sample preparation of mineral raw materials and industrial process products for XRF and XRD analysis**
Franziska Setzer, Herbert Pöllmann (Halle/Saale/DE)
Roger Meier (Wuppertal/DE)
- MOD-P04 **New perspectives for lower mantle reaction mechanism research using modern x-ray sources**
Karen Appel, Manuela Borchert (Hamburg/DE)
Wolfgang Morgenroth (Frankfurt/DE)
Motoaki Nakatsutsumi (Hamburg/DE)
Sylvain Petitgirard (Bayreuth/DE), Gerd Priebe
Thomas Tschentscher (Hamburg/DE), Max Wilke (Potsdam/DE)
- MOD-P05 **Low-temperature and high-temperature infrared properties of spinel and corundum and their application to stardust spectra**
Thomas Posch, Simon Zeidler, Harald Mutschke (Jena/DE)
- MOD-P06 **Crystal chemistry of amphiboles studied by Raman spectroscopy**
Lisa Leißner, Jochen Schlüter, Boriana Mihailova (Hamburg/DE)
- MOD-P07 **Quantitative estimation of radiation-induced defect accumulation in zircon (ZrSiO_4) – A REE^{3+} photoluminescence and Raman spectroscopic approach**
Christoph Lenz, Andreas Artac (Vienna/AT)
Shavkat Akhmadaliev (Dresden/DE), Lutz Nasdala (Vienna/AT)
- MOD-P08 **A new procedure for trace element analysis of fluid inclusions with UV-fs-LA-ICP-MS and its Application on tin granites**
Moritz Albrecht, Insa Theresa Derrey, Ingo Horn (Hannover/DE)
Axel Müller (Trondheim/NO), Stephan Schuth
Stefan Weyer (Hannover/DE)

MOD-P09 **Einsatz eines Versuchsplanungsprogramms zur Optimierung der technischen Eigenschaften von Deponiestabilisaten aus calciumreichen Braunkohlenfilteraschen**
Marko Ranneberg, Herbert Pöllmann (Halle/Saale/DE)

MOD-P10 **New perspectives of synchrotron radiation based techniques for mineralogical research at ANKA**
Jörg Göttlicher, Krassimir Garbev, Biliana Gasharova
 Stefan Mangold, Jörg Rothe, Rolf Simon, Ralph Steininger
 Tonya Vitova (Eggenstein-Leopoldshafen/DE)

Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-P01 **Fe isotope fractionation in carbonatite melt systems**
Maria Stüff, Jan A. Schuessler, Max Wilke (Potsdam/DE)

ISO-P02 **The GFZ Potsdam 1280-HR SIMS Laboratory – current state**
Alexander Rocholl, Michael Wiedenbeck, Robert Trumbull
 Frédéric Couffignal, Sarah Glynn, Abiel Kidane (Potsdam/DE)

ISO-P03 **Zircon M127 – a future reference material for U-Pb combined with Hf- and O-isotope analysis***
 Lutz Nasdala (Vienna/AT), Wolfgang Hofmeister
 Tobias Häger (Mainz/DE), Manuela Zeug (Vienna/AT)
 James M Mattinson (Santa Barbara, CA/US)
 Fernando Corfu (Oslo/NO), Fuyuan Wu, Qui-Li Li (Beijing/CN)
 John W Valley (Madison, WI/US), Dirk Frei (Matieland/ZA)
 Andreas Kronz (Göttingen/DE), Carsten Münker (Cologne/DE)
 Christopher M. Fisher (Pullmann, WA/US)
 Allen K Kennedy (Perth/AU), Peter W Reiners (Tucson, AZ/US)
 William R Guenther (Champaign IL/US)
 Katharina Scheidl (Vienna/AT)
 Alfred Kröner (Mainz/DE, Beijing/CN)

Technical mineralogy – cements, ceramics and glasses

- TEC-P01 **Phase transitions of $\text{Ca}(\text{Ti,Fe,Mn})\text{O}_{3-d}$ perovskites**
Stefan Stöber (Halle/Saale/DE), Herbert Pöllmann (Halle/DE)
- TEC-P02 **Hydrothermal Solution of Heavy Metals from MSWI Residues**
Amanda Günther, Karl Thomas Fehr
Rupert Hochleitner (Munich/DE)
- TEC-P03 **Usage of secondary raw materials (residual bauxite, laterite and residual kaolin) for the synthesis of CSA-based cements**
Sabrina Galluccio, Herbert Pöllmann (Halle/Saale/DE)
- TEC-P04 **Investigations of lamellar tetrastrontium aluminate hydrates $[\text{Sr}_3\text{A} \cdot \text{SrX} \cdot n\text{H}_2\text{O}]$ ($\text{X} \in \{(\text{OH})_2, \text{Cl}_2, (\text{NO}_3)_2, \text{CO}_3, \text{SO}_4\}$)**
Martin Kettmann-Pommnitz (Halle/Saale/DE)
Herbert Pöllmann (Halle/DE)
- TEC-P05 **In-situ studies on Li-mobility in compacted powdered solids**
Dawid Murawski, Harald Behrens, Sebastian Ross (Hannover/DE)
Martin Lerch, Dennis Wiedemann, Suliman Nakhal (Berlin/DE)
- TEC-P06 **Modeling of Blast Furnace Slag induced Corrosion of fully Y_2O_3 -Stabilized Zirconia**
Yannick Hemberger, Christoph Berthold
Klaus Georg Nickel (Tübingen/DE)

Archeometry and monument conservation

- ARC-P01 **Fast non destructive and chemical imaging of archaeological artifacts with an X-ray color camera**
Christoph Berthold (Tübingen/DE), Oliver Scharf (Berlin/DE)
Klaus Bente, Klaus Georg Nickel (Tübingen/DE), Rainer Wedell
Aniouar Bjeoumikhov (Berlin/DE)
- ARC-P02 **A multimethodical approach to post mortem coral alteration hypothesis**
Klaus Bente, Christoph Berthold, Ulrike Teschner, T. Münster
Claudia Birkemeyer, S. Nagl, D. Belder, D. Hirsch (Leipzig/DE)
G. Reinicke (Stralsund/DE)
- ARC-P03 **Characterization of historic and modern mortars used at the Freiburg Minster**
Tobias Bader, Hiltrud Müller-Sigmund (Freiburg/DE)

- ARC-P04 **Phaseanalysis on attic silver coins**
Oliver Baehre, Gerald Eisenblaetter, Gert Klöß (Leipzig/DE)
- ARC-P05 **Melting behaviour of alkali feldspar temper clasts in Sue ware**
Michael M. Raith, Radegund Hoffbauer, Beate Spiering (Bonn/DE)
 Maria Shinoto (Heidelberg/DE)
- ARC-P06 **The weathering of magmatic rocks – an approach to quantify the process by an index**
 Klaus Bente (Leipzig/DE), Robert Sobott (Erlangen/DE)
 H.-J. Höbler (Leipzig/DE), G. Klingelhöfer (Mainz/DE)
- ARC-P07 **Microanalysis of Neolithic pottery from northern Syria: insights to provenance and production technology**
Kirsten Drüppel, Markus Federkeil
 Benedikt Rampf (Karlsruhe/DE), Jörg Becker (Halle/DE)
- ARC-P08 **Archaeometric analyses of Paracas ceramics (800-200 BC), southern Peru**
Daniela B. Oestreich, Debora Faller
 Ulrich A. Glasmacher (Heidelberg/DE), Markus Reindel
 Angelika Wetter, Heike Otten (Bonn/DE), Johny Isla (Lima/PE)
- ARC-P09 **Colouring minerals on a Classic Kerma tulip beaker**
 Tom Muenster, Gerald Eisenblaetter (Leipzig/DE)
 Alexandra Franz (Berlin/DE), Ulrike Teschner, Dietrich Raue
Gert Klöß (Leipzig/DE)

Crystal structures and properties of materials

- CSP-P01 **Wavellite from lateritic phosphate deposits in Amazon, Brazil**
Ronny Kaden, Herbert Pöllmann (Halle/DE)
 Marcondes Lima da Costa (Pará/BR)
- CSP-P02 **Dispersion analysis of triclinic crystals**
Sonja Höfer, Thomas Mayerhöfer (Jena/DE)
 Roberto Moreira (Belo Horizonte/BR), Jürgen Popp (Jena/DE)
- CSP-P03 **Single crystal growth of members of the triphylite: lithiophilite, Li(Fe,Mn)PO_4 solid-solution series**
Peter Schmid-Beurmann, Joshua Sibbing
 Jan Thiäner (Münster/DE), Werner Lottermoser (Salzburg/AT)

- CSP-P04 **Phase content and structural analysis of off-stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ (CZTS)**
Kai Neldner, Susan Schorr (Berlin/DE)
- CSP-P05 **Synthesis and characterization of complex lithium-containing layered double hydroxides**
Anton Niksch, Herbert Pöllmann (Halle/Saale/DE)
- CSP-P06 **Crystal structures and photoluminescent properties of the disilicates $\text{K}_3\text{Pr}(\text{Si}_2\text{O}_7)$, $\text{K}_{2.40}\text{Rb}_{0.60}\text{Pr}(\text{Si}_2\text{O}_7)$ and $\text{K}_{2.84}\text{Rb}_{0.16}\text{Sm}(\text{Si}_2\text{O}_7)$**
Maria Wierzbicka-Wieczorek, Martin Göckeritz (Jena/DE)
Uwe Kolitsch, Christoph Lenz, Gerald Giester (Vienna/AT)
- CSP-P07 **Synthesis and structural study of new trigermanates $\text{CaRE}_2\text{Ge}_3\text{O}_{10}$, $\text{RE} = \text{La-Yb}$**
Olga Lipina, Ludmila Surat, Alexander Tyutyunnik, Ivan Leonidov
Vladimir Zubkov (Ekaterinburg/RU)
- CSP-P08 **Crystal structure of Cr-substituted lawsonite from powder diffraction**
Martin Ende (Vienna/AT), Monika Koch-Müller
Bernd Wunder (Potsdam/DE), Eugen Libowitzky (Vienna/DE)
- CSP-P09 **On the relation between structural disorder and modulation in mullite**
Johannes Birkenstock (Bremen/DE), Václav Petříček (Prague/CZ)
Bjoern Pedersen (Garching/DE), Hartmut Schneider
Reinhard X. Fischer (Bremen/DE)
- CSP-P10 **New oxynitride compounds with transition metal elements and extraordinary magnetic properties**
Ulrich Bläß, Marcus Schwarz, Edwin Kroke (Freiberg/DE)

Functional materials

FUN-P01 Comprehensive study of actinide reference materials for electron probe micro-analysis
Xenia Ritter, Philipp Pöml, Stéphane Brémier (Karlsruhe/DE)
 Jasper Berndt-Gerdes (Münster/DE)

FUN-P02 Growth of synthetic Ga-rich tourmaline in hydrothermal solutions
Tatiana Setkova, Vladimir Balitsky (Chernogolovka/RU)

Metamorphic rocks – petrology, geochemistry, geochronology

MOR-P01 Gneisses and charnockites related with UHT metamorphism in Angara-Kan block (Siberian Craton, Russia)
Vasilij Sukhorukov (Novosibirsk/RU)

MOR-P02 Metamorphic evolution of peridotites from the Schwarzwald: evidence from mineral trace element data and P-T pseudosections
Kirsten Drüppel, Alexandra Steiger (Karlsruhe/DE)
 Alexander Heuser (Bonn/DE)

MOR-P03 Petrologic and structural constraints on the late Variscan exhumation of lower crustal migmatitic gneisses of the Peterstal antiform (Central Schwarzwald, SW-Germany)
 Maximilian Zundel, Kirsten Drüppel, Jens Grimmer (Karlsruhe/DE)

MOR-P04 Pressure-temperature evolution of a garnet-bearing metapelite from the northern Fichtelgebirge, Upper Palatinate
Gelareh Rahimi, Hans-Joachim Massonne (Stuttgart/DE)

MOR-P05 Chemical composition of Ti-rich garnets as indicator for skarn zones from the contact aureole of Maronia pluton, western Thrace, Greece
Manuela Zeug (Vienna/AT), Panagiotis Voudouris (Athens/GR)
 Alexander Repstock (Freiberg/DE), Helmut Schleicher (Hamburg/DE)

MOR-P06 Protolith determination of a metasedimentary series in the western Tauern Window
Gerhard Franz, Anselm Loges, Dina Schultze (Berlin/DE)
 Eleanor Berryman, Martin Kutzschbach (Berlin, Potsdam/DE)

Meteorites and the early solar system

- MET-P01 Accessory Ca-phosphates in meteorites – distribution and composition**
Dustin Ward (Münster/DE), Roszar Julia (Vienna/AT)
Addi Bischoff, Leschner Lina (Münster/DE)
- MET-P02 Synthesis of refractory metal nuggets (RMNs) and clues to the cooling rate of RMN bearing CAIs**
Daniel Schwander, Stephan Buhre (Mainz/DE)
Ulrich Ott (Szombathely/HU), Gerd Schönhense (Mainz/DE)
- MET-P03 Partial melting of harzburgite in the Yurtuc meteorite of the HED series**
Rainer Abart, Georg Gravogl (Vienna/AT)
Natalia Khisina (Vienna/RU), Elena Petrishcheva, Gerlinde Habler
Theodoros Ntaflos (Vienna/AT)
- MET-P04 Shock Classification of Martian Meteorites by Micro Raman Spectroscopy – clue for a better understanding of the magnetic signature and record**
Viktor H. Hoffmann (Tübingen, Munich/DE), Rupert Hochleitner
Melanie Kaliwoda (Munich/DE), M. Funaki (Tokyo/JP)
M. Torii (Japan/JP), Y. Yamamoto, K. Kodama (Kochi/JP)
T. Mikouchi (Tokyo/JP)
- MET-P05 Raman spectroscopy on terrestrial and meteoritical natural glasses**
Viktor H. Hoffmann (Munich, Tübingen/DE), Melanie Kaliwoda
Rupert Hochleitner (Munich/DE)
- MET-P06 New Results on mineralogy, Raman Spectroscopy and magnetic signature of the Chelyabinsk meteorite**
Hoffmann Viktor H. (Munich, Tübingen/DE), Rupert Hochleitner
Kaliwoda Melanie (Munich/DE), Funaki M. (Tokyo/JP)
Y. Yamamoto, Kodama K. (Japan/JP), Karl Thomas Fehr (Munich/DE)
- MET-P07 Fractionation of major elements, chalcogens and highly siderophile elements in components of the unequilibrated L-chondrite QUE 97008**
Franziska Schubring, Tanja Giebner, Yogita Kadlag
Harry Becker (Berlin/DE)

- MET-P08 **Infrared spectra of meteoritic analogs to protoplanetary disk material**
Pierre Mohr, Harald Mutschke (Jena/DE), Thomas Posch (Vienna/AT)
- MET-P09 **Mid-infrared absorption spectra of five meteorites: comparison with observed spectra obtained by vega-type stars**
Akemi Tamanai (Heidelberg/DE), Harald Mutschke (Jena/DE)
Annemarie Pucci (Heidelberg/DE)

Minerals – fluids – rocks

- FLU-P01 **Zur Mineralogie des Eisenerzvorkommens von Kakopetros, Chania-Kreta (Griechenland)**
Georgios Alevizos, Nikolaos Katzagiannakis
Antonios Stratakis (Chania/GR)
- FLU-P02 **Time resolved alteration of gabbro in high-temperature hydrothermal systems – an experimental study**
Steffen Schächinger, Oliver Beermann, Dieter Garbe-Schönberg
Astrid Holzheid (Kiel/DE)
- FLU-P03 **The formation of the rare earth mineral parisite in emerald bearing carbonate veins of Muzo/Colombia**
Julia Artel, Uwe Altenberger, Christina Günter (Potsdam/DE)
Jimmy Fernandez Lamus (Bogota/CO)
- FLU-P04 **Contributions to the formation of accessory minerals in the emerald deposits of Muzo/Colombia**
Henrike Wilborn, Uwe Altenberger
Christina Günter (Potsdam/DE), Jimmy Fernandez Lamus
Ana Elena Concha Perdomo (Bogota/CO)
- FLU-P05 **Molecular structure of Na(OH) solutions at high P and T: Insights from in-situ Raman spectroscopy and ab initio molecular dynamics simulations**
Johannes Stefanski, Sandro Jahn, Christian Schmidt (Potsdam/DE)

Minerals in the environment – from geo- to biosphere

- ENV-P01 **Arsenical acid mine drainage with colossal arsenic concentration from Jáchymov in Czech Republic – mineralogy, geochemistry, microbiology**
Juraj Majzlan, Jakub Plášil, Radek Skoda, Johannes Gescher
Felix Kröglér, Anna Rusznyak, Kirsten Küsel, Stefan Mangold
Jörg Rothe (Jena/DE)
- ENV-P02 **Elemental composition of detrital magnetite from the upper Yangtze River sediments – implication for the provenance discrimination**
Jiang Huajun, Chang'an Li, Chunguo Kang (Wuhan/CN)
- ENV-P03 **Clay minerals in Zhoulao core sediments since late Cenozoic, Jiangnan Plain, Central China – implication for the time of modern Yangtze River's formation**
Juxing Zhao, Chang'an Li, Lei Shao (Wuhan/CN)
- ENV-P04 **Microbial impact on calcite precipitation**
Aileen Weist, Manu Singh, Anne Kastner, Gerd Gleixner
Georg Büchel, Reinhard Gaupp, Erika Kothe (Jena/DE)
- ENV-P05 **Quantifying the kinetics of olivine dissolution in partially closed and closed batch reactor systems**
Raul Martinez, Sebastian Weber, Kurt Bucher (Freiburg/DE)
- ENV-P06 **Geosphere-Biosphere processes between mine waste, water and Phragmites australis at San Giorgio river (SW Sardinia, Italy)**
Claudia Pusceddu, Daniela Medas, Francesca Podda, Rosa Cidu
Pierfranco Lattanzi (Cagliari/IT), Carlo Meneghini (Roma/IT)
Richard B. Wanty (Denver, CO/US), Alessandra Gianoncelli (Trieste/IT)
Giovanni De Giudici (Cagliari/IT)
- ENV-P07 **Geogenic arsenic enrichment in Upper Permian and Lower Triassic sedimentary rocks of Thuringia, Germany**
Michael Abratis, Lothar Viereck, Juraj Majzlan (Jena/DE)
- ENV-P08 **The fate of As⁵⁺ during the thermal transformation of As-bearing rhomboclase to (H₃O)Fe(SO₄)₂**
Ralph Bolanz (Jena/DE)

ENV-P09 **Carbon and Oxygen isotope signature of hydrozincite biomineralization in Zn-Pb mine (South-West Sardinia, Italy)**
Patrizia Onnis (Cagliari/IT), Pierpaolo Zuddas (Paris/FR)
Giovanni De Giudici, Daniela Medas
Francesca Podda (Cagliari/IT)

ENV-P10 **X-ray powder diffraction versus sequential chemical extraction – a new combined method for exacting mineralogical speciation of sulphidic mining wastes**
Moricz Ferenc, Madai Ferenc, Kristaly Ferenc (Miskolc/HU)

The mineral record of impact events

IMP-P01 **A martensitic mechanism for the zircon-to-scheelite transformation**
Doreen Turner, Kilian Pollok, Falko Langenhorst (Jena/DE)

IMP-P02 **Laser shock experiments on olivine**
Stefanie Hauber, Sven Döring, Dennis Harries, Stefan Nolte
Falko Langenhorst (Jena/DE)

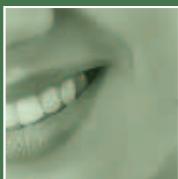
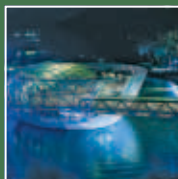
IMP-P03 **TEM-studies on the Tissint meteorite – chemical and structural characterisation of dendritic olivine in melt pockets**
Susanne Rempt, Frank Brenker (Frankfurt/DE)

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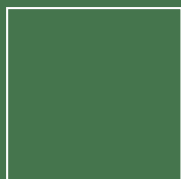
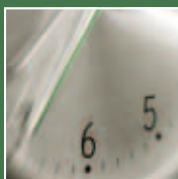
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conventus (lat.) = Coming together, Congress, Convention

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P03

Open-framework silicates at extreme conditions

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Zeolites are a class of “microporous materials” characterised by open-structures with cavities, in the form of channels or cages, with free diameters smaller than 20 Å. In Nature, zeolites with SiO₄-AlO₄-PO₄-tetrahedra form open frameworks; polar molecules (in particular H₂O) and monovalent or divalent cations, which are commonly exchangeable, are the extra-framework species. The selective cation-exchange capacity, the *T*-induced reversible hydration/dehydration and the catalytic activity of zeolites have made this class of natural or synthetic materials an object of attention for their advanced technological applications, spanning from water treatment, soil remediation, cements production, biomedical and veterinary applications, gas separation to catalysis in the petroleum industry and nuclear-waste. Many experiments have addressed the behaviour of zeolites in response to applied temperature, and the mechanisms of *T*-induced dehydration, cation migration and the rearrangement of extra-framework species have been investigated extensively. On the other hand, experiments on zeolites at high pressure have been done only recently, shedding new insight into the elastic behaviour and phase stability in response to changing pressure, coupled with the *P*-induced deformation mechanisms at the atomistic level, *P*-induced over-hydration, *P*-induced amorphization processes along with the effect of pressure on the ionic conductivity of zeolites. In this presentation, a comparative analysis based on the experimental findings on zeolites at extreme conditions will be done, in order to describe: 1) the relation between compressibility and microporosity, 2) the framework flexibility, through deformation mechanisms at the atomistic level, 3) the different role played by framework (i.e. Si/Al-ordering, different cross-linking of the building block units) and extra-framework configuration (i.e. nature of cations and absorbed molecules, ionic valence, ionic radii, coordination number) on the behaviour of zeolites, 4) the crystal-fluid interaction at high pressure and the “hyper-confinement” regime of supramolecular nanoaggregates in zeolitic framework in response to the applied pressure.

The author acknowledges the Italian Ministry of Education, Project: “ImPACT-RBFR12CLQD.

Plenary talks

P04

Biomining by magnetotactic bacteria and the biomimetic synthesis of magnetic nanoparticles

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Magnetotactic bacteria form 'magnetosomes', which are intracellular, membrane-bound magnetic nanoparticles. Each bacterial strain produces magnetite (Fe_3O_4) or greigite (Fe_3S_4) nanocrystals with specific shapes and sizes. The crystals are assembled in linear chains, thereby creating a 'compass needle' that aligns the cell with an external magnetic field. Since tailor-made magnetic nanoparticles have a wide variety of technological and medical applications, it is of interest to understand how the biomining process is controlled by the organism and how the sizes, shapes, structures and arrangements of the nanoparticles affect their magnetic properties.

We have used several advanced transmission electron microscopy techniques, including off-axis electron holography, to study the physical properties of magnetite particles from cells of magnetotactic bacteria. Our results show that in wild-type bacteria the magnetosome particles contain single magnetic domains and that the direction of the magnetic field inside them is governed primarily by their shapes and by magnetostatic interactions between the particles. Whereas in wild-type *Magnetospirillum gryphiswaldense* most magnetosomes contain structurally perfect magnetite crystals, some strains carrying mutants in various magnetosome biosynthesis genes produce particles that are composed of several crystals. The magnetic moments of such aggregated magnetosomes are reduced when compared to those of single-crystal particles.

Studies of genetically-engineered bacteria revealed the roles of distinct proteins in the nucleation and growth of the magnetite crystals. This information is being used to design biomimetic synthesis pathways for the laboratory production of magnetite nanoparticles with special properties. Our approach is to combine two known bacterial functions, filament formation and magnetosome synthesis, in order to produce one-dimensional magnetic nanostructures. The subunit protein of bacterial flagellar filaments, flagellin, was genetically modified by inserting iron-binding motifs known from magnetotactic bacteria. Filaments constructed from these recombinantly expressed fusion proteins display periodically-repeated iron-binding sites on their

surface and can thus serve as templates for the nucleation of magnetite from solution. By using the biological templates our goal is to produce magnetic nanorods.

ARC-T01

Ramanspektroskopische Differenzierung von organischen Pigmenten in biomineralischem Verbund

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Bioorganische Pigmente sind wesentliche farbgebende Bestandteile von Muschelschalen, Korallen, Austernperlen und anderer metabolisch gesteuerter Systeme. So treten entsprechende Pigmente dominant in biomineralischen Karbonaten wie Vaterit, Kalzit und Aragonit als Mischungen von methylierten bzw. unmethylierten konjugierten C=C-Doppelbindungssystemen, d.h. Karotinoiden bzw. Polyenen auf. Diese Mischungen erzeugen in Ramanspektren in der Regel wenig differenzierte Messsignale, die sich jeweils aus einer Reihe von Raman-Banden verschiedener Verbindungen zusammensetzen. Ihre ganzzahligen Doppelbindungsanzahlen ($8 < N < 15$) können über den Schwerpunkt einer Umhüllenden mit einem N_{eff} definiert werden. Die beteiligten Polyene werden dabei über den empirischen Ansatz von Barnard (2006) [1] genähert. Da offensichtlich die C=C-Bindungen durch unterschiedliche LASER-Wellenlängen verschieden angeregt werden, ergeben sich je nach Wellenlänge für eine Pigmentkombination Banden mit verschiedenen Schwerpunkten und Formen. Während statistische Berechnungen zu N bzw. Rechnungen nach Barnard (2006) zu gemittelten N_{eff} führen, liegen jedoch zur Selektion der für die einzelnen Polyene und Karotinoide geltenden Wellenzahlen und deren bandenspezifischen Ursachen ab initio Berechnungen nur zu einigen wenigen Polyenen wie Canthaxanthin [2] vor.

Anhand von Ramanmessungen einzelner Polyene, die als Referenz dienen, werden unterschiedliche im Mineralverbund auftretende Polyene verschiedener Farbeffekte studiert. Dabei werden Banden über empirische Ansätze und im Rahmen von ab initio Rechnungen zugeordnet. Die Ergebnisse werden allgemein sowie auf archäologisch relevante Materialien angewendet.

[1] Barnard et al. J. *Raman Spectroscopy* 37 (2006)

[2] Wu Nan-Nan et al. *Chin. Phys. B* 21(2010)

ARC-T02

White coral beads of Latène and Hallstatt age: original color or decolorated material?

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Corals used for decoration on fibulae and other artifacts are well known e.g. from Latène and Hallstatt age. Fibulae from Hallstatt age (Dürrnberg, Austria) contain both, white and red decorations, but only the white ones are characterized as calcite corals. Contrary to this, the red ones are enamel and amber. Comparing studies of Latène age fibulae of the same type from Central Germany (Hänichen, Kleinkorbetha, Gräfenhainichen) only show white beads which are attributed to fossil calcite material. Our Raman spectroscopic studies on white beads from south Germany and Austria show typical polyene pigment spectra being comparable with those of recent red corals. But in contrast to recent red coral calcites with up to 16% MgCO_3 , the white coral beads showed MgCO_3 contents of app. 8% being in agreement with minimal MgCO_3 contents of leached corals confirmed by our experiments. Contrary to these data, the fibulae beads from central Germany contain neither MgCO_3 nor polyenes and are suggested to derive from fossil corals, other biogenic lime stones or calcites transformed by meteoric water from Fakse aragonite corals. But these beads may also derive from glacier debris within quarries from north Germany. From our findings, only the beads from South Germany (Langenau) and Austria (Dürrnberg) can be attributed to corals from the Mediterranean Sea.

After archaeological suggestions, the fibulae white beads should be caused by post mortem bleaching of red corals by means of workman treatments or deposition conditions. Because these suggestions do not agree neither with concrete contextural aspects nor with biological data on red corals, the contradictions between archaeological arguments and biological as well as material science data will be resolved by systematic studies on experimentally treated corals.

ARC-T03

p-ED-XRF analyses including Na and Mg of ancient glasses

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The best non-destructive way to analyse glasses is by using hand-held devices. Over the past decade these gadgets have been used in an increasing number of studies to analyse ancient glasses in museums all over the world.

Unfortunately, light elements cannot easily be included in measurements using portable energy-dispersive X-ray analysers (p-ED-XRF). Elements of particular significance, such as Na and Mg, are mostly excluded from analyses. In many cases, Na is documented as part of the not-analysed “balance” which includes all light elements. The reason for this is the low X-ray energy of this element. The light elements are almost completely absorbed by air and by the physical parts of the detectors.

As little as 1 mm (2 mm) of air causes an absorption of Na radiation of 31% (53%) and Mg radiation of 20% (36%) of their initial amounts. This means that the presence of any air-filled gap between X-ray source and detector will have a huge influence on the analytical results.

Generally, helium is used instead of air as the medium between the exited sample and the detector to reduce absorption of low-energy X-rays. Intensity loss is reduced to less than 1 % by using He.

We allow for the detection of Na peaks in our standard p-ED-XRF by introducing a simple modification that enables us to analyse Na down to concentrations of about 0.5 wt%.

To calibrate this improved method we prepared approximately 100 glasses of different ages, colours and geographic origins. These glass samples with a diameter of more than 1 cm were mounted in epoxy and polished.

These glasses cover a broad chemical compositional range for more than 20 important elements. The samples were analysed by electron microprobe, energy-dispersive analyses at the SEM and wavelength dispersive X-ray fluorescence analyses for major and trace elements. In addition, we used 19 international glass reference materials and included them in the calibration.

Measurements of unknown samples outside the optimized laboratory conditions produce additional pitfalls, because of small air-filled gaps between the sample and the foil of the detection unit. This causes absorption of radiation emitted in particular from light elements, such as Na and Mg. A series of analysis are conducted on the sample surface, after which additional corrections can be applied to enhance the accuracy of the analyses.

ARC-T04

Zerstörungsfreie Untersuchungen an weissgrundiger attischer Keramik mit modernen hoch ortsauflösenden Röntgenanalyseverfahren und der μ -Ramanspektroskopie

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Bei attischen Keramiken spielen neben schwarz- und rotfigurigen auch die sog. weißgrundigen Keramiken sowohl künstlerisch als auch material- und herstellungstechnisch eine wesentliche Rolle. Ein typisches Beispiel sind weißgrundige Lekythen, die als keramische Erzeugnisse regional in Athen und Umgebung hergestellt wurden, und weit über die Grenzen Attikas hinaus vor allem als Beigaben im Grabkontext nachzuweisen sind. Generell werden bei diesem Keramiktypus vor oder nach dem Brennprozess weiße Grundierungen aufgetragen, die dann als Basis für polychrome Bemalungen mit unterschiedlichen Pigmenten dienen. In diesem Zusammenhang stellen sich entscheidende Fragen zur Herstelltechnik: welche der Gefäßdekorationen wurden vor und welche nach dem Brennvorgang, d.h. kalt, auf den Arbeitston aufgebracht? Gibt es unterschiedliche Brennprozesse bei der Herstellung einer Vase? Sind beispielsweise die Weißgrundierungen auf kaolinitischer Basis aber auch die typischen schwarzen Glanztonpigmente der Fe-Spinelle, die vor dem Brennprozess aufgetragen wurden, abgrenzbar von nach dem Brennen erzeugten Gipsgrundierungen und Farbauftragungen von möglicherweise in separaten Brennprozessen hergestellten und dann kalt aufgetragenen Spinellpigmenten und anderen Kaltpigmenten? Haben sich die Farbpigmente während der Lagerung möglicherweise verändert?

Wie diese und weitere Fragen durch den Einsatz moderner nichtzerstörender und hoch ortsauflösender Röntgenanalyseverfahren wie μ -XRD², μ -RFA und einer Röntgenfarbkamera in Kombination mit der μ -Ramanspektroskopie beantwortet werden können, wird im Beitrag dargestellt werden.

ARC-P01

Fast non destructive and chemical imaging of archaeological artifacts with an X-ray color camera

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²IfG-Institute for Scientific Instruments GmbH, Berlin, Germany

³IAP-Institut für angewandte Photonik e.V., Berlin, Germany

Until now spatially resolved X-ray fluorescence (XRF) mappings are only possible by using typical μ -XRF setups which combine microfocus X-ray sources with polycapillary optics to decrease the spotsize down to the 10 μ m-range. The X-ray spectrum of each location is then analyzed by a classical EDX-detector. Therefore, a chemical mapping of a whole object is typically done measuring each point separately by moving the sample step by step which is not only a time consuming procedure. But nowadays the development of modern X-ray detector systems gives the opportunity to perform a direct locally highly resolved chemical image of a sample especially if a pnCCD detector (developed by PnSensor GmbH, Munich) is used with a 264x264 pixel resolution and a energy resolution of 152eV (MnK α) for each pixel. With this type of detector it is now possible to measure a full-field energy-resolved X-ray image (FF-XRF) of a sample surface if an X-ray optic is mounted in front of the detector ^(1,2). Using different types of such X-ray polycapillary optics with varying magnification it is also possible to change simply the magnification of the camera setup to increase or decrease the local resolution or vice versa the area, which is measured. Moreover, using a non magnifying 1:1 optic 3-dimensional objects can be characterized chemically for the first time without any focussing effort due to the almost infinite depth of sharpness of this kind of optic ⁽³⁾. This unique advantage of the SLcam[®] is a big step forward for an efficient chemical imaging of 3-dimensional surfaces. The opportunity of a nondestructive and time efficient locally resolved chemical analysis of sample surfaces in a common laboratory setup is a breakthrough in the characterization of sensitive archaeological artifacts objects independent from their size and morphology.

In our presentation we will show results from different archaeological artifacts to demonstrate the potential of the X-ray color camera.

⁽¹⁾ Scharf, O. et al., (2011) *Compact pnCCD-Based X-ray Camera with High Spatial and Energy Resolution: A Color X-ray Camera*, Anal. Chem., Vol. 83(7), pp. 2532-2538

⁽²⁾ Ordavo, I. et al., (2011) *A new pnCCD-based color X-ray camera for fast spatial and energy-resolved measurements*, Nucl. Instrum. Methods Phys. Res. Sec. A 654(1) pp. 250 - 257.

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ARC-P02

A multimethodical approach to post mortem coral alteration hypothesis

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Related to material culture questions, we studied fibulae beads from Latène and Hallstatt ages. Because instead of mythologically expected red corals, white beads are archaeologically suggested to derive from post mortem bleaching. Additionally to fibulae beads, we analyzed red and white corals submitting them to experimental procedures regarding their morphology, chemical composition, pigments, carbonate transformation and simulated cyanobacteria influences.

Experimental parameters were deduced from sea water chemistry, in vivo changes and coral detritus decay. We used oxidizing and reducing, acidic, alkaline conditions, sulfate and nitrate solutions, thiourea, urine, soil material, H₂S and reaction accelerating microwave and higher temperatures. Additionally bacteriae influences on the coloring polyenes are in progress. The original and experimentally treated corals as well as the bead materials were characterized by optical microscopy, x-ray m-CT, UV-Vis and Raman spectroscopy, XRD, TEM, SEM, EDX and HPLC-MS.

In contrast to red coral calcites with max. ~16% MgCO₃, white fibulae beads as from Langenau (South Germany) and Dürrenberg (Austria) showed polyenes with $8 < N_{\text{eff.}} < 12$ (Raman spectroscopy) and ~8 % MgCO₃ agreeing with solvus minima of leached Mg containing calcites (XRD). Contrary to these results, fibulae beads from Hänichen, Kleinkorbetha, Gräfenhainichen (Central Germany) contain neither MgCO₃ nor polyenes. The latter are characterized to derive from fossil corals, biogenic lime stones or calcites pseudomorphically transformed from aragonite corals.

Calcite and aragonite corals from Baltic and Mediterranean Sea showed different reactions depending on experimental treatment which can be attributed to surface, interface and volume phenomena. Time depending effects are related to the decrease and degradation of polyenes showing shifts and splitting of Raman bands (Raman) and to Mg leaching as well as to morphological and phase transformations. During bleaching, UV-Vis spectra show decreases of signals of colored corals. For to differentiate the polyenes, HPLC-MS studies are carried out.

ARC-P03

Characterization of historic and modern mortars used at the Freiburg Minster

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The medieval Minster depicts the most prominent landmark of Freiburg, Baden-Wuerttemberg. Its construction started around 1200 in Romanesque style and proceeded in Gothic style from 1230 on. Since then, several episodes of restoration took place, each with its contemporary mortar types. As part of the actual major restoration activities, mortar samples from the Gothic spire and the late Gothic choir were studied with respect to petrography, mineralogy, and microstructures.

In order to identify the aggregates, mineralogy, and textures, thin sections were prepared and analyzed. The aggregates consist predominantly of granitic grit. In one sample relics of smithing waste were observed. The binders were investigated with the help of X-ray diffraction and revealed calcite as major phase. Samples with suspected hydraulic binder phases were further analyzed by electron microprobe.

The characterization revealed a combination of different types of mortars: Original lime mortars on the one hand, modern hydraulic lime mortars of different restoration stages on the other. The further differentiation between hydraulic lime mortars and lime cement mortars was based on the presence of the mineral phase alite. An exception represents one mortar-like substance which was in direct contact with the peripheral tie beam of the tower. From there iron migrated into the mortar and replaced the original binder completely by goethite.

ARC-P04

Phaseanalysis on attic silver coins

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XRD measurements were performed on nine attic silver coins to determine surface contaminations and corrosion products. The silver coins are dated to the 5th century BC. The XRD experiments with high lateral resolution show significant lateral changes in the intensity of identified surface phases. This applies to single coins as well as between the coins. Diffraction patterns of two areas measured on coin 865 are showing this circumstance (see figure 1). The chlorargyrite peaks are surprisingly high. Beside the silver from the bulk and the chlorargyrite, acanthite could be detected on each coin. The peak intensity of all detected phases strongly depends on the measured area. Therefore we restricted the focal-spot size to 1 x 2 mm². Other identified phases on the coins are quartz, calcite, akaganeite, litharge, and massicot.

In addition to XRD, XRF measurements were carried out. The measured content of silver, lead and copper reveal a typical composition of this mint. A significant amount of bromine could be detected on some coins. It is assumed that the bromine is located in the chlorargyrite. Precision lattice constant measurements are in progress to verify this expectation. Peak shifts of the chlorargyrite peaks to lower diffraction angles should be measured in dependence of the bromine content. The archaeological challenge is where the bromine does come from? Is this an evidence of underwater storage?

Many thanks to Professor Dr. Ulrich Johannes Schneider, Dr. Christoph Mackert and Jörg Graf from Leipzig University Library.

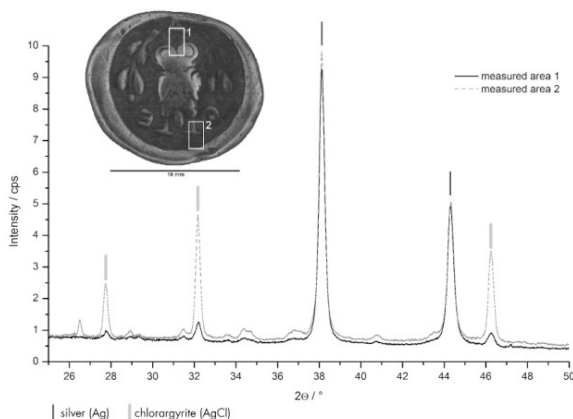


Figure 1: Diffraction patterns of two measured areas on coin 865. Not labelled peaks of lower intensity refer to acanthite, calcite and/or quartz. Data acquisition was done using a Bruker D8-Discover X-ray diffractometer (Cu-K α ; 300 s/frame; frame centre at 2 Θ 30°, 45° and 60°; 40 kV and 40 mA; spot size: 1x2 mm²; VÅNTEC-500 area detector).

ARC-P05

Melting behaviour of alkali feldspar temper clasts in Sue ware

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This contribution examines the melting behaviour of alkali feldspar clasts in 9th century Sue ware from the southernmost Sue kilns of Japan in Kagoshima prefecture (Kyūshū). Sue ware is high-fired stoneware of typical grey to brownish-grey appearance and surfaces that may be unglazed or covered by natural ash glaze. Firing was performed in sloping single-chamber tunnel kilns at reducing conditions and temperatures over 1000 °C. Set in a variably vitrified matrix (glass, mullite, minor spinel and cristobalite), alkali feldspar clasts constitute a major temper component. Melting phenomena range from few microns thin vitreous margins to completely melted clasts which correlates with the vitrification degree of the ceramics (15-50 wt% vitreous phase) and reflects temperature gradients in the kilns. Irrespective of the degree of melting, the clasts retained their original angular shape. Back scattered electron images and element maps of alkali feldspar clasts document chemical zonations that become increasingly pronounced with the degree of melting. Zoning patterns of the clasts show continuous gradations from potassic core compositions ($\text{Or}_{90-80}\text{Ab}_{10-20}\text{An}_{0-1}$) to sodic compositions ($\text{Or}_{68-51}\text{Ab}_{30-46}\text{An}_{2-3}$) in domains adjoining the vitreous domain. Compositions of the vitreous phase show little variation (SiO_2 65-68, Al_2O_3 19.5-20, FeO 2-1.3, MgO 0.6-0.3, CaO 1-0.7, Na_2O 2.5-2, K_2O 6.5-5 wt%). When recalculated to the feldspar formula unit, Si and Al retain the 3:1 cation proportion of the precursor feldspar framework, whereas K and Na are depleted ($\text{K}+\text{Na} = 0.60\text{-}0.45$ a.p.f.u.), and Ca, Fe and Mg ($\text{Ca}+\text{Fe}+\text{Mg} = 0.20\text{-}0.15$ a.p.f.u.) enriched relative to the precursor feldspar.

The compositional systematics show that (1) alkali feldspar did not melt through the incongruent reaction $\text{K-feldspar} \rightarrow \text{leucite} + \text{liquid}$; (2) prior to or synchronous with the onset of melting, the pristine alkali feldspar clasts experienced diffusive K-Na exchange with the matrix, thereby shifting the composition towards the thermal minimum ($\text{Or}_{40}\text{Ab}_{60}$) in the Ab-Or binary system; (4) melting affected exclusively the sodic feldspar domains, occurred in the temperature range 1050-1100 °C, and involved bi-directional element exchange between melt domains and the ceramic matrix, viz. influx of $\text{Ca}+\text{Fe}+\text{Mg}$ to the melt and concomitant loss of $\text{K}+\text{Na}$ to the matrix.

ARC-P06

The weathering of magmatic rocks – an approach to quantify the process by an index

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The term weathering summarizes a number of chemical and physical processes which effect measurable changes of the chemical composition and physical properties of a (magmatic) rock. The chemical weathering of rock-forming minerals such as feldspars, amphiboles, pyroxenes and micas is effected by hydrolysis and leads to the formation of sheet silicates such as clay and serpentine minerals. The degree of weathering depends on the chemical and structural constitution of a rock as well as on the duration and intensity of the chemical and physical processes. Where natural rocks are used for building and construction work it would be practical to have an index for the extent of alterations. Changes in colour, density, uptake of water, ultrasonic velocity and chemistry lend themselves to this purpose. The freshly quarried rock usually serves as reference material although one has to keep in mind that weathering sets in immediately after rock emplacement and also bears on rocks exposed in a quarry. In the case of magmatic rocks used for monuments it would be desirable to carry out the necessary analyses in a non-destructive way or with the minimum interference with the monuments integrity.

As the interaction of oxygen-containing water with rock-forming minerals containing Fe^{2+} ions (amphiboles, pyroxenes and micas) leads to the oxidation of Fe^{2+} to Fe^{3+} the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in these minerals which are individually or collectively present in most magmatic rocks was regarded as a possible weathering index.

To put the idea to the test seemingly unweathered and weathered granite and diorite samples from quarries and outcrops in Demitz-Thumitz (Saxony) and Brotterode (Thuringia) and single crystal specimen from the mineral collection of the TH Freiberg were analysed by different methods with emphasis on the mineral biotite. Also the state of the glacial boulders used for the building of the "Gletschersteinpyramide" (glacial boulder pyramid) in Leipzig Stötteritz and the Romanesque church Hohen-Thekla in Leipzig were investigated. The study of natural weathering was supplemented by controlled weathering experiments in

Archeometry and monument conservation

which fresh granite samples were subjected in a closed systems to percolating water with a pH of 3 - 5 for 853 days.

For analytical data collection we used conventional destructive methods (optical microscopy, X-ray diffraction, electron microprobe analysis) but also innovative non-destructive methods such as computed tomography, μ XRD² and the portable MIMOS II Moessbauer spectroscopy device. The studies were focused on chemical composition (cation substitution), Fe oxidation state and microstructure (zonation, intercrystalline cracks).

The results reveal that the idea of using the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio as a weathering index for magmatic rocks is correct in general but not very suitable for practical purposes which rely more on physical parameters such as compressive strength and/or Young's modulus. The portable Moessbauer spectroscopy device in reflecting mode (MIMOS II) works very well as a tool for quantifying the Fe^{2+} and Fe^{3+} contents in respective minerals even with complex samples. However, in the case of biotite the determination of optical constants (n_z , D) produces also useful information about the oxidation state of iron and with much less experimental effort at that.

ARC-P07

Microanalysis of Neolithic pottery from northern Syria – insights to provenance and production technology

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Petrographic and chemical analyses were carried out on 30 selected potsherds from Neolithic sites of Northern Syria (Tell Halaf, Tell Harubi, Mishrifeh, Hagg Badran, Agila-South, and Tell Tawila), covering the pre-Halaf to Ubaid-period. Most shards display greenish cores and narrow red margins, pointing to firing under reducing conditions. Only potsherds from Tell Tawila are characterized by a red color, pointing to oxidation atmosphere. Most samples contain subrounded fragments of quartz, plagioclase, K-feldspar, ilmenite, and biotite of 0.02 to 0.5 mm in size. These phases presumably represent sand deposits. Limestone inclusions are abundant whereas fragments of mollusk shells are identified in only two samples. These inclusions are set in a fine-grained to vitric matrix. Porosity is represented by sub-millimeter sized voids, channels and, especially in case of potsherds of the Ubaid-period, elongated pores of up to 3 mm in length, suggesting addition of organic fibers.

Scanning electron microscopy and electron microprobe analysis of the fine-grained to glassy matrix reveal that clinopyroxene (fassaite with 15-24 wt% Al_2O_3) is the main neocrystallized phase in most of the shards. In addition, minor gehlenite, anorthite, and sanidine may occur. Small limestone fragments are surrounded by a narrow rim of wollastonite. These phases are held together by a porous, Si-Al-Fe-Mg-Ca-rich glass phase. The amount of vitreous material strongly increases with increasing amounts of fassaite. The fassaite-anorthite-wollastonite-gehlenite-glass assemblage of the samples indicates high firing temperatures of c. 900-950°C, with highest temperatures of > 1000°C being experienced by the fassaite- and glass-rich potsherds from the Ubaid-period. Only two samples from the Halaf-period, one from Tell Halaf and one from Agila, lack both newly formed fassaite and glass phase but instead contain illite and show high carbonate contents, pointing to significantly lower firing temperatures of < 800°C.

The wide variety of the type and size of the raw material particles and the newly formed mineral assemblages in the groundmass, the latter indicating variable firing conditions, are consistent with local production of the pottery. Consistently high glass contents in Ubaid-period shards suggest improved temperature control.

ARC-P08

Archaeometric analyses of Paracas ceramics (800-200 BC), southern Peru

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The Peruvian south coast, located within the northern extension of the Atacama Desert, is one of the driest regions on the planet. Nevertheless, it witnessed the rise of indigenous civilizations, notably the Paracas Culture (800-200 BC) and Nasca Culture (200 BC-600 AD; Van Gijseghem and Vaughn, 2008). The ceramics of the Paracas Culture are characterized by a wide range of intentional burning variants, shapes, and complex decorations. The combination of archaeological analysis and natural scientific methods can reveal new insights in manufacturing techniques and cultural processes. While macroscopic descriptions allow the identification of the materials used in the production process, detailed knowledge of the mineral composition of the ceramic provides the basis for additional interpretations regarding e.g. provenance analysis. Interdisciplinary cooperation between archaeologists and geoscientists enables comprehensive descriptions and analyses of ceramics (Reindel and Isla, 2005; Wetter, 2005).

This study will present data sets from archaeometric investigations (Wetter, 2005; Faller, 2013) on Paracas ceramics from Jauranga, a settlement located near the town of Palpa. Macroscopic and microscopic description, XRD, ICP-ES, and ICP-MS analytical techniques as well as Raman-spectroscopy, Neutron activation analysis, and Electron microprobe analysis were used to characterize the ceramics. Also, this data will be complemented by first results from petrological and geochemical analysis of ceramics from two Paracas locations in the Andean Highlands.

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ARC-P09

Colouring minerals on a Classic Kerma tulip beaker

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The Classic Kerma tulip beaker (1650 BC) is stored at the Egyptian Museum - Georg Steindorff- Leipzig. The red and black ware is made of fine Nile silt and has a variegated grey-purple band on the exterior as a special decor. Besides of the egyptological classification of the Kerma beaker, the mineral phase composition should be investigated to discuss details of the production process, the raw materials and what is so special on the grey-purple band.

As far as investigated by XRD, iron oxides like hematite, goethite, and magnetite are detected in the red part of the beaker but not in the black one. In contrast, graphite is detected in the black part only. Raman spectroscopy was used to verify the graphite found by XRD.

XRF studies proofed that the typical red and black colouring is not the result of a different element contribution but rather due to the firing process. The matrix consists of only one material stating quartz and feldspar as main phases. The grey-purple band seems to be made of the same or very similar material, probably stone dust or ground pottery.

X-ray tomography is additionally used to image density differences within the beaker and the band.

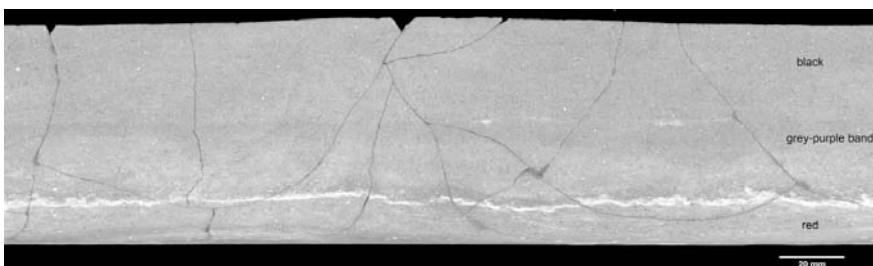


Figure 1: Visualization of the Classic Kerma tulip beaker (No. 3858) by μ XRCT cylindrical projection (53.1 μ m pixel size; measured at IMKM, Leipzig)

Crystal structures and properties of materials

CSP-T01

Analyzing *in-situ* powder diffraction data of minerals and inorganic compounds with symmetry mode approaches

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The formation of high-pressure and/or high-temperature polymorphs of minerals and crystalline compounds can be observed with e.g. *in-situ* powder diffraction methods, as these methods allow a direct observation of structural changes within the crystal. In the case of second order phase transitions these structural changes often can be described as motions of whole atomic groups or polyhedra, which obey group theory and the corresponding group-subgroup relations. Traditionally, the investigation of *in-situ* powder data sets is done by using relative atomic coordinates within a Rietveld refinement^[1], which determine the basis of the atomic configuration space. Unfortunately, this choice of basis with relative atomic coordinates is not a natural choice, as the motion of atomic groups or polyhedra can be described with a smaller set of parameters. In order to change the basis of the atomic configuration space to a more natural choice, symmetry mode^[2,3] approaches which account for the group theoretical nature of the phase transition can be used, as these approaches inherently describe the distortion of atomic coordinates of a real or hypothetical high-symmetry structure to the coordinates of a low-symmetry structure.

In the presentation, the application of rotational rigid body symmetry modes^[4] on minerals (high temperature investigations of lueshite (NaNbO₃)^[5], high pressure investigations of schafarzikite (FeSb₂O₄)^[5]) and inorganic compounds (high pressure investigations of lanthanum ferrite (LaFeO₃)^[6]) will be shown.

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CSP-T02

Determining verticillated crystals and finding their optical axis with IR-spectroscopy

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The measurement scheme developed and described in [1] for triclinic crystals can be used to find the optical axis of verticillated single crystal samples (trigonal, tetragonal and hexagonal systems, but as they cannot be distinguished with this method, we refer to trigonal crystal for convenience).

The spectra set is measured equally to triclinic crystals, of which 12 spectra of three perpendicular crystal faces are recorded in the measurement scheme developed in [1] and then fitted with the “triclinic” routine, meaning without any constraints concerning the oscillator parameters.

The resulting oscillator parameters show two classes of oscillators, one class of oscillators occurs in pairs with similar values for resonance wavenumber, strength and damping constant, and are roughly orthogonal to each other and fixed within one plane. The other oscillators which indicate the optical axis occur singly and perpendicular to the planes in which the first kind is restricted to.

The fit is then performed a second time with “trigonal” constraints, i.e. using an oscillator model particularly developed for verticillated materials. The orientation of the optical axis can be found up to $\pm 2^\circ$ depending on the spectral distance of the oscillators. The method is a suitable alternative to x-ray orientation with additional information about the components due to the oscillator parameters.

We investigated three trigonal crystals: Calcite, which shows almost “cubic” spectral behavior except for one vibrational transition, Quartz, whose vibrations are sufficiently strong and separated that already the unconstrained fit reveals its kind of anisotropy and the correct orientation of the optical axis, and Lithiumniobate, which has intense bands very near to weak bands, which shows that for a reliable fit some kind of Rayleigh criterion has to be fulfilled.

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CSP-T03

Actinide chemistry under extreme conditions – the first example of a mixed valence As(III)/As(V) actinide compound

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The chemistry of Actinides is of special interest because the knowledge of their chemical behavior is of great importance for applications linked to nuclear energy production and nuclear repositories. In addition, these elements are very interesting as the objects for basic experimental and theoretical study because they possess 5f-electrons.

Recently, most experimental studies on Actinide chemistry are done at ambient or mild hydrothermal pressures. The use of high pressure/ high temperature equipment like piston cylinder or multi anvil presses could expand the range of experimental spectrum and therefor the understanding of actinide chemistry enormously. First results of high temperature/high pressure experiments in a piston cylinder apparatus from investigation of the crystallization in $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ - As_2O_3 - CsNO_3 system will be presented.

The initial finely grounded mixture of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, As_2O_3 , and CsNO_3 in a ratio of 1 : 8 : 2 was sealed in a Pt capsule and placed in a high pressure assembly which was inserted in the piston cylinder module of a Voggenreiter LP 1000-540/50 (FZ Jülich). The experiment was performed at a pressure of 3 GPa and a temperature ranging from 1200 to 300°C. After quenching the experiment the capsule was opened and transparent crystals were picked from a white media. The resulting compound obtained is $\text{Th}(\text{As}^{\text{III}}_4\text{As}^{\text{V}}_4\text{O}_{18})$ (see figure 1) which is representative of rare class of mixed valence $\text{As}^{\text{III}}/\text{As}^{\text{V}}$ compounds. This compound was studied with SG XRD, EDX, and Raman spectroscopy. Crystallographic data shows $\text{Th}(\text{As}^{\text{III}}_4\text{As}^{\text{V}}_4\text{O}_{18})$ built of $(\text{As}^{\text{III}}_4\text{As}^{\text{V}}_4\text{O}_{18})^{4-}$ layers connected to each other through coordinated Th atoms. The arsenic layers in the crystal structure of the novel compound are found to be isorecticular to those in previously reported As_2O_3 and $\text{As}_5\text{O}_{13}(\text{OH})$.

Two more obtained structures in the $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ - As_2O_3 - CsNO_3 system that will be presented are $\text{CsTh}(\text{As}_3\text{O}_{10})$ and $\text{Cs}_2\text{Th}_2\text{As}_6\text{O}_{19}(\text{OH})_2$. These structures are just a small example which shows the great diversity of chemical compounds which can be expected from actinide high temperature/ high pressure experiments.

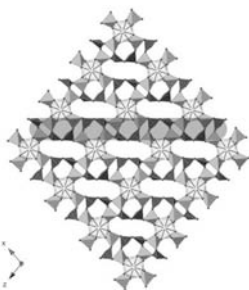


Figure 1. A view on the crystal structure of $\text{Th}(\text{As}^{\text{III}}_4\text{As}^{\text{V}}_4\text{O}_{18})$. ThO_8 , AsO_4 , and AsO_3 coordination polyhedra are yellow, green, and magenta, respectively, and O atoms are red. An $(\text{As}^{\text{III}}_4\text{As}^{\text{V}}_4\text{O}_{18})^{4-}$ layer is marked with blue.

CSP-T04

Thermodynamic mixing properties and behavior of grossular-spessartine, $(\text{Ca}, \text{Mn}_{1-x})_3\text{Al}_2\text{Si}_3\text{O}_{12}$, solid solutions

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The heat capacity, C_p , for nine synthetic solid-solution members of the grossular(Gr)-spessartine(Sp) binary was measured in the temperature range between 2 and 300 K using relaxation calorimetry and from 280 K to 764 K using DSC methods. All solid-solution garnets exhibit normal heat capacity behavior from 764 K down to 7 K. Below 7 K, a heat-capacity anomaly, originating from a paramagnetic to antiferromagnetic phase transition related to an ordering of the electron spins of the Mn cation, is observed. This lambda anomaly is sharp and pronounced for Mn-rich solid-solution members and it becomes more flattened and rounded with decreasing Mn concentration in the garnet. The corresponding Neel temperature decreases monotonically from 6.2 K in pure Sp to less than 2 K in Gr-rich garnets with $X_{\text{Mn}}^{\text{grt}} < 0.5$. The calorimetric entropy, S_{cal} , at 298 K for all intermediate composition garnets shows a slight positive deviation from ideality, resulting in an excess calorimetric entropy, $\Delta S_{\text{ex,cal}}$, of approximately 2 J/mol·K. The vibrational and magnetic parts of the total calorimetric entropy, S_{vib} and S_{mag} , respectively, were separated and calculated using the single-parameter phonon dispersion model of Komada and Westrum (1997). A symmetric entropy interaction parameter of $W_{\text{S,CaMn}}^{\text{grt}} = 3.8 \pm 2.0$ J/cation·mol·K is calculated for Ca-Mn mixing across the Gr-Sp binary based on garnets with $X_{\text{Mn}}^{\text{grt}} \geq 0.5$. More Gr-rich garnets have impurity phases, complicating their exact C_p behaviour and, thus, they were not used in this calculation. S_{mag} behaviour was also determined for intermediate garnets where the lambda anomaly is well pronounced and measurable. A thermodynamic analysis of published displaced phase equilibrium experiments was also made. The analysis yields a symmetric enthalpy interaction parameter of $W_{\text{H,CaMn}}^{\text{grt}} = 3.2 \pm 0.3$ kJ/cation·mol. ΔG_{ex} for Gr-Sp garnets is slightly positive at 500°C and becomes more negative with increasing temperatures. Its absolute values are small though and, thus, Ca-Mn mixing in garnet can be considered nearly ideal at most geological P-T conditions of the Earth's crust.

Crystal structures and properties of materials

CSP-T05

Calorimetric studies of boron minerals: danburite ($\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$) and olenite ($\text{NaAl}_3\text{Al}_6[(\text{BO}_3)_3\text{Si}_6\text{O}_{18}\text{O}_3(\text{OH})]$)

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Experimental thermodynamic data for all borosilicates including the minerals of the tourmaline group are very limited. Consequently, the inclusion of tourmaline in thermodynamic modeling packages based on careful thermodynamic measurements is listed as a key research question [1].

In this study, we present low- and high-temperature heat-capacity (C_P) data for natural danburite ($\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$) and the tourmaline endmember olenite (ideally, $\text{NaAl}_3\text{Al}_6[(\text{BO}_3)_3\text{Si}_6\text{O}_{18}\text{O}_3(\text{OH})]$) which we obtained synthetically. Standard entropies were derived from these measurements.

Danburite was chosen to check the applicability of the PPMS method [2] to boron minerals. The standard entropy of the pure sample (Charcas, Mexico) was derived from PPMS heat capacity measurements in the temperature range $5 \text{ K} < T < 300 \text{ K}$: S_{298}^0 (danb.) was obtained to $153.9 \pm 0.8 \text{ JK}^{-1}\text{mol}^{-1}$. This value agrees very well with S_{298}^0 (danb.) = $154.8 \pm 2.1 \text{ JK}^{-1}\text{mol}^{-1}$ obtained by adiabatic calorimetry [3]. Additionally, DSC measurements with a Perkin Elmer Diamond DSC in the temperature range $280 \text{ K} < T < 760 \text{ K}$ were performed to check the reproducibility of the PPMS measurements around ambient temperature. The heat capacity curve was fitted to the experimental values: $C_P(T) = 367.24 - 1289.57 \cdot T^{-0.5} - 0.2047593 \cdot 10^8 \cdot T^{-2} + 0.3213486 \cdot 10^{10} \cdot T^{-3}$.

Analytical data on an olenite sample prepared at 2.5 GPa, 600°C in a piston cylinder device, show excess boron and water relative to the theoretical formula, coupled with deficiencies in Si, Al, and Na. Thus, a provisional structural formula was derived as $(\text{Na}_{0.65} \dots) (\text{Al}_{2.72} \dots) (\text{Al}_{5.42} \text{Si}_{0.58})$

$[\text{Si}_{3.73} \text{B}_{2.27} \text{O}_{18}] (\text{BO}_3)_3 (\text{OH})_{3.87} \text{O}_{0.13}$ [4]. S_{298}^0 of a similar sample, No. V 81 [5], was obtained to $574.2 \pm 2.0 \text{ JK}^{-1}\text{mol}^{-1}$ assuming the composition of the first sample [4]. The C_P curve can be described by the polynomial: $C_P(T) = 1198.85 + 2809.47 \cdot T^{-0.5} - 0.1201668 \cdot 10^9 \cdot T^{-2} + 0.1915016 \cdot 10^{11} \cdot T^{-3}$.

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CSP-T06

Crystal structures and vibrational properties of germanates comprising [Ge₄O₁₂] ring units

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The lanthanide-doped germanates CaY₂Ge₄O₁₂ [1], CaY₂Ge₃O₁₀ [2], Ca₂Ge₇O₁₆ [3] have been studied as promising phosphors for light upconversion and pcLED applications, and persistent luminescent materials. The present report will be focused on structural features and lattice dynamics of CaY₂Ge₄O₁₂ and Ca₂Ge₇O₁₆ containing [Ge₄O₁₂] ring units. Two space groups *P4/nbm* and *Cmme* have been considered for CaY₂Ge₄O₁₂. The former corresponds to a mixed (0.5 Ca + 0.5 Y) distribution at the octahedral sites found from the results of Rietveld refinement of room temperature powder XRD pattern, the latter refers to the model of crystallographically nonequivalent Ca and Y atomic setting in distorted oxygen octahedrons on the results of *ab initio* calculations in the DFT framework. The LDA, GGA and hybrid functionals have been applied. While the most accurate geometry description has been obtained with the WC1LYP and PBE (*n* = 6) hybrids, the B3LYP calculation provides the best agreement between the recorded and computed infrared and Raman spectra [4]. Afterwards, the WC1LYP and B3LYP approaches have been employed in the description of the crystal structure and vibrational properties of Ca₂Ge₇O₁₆. A more clear assignment of observed IR bands and Raman lines to certain internal vibrations of the [Ge₄O₁₂] ring and lattice modes has been facilitated by the performance of periodic *ab initio* calculations combined with the conventional factor group analysis. The obtained results may be useful not only for multiphonon relaxation estimations for germanate optical hosts, but also for further lattice dynamics studies of arsenates, phosphates, vanadates, and silicates whose crystal structures comprise the ring anions [A₄O₁₂]^{*n*-}, A = As, P, V, Si; *n* = 4, 8.

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Crystal structures and properties of materials

CSP-P01

Wavellite from Lateritic Phosphate Deposits in Amazon, Brazil

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Wavellite $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$ is a typical secondary aluminium phosphate mineral that can occur in phosphate deposits as like phosphorous laterites and bauxites. In the area of Bonito, north-eastern of the province Para (Amazon region, Brazil), large occurrences of lateritic aluminium phosphates are located. Owing to the high phosphor content this material became of interest for the production of agricultural fertilizers. Within the geochemical profile an aluminium phosphate horizon in 3.5 - 8.5 m depth is covered by a breccia iron crust, under yellow clay soil and a humus layer [1]. Whereas the aluminium phosphate horizon mainly bears crandallite, goyazite and florencite, wavellite was found as crystal druses in the iron crusts (Fig. 1a).

The orthorhombic crystal structure (SG oPcmn) of wavellite consists of 2 different types of $[\text{AlO}_6]$ -chains [2,3]. Whereas the Al–O octahedrons are interconnected via hydroxide, the chains are interlinked by phosphate tetrahedrons, resulting in a chessboard like cross-section with infinite channels parallel to the chain elongation, Fig. 1b. The one constitutional water molecule is relatively loosely located within these channels.

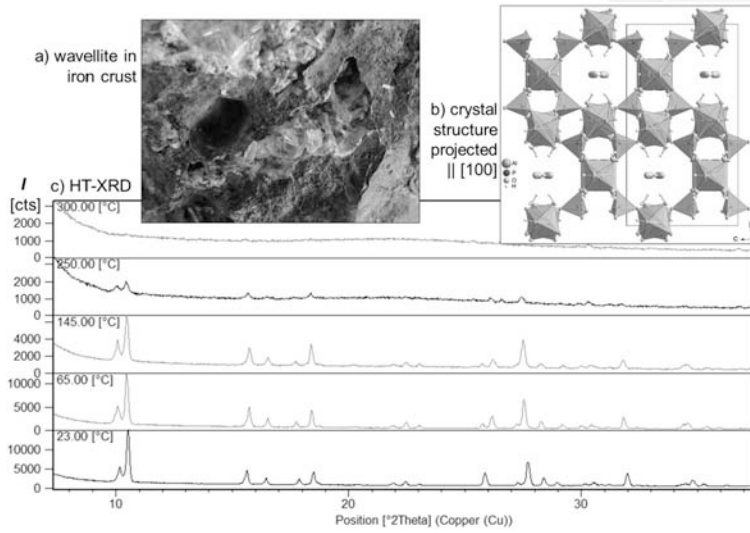
The thermal dehydration was reported to take place mainly between 110 ° and 280 °C in a single step slowly continuing towards 1000 °C [2]. Own thermal analysis of wavellite (N_2 flow, $dT/dt = 1 \text{ K/min}$) revealed an additional dehydration below 65 °C corresponding to a loss of 0.5 H_2O which is accompanied by a phase transition from SG oPcmn to $mP2_1/c$ detected by HT-XRD (Fig. 1c). This can be attributed to a loss of the half of the water molecules within the channels, slowly continuing to a complete loss of this water towards 110 °C. The structure appears to keep stable up to 145 °C, during the further loss of ca. 3 of 4 water molecules involved in the $[\text{AlO}_6]$ coordination polyhedral. With increasing temperature the reflections in HT-XRD become weaker and finally disappear at 300 °C. This corresponds to a lattice break down by the loss of the complete structurally bonded water molecules. The remaining hydroxide then slowly casts out towards 760 °C without a noticeable recrystallisation of the residual material.

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Crystal structures and properties of materials



Crystal structures and properties of materials

CSP-P02

Dispersion analysis of triclinic crystals

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In this contribution we present the results of dispersion analysis of triclinic crystals. Dispersion analysis (DA) is the determination of oscillator parameters of a crystal and is the basis to calculate the dielectric tensor function of the crystal and builds the bridge between material and optical properties.

The first successful DA of a triclinic crystal has been performed on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and is presented in [1]. The measurement scheme is based on a cube cut of the crystal, of which 12 IR-spectra from three orthogonal cube faces are recorded with polarized light. To take the spectra the cube is rotated within the spectrometer in a fixed sequence developed by the authors. Based on a 4×4 matrix formalism [2], all 12 spectra are analyzed in parallel with resonance wavenumber, strength and damping and two orientation angles for each oscillator.

Since [1], dispersion analysis has been performed on two more triclinic crystals, potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ and Montebrasite $\text{LiAlPO}_4(\text{F},\text{OH})$. The copper sulfate and potassium dichromate crystals have inversion symmetry, the Montebrasite crystal is a natural sample from Brazil with space group 1.

We found out that the orientation of the transition moments resemble the expected spectral behavior of the crystal, e.g. almost orthorhombic behavior of the transition moments for the copper sulfate crystal due to the only weakly distorted, tetrahedral SO_4^{2-} molecule. The results found for [m1] potassium dichromate and Montebrasite also represent their structure.

To check the fitted oscillator parameters for the copper sulfate and potassium dichromate crystals, a spectrum of a polycrystalline sample was evaluated. The sample dimensions of Montebrasite were only $2 \times 2.5 \times 4$ mm. The reflection spectra were recorded by Roberto Moreira [m2] and his group in Minas Gerais, Brazil. To check the fitted oscillator parameters, spectra with large incidence angle (34°) were recorded instead of crushing the crystal into powder.

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CSP-P03

Single crystal growth of members of the triphylite – lithiophilite, Li(Fe,Mn)PO_4 solid-solution series

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The primary phosphates of the triphylite - lithiophilite, $\text{Li(Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$ solid-solution series are the educt of several reactions leading to secondary phase associations which can be used to characterize the conditions of pegmatitic evolution (Fransolet et al., 1985). One of them is the oxidation of triphylite, $\text{Li(Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$ to ferrisicklerite, $\text{Li}_{1-x}(\text{Fe}^{3+}_x, \text{Mn}^{2+}_{1-x})\text{PO}_4$. This reaction was investigated experimentally (Schmid-Beurmann et al., 2013) using cuboids cut from a natural single crystal of triphylite. Unfortunately natural phases suffer from the lack of pure end-member compositions, the presence of additional components as well as inclusions and cracks. For the investigation to the complete solid-solution it would be desirable to have synthetic single crystals of mm-size. Therefore we synthesized crystals of the triphylite - lithiophilite solid-solution series in steps of 12.5 molar% using the flux growth method with LiCl as flux. Our procedure was derived from the method of Zambonini & Malossi (1931) applied to lithiophilite, LiMnPO_4 . In order to prevent the oxidation of Fe^{2+} we used welded Au-capsules ($\varnothing$ 4mm, L = 40mm) with the addition of elemental Fe as oxygen getter. Homogenized mixtures of LiCl, FePO_4 , $\text{Mn}_3(\text{PO}_4)_2$, Li_3PO_4 and Fe were heated to 900°C and then cooled down slowly to 600°C to allow crystallization. The growth resulted in mm-sized euhedral single crystals of gem-quality with colors ranging from brownish to pink with increasing Mn-content. Mapping by EPMA proved the homogeneity of the crystals with the exception of a rim of 20 to 30 μm . ⁵⁷Mössbauer-spectroscopy revealed an $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio of 5 to 7 %. As a result crystals of the triphylite - lithiophilite solid-solution series of good quality and homogeneity can be prepared by the flux growth method.

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CSP-P04

Phase content and structural analysis of off-stoichiometric

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS)

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Quaternary chalcogenides have seen a rapid development in the last years leading to a world record efficiency for thin film solar cells based on $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) of 12.6%[1].

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) belongs to the $A_2^I B^I C^{IV} X_4^{IV}$ compound family and crystallizes in the tetragonal kesterite type structure, the certain ordering of the Cu and Zn cation layers results in the space group [2]. According to literature [3] the stability field of single phase CZTS is assumed to be quite narrow. Typical secondary phases coexisting with a quaternary kesterite type phase are ZnS, CuS, Cu_2S , SnS, Sn_2S_3 , SnS_2 and Cu_2SnS_3 . Nevertheless there is still a lack of knowledge about existing phases and phase relations in the vicinity of the intersection point of CZTS. In literature [4] four off-stoichiometric CZTS compounds, named A-, B-, C- and D-type, have been proposed.

Off-stoichiometric CZTS powder samples were synthesized by solid state reaction. The pure elements, weighted in the calculated composition, are placed in a pyrolytic graphite boat and sealed in evacuated quartz ampoules. The tubes were placed in a one-zone furnace and heated with 10 K/h in 4 steps up to 750°C and after holding the final temperature for 240 h cooled to room temperature. After a homogenization step and pressing pellets an annealing in evacuated silica tubes at 750°C for 240 h followed. The obtained powder samples have been characterized by wavelength-dispersive X-ray spectroscopy (WDX) using an electron microprobe system and by X-ray diffraction (XRD). Furthermore Rietveld analysis was used to obtain the lattice constants. The phase content analysis presented here considers the samples before (intermediate samples) as well as after the annealing step.

The results of the XRD and WDX analysis show that CZTS is the main phase in all samples synthesized. The CZTS grains in the intermediate samples exhibit a slight variation of the chemical composition. The presence of secondary phases like CuS, ZnS and Cu_2SnS_3 was noticed for all samples. Moreover a limited solubility of Cu and Sn in ZnS, Zn and Sn in ZnS as well as Zn in Cu_2SnS_3 was determined. These results have been assistant to understand the growth process of CZTS and to improve the solid state synthesis procedure.

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CSP-P05

Synthesis and characterization of complex lithium-containing layered double hydroxides

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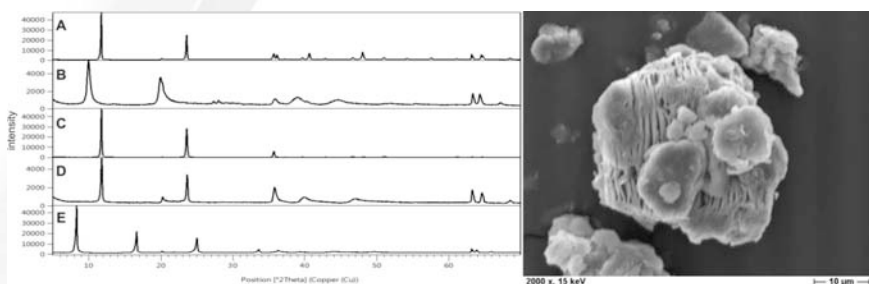
Layered double hydroxides (LDHs) consist of alternate positively charged mixed metal hydroxide layers and negative charged interlayer anions. Usually these materials can be formulated as $[M_{1-x}^{Z+}M_x^{3+}(\text{OH})_6]^{p/n}(Y^{n-})_{p/n}\cdot m\text{H}_2\text{O}$ with $Z = 2^+$, $M = \text{bi- and trivalent metallic elements}$, $Y = \text{organic or inorganic anion}$ and $m = \text{amount of Interlayer H}_2\text{O}$ depending on the temperature, relative humidity and hydration level [1].

The aim of this research is to synthesize and characterize lithium-aluminium LDHs with different anions. At first the synthesis of a precursor lithium-LDH $[\text{LiAl}_2(\text{OH})_6][\text{Cl}\cdot m\text{H}_2\text{O}]$ for the anion exchange was done. For this purpose a NaOH solution was added dropwise to a mixed solution of $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ and LiCl with the Al:Li ratio of 1:0,5 at RT until a basic pH of 9.5 was reached [2]. The synthesis was done in a nitrogen atmosphere to avoid carbonisation of the LDH. After the titration, the product was shaken at 45°C for 3 weeks, then filtered, washed and dried in an exsiccator (RH 30%). XRD (Fig. 1) and IR spectroscopy proved a pure, noncarbonated $[\text{LiAl}_2(\text{OH})_6][\text{Cl}\cdot m\text{H}_2\text{O}]$. The same procedure was performed with $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and LiNO_3 to obtain $[\text{LiAl}_2(\text{OH})_6][\text{NO}_3\cdot m\text{H}_2\text{O}]$.

For the anion exchange, parts of the precursor were added to aqueous solutions of different inorganic salts (Li_2CO_3 for CO_3^{2-} , LiOH for OH^- , Na_2SO_4 for SO_4^{2-}). The solution was stirred and heated to 50°C for 3-6 hours. Afterwards the product was filtered, washed, dried in an exsiccator (RH 30%) and investigated by XRD (Fig. 1) and IR spectroscopy.

It is possible to produce pure $[\text{LiAl}_2(\text{OH})_6][\text{Cl}\cdot m\text{H}_2\text{O}]$ by the titration-method, which then can be used successfully as a precursor for the anion exchange.

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[LiAl₂(OH)₆]₂[CO₃·1,43H₂O], D) [LiAl₂(OH)₆][OH·1,97H₂O], E)
[LiAl₂(OH)₆]₂[SO₄·2,2H₂O]

Fig. 2: SEM of [LiAl₂(OH)₆]₂[SO₄·2,2H₂O]

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CSP-P06

Crystal structures and photoluminescent properties of the disilicates $K_3Pr(Si_2O_7)$, $K_{2.40}Rb_{0.60}Pr(Si_2O_7)$ and $K_{2.84}Rb_{0.16}Sm(Si_2O_7)$

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The previously unknown title compounds were grown from MoO_3 - or MoO_3 -KF-based flux mixtures as part of a study focusing on preparation, structural and optical characterisations of novel silicates containing Pr^{3+} , Sm^{3+} , Tb^{3+} and Dy^{3+} . The three disilicates crystallise in the structure type of $K_3Eu(Si_2O_7)$ [1] (space group $P6_3/mcm$) which is also adopted by other, large to small REE³⁺ (REE = Nd [2] and Gd-Yb [3]). They represent the first Rb-bearing members; pure $Rb_3REE(Si_2O_7)$ do not seem to be stable, however. Green $K_3Pr(Si_2O_7)$ and $K_{2.40}Rb_{0.60}Pr(Si_2O_7)$ (hereafter KPr and KRbPr) and colourless $K_{2.85}Rb_{0.15}Sm(Si_2O_7)$ (KRbSm) have the following unit-cell parameters: $a = 10.0710(14) / 10.0922(14) / 9.9830(10) \text{ \AA}$, $c = 14.589(3) / 14.587(3) / 14.484(3) \text{ \AA}$, $V = 1281.4(4) / 1286.7(4) / 1250.1(3) \text{ \AA}^3$. Their crystal structures were refined from single-crystal X-ray intensity data to $R(F) = 0.0303 / 0.0211 / 0.0221$, respectively.

The crystal structures contain Si_2O_7 groups (eclipsed alignment) with two [6]-coordinated REE³⁺ cations (REE = Pr, Sm) and three different K⁺ coordination environments. The isolated REEO₆ polyhedra (octahedra and trigonal prisms) share each of their apices with oxygen atoms of the Si_2O_7 groups to form a three-dimensional framework. The [9]-coordinated K1 and [8]-coordinated K3 sites in KRbPr and KRbSm are the main hosts of the Rb atoms, whereas the [6]-coordinated K2 site contains only very minor to trace amounts of Rb.

Photoluminescence spectra were obtained at room temperature using a Horiba Jobin Yvon LabRAM-HR Evolution spectrometer with 473 nm laser-excitation. Pr^{3+} present in the KPr and KRbPr results in dominant luminescence bands around 500 nm due to the $^3P_0 \rightarrow ^3H_4$ transition, showing a blue-green emitting colour. The luminescence emissions of KRbSm is caused by Sm^{3+} cations, which show two dominant luminescence transitions in the visible orange to yellow spectral range at 600 and 570 nm, which are interpreted as $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition, respectively.

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Crystal structures and properties of materials

CSP-P07

Synthesis and structural study of new trigermanates $\text{CaRE}_2\text{Ge}_3\text{O}_{10}$, $\text{RE} = \text{La-Yb}$

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In this report, we characterize the crystal structure of $\text{CaRE}_2\text{Ge}_3\text{O}_{10}$ ($\text{RE} = \text{Y, La-Yb}$) prepared via the EDTA complexing process. The germanates belong to the compounds $\text{MRE}_2\text{T}_3\text{O}_{10}$ ($\text{M} = \text{Ca, Co, Sr, Ba}$; $\text{RE} = \text{lanthanide, Sc, Y}$; $\text{T} = \text{Si, Ge}$) whose structures comprise the tritetrahedral $[\text{T}_3\text{O}_{10}]^{8-}$ anions. The crystal structures of $\text{MRE}_2\text{Si}_3\text{O}_{10}$ ($\text{M} = \text{Co, Sr, Ba}$; $\text{RE} = \text{Sc, Y, Eu, Gd, Er, Yb}$) [1-3] and $\text{CaY}_2\text{Ge}_3\text{O}_{10}$ [4] had been previously reported, and the latter has been used as a starting model for Rietveld refinement of room temperature powder XRD patterns.

XRD study shows that $\text{CaRE}_2\text{Ge}_3\text{O}_{10}$ ($\text{RE} = \text{Y, La-Yb}$) crystallize in the monoclinic system with the space group $P2_1/c$, $Z = 4$. The lattice parameters and volume follow the linear dependence upon the ionic radius of RE^{3+} with two morphotropic phase transitions. The first one between the La and Pr compounds is related by step-like changes in all the unit cell parameters, while the second ($\text{Eu} \rightarrow \text{Gd}$) is accompanied by a decrease in c and β .

The metal cations occupy three nonequivalent sites and form layers along [001] connected into the framework through $[\text{Ge}_3\text{O}_{10}]$. The calcium and rare earth ion site occupancies vary from mixed in $\text{CaRE}_2\text{Ge}_3\text{O}_{10}$, $\text{RE} = \text{Y, Pr-Yb}$, to partially ordered in $\text{CaLa}_2\text{Ge}_3\text{O}_{10}$. In its turn, the RE^{3+} ionic radius decrease leads to a change in the cation layer thickness, which results in a variation of the $[\text{Ge}_3\text{O}_{10}]$ geometry. In the group of compounds $\text{CaYb}_2\text{Ge}_3\text{O}_{10}$ - $\text{CaPr}_2\text{Ge}_3\text{O}_{10}$ the angle Ge-Ge-Ge increases from 144.7° (Yb) to 148.4° (Pr), but in the case of $\text{CaLa}_2\text{Ge}_3\text{O}_{10}$ this angle becomes equal to 116.2° and the conformation changes, that leads to variation in the first and second coordination spheres of $\text{Ca}^{2+}/\text{RE}^{3+}$.

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CSP-P08

Crystal structure of Cr-substituted lawsonite from powder diffraction

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In Ca-Al lawsonite chains of AlO_6 octahedra plus Si_2O_7 groups build up a framework structure [e.g. 1] which can incorporate a distinct amount of Cr^{3+} substituting Al^{3+} . The Cr/Al ratios observed in natural samples reach up to 0.28/1.72 [2] and 0.36/1.64 [3].

We synthesised Al-Cr solid solutions of the sorosilicate lawsonite, $\text{CaAl}_2[(\text{OH})_2|\text{Si}_2\text{O}_7]\cdot\text{H}_2\text{O}$, with different input compositions of $\text{Cr}_{0.2}\text{Al}_{1.8}$ (1), $\text{Cr}_{0.5}\text{Al}_{1.5}$ (2) and CrAl (3) at 11 GPa and 700 °C using the multi-anvil press at GFZ Potsdam, Germany. Crystals of experiments 1 and 2 had a size of up to $10\times4\times4\text{ }\mu\text{m}$ and were characterised by SEM and semiquantitative EDS analysis. A mean Cr/Al ratio of 0.17/1.75 (1) and 0.32/1.6 (2) could be obtained, with a maximum of 0.49/1.42 at the rim of one crystal. The synthesis with Cr/Al ratio of 1/1 (3) resulted only in nano-crystalline lawsonite with additional phases such as stishovite, guyanaite ($\beta\text{-CrOOH}$) and Ca-silicates.

Assuming a linear increase of the a-lattice parameter with increasing Cr-content resulted in a Cr/Al ratio of about 0.51/1.49 in lawsonite of experiment (3), which seems to be the maximum at the given p/T conditions.

Compared to pure Ca-lawsonite, X-ray diffraction patterns of Cr-lawsonites show a slight shift of the (110) reflection, but almost no shift of the (002) and (021) reflections. The a-lattice parameter of Cr-lawsonite changes by about 0.7 % from 5.847 Å for pure Al to 5.888 Å for $\text{Cr}_{0.51}\text{Al}_{1.49}$. Changes of b and c are within the error levels. This can be explained by extension of the octahedral chains parallel to the a-axis. A possible space group change as in Sr-Ca solid solutions of lawsonite [4] was not observed. X-ray powder diffraction patterns of the Cr-lawsonites (2, 3) show no further diffraction peaks, which would be expected in case of a symmetry reduction or superstructure. As a consequence, the crystal structure of saturated Cr-lawsonite is identical to lawsonite at RT (space group No. 63, setting *Cmcm*) with statistically allocated chromium in the octahedral site.

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CSP-P09

On the relation between structural disorder and modulation in mullite

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The crystal structure of mullite is simple on average but complex in detail. Octahedral AlO_6 chains are cross-linked by two or three $(\text{Si,Al})\text{O}_4$ tetrahedra ("diclusters" and "triclusters"), the latter are superimposed with partial occupancies in a small average unit cell. Most typical compositions of synthetic mullites (per average unit cell) are either $\text{Al}_{4.8}\text{Si}_{1.2}\text{O}_{9.6}$ ($\text{Al/Si} = 4/1$, usually "2/1 mullite", as referred to oxides: $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) or $\text{Al}_{4.5}\text{Si}_{1.5}\text{O}_{9.75}$ ($\text{Al/Si} = 3/1$, "3/2 mullite"). Different from the similar sillimanite the Al/Si ratio is larger than 2/1 leading to Al,Si disorder in the tetrahedra and a lack of oxygen in the O3 position linking the tetrahedra. Diclusters, triclusters and oxygen vacancies share the same average location in the average structure but build up a complex pattern in the real structure where the octahedral chains are virtually unaffected. Diffraction studies on mullites show significant diffuse scattering and regularly arranged satellite reflections together, which we perfectly reproduced in our own study. The former clearly indicates structural disorder, the latter long-range order which appears contradictory.

We found that only n-5-fold superstructures would be compatible with the chemical composition of 2/1 mullite and similarly only n-4-fold superstructures with that of 3/2 mullite. However, for small n the corresponding long-range ordered structures inevitably would produce linear and/ or planar alignments of vacancies and likewise for the triclusters and for the diclusters. Since all the three units are located in the same environment of octahedral chains any such perfectly ordered arrangement would be energetically unfavorable for the strong differences in the local energies. For large n the correlation between the local energy fields gets lost and thus a perfect ordered structure cannot result for large n as well. However, a weak long-range order in the occupation probabilities of the structural units still develops accounting for the general tendency for long-range order in the crystalline state. For the first time we refined successfully the modulation parameters associated with the first out of three modulation vectors in the framework of the superspace approach.

CSP-P10

New oxynitride compounds with transition metal elements and extraordinary magnetic properties

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Several oxide compounds belonging to structure types like spinels or perovskites are known to exhibit extraordinary magnetic properties, if containing rare earth or transition metal elements. Magnetic frustration for example occurs, if magnetic spins cannot order properly due to geometrical reasons. The spinel phase of Co_3O_4 containing magnetic Co^{2+} and non-magnetic Co^{3+} e.g. is known as a highly correlated A-site spinel which develops a spin liquid originating from A-site magnetic frustration. Its changes in magnetism at high pressures have recently been investigated (Hirai and Mao, 2013). Germanate spinels like GeFe_2O_4 or GeCo_2O_4 show magnetic frustration due to long-range antiferromagnetic exchange interactions. If germanium is replaced by Mg, Zn or Cd, highly magnetic frustrated antiferromagnets develop (Tagaki and Niitaka, 2011).

In contrast to oxide phases, nitride spinels are known only from group IV elements at high pressure up to now (e.g. Zerr et al., 1999), but oxynitrides exist over a wide compositional range. Here we report first results on the synthesis of new compounds of group IV spinel-type oxynitrides and of perovskite-type, in which one site is substituted by *3d* or *5d* transition metal elements in order to find new compounds showing magnetic frustration. The compounds have been synthesised via solid-state reactions of oxide and nitride precursors at high pressures and temperatures. Recovered samples were characterised by X-ray powder diffraction and electron microscopic techniques. Crystallographic data were obtained from Rietveld refinements and are discussed in relation to crystallographically similar phases and measured physical properties.

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Economic minerals – formation, characterization, and applications

ECO-T01

Mineralogy and Geochemistry of PGE-Ni-Cu ore-forming processes in basic/ultrabasic magmatic complexes – system and applied approaches

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Sulphide ore-forming processes and their products in basic /ultrabasic complexes are developing in magmatic ore-forming systems limited space and life time. They start early in mantle plume melts in the Earth's deeps and finish as final products of several etaps of magmatic system development: sulphide preliquation, mass sulphide liquation and differentiation, sulphide postliquation transformation, postsulphide hydrothermal deposition. They can be qualified as open dynamic nonlinear developing systems and tested with quality system analysis methods.

Having started in different geodynamic positions and conditions in the earth interior, those ore-magmatic systems have different fluid, silicate melt and metal compositions, major/minor metal species and their quantity interrelations in magmatic-hydrothermal ores [Barnes et al, 1988].

Analysis of ore mineral species and assemblages and their chemical compositions in those developing ore-forming systems (quality system analysis) on all stages of their development had revealed two universal trends: 1) exhaustion and transformation of ligands roles as cations or anions (S, As, Sb, Bi, Te, Se); 2) exhaustion of (Fe, Cu, Ni, Co)/accumulation of ore-forming metals as incompatible chemical species (PGE, Ag, Au, Sn, Pb, Sb, Bi, Te, Se, et al.) in mineral formation processes to final stages of system life time.

Qualitization of mineral assemblages successions and quantization of some elements interrelations in particular world PGE-Ni-Cu ore-forming systems over Wilson's geodynamic positions series have been discussed and illustrated by specific examples. Some of the results from ores in nondifferentiated PGE-Ni-Cu systems (greenstone belts) to ores deposited from volcanic exhalations of operating volcanoes may be recommend to PGE-Ni-Cu ore prognostic, exploration, assessment practice.

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Economic minerals – formation, characterization, and applications

ECO-T02

Cu-Ag-Au-mineralization of the German copper belt - new results from the Spremberg Kupferschiefer deposit, Lausitz, Germany

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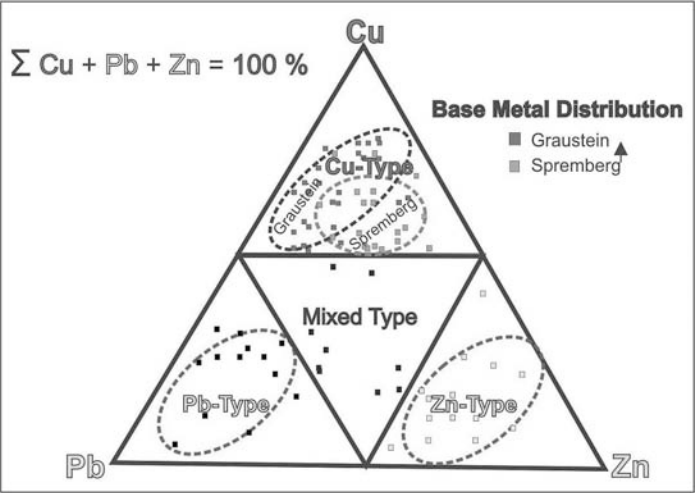
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Bornite Cu_5FeS_4 , very strongly digenite Cu_9S_5 , djurleite, idaite and chalcocite Cu_2S are the dominant minerals in the high grade Cu-Ag-Au Kupferschiefer deposit Spremberg-Graustein-Schleife, Lausitz, Germany. The vertically zoned, high temperature hydrothermal assemblage consists predominantly of a footwall layer of chalcocite, bornite occasionally with tennantite, and chalcopyrite in the Permian Rotliegend-Weissliegend sandstone. The Kupferschiefer main ore body starts with a bottom layer of Cu-mineralisations rich in bornite with electrum, AuAg, exsolutions, chalcocite with disseminated silver and a high percentage up to 22 % of hydrocarbons and pyrobitumina. Within the Kupferschiefer so called "Lineals" occur composed of layers of chalcocite-digenite-covellite-phases with minor bornite, chalcopyrite and idaite. Silver and gold also occur as native grains. In the overlaying Zechstein dolomite the dissemination of chalcopyrite and pyrite is widespread. Chalcocite, bornite and chalcopyrite veinlets crosscut the Kupferschiefer mineralization and have been determined through sulfide isotopic analysis to be also of hydrothermal origin. Pyrite, galena and sphalerite are present in minor amounts in all parts of the high grade copper deposit.

Detailed pol.-microscopic, REM and Raman-spectroscopic investigations have shown that parageneses display a certain amount of geochemical "telescoping": contemporaneous crystallization of Cu-minerals with variable Fe content. Also, sphalerite and galena occur next to chalcocite-digenite. Frequently a mixed phase of chalcocite-digenite-covellite is observed with non-stoichiometric compositions. This "disintegrated digenite" is a major ore mineral in the deposit and has a variable Cu content between 35 and 73 %.

The Cu-Ag-Au-PGM-hydrocarbon(+Pb+Zn) mineralization at Spremberg is vertically and laterally zoned typical for Kupferschiefer sediment hosted deposits with geochemical overprint and tectonic geological control.

Economic minerals – formation, characterization, and applications



Economic minerals – formation, characterization, and applications

ECO-T03

Automated quantitative mineralogy of sandstones – examples of QEMSCAN applications for the study of hot water storage in geothermal aquifers and diagenesis

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Sandstones play an important role as oil and gas reservoirs, and are prominent target rocks for CO₂-sequestration and/or energy storage by the injection of hot water. Their properties are highly dependent on diagenetic reactions during burial or on mineral reactions caused by the injected fluids. Understanding and quantification of such processes is crucial for prediction of storage potential or technical applications. Automated QEMSCAN mineralogy offers unique possibilities to study diagenetic processes as well as fluid rock interaction in sandstones. A first important step is the identification of a minimum representative area (MRA) to obtain relevant data for a larger rock volume. Worked examples from Palaeozoic sandstones from the RWTH-1 well (Aachen, Germany) and Triassic to Jurassic sandstones from the Norwegian-Danish Basin as well as of the Berea sandstone demonstrate that the MRA for the dominant mineral quartz may not be representative for other mineral phases. In particular, MRA values for heterogeneously distributed phases such as carbonates or sulfates are high and locally exceed 100 mm². Heterogeneity due to patchy cementation or lamination can be quantified by sub-sectioning of images. For the Berea sandstone it is shown that siderite-iron oxide / hydroxide redox reactions caused by hot water injection enhanced existing lamination. To relate microscopic studies to core scale image analysis of sandstones requires sample areas in the order of several mm to cm, underlining the importance of automated systems like QEMSCAN. The study highlights the crucial role of image resolution for the determination of porosity and pore-mineral interfaces. This is of importance for the quantification of reactive mineral surface areas. Image derived specific surface area can be used to calculate permeability applying Kozeny's equation. After optimisation of spatial resolution and using a constant ratio of pixel length to effective specific surface area, calculated permeability of sandstone samples from the Norwegian-Danish Basin as well as of the Berea sandstone reproduced measured Klinkenberg permeabilities within limits better than 50%.

Economic minerals – formation, characterization, and applications

ECO-T04

Gangue mineralogy and deportment of titanium (Ti) and vanadium (V) in the Kiirunavaara iron ore deposit, Northern Sweden

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The Paleoproterozoic Kiirunavaara Fe oxide-apatite intrusive body has long been known as the most productive iron ore deposit of Europe. Because of the production in the mine is advancing deeper levels and demand for iron ore is increasing, the importance of understanding the deposit from both mineralogical and geochemical point of view is obvious. Among other it is thus important to characterise the abundance and chemical composition of ore and gangue minerals in terms of their variable impact as potential Ti-V hosts, which might be critical elements for production in the future. For this purpose, 55 samples from deeper parts of the orebody were studied combining optical microscopy, SEM-based MLA, and EPMA. Three minerals with stoichiometric Ti-contents have been identified: titanite, ilmenite, and rutile. Moreover, phlogopite hosts Ti in significant amounts (Ø 4300 ppm). For the P-poor parts of the orebody (B-type ore), ilmenite and rutile form the major Ti-hosts in Fe-rich intervals (Fe > 66 wt. %), whereas titanite is predominant in P-poor intervals with slightly lower Fe contents. In contrast, Ti-minerals are fairly rare in P-rich zones of the orebody (P > 0.1 wt. %, D-type ore) and, if present, represented by titanite. Magnetite, being the major commodity at Kiirunavaara, has not revealed any significant Ti contents in its crystal structure. However, Ti is associated with magnetite in the form of Ti-rich exsolution lamellae, being restricted to magnetite crystals in B-type ore (Fig. 1). Incorporation of V has been exclusively detected in magnetite and titanite, revealing average concentrations of c. 600 ppm and 650 ppm respectively. Due to the exploration and grade control drilling the Ti-grade increases with depth. Consequently also the abundance of Ti-bearing silicate (titanite, phlogopite) and oxide (ilmenite, rutile) rises. In the future, additional flotation steps besides the reverse apatite flotation may be required to ensure their efficient elimination during the beneficiation process. It also appears unreasonable to mechanically separate the Ti-rich exsolution lamellae and lattice-bound V from the magnetite sinter feed product of the Kiruna Mine.

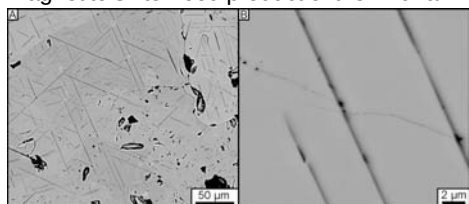


Fig. 1: BSE image displaying Ti-rich exsolution lamellae, representing a Fe-rich, P-poor ore type (A). The width of a single lamella ranges at nm scales (B).

Economic minerals – formation, characterization, and applications

ECO-T05

Variation in chromite chemistry across the UG2 chromitite layer, Eastern Bushveld Complex

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The Bushveld Complex is the largest known layered intrusion on Earth and hosts with the Upper Group 2 (UG2) an excellent example of magmatic layering as well as one of the largest resources of PGE. The origin and formation process of the UG2, a massive chromitite layer, is still not well-understood and part of an ongoing debate. Existing models involve processes like magma mixing, assimilation, mechanical sorting and injection of crystal slurries (e.g. [1] and references therein). This study focuses on the petrogenesis of the UG2 by investigations of the chromite chemistry on a microscale. This was done on samples provided by Nkwe Platinum (Pty) Ltd, which were taken from diamond drill core material of HPK 016, that was drilled ~12 km NW of Steelpoort on Hoepakrantz 291KT farm in the Eastern Bushveld Complex. Detailed microprobe analysis on chromite grains on a 1 m profile covering the UG2 (~60cm) and the footwall pyroxenites were carried out.

The major and trace element composition of chromites of the UG2 differs from those in the pyroxenite footwall. The chromites in the UG2 have higher Mg and Cr as well as lower Fe and Al contents. The chromites of the UG2 are also more homogenous in chemical composition than the chromites of the footwall pyroxenite, which scatter much stronger. The UG2 chromites nevertheless show rhythmic variations, which is seen in Mg# and Cr# across the UG2, whereby Cr# correlates negatively with Mg#. Similar rhythmic variations in chromitites recently observed in the Western Bushveld [2] were interpreted as continuous fractionation repeatedly interrupted by the influx of more primitive magma. Compared to the major elements, the trace elements of the chromites show a much stronger variation along the UG2 profile. Towards the top and bottom of the UG2 the Ni, Ti and V contents increase substantially. Likewise there are significantly higher PGE-concentrations and higher Sr-initial ratios [3] at the top and bottom of UG2. This suggests a link between chromite chemistry and magmatic and/or late-to-post-magmatic PGE-enrichment.

Economic minerals – formation, characterization, and applications

ECO-T06

Factors of ore-metals concentration during the formation of a large auriferous Bugdaya Mo-porphyry deposit (Eastern Transbaikalia, Russia): Results of thermodynamic modeling

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Introduction: The geological structure, mineralogy, geochemistry and ore formation conditions of Mo-porphyry Bugdaya deposit, as well as influence of magmatism, fluid regime, sources of fluids and metals were considered earlier [Kovalenker *et al.*, 2011]. Here the factors of metal concentration based on results of numerical simulation are discussed.

Methods: Equilibria in the multicomponent (Ag-Al-As-Au-C-Ca-Cl-Cu-Fe-HK-Mg-Mo-Na-O-Pb-S-Si-W-Zn) system were under research. Magmatic fluid initially in equilibrium with the Bugdainsky rhyolite porphyry at $T = 550^{\circ}\text{C}$ and $P = 1500$ bar, flows outward from the stock, interacting with the surrounding a granite of the Undinsky pluton while falling temperature. At each point along the flow line the fluid which came from a previous high-temperature zone interacts with the rock at lower temperature. Moreover, the model considers definite part of meteoric water in equilibrium with granite that is admixed with the changed magmatic fluid. The fraction of the admixed meteoric water increases exponentially as temperature decreases. The process of such interaction is repeated many times that imitates influence of new portions of ore bearing magmatic fluid on ore deposition.

Results: The thermodynamic calculations show that such kind of interaction leads to the appearance of stationary zones deposition of ore minerals. The formation of native Au occurs in a low-temperature zone ($T < 250^{\circ}\text{C}$), while argentite - in a relatively high-temperature region ($350 < T < 420^{\circ}\text{C}$). At low temperatures ($220 < T < 270^{\circ}\text{C}$) gold deposition occurs together with native silver that in reality corresponds to the electrum deposition. The main accumulation of Cu, Zn and Pb in the form of chalcopyrite, sphalerite, and galena correspondingly occurs in the range from ~ 350 to 250°C . Wolframite deposition takes place at high temperatures, while the area of molybdenite deposition extends to a cooler domain.

Conclusions: Numerical simulation indicates that cooling of ore-bearing fluids, which occurs when they are mixed with meteoric water, can be significant factors of ore formation and accumulation of ore minerals in definite spatial areas of the host rocks.

This work was supported by RFBR, projects 13-05-12043-ofi-m and 13-05-00622 Kovalenker et al. (2011). Geol. Ore Dep. 53, 93-125

Economic minerals – formation, characterization, and applications

ECO-P01

Minerals of hydrothermal copper-deposits from northern Chile.

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Chile is the most important mine producer of copper worldwide. 35 % of the world-copper-production takes place in Chile. The occurrence of the copper-deposits in the middle Andes is associated with the active continental margin and the subduction of the Nazca plate below the South-American plate. By reason of intrusions of granitic to granodioritic magma and their subvolcanic extensions as Trachyte, Andesite or Dacite, with porphyritic texture, the large scaled porphyry copper ore bodies were formed. A late hydrothermal alteration remobilized the pluton and the host rock which lead to the occurrence of hydrothermal copper veins.

The Chilean mining already boomed in the 19th century. In numerous Mines Au, Ag and Cu were explored. The Mineralogical Collection of the Friedrich-Schiller University includes the "Ferber Collection"¹, which contains about one hundred Cu-minerals collected during the mining period of the 19th century in Chile. Well-known Copper-Ore minerals like Bornite (Cu_5FeS_4), Chalcocite (Cu_2S), Covellite (CuS), Cuprite (Cu_2O), Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) and further secondary minerals like Brochantite $\text{Cu}_4[(\text{OH})_6](\text{SO}_4)$, Atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), Tyrolite ($\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{OH})_8(\text{CO}_3)(\text{H}_2\text{O})_{11} \cdot 1-2\text{H}_2\text{O}$), Linarite ($\text{PbCu}(\text{SO}_4)(\text{OH})_2$) and Domeykite Cu_3As are part of this historical pool.

In the course of a bachelor thesis the Minerals were prepared to receive a new compilation of the geological background of the mining-localities and examine the specimens for further mineral-phases.

¹ Moritz Rudolf Ferber (1805 - 1875) collected minerals since his first steps at school. One of his sons worked as a mining engineer in South America and sent a lot of unknown specimen to his father's place.

Economic minerals – formation, characterization, and applications

ECO-P02

Mineralogy, formation conditions and hydrothermal alteration at the Ag-Au epithermal deposit Nová Baňa (Slovakia)

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The Nová Baňa epithermal Ag-Au deposit is located in the peripheral zone of a large Miocene andesite stratovolcano within the Central Slovakia Volcanic Field. The mineralization occurs in extensional or stockwork-like veins, and as disseminations in partly brecciated rhyolite and andesite or their pyroclastics.

The base-metal sulfide association consists of pyrite, marcasite, stibnite, arsenopyrite, realgar, chalcopyrite, sphalerite, galena, plagioclase, and tetrahedrite-tennantite. The Ag carriers are dominated by polybasite-pearceite, freibergite, and miargyrite. Minor Ag bearing phases are acanthite, andorite, argentotetrahedrite-argentotennantite, diaphorite, and proustite-pyrargyrite. Gold occurs as Au-Ag alloy (electrum).

Hydrothermal alteration comprises extensive silicification, argillic alteration, adularization, hematitization, and propylitic alteration. The argillic alteration occurs in the central part and has a zonal distribution; the illite zone in the proximal part to the illite-smectite zone and the smectite zone in the distal part.

Analyses of fluid inclusions show fluids with low salinity (0-3 wt.% NaCl eq.). Abundant co-existence of liquid- and vapor-rich inclusions indicates boiling during the entrapment. That was the likely reason for the precipitation of gold. Eutectic temperatures (-42°C to -24°C) suggest the presence of NaCl and other minor salts (FeCl₂, MgCl₂ and CaCl₂). Homogenization temperatures vary mostly between 190 and 240 °C. Assuming hydrostatic pressures, boiling occurred from 12 to 35 bars, corresponding to paleodepths of 130 to 400 m, reflecting variable erosion level of individual parts of the vein system at various stages of its evolution. The fluids at Šibeničný vein show a different character, some with much higher salinity (up to 24 wt.% NaCl equivalent), which needs extensive boiling. All fluid inclusions reveal constant but relatively lower homogenization temperatures of approximately 160-180°C. Assuming hydrostatic pressures, boiling occurred from 4 to 15 bars, corresponding to paleodepths 34 to 160 m.

Isotopic composition of vein quartz ranged from 4.5 to 10.3 ‰ δ¹⁸O (mostly 5.3 to 5.8 ‰), while illite-smectite from wall-rock alteration had 1.9 to 6.9 ‰ δ¹⁸O and -66 to -98 ‰ δD. Composition of fluids in equilibrium with quartz (-5.9 to -3.0 ‰ δ¹⁸O) and illite-smectite (-5.5 to -0.6 ‰ δ¹⁸O; -80 to -46 ‰ δD) indicate mostly meteoric origin of fluids affected by isotopic reequilibration with country rocks.

Economic minerals – formation, characterization, and applications

ECO-P03

Influence of submarine and subaerial alteration on trace element distribution in VMS ores from the Oman Ophiolite

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In the Oman Ophiolite, volcanogenic massive sulfide deposits near the city of Sohar in northern Oman were investigated using QEMSCAN® analysis (Quantitative Evaluation of Minerals by Scanning Electron Microscopy), optical microscopy, XRD, EMP, and LA-ICP-MS. Combined, these techniques provide salient information for the interpretation of mineral reactions, the dynamics of metal enrichment and mobilization processes. The main ore bodies, hosted in oceanic basalts, consist of mainly pyrite, chalcopyrite and smaller amounts of sphalerite as well as secondary chalcocite. The focus of this study is on trace element distributions in the hypogene sulfides and their behavior during supergene, subaqueous and subaerial alteration processes. In addition to sulfides, trace element abundances were also determined for iron oxides and hydroxides from both, submarine alteration zones and subaerial gossans.

Supergene weathering of VMS ore bodies with concomitant gossan formation is widespread in the area. Gossans consist of the mineral assemblage including quartz, hematite, goethite, and clay minerals. Close to the surface, where mineral components are cemented by calcite, they are conspicuous by the loss of almost all trace elements. The underlying supergene zone, characterized by secondary chalcocite and iron oxides, is significantly enriched in copper and arsenic, but in contrast to the hypogene VMS ore depleted in cobalt (76-926 ppm) and selenium (<48 ppm). These two elements have highest concentrations in the massive sulfide ore (Co: 717-1211 ppm; Se: 15-658 ppm). Concentrations of all other metal trace elements in the sulfides are less than 100 ppm. Preserved submarine alteration of the VMS bodies is rare; however, some VMS lenses are overlain by a few centimeter-thick Fe-Mn rich oxide layer. Sulfides in contact to this zone are depleted in nearly all elements except for manganese.

The aim of this study is to map-out the distribution of trace elements in massive sulfide ores, their submarine alteration zones, and concomitant subaerial gossans from VMS deposits in the Sultanate of Oman, and to gain insight into the behavior of trace elements during supergene, subaqueous, and subaerial alteration processes.

Economic minerals – formation, characterization, and applications

ECO-P04

The Rietveld refinement applied to the bauxite and its clayey cover at Juruti, Pará, Brazil.

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Bauxites are the main raw materials of aluminum and refractory industry. Brazil currently stands as the third largest producer of this ore, also being the country that has its third largest reserves, of which 97% are in the Amazon region. The main restriction of the bauxite's mining in Amazon region is the up to 20 m thickness overburden made of yellowish clays (Belterra Clay), besides the difficulty and costly of chemical and mineralogical quantification of bauxites, particularly of available alumina and reactive silica. This paper evaluates the use of the Rietveld refinement to address these deficiencies. For this purpose, 17 samples were selected from a bauxite ore and its clay overburden in Juruti, Brazil. After mesoscopic description the samples were analyzed by X-ray diffraction and fluorescence. The amorphous content was characterized mixing 20% of rutile as standard crystalline phase. Cluster analysis was used to arrange similar x-ray patterns in order to apply different refinement's strategies for the distinct x-ray patterns types recognized. The bauxite bearing regolith, with 23 m in depth, comprises a mottled horizon at the bottom; a bauxitic horizon consisting mainly of gibbsite; an iron crust; a horizon with ferruginous nodules and clayey matrix; a horizon with bauxitic nodules and clayey matrix, and; clay cover horizon comprising mainly to kaolinite group minerals. Mineral quantification obtained by the Rietveld method reveled two generations of gibbsite with distinct crystallinity, resulting mainly in asymmetric gibbsite peaks. The quantified amorphous content of bauxite was up to 9,1%, increasing in the clay cover horizon. The use of different kaolinite's polymorphs structures as dickite, dickite 2m and halloysite resulted in better profile fittings, suggesting the coexistence of these phases. The evaluation of the Rietveld refinement was made by the goodness-of-fit, the R factor values, the fitting of the calculated profile and the reproducibility of the method. The refinement indices and results appear to be satisfactory and proving that the Rietveld method is applicable and feasible to exploit bauxite due to its convenience and speed, crucial to discover new reserves.

Economic minerals – formation, characterization, and applications

ECO-P05

Fluid mixing processes involving red bed- and basement-interacted fluids recorded in fluid inclusions from a hydrothermal Mn-Fe vein system at Sailauf (Germany)

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The reconstruction of fluid sources and pathways by analysis of ore fluids is one of the most important aspects in the study of hydrothermal ore deposits. It provides invaluable information about crustal fluid flow, enables identification of metal sources and allows for physicochemical reconstruction of ore forming processes. In this study, we carried out LA-ICPMS microanalysis of carbonate-hosted fluid inclusions from a hydrothermal Mn-Fe vein system at Sailauf, Bavaria. The veins are hosted by a subvolcanic rhyolite body and are structurally related to the unconformity separating Variscan basement and Upper Permian Zechstein dolomite. A complex sequence of carbonate and Fe- and Mn-oxide minerals records a protracted fluid evolution and significant variation in physicochemical conditions during formation of two major ore stages. Mn-oxides associated with calcite constitute the Mn-oxide stage, which is postdated by hematite and Mn-calcite during the hematite stage. Microthermometry of calcite-hosted fluid inclusions from both ore stages showed no differences in bulk fluid properties; all fluids were found to be highly saline sodic-calcic brines. LA-ICPMS fluid inclusion microanalysis, however, revealed significant and systematic differences with regard to light element (Li, B) and base metal (Pb, Zn) concentrations. The fluids present in hematite stage Mn-calcite possess Li/B and Pb/Zn ratios typical of basement-interacted fluids, generally thought to represent the principal metal supply for basement- and sediment-hosted Pb-Zn deposits. Conversely, the fluids associated with the Mn-oxide stage possess anomalous Li/B and Pb/Zn ratios, compositionally resembling red-bed interacted fluids, which by some are thought to play an essential role in the formation of Kupferschiefer-type sediment-hosted Cu deposits. Vein formation at Sailauf was facilitated by mixing with a metal-depleted third fluid type, most likely derived from the overlying Zechstein dolomite. Our study highlights the potential of LA-ICPMS microanalysis in fluid source fingerprinting, especially in cases unresolvable by conventional bulk analytical techniques, and the benefits it might provide in future studies on formational mechanisms of controversially discussed ore deposit types, such as the Kupferschiefer.

Economic minerals – formation, characterization, and applications

ECO-P06

Arsenic in pyrite – commonalities and disparities – an overview

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Pyrite is the most common sulfide mineral in the earth's crust. Despite its simple nominal stoichiometry, pyrite tends to incorporate various amounts of trace elements, a fact that is well known and investigated for many years (e.g. Hawley & Nichol 1961), for different formation types (e.g., Huston et al. 1995) and with different investigation methods (e.g. Simon et al. 1999). The most common trace element in pyrite is arsenic, where the contents can reach up to 10 weight percent. Reactions evolving pyrite can therefore be important sinks or sources for arsenic in the environment. In this study, we present selected literature data combined with original data of arsenic contents in pyrite from different locations and formation conditions. Derived from the arsenic distribution in pyrite, EXAFS data and the sulfur to arsenic and arsenic to metal ratios, we furthermore present possible differences in the bound arsenic species and therefore in the form of arsenian pyrite.

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Economic minerals – formation, characterization, and applications

ECO-P07

Formation of REE-rich veins in ferrocarbonatite, NW Namibia

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In NW Namibia, REE-carbonatite veins crosscut Mesoproterozoic (c. 1.1 Ga) ferrocarbonatite dykes (Drüppel et al., 2005). The veins display extreme enrichment of both Sr (up to 9 wt%) and the LREE, especially La, Ce, Pr, and Nd (up to 17 wt% LREE), whereas the HREE contents resemble those of the associated ferrocarbonatites. The primary mineral assemblage includes medium grained, euhedral magnetite and granoblastic ankerite, fine grained, euhedral strontianite, and mm- to cm-sized, hexagonal-prismatic remondite-(Ce), a Sr- and LREE-rich member of the burbankite family. Albite and sodalite, both forming small, subhedral crystals surrounded by the carbonatite matrix, are minor phases. Dolomite is an accessory phase. The exotic mineralogy of the veins as well as their massive texture and large grain size suggests injection of a highly fractionated, Sr-, Na-, and volatile-rich REE-carbonatite melt, characterized by pegmatite-like delayed nucleation and high growth rates.

The primary vein minerals underwent partial to complete replacement by a secondary metasomatic assemblage. Albite is transformed into sodalite, which is subsequently replaced by a Si-free sodium-aluminate. Remondite-(Ce) is altered to a fine grained intergrowth of calcite, barite, carbocernaite, and other REE-carbonates with up to 64.5 wt% CeO, possibly belonging to the burbankite group. The latter phases also fill cracks in the veins and occur along grain boundaries between primary minerals, suggesting fluid-assisted REE-mobility during alteration. The species involved in the reactions vary but mainly include Na, Ba, Ca, Sr, and the LREE, as well as sulphate, water and carbonate, but exclude silicon. These observations agree with synchrotron micro-XRF data for NaCl-rich hydrous fluid inclusions in sodalite and ankerite that reveal remarkably high amounts of Sr, Ba, and the LREE. Late cracks in the veins are invaded by sulphides, including pyrite, chalcopyrite, millerite and thiospinels, representing the latest recognizable mineralization stage. To summarize, the formation of REE-carbonatite veins is due to strong fractionation of the precursor ferrocarbonatite magma, followed by subsequent REE-remobilization due to fluid-assisted metasomatic reactions.

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Economic minerals – formation, characterization, and applications

ECO-P08

Occurrence of Ilmenite on the Ti-bearing Ore deposit in Jikjeon-Ri, Hadong, Korea

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The Ti-bearing ore deposit of Hadong is located in the Precambrian Hadong-Sancheong anorthosite complex that is part of Yeongnam massif of the south Korea. The ore bodies are developed as several vein-shaped intrusion, estimating about $2.5 \times 10^6 \text{ m}^3$ in volume by 3D-ore bodies modeling, which are of Ti-rich gabbroic-anorthosites made up of ilmenite (48.9wt% TiO_2 in average), plagioclase, hornblende and apatite. Main ore bodies as intercumulated-type and/or layered-type anorthosites enriched in Jikjeon area. They have sharp or gradual contacts with the host anorthosite and adjacent intrusive rocks of diorite which were intruded in the south-western of the anorthosite. The Ti-ore bodies also extended into the diorite that is unusual occurrence in study area. There is gradational contact between host diorite and Ti-bearing ore bodies. This Ti-ore bodies consist of ilmenite, hornblend, quartz and apatite.

This study aims to compare characteristics of the Ti-bearing ore occurrence in between the anorthosite and the diorite. The ilmenite in the diorite are as disseminated or massive, whereas the ilmenite in the anorthosite are as massive or layered. Higher Ti concentrations in ore bodies are found in the diorite rather than the anorthosite. SEM study reveals that exsolution textures exist in the ore bodies in diorite, whereas they are not found in those in the anorthosite. The ilmenite minerals are separated into two phase of rutile and Fe-oxide because of high temperature from the intrusive rock (diorite).

Economic minerals – formation, characterization, and applications

ECO-P09

Resource potential of REE as by-product of an existing mining operation - A geometallurgical assessment

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A systematic geometallurgical study of the rare earth mineralogy and beneficiation potential as by-product was performed based on a currently operating flow sheet of an existing large-scale industrial mining and beneficiation operation. For this purpose, a representative suite of samples was collected from a single mining block prior to blasting. The material derived from this mining block was then tracked through beneficiation by comminution and a sequence of flotation steps. Samples were collected at all crucial steps of the beneficiation plant. Whole rock geochemical analyses and quantitative mineralogical and microstructural analyses (by MLA), complemented by mineral chemistry data for relevant REE minerals, were obtained for a suite of more than 60 samples. These data were then used to assess the deportment of REE and to track the route of REE-minerals within the beneficiation process.

Apatite was found to be the most important primary host mineral for REE. Postdepositional alteration evidently led to the breakdown of apatite, resulting in the formation of microcrystalline xenotime and monazite of secondary origin. The latter are the two most abundant rare earth minerals identified in the mining block studied. Additionally identified rare earth minerals occur only in minor or trace amounts. Other minerals were found to contribute only limited amounts to the total REE content of the ore.

Process samples from the flotation circuit illustrate that the material from the cleaner circuit tailing, being usually considered as waste, is strongly enriched in monazite and xenotime, i.e., the two most common REE minerals. The REE minerals are well liberated, thus leading to the conclusion that it may be feasible to produce REE minerals as a future by-product by only slight modification of the current flow sheet.

FUN-T01

Garnet-like structured solid solutions $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{M}_x\text{O}_{12}$ ($\text{M} = \text{Nb}^{5+}$, Ta^{5+}) for all-solid-state-lithium-ion batteries - a comparison between solid state reaction and sol-gel synthesis

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Delocalized stationary and mobile energy storage systems are key technologies for the present and for the immediate future. Conventional Li-ion batteries offer high energy density, long cycle life and light weight. But due to their liquid electrolytes these batteries are potentially unsafe. Solid-state Li-ion electrolytes have therefore been extensively studied in recent years.

Garnet-like structured ceramics $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{M}_x\text{O}_{12}$ ($\text{M} = \text{Nb}^{5+}$, Ta^{5+}) (LLZMO) are highly promising solid-state electrolytes. Through appropriate doping LLZMOs may also be used as materials for anodes or cathodes.

At ambient conditions pure $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has a tetragonal structure $I4_1/acd$ with a low conductivity of about $10^{-6} \text{ S cm}^{-1}$ [1]. Around 700°C LLZO transforms to the cubic symmetry $Ia-3d$ with a higher conductivity of approximately $10^{-4} \text{ S cm}^{-1}$ [2]. However, this cubic phase is not quenchable.

On the other hand pure $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (LLMO) occurs only in a cubic structure and exhibits a conductivity of roughly $10^{-6} \text{ S cm}^{-1}$ [2].

LLZMOs combine the advantages of the end members by having cubic symmetry and conductivities of at least $10^{-4} \text{ S cm}^{-1}$ [1] [3]. The stabilization of the cubic phase depends on temperature and pressure as well as on the Li-content.

Li-loss through an isobaric heat treatment is a function of mainly temperature and time but also of sample compaction, crucible shape, and so forth, and it cannot be controlled well. Solid state reactions of LLZMO evaporate Li during devolatilization and sintering. On the other hand, in sol-gel syntheses the sample-components are mixed on the molecular level and therefore the time and/or the temperature of calcination and of sintering can be reduced in relation to solid state reactions, resulting in better control of Li-loss.

This study presents a comparison between solid state reaction and sol-gel synthesis by using a broad spectrum of analytic methods. The results provide an overview of the advantages and disadvantages of different synthesis routes and their consequences for material properties.

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FUN-T02

Synthesis of coarse-grained garnet-type Li-ion conductor**Li₇La₃Zr₂O₁₂**R. Wagner¹, D. Rettenwander¹, M. Maier¹, G. Amthauer¹¹*University of Salzburg, Department of Materials Research and Physics, Salzburg, Austria*

Li-stuffed oxide garnets containing more than three Li cations per formula unit attract a lot of interest as they show a high Li-ion conductivity, making them ideal candidates for solid Li-ion electrolytes [1, 2]. Among this group, the garnet of nominal composition Li₇La₃Zr₂O₁₂ (LLZO) is one of the most promising materials. Pure LLZO has a tetragonal structure and shows conductivities of approximately 10⁻⁶ S cm⁻¹ [3]. The incorporation of certain cations such as Al³⁺ [3, 4], Fe³⁺ [5] or Ga³⁺ [6] stabilizes the cubic LLZO phase, which crystallizes in the cubic space group *la-3d* with $a_0 \approx 12.97$ Å. The cubic phase shows higher conductivities in the order of 10⁻⁴ S cm⁻¹ [3, 7].

The comparison of different conductivity measurements is difficult as the bulk conductivity depends on various parameters such as grain size, presence of impurities and bulk density. Conductivity measurements on single crystals would provide comparable values, but this was not yet possible as the grain sizes were too small. The grain size of LLZO prepared by conventional solid state synthesis is influenced by several parameters such as particle size of the reagent, Li content and sintering temperature [7]. We improved existing synthesis methods and developed a method for the synthesis of comparatively large grained and dense LLZO samples with grain sizes up to several hundreds of micrometres. These samples will be used for single-grain conductivity measurements to compare the influence of different dopants and dopant concentrations.

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FUN-T03

Structure-property relationship of transition metal catalysts

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Transition metals containing inorganic materials are essential as catalysts for many chemical reactions. For example Co_3O_4 is a suitable catalyst for low temperature CO oxidation while CuO has been intensively investigated as catalyst for methanol synthesis. Ammonia is an interesting hydrogen carrier with respect to the gravimetric hydrogen content. However, the decomposition of ammonia to hydrogen and nitrogen requires high reaction temperatures. The use of catalysts leads to a significant decrease of temperatures from more than 1000°C to less than 600°C. In this paper we focus on the catalytic decomposition of ammonia over different inorganic catalyst. Aim of the work is to understand activity differences of various catalysts and how modifications of the catalysts influence the properties. From previous studies we know, that the state of a catalysts changes significantly during the reaction. Removing the catalysts from the reaction may transform the material into a state which does not reflect the state under reaction conditions. In order to analyze a catalyst in action, in situ diffraction studies are required. Starting mainly from oxides, the formation of the active catalyst was followed during reaction. The experiments were conducted in a catalysis chamber attached to a laboratory diffractometer under elevated temperatures and controllable gas flows. Microstructure properties in terms of crystallite size or defect concentrations were evaluated by line profile analysis. The influence of crystal structure changes as well as of compositional alterations and microstructure features are discussed with respect to the catalytic properties. The studies show that mostly more than one property contributes to the final catalytic performance of an inorganic solid-state catalyst. The knowledge of the different contributions provides the deeper understanding of structure properties relationship of inorganic solids used in heterogeneous catalysis.

FUN-T04

Molecular dynamics modeling of irradiation damage in zircon, monazite, lakargiite and $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore

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The prospects of development of nuclear power engineering are associated with the ability of effective manipulation with nuclear wastes. Vitrification, or immobilization of nuclear wastes into glass, is the most widespread method of their treatment. However, the service life of such matrices is no longer than 30-40 years. An alternative to vitrification of nuclear wastes is utilization of high-level radioactive waste (HLW) in ceramic matrices and materials. The question of how effectively the matrix will maintain the barrier for the required time interval, which ranges from tens of years to tens of thousands of years for various isotopes, is most important.

The purpose of the present work was to investigate the relation between the radiation stability of zircon ZrSiO_4 , monazite LaPO_4 , lakargiite $\text{Ca}(\text{Zr,Ti,Sn})\text{O}_3$ and compounds $\text{Gd}_2\text{Zr}_2\text{O}_7$ with the structure of pyrochlore using method of molecular dynamics (MD).

The kinetics of accumulation and annihilation of Frenkel pairs (FP) in a cascade of atomic displacements after the passage of a primarily knocked thorium atom with an energy of 20 keV in the structure of investigated minerals has been calculated (fig. 1).

In addition to the data of the MD calculation the formation energy of FPs was calculated with the help of the Mott-Littleton classical model of “two inserted spheres” using the GULP software complex.

Based on these data, we evaluated parameter δ , which characterized susceptibility to amorphization of minerals under radiation damage. This parameter numerically equal to a part of the energy of Th atom, which is consumed for the formation of Frenkel pairs in a cascade of displaced atoms [1].

The results show that this parameter is equal to 0.68, 0.39, 0.07 and 0.05 for zircon, monazite, lakargiite and $\text{Gd}_2\text{Zr}_2\text{O}_7$. Thus, by the results of this MD investigation, we can conclude the following: the radiation stability of a lakargiite mineral matrix and $\text{Gd}_2\text{Zr}_2\text{O}_7$ chemical compound are one of highest among the chemical compounds studied up to date.

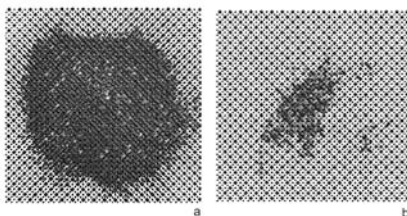


Figure legend. Radiation damage, produced by 20 keV Th recoil in pyrochlore at the peak of the damage (a) and after structure relaxation (b).

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FUN-P01

Comprehensive study of actinide reference materials for electron probe micro-analysis

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Electron probe micro-analysis (EPMA) is an important method for a broad range of applications in nuclear sciences. One main target is to improve the safety of the nuclear fuel cycle, by studying the chemical and physical properties of spent nuclear fuel and, in particular, of the fission products, either solids, volatiles, or gases, generated in the fuel during reactor irradiation [1].

Quantification of elements can only be achieved if the unknown sample is referenced to a sample of known concentration. In this study we investigate the options to prepare and use reference materials for the actinides Am and Cm.

Actinides are highly radioactive (especially the transuranic elements), hence difficult to handle. Two Am oxide compounds are currently investigated in the shielded facilities of the Institute for Transuranium Elements (ITU): $(U_{0.9}Am_{0.1})O_2$ and $(U_{0.8}Am_{0.2})O_2$. These ceramics are being characterized by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Element 2) for their bulk chemistry and impurities and by EPMA (Cameca SX100R) for their precise chemical composition and homogeneity. The Am content of the two compounds is cross-checked by EPMA using a calibration-curve approach described in [2]: the X-ray Ma and Mb intensities of Th, U, Np, and Pu are measured, and the resulting curve fitted. The Am intensity can be linked to the U intensity; this allows using the U signal as a standard for Am. Both the analytical characterization and the calibration curve method are expected to yield the same result.

The new Am standard can be used not only to measure Am in nuclear fuels, but also to accurately measure the content and monitor the in-growth Am in other actinide specimens, namely in PuO_2 . In addition, a calibration curve for Cm can be determined using the elements Th, U, Np, Pu, and Am. Similarly to the case of the Am standard, this will link the Cm intensity to the intensity of U, which will be used as a standard for Cm. This standard will allow the quantitative measurement of Cm in nuclear fuels.

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[2] Pöml, P., Brémier, S., Laheurte, F., Hasnaoui, R. and Walker, C. T. 2010. IOP Conf. Series: Materials Science and Engineering 7. doi: 10.1088/1757-899X/7/1/012025

FUN-P02

Growth of synthetic Ga-rich tourmaline in hydrothermal solutions

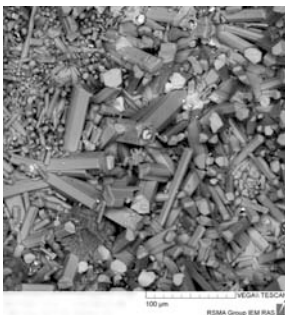
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The tourmaline crystals possesses by valuable pyro and piezoelectric properties. However crystal growth of tourmaline connected to a number of difficulties such as high temperature and pressure of crystallization, low growth rate, etc. (Setkova et al, 2011; London, 2011). At the same time, the synthesis of structural analogues of natural minerals in which aluminum and silicon are completely or partially substituted by gallium and germanium (gadolinium gallium, yttrium aluminum, and other garnets, germanium oxide, etc.) can reduce significantly the temperature and pressure of the process and to improve functional properties.

Studies were performed under thermogradient conditions using chromium-nickel alloy autoclaves at temperature of 450-650° C and pressure of 100 MPa in boric, boric-fluoride, boric-alkaline hydrothermal solutions. Plates made from natural tourmaline crystals of elbaite (chemical formula is $\text{Na}(\text{Li,Al})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH,F})_4$) were used as seed crystals in the experiments. Single crystals of quartz and corundum with addition of gallium oxide was used as charge material. The autoclave was filled with solution in accordance to autoclave-filling factor, then sealed, and placed into electric furnace with two-section heaters. The duration of the runs was 14 days.

As a results, the Ga-rich tourmaline wherein part of aluminum are substituted by gallium was grown on natural elbaite seed for the first time. The thickness of newly formed layer was up to 100 μm , and the gallium content was up to 12 wt. %. Growth of Ga-rich tourmaline took place in boric, boric-fluoride, boric-alkaline hydrothermal solutions. Along with single crystal growth of Ga-rich tourmaline, the fine long prismatic (10-100 micron in size) Ga-rich tourmaline crystals of spontaneous nucleation were observed on surface of the seed crystals and in the charge (Fig.). In boric-alkaline solutions, the largest size crystals of Ga-rich tourmaline and Ga-rich albite were formed simultaneously.



London, D. (2011). Canadian Mineralogist, 49, 117-136. T. Setkova, Yu. Shapovalov, V. Balitsky (2011). Journal of Crystal Growth, 318, 904-907.

Magmatic petrology – from melt to rock

MAG-T01

From a supercritical fluid to pegmatite

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Beginning in 1999 we performed hundreds of homogenization experiments on granite and pegmatite samples using the cold-seal pressure vessel and rapid-quench techniques at pressures between 1 and 5 kbar, complimented by Raman spectroscopy and hydrothermal diamond-anvil cell (HDAC) experiments.

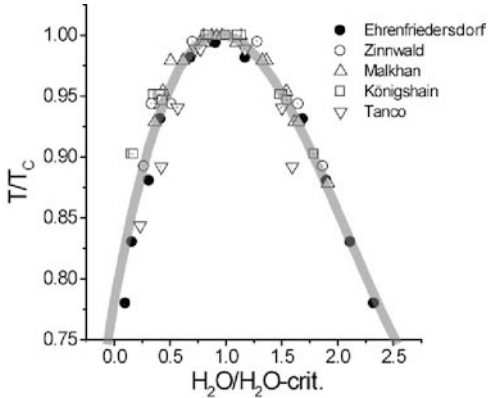
The general results obtained from melt inclusions in quartz from pegmatites (Ehrenfriedersdorf, Zinnwald, Malkhan, Königshain, and Tanco) plot as a pseudo-binary solvus. To show the five different systems on the same plot the temperature has been adjusted to the critical ones of the single systems (see Fig. 1). This type of presentation shows that all five systems have a very similar pattern of melt-melt immiscibility.

The following conclusions can be derived from this plot:

- Despite of some skeptical discussions to the possibility of liquid-liquid-fluid immiscibility in the past, the processes are real and widespread in nature.
- Type-A and type-B melt inclusions represent conjugate melts resulting from melt-melt immiscibility along a pseudobinary solvus boundary. The two conjugate melt fractions evolve to more peraluminous and less water-rich compositions (type-A melts) and to more peralkaline and very water-rich compositions (type-B melts).
- Independently of the different host granites the homogenization temperatures and the water concentration of melt inclusions in quartz of the related pegmatites plot in a consistent manner.
- For the critical temperature t_c we obtain a value of $731 \pm 21^\circ\text{C}$, valid for the pressure range from 1 to 5 kbar, thus the different run conditions fall within the given standard deviation of 1s.
- The critical water concentration ($\text{H}_2\text{O-crit.}$) for the five systems is $26.5 \pm 1.5\%$.
- Compared to standard melt systems the supercritical state is characterized by properties such as diffusion rate, density and viscosity which are completely unusual.
- the maximum rate of isotope fractionation is achieved at the critical region.

Magmatic petrology – from melt to rock

Using two extreme examples - the behavior of Be and P in relationship to the pseudobinary solvus - we show, that the water-rich pegmatite-forming systems cannot be derived from experimental results obtained for “condensed” granitic systems. An evolved granite is not a pegmatite!



Magmatic petrology – from melt to rock

MAG-T02

In-situ observation of crystal growth in a basalt melt and the development of crystal size distribution in igneous rocks

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Igneous rocks are formed by the solidification of silicate melts. From a microscopic perspective, melt solidification is known to involve a series of physico-chemical processes, including crystal nucleation, crystal growth, Ostwald ripening, and others. A good understanding of these processes and their collective operation is therefore fundamental in deciphering magma history from rock texture. To understand the solidification processes of natural magma and the texture evolution of igneous rocks, we have studied the crystallization of a high-K basaltic melt cooling from ~1240 °C by in-situ observation in a moissanite cell. In a series of experiments with different thermal history, olivine or clinopyroxene (cpx) appeared as the liquidus phase before the formation of plagioclase. Nucleation of olivine occurred only in a narrow temperature and time interval below the liquidus. During cooling at 100 °C/hr, the morphology of olivine and cpx transitioned from tabular to hopper habit. To first order approximation, crystal growth rate is proportional to crystal size. This causes a counterclockwise rotation of the crystal size distribution (CSD) curves, whereas Ostwald ripening reduces the population density of the smaller crystals.

Our experiments provide the first observation of proportionate crystal growth and suggest that conventional analyses of crystal size distributions of igneous rocks may be in error - the slope of the CSD cannot be interpreted in terms of a uniform growth rate and the intercept with the vertical axis does not correspond to a nucleation density. In reality, nucleation of each mineral is probably limited to a short event, which is followed by a long period of crystal growth (with growth rates proportional to crystal size) and annealing.

MAG-T03

Experimental approach to form anorthositic melts: phase relations in the system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{CaMgSi}_2\text{O}_6$ - Mg_2SiO_4 at 6 wt.% H_2O

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Massive anorthosite dykes are documented for the first time from the Limassol Forest Complex (LFC) of Cyprus, the LFC being a deformed equivalent of the Troodos ultramafic massif. Both the Troodos and LFC complexes are part of the Tethyan realm consisting of Cretaceous oceanic crust that formed within a backarc basin 90 Ma ago and was obducted during late Miocene.

From crosscutting relations with the sheeted dyke complex, it follows that the anorthosites belong to one of the latest magmatic events on Cyprus. In hand specimen, the rocks appear massive and unaltered, although in thin section magmatic plagioclase (An93) is partially replaced by albite and thomsonite (zeolite). Where magmatic textures are preserved, plagioclase forms cm-sized, acicular, radially arranged crystal aggregates that remind of spinifex textures.

The origin of these anorthosite dykes remains poorly understood. Even though they occur as intrusive dykes, it is evident that they cannot represent liquidus compositions, at least under dry conditions. Whole-sale melting of pure An93 would require temperatures in excess of 1450 °C.

The working hypothesis is that boninitic melts with approximately 4 wt.% H_2O , as found in the cyprian upper pillow lavas (UPL), could produce such rocks by olivine-pyroxene fractionation. Experiments at various temperatures are being performed in the ol-cpx-plag- H_2O system. The materials are ground and mixed in the desired proportions, then equilibrated with 6 wt. % H_2O at 0.5 GPa total pressure in a piston-cylinder press. Indeed, experiments indicate that such lithologies can be generated by medium-pressure fractional crystallization of hydrous basaltic melts followed by decompression-degassing. High pH_2O stabilizes olivine but tends to suppress plagioclase as the highest polymerized phase. Hence the An component is accumulated in the (late-stage) melt. When such a system experiences sudden decompression, the aqueous phase will exsolve and will trigger massive precipitation of anorthite. Aim is to delineate the anorthite saturation field in the ol-cpx-plag- H_2O system, and to assess to which extent plagioclase can be suppressed as a liquidus phase when a basaltic melt fractionates under hydrous conditions.

MAG-T04

Petrological and Geochemical Characterization of Abyssal Peridotites from the East Pacific Rise and Incorporation of OH-Defects in Nominally Anhydrous Orthopyroxene (ODP Leg 147: Hess Deep)

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Spinel peridotites from Hess Deep were investigated concerning mineral chemistry and the incorporation of hydroxyl point defects in the crystal structure of orthopyroxene. Therefore, analyses were taken by EPMA, LA-ICP-MS, and FTIR-spectroscopy.

Primary minerals of the harzburgite are olivine, orthopyroxene, clinopyroxene, and spinel. Serpentinization ranges from 60 to >95 % with secondary phases like serpentine, bastite, and magnetite. Analyses reveal Mg# ($\text{Mg}/(\text{Mg}+\text{Fe})$) between 0.90 and 0.92 for ol and opx. Mean enstatite component of opx varies between 78.6 and 85.5 % with Cr# ($\text{Cr}/(\text{Cr}+\text{Al})$) ranging from 0.15-0.24. Al_2O_3 varies between 0.49 and 2.88 wt. %. Cpx has Mg# of 0.91-0.96 and Cr# of 0.18-0.72. Al_2O_3 contents range from 0.07-3.58 wt. %. Measurements of spl reveal Mg# of 0.44-0.54 and Cr# of 0.55-0.69. Trace element data indicate an extreme depletion, characteristic for the restitic nature of abyssal peridotites after melt extraction. Water contents in opx range from 80-240 wt. ppm H_2O .

Equilibrium conditions were evaluated using various thermobarometers. Mean temperatures determined by two-pyroxene thermometers range from 914-1134 °C (e.g. Köhler & Brey). Pressures vary between 7.0 and 35.6 kbar. The degree of partial melting amounts to 16-18 % of fractional melting in the spinel peridotite stability field (Hellebrand et al.). Comparison of water contents to mineral chemistry or calculated pressures gives moderate correlations. A relation to temperature or stratigraphy cannot be identified.

In contrast to MAR peridotites, the samples contain intermediate to high water concentrations, experienced a high degree of partial melting, and intermediate temperatures. Elevated water contents as opposed to the high degree of melting indicates re-introduction of water into the opx after melt removal. Re-equilibration took place under spinel-facies conditions before exhumation of the tectonite since elevated P/T enhance diffusion and H uptake. Uplift was fast and accompanied by cooling such that re-equilibration to lower pressure assemblages and decompression-induced water loss were prevented.

Hellebrand, Snow, Dick & Hofmann (2001): Coupled major and trace element [...]. *Nature* 410: 677-681.

Köhler & Brey (1990): Calcium exchange between olivine and [...]. *Geochimica et Cosmochimica Acta* 54: 2375-2388.

MAG-T05

Crystallization of interstitial liquid and latent heat buffering in solidifying gabbros: Skaergaard Intrusion, Greenland

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Compositional profiles across plagioclase grains from the Layered Series (LS), Marginal Border Series (MBS) and Upper Border Series (UBS) of the Skaergaard intrusion are used to understand the mechanisms of cumulate rock solidification and the fate of the interstitial liquid. The data show that plagioclase crystals display three types of compositional profiles over the whole intrusion: (1) grains with normal zoning which dominate the MBS and UBS. These are interpreted as having formed at the top of crystal mush and then buried in the cumulate pile. Crystallization of the interstitial melt resulted in liquid differentiation and produced normally zoned rims on plagioclase cores; (2) unzoned crystals which dominate the upper part of the LS also crystallized at the top of the mush and were then buried in a mush with low interstitial liquid fraction or experiencing convective movements that kept the liquid to a constant composition; and (3) crystals with a mantle of decreasing An-content followed by a rim of constant composition. Grains showing this complex zoning mostly occur in the lower parts of the LS. Depending on the stratigraphic position within the intrusion, the composition of the rim can be An₅₆, An₅₁ or An₄₀. In the main magma body, these compositions (An-contents) correspond to those of plagioclase primocrysts (e.g. cores) at the appearance of cumulus clinopyroxene (An₅₆), Fe-Ti oxides (An₅₁) and apatite (An₄₀). Compositional buffering of plagioclase rims is interpreted as being a consequence of enhanced release of latent heat of crystallization at the appearance of new interstitial phases in the crystal mush. When a new phase saturates, the latent heat contribution to the global enthalpy budget of the system becomes sufficiently high to keep the interstitial melt to its liquidus temperature for a period of time that could exceed thousands of years. Under these conditions, equilibrium, adcumulus growth together with diffusion and possibly advection of chemical components result in the formation plagioclase rims of constant compositions (An-contents). Efficient thermal buffering of the mush liquid is shown to depend on the porosity (e.g. fraction of liquid within the mush) and the degree of compositional homogeneity of the mush.

MAG-T06

"Gabbro glacier" or "sheeted sills"? New constraints on the accretion mode of oceanic crust at fast-spreading oceanic ridges

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²*Christian-Albrechts-Universität zu Kiel, Institut für Geowissenschaften, Kiel, Germany*

In contrast to the upper oceanic crust which consists generally of effusive MOR-basalts, the structure, composition, mineralogy, and in situ physical properties of the lower, plutonic crust and the mechanisms by which it forms is poorly constrained. Prominent conceptual models for the formation of the deep, fast-spread crust are the "gabbro-glacier" model, where the lower crust is formed in the axial melt lens, and the "sheeted sill" model, where the lower gabbros are generated by the intrusion of sills of gabbroic mushes in the depths.

Here we present new petrological/geochemical/structural data providing evidence for the "sheeted sill" model: (1) recently established downhole logs for bulk Mg# and for the plagioclase / olivine co-variation both in the actual EPR (East Pacific Rise) oceanic crust as well in the Oman ophiolite reveal systematic trends with depth. (2) IODP Expedition 345 revealed delicate fast-crystal growth structures in olivine, which is not compatible with a crystallization in the axial melt lens and down transportation of several km. (3) A quantification approach of the variations of crystallographic orientations with crustal depth in gabbros from a profile in the Oman ophiolite using EBSD (Electron BackScatter Diffraction) is only compatible with the predictions for the "sheeted sill model".

A requirement for the "sheeted sill" model, however, is a substantial cooling of the deep oceanic crust. We believe that this is established by 100 m wide fault zones cutting the layered gabbro at several places which were recently discovered in the Oman ophiolite. These zones are characterized by the record of intense hydrothermal alteration at moderate (greenschist facies), high (amphibolite facies) and very high temperatures (magmatic regime). We identified these faults as zones where high hydrothermal flux was introduced into the lower crust starting at very high temperatures, which have the potential for effective cooling the deep crust.

MAG-T07

Rapid hydrothermal cooling above the axial melt lens at fast-spreading mid-ocean ridge

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Axial melt lenses sandwiched between the lower oceanic crust and the sheeted dike sequences at fast-spreading mid-ocean ridges are assumed to be the major magma source of oceanic crust accretion^[1]. According to the widely discussed “gabbro glacier” model^[2], the formation of the lower oceanic crust requires efficient cooling of the axial melt lens, resulting in partly crystallization and leading to crystal-melt mush which may subside down to form the lower crust. These processes are believed to be controlled dominantly by periodical magma supply and hydrothermal circulation above melt lens^[3]. Here we quantify the cooling rate above the melt lens using chemical zoning of plagioclase from former sheeted dikes recrystallized to granoblastic hornfelses, overlying the uppermost gabbros which are interpreted as part of the frozen melt lens system. The samples used were drilled from the Integrated Ocean Drilling Program at Site 1256 in the eastern equatorial Pacific, where for the first time the dike-gabbro transition zone of an intact oceanic crust was penetrated^[4]. The measured zoning patterns are supposed to be a combined result of diffusion during both off-ridge and on-ridge cooling. We estimate the on-ridge cooling rate using a forward modelling approach based on CaAl-NaSi interdiffusion in plagioclase. The results show that the recrystallized sheeted dikes have been cooled from the peak thermal overprint at 1000-1050 °C to 600 °C within about 5-30 years (see the figure below as an example) as a result of hydrothermal circulation above a melt lens during a period of magma starvation. The estimated rapid hydrothermal cooling coincides with the observed annual to decal episodes of melt lens fluctuation^[5] and lava eruption^[6], which supports the “gabbro glacier” model and explains how the effective heat extraction from melt lens is achieved at fast-spreading mid-ocean ridges.

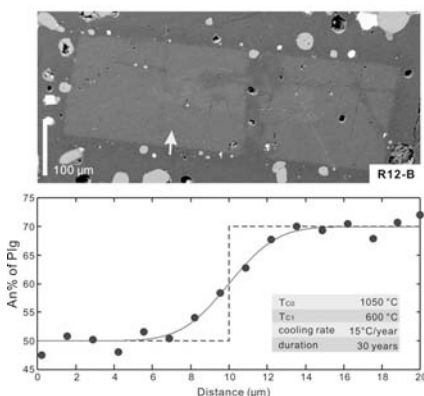


Fig 1. Image, concentration-distance profile and modeled profile for intra-plagioclase CaAl-NaSi couple interdiffusion.

- [1] Detrick, et al. Nature 326, 35-41 (1987).
- [2] Phipps Morgan, & Chen. J. Geophys. Res. 98, 6283-6297 (1993).
- [3] Henstock et al. J. Geophys. Res. 98, 4143-4161 (1993).
- [4] Wilson et al. Science 312, 1016-1020 (2006).
- [5] Mutter, et al. AGU Fall Meeting; p. 0321 (2008).
- [6] Carbotte, et al. Nature Geosci. 6, 866-870 (2013).

MAG-T08

First report on PGM inclusions hosted by chromian spinel from high-Cr podiform chromitites, Sabzevar ophiolite, NE Iran

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High-Cr podiform chromitites of Sabzevar ophiolite in Forumad area, west of Sabzevar ophiolite, NE Iran were investigated for PGM and other solid inclusions. Following the recently published papers on PGM in Neyriz and Faryab ophiolitic chromitites, SW and S of Iran respectively [1,2], this paper reports for the first time the presence of PGM in the Sabzevar Ophiolite. The detected solid phases in the chromitites are divided into three categories: PGM, base-metal minerals (BMM), and silicates (Fig. 1). Most of the studied PGM occur as very small (generally <10 µm in size) primary single or composite inclusions of Os-rich laurite. BMM are of Ni-Fe or Cu-Ni sulfide and alloy types. The presence of laurite in association with abundant base-metal sulfides shows increasing of f_{S_2} at the crystallization milieu of the chromian spinel. The silicate phases are pyroxene and amphibole. One large zircon grain (~40 µm in size) with K-feldspar inclusions was also detected as interstitial silicate in the studied chromitites, probably as xenocryst that originated from continental materials during subduction. This mineral was incorporated into podiform chromitite during melt-rock interaction [3]. Chemical data indicated that the studied chromitites were precipitated from boninitic melt in a SSZ setting in which slab-derived fluids and molten sediments interacted with sub-lithospheric mantle wedge.

[1] Rajabzadeh, M.A., Moosavinasab, Z., 2012. Mineralogy and distribution of platinum-group minerals (PGM) and other solid inclusions in the Neyriz ophiolitic chromitites, southern Iran. *Can Mineral* 50 (3), 643-665.

[2] Rajabzadeh, M.A., Moosavinasab, Z., 2013. Mineralogy and distribution of Platinum-Group Minerals (PGM) and other solid inclusions in the Faryab ophiolitic chromitites, Southern Iran. *Mineral Petrol* 107, 943-962.

[3] Yamamoto, S., Komiya, T., Yamamoto, H., Kaneko, Y., Terabayashi, M., Katayama, I., Iizuka, T., Maruyama, S., Yang, J., Kon, Y., Hirata, T., 2013. Recycled crustal zircons from podiform chromitites in the Luobusa ophiolite, southern Tibet. *Island Arc* 22, 89-103.

Magmatic petrology – from melt to rock

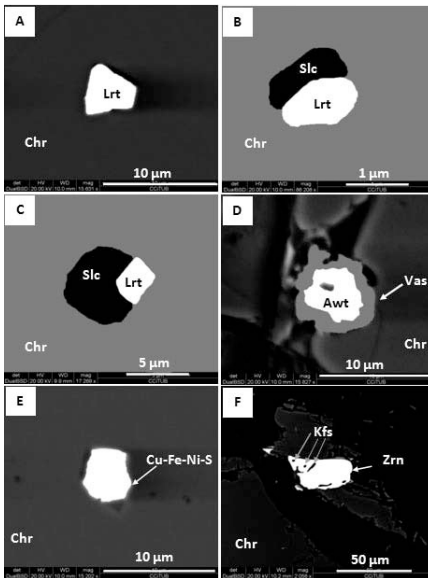


Figure 1: Solid inclusions within Sabzevar chromitites. Chr: chromite, Lrt: laurite, Slc: silicate mineral, Awt: awaruite; Vas: vaesite; Kfs: K-feldspar; Zrn: zircon; Cu-Fe-Ni-S: unknown base metal sulfide.

Magmatic petrology – from melt to rock

MAG-T09

Supra-chondritic Nb/Ta ratios and other exotic geochemical signatures in rejuvenated Hawaiian magmas as fingerprints of carbonatitic auto-metasomatism in parts of the Hawaiian mantle plume

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The rejuvenated Honolulu Volcanics (HV), Oahu, Hawaii, comprise small-volume magmas ranging from alkali basalt through basanite and nephelinite to melilitite. Their origin is enigmatic and debated, because the magmas are highly enriched in incompatible trace elements but isotopically depleted and erupted some 1.3 Myrs after the Koolau shield building phase had ceased. We have analysed 26 HV basanitic to melilitic tuffs from Salt Lake Crater at Honolulu, Oahu (SLC). While trace element patterns of most samples overlap with those of magmas from other HV localities, four melilitites display 2 to 4-times higher concentrations for “carbonatite-affine” elements such like P, Mn, REE, Sr, Ba. These samples also show carbonatite-like supra-chondritic Nb/Ta (up to 40) and Zr/Hf (up to 60) ratios, suggesting the presence of a carbonatitic component, which is also supported both by modal mineralogy and mineral chemistry. For example, magnetite compositions differ significantly from those of mantle peridotites and basaltic magmas, varying between oceanic carbonatites and SLC Hawaiian plume xenoliths. In addition, many such xenoliths bear multiple evidence of carbonatitic (as well as silicate) metasomatism, e.g. aragonite, diamond, graphite (Wirth & Rocholl, 2003). The carbonatitic agents must therefore be derived from the Hawaiian plume itself, thus documenting auto-metasomatic processes within the rising plume. Because the formation of melilitite requires a carbonated peridotite mantle (Brey 1978), the SLC melts probably derived from such auto-metasomatised parts of the plume, with a possible derivation of the carbonatite agents from carbonated eclogite (Yaxley & Brey 2004). This model is consistent with a HV-source being intrinsic to the Hawaiian plume (Fekiacova et al., 2007), Sr-Nd-Hf systematics in SLC magmas and xenoliths (Bizimis et al. 2005) and very similar to a model proposed by Dixon et al. (2008) for the origin of Niihau rejuvenated lavas.

Bizimis et al. (2005) *Geochim. Cosmochim. Acta*, 69, 2629-2646.

Brey, G. (1978) *J. Volc. Geotherm. Res.* 3, 61-88.

Dixon et al. (2008) *Geochem. Geophys. Geosyst.* 9, 1-34.

Fekiacova et al. (2007): *Earth Planet. Sci. Lett.* 261, 65-83.

Wirth R. and Rocholl A. (2003) *Earth Planet. Sci. Lett.* 211, 357-369.

Yaxley, G.M. and G.P. Brey (2004) *Contrib. Mineral. Petrol.* 146, 606-619.

MAG-T10

Petrology of Late Miocene calc-alkaline (shoshonitic) lamprophyres from Kos (Greece)

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The island of Kos is part of the Quaternary to Recent Aegean volcanic arc. In the eastern part of the island, Permo-Carboniferous sedimentary and mafic volcanic rocks were intruded by an I-type monzonite at ~12 Ma. Numerous lamprophyric dykes (spessartite, vogesite, kersantite, minette) cut the monzonite and its contact metamorphic aureole (Wimmenauer 1977; Altherr et al. 1988, Altherr and Siebel 2002). Mg# values [$= 100 \text{ Mg}/(\text{Mg} + 0.9 \text{ Fe}_{\text{tot}})$] range from 71.5 to 54.1. Chondrite-normalized (cn) REE patterns are concave upwards and do not show a Eu anomaly. All REE patterns exhibit steep slopes from La to Ho with $(\text{La}/\text{Ho})_{\text{cn}} = 14\text{--}55$, whereas the HREE show rather flat patterns with $(\text{Ho}/\text{Lu})_{\text{cn}}$ values between 1.1 and 1.5. Such patterns demonstrate that there was no residual garnet present during partial melting of the source rocks. Primitive mantle-normalized element abundance patterns are characterized by negative anomalies for Nb-Ta and Ti and a positive anomaly for Pb. Zr/Hf ratios (34.8–50.2) are negatively correlated with Mg#. Except for the most fractionated samples, Nb/Ta ratios (16–31) correlate with Zr/Hf. Th/La ratios of the lamprophyres range from 0.13 to 0.44, while Sm/La ratios (0.09–0.16) are extremely low. High Th/Yb ratios (4.5–19.5) and low Ba/La ratios (< 32) suggest a dominant role of sediment-derived melts vs slab-derived fluids.

Sr, Nd and Pb isotopic compositions fall in very narrow ranges. $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{init}}$ values (0.51253 to 0.51267) and $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{init}}$ values (0.70424 to 0.70546) are negatively correlated and extend from the unradiogenic end of the mantle array toward crustal compositions. The lead isotopic compositions fall in the range typically encountered for crustal rocks [$(^{206}\text{Pb}/^{204}\text{Pb})_{\text{init}}$: 18.64–18.94; $(^{207}\text{Pb}/^{204}\text{Pb})_{\text{init}}$: 15.61–15.66; $(^{208}\text{Pb}/^{204}\text{Pb})_{\text{init}}$: 38.46–38.86]. There is no systematic relationship between the different types of lamprophyre and their isotopic compositions.

Geochemical signatures of the lamprophyres indicate that the primary lamprophyric melts were derived from a strongly depleted mantle source that was re-enriched by melts derived from subducted sedimentary rocks.

Altherr et al. (1988) *Contrib Mineral Petrol* 100: 528–541; Altherr and Siebel (2002) *Contrib Mineral Petrol* 143: 397–415; Wimmenauer (1977) *Ann Géol Pays Helléniques* 28: 427–435

Magmatic petrology – from melt to rock

MAG-T11

Tracing crustal assimilation and basement compositions in differentiated volcanic rocks from the Siebengebirge Volcanic Field (SVF) – insights from Sr-Nd-Hf-Pb isotopes

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The Cenozoic Siebengebirge Volcanic Field (SVF) comprises the entire range of volcanic rocks from mafic basanites and alkali basalts to differentiated latites and trachytes. Prior studies (Vieten, 1961; Jung et al., 2012; Kolb et al., 2012) mainly focused on characterising the source of the mafic volcanic rocks and their evolution, but relatively little work has been carried out on the more felsic suites found in the SVF. These differentiated felsic lithologies can potentially shed some light on differentiation of SVF magmas and on potential crustal assimilation, namely its extent and the nature of the assimilant. These processes might provide further insights into assimilation-fractional crystallisation (AFC) and the geodynamic evolution of intraplate volcanic settings such as the CEVP.

Samples of the differentiated SVF lithologies include tephriphonolites, latites and trachytes with SiO₂ contents between 53 and 66 wt. %. Moreover, the differentiated lavas have positive Pb anomalies and negative Nb anomalies in comparison to the mafic lithologies with positive Nb and negative Pb anomalies, pointing towards the assimilation of crustal components. The unradiogenic ¹⁴³Nd/¹⁴⁴Nd (εNd = -0.31 to +1.79) and ¹⁷⁶Hf/¹⁷⁷Hf (εHf = -0.12 to +4.98) coupled with radiogenic ⁸⁷Sr/⁸⁶Sr (0.704296-0.705689) and ²⁰⁷Pb/²⁰⁴Pb (15.66-15.70) confirm the interpretation that compositions of the differentiated volcanic rocks can be explained by assimilation of crustal material. In part, the isotope compositions can be explained by assimilation of lower crustal granulites from the Eifel, but some material with a long term elevated U/Pb is required to account for the high ²⁰⁷Pb/²⁰⁴Pb in many samples.

Altogether, differentiation of the SVF lithologies can be explained by ca. 30-47% fractional crystallisation and up to 1-15% of crustal assimilation using energy-constrained assimilation-fractional crystallisation (EC-AFC) model calculations.

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MAG-T12

The origin of sapphire megacrysts in alkaline basalts from the Siebengebirge Volcanic Province, W Germany

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Although basalt is known to not contain corundum in the norm, sapphire megacrysts were found in alkaline basalts of the cenozoic Siebengebirge Volcanic Province, W Germany. A rim of hercynitic spinel surrounding all sapphires reflects a state of disequilibrium between the sapphire and the hosting basalt, supporting a xenocrystic rather than a phenocrystic nature. The mineral inclusion suite comprising Ca-, Mg- carbonates, feldspar, and Nb, Ti, Fe, and Th-rich oxides, as well as the overall enrichment in the High Field Strength Elements Nb, Ta, Zr, Hf, Th, and in W up to five orders of magnitude compared to the Primitive Mantle, indicate the sapphires to originate from a reservoir highly enriched in these incompatible elements. A likely candidate for the reservoir parental to the sapphires is a carbonatitic magma, as these magmas are produced at very low melt fractions (< 1%), enhancing the enrichment in highly incompatible elements such as the HFSE. Testing the feasibility of a petrogenetic model for an origin of the sapphires related to carbonatitic magmatism, Piston Cylinder experiments at upper mantle conditions were conducted and presented here.

Magmatic petrology – from melt to rock

MAG-T13

Partial melting of carbonates – evidence from a diatexite migmatite from Øksfjord, Finnmark, Northern Norway

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Every now and then the question on the existence of crust-derived carbonate melt, as opposed to mantle carbonatites, appears. Although it is experimentally proven that it is possible to melt calcite at reasonably low temperatures (1), only little field evidence was reported (2). Investigated granulites from a 60 x 20m-calc-silicate raft contained in Syenogabbros of the Seiland Igneous Province from Øksfjord, Finnmark, Northern Norway, exhibit abundant partial melting structures with calcite as the dominant neosome mineral. The neosome consists of a Cc-Cpx leucosome and Cpx-Bt melanosome, emplaced into strongly deformed calc-silicate paleosome. Partial melting reaches high proportions, classifying the migmatite as a schollen diatexite. A genetic relation to intrusive mantle-derived carbonatites of the nearby island of Stjernøya could be excluded due to distinct bulk chemistry and lacking enrichment of Nb, La, Ce, Nd and apatite. Furthermore, stable isotope analysis of calcite yielded values of 1.75 - 3.81 ‰ $\delta^{13}\text{C}$ VPDB and 17.38 - 20.86 ‰ $\delta^{18}\text{O}$ VSMOW, hinting to a sedimentary or recrystallized origin. No isotope fractionation between neosome and paleosome during partial melting could be observed in this study. Therefore, a genesis in a closed system is proposed. Paleosome mineral assemblages of Scp-Cpx-Grt-An indicate granulite facies metamorphic conditions, featuring textures of the following reactions: (I) $3\text{An} + \text{Cc} \rightarrow \text{Scp}$; (II) $\text{Scp} + 3\text{Wo} + 2\text{Cc} \rightarrow 3\text{Grs} + 3\text{CO}_2$ and (III) $\text{Wo} \rightarrow \text{Cc} + \text{Qtz}$. Petrogenetic phase modelling represents well the observed reaction textures, giving minimum peak metamorphic conditions of 820°C and 6-7 kbar. The intrusion of the surrounding ~565 Ma gabbro (3) is thought to have facilitated partial melting of carbonate within the assimilated calc-silicate raft via influx of heat and H₂O-rich fluids. During the process of partial melting, the activity of CO₂ in the fluid is believed to have increased, allowing the formation of carbonate scapolite selvages as in prograde reaction (I). Grossular-forming reaction (II) would then represent another change in fluid composition during a later phase of metamorphism, possibly related to the Scandian phase (420 Ma) of the caledonian orogeny.

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MAG-T14

Geothermometry in highly evolved peralkaline magmatic systems

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Geothermometry in highly evolved peralkaline igneous rocks is often complicated by the absence of Fe-Ti oxides, olivine and Ca-rich clinopyroxene; only few other approaches to calculate crystallization temperatures are available. Instead, complex Na-Fe-Ti-Zr silicates like eudialyte and aenigmatite occur in such rocks.

In this study, data from phase equilibrium experiments on an iron-rich peralkaline phonolitic composition (100 MPa, $\Delta \log \text{FMQ}$ -1.5; Giehl et al. 2013, 2014) are used to test existing geothermometers. In these experiments, titanomagnetite, fayalitic olivine, Ca-Na-Fe clinopyroxene, alkali feldspar, nepheline, aenigmatite, sodalite, eudialyte, fluorite and hiortdahlite occur, coexisting with residual melt. Calculated temperatures using both olivine - clinopyroxene - Fe-Ti oxide equilibria and clinopyroxene - melt element partitioning are in reasonable agreement with experimental temperatures when using Na-poor (<0.1 apfu) clinopyroxene. However, calculated and experimental temperatures show increasing misfit (± 50 - 200 °C) with increasing Na content (0.1 - 0.8 apfu) in clinopyroxene, confirming serious problems of these thermometers in highly peralkaline systems.

We provide calibrations for the following potential geothermometers based on the partitioning of Mn between minerals and between minerals and melt:

$\log K_d (\text{cMn, eudialyte/clinopyroxene}) = 0.38 \cdot (10000/T \text{ (K)}) - 3.86$ ($n=7$, $R^2=0.94$, $T_{\text{int}}=800\text{-}650^\circ\text{C}$)

$\log K_d (\text{cMn, aenigmatite/clinopyroxene}) = 0.29 \cdot (10000/T \text{ (K)}) - 2.72$ ($n=6$, $R^2=0.87$, $T_{\text{int}}=800\text{-}700^\circ\text{C}$)

$\log K_d (\text{cMn, clinopyroxene/melt}) = -0.31 \cdot (10000/T \text{ (K)}) + 3.14$ ($n=16$, $R^2=0.95$, $T_{\text{int}}=900\text{-}650^\circ\text{C}$)

with Mn in wt% and T in K; n is the number of calibration experiments, R^2 the coefficient of determination and T_{int} the T interval where calibration experiments were conducted. These calibrations were tested using literature data, both from experiments and from natural rocks with independent temperature estimates. Temperature calculations reasonably match the expected temperatures within 50 °C, however, they imply increasing misfit at oxygen fugacities significantly higher compared to calibration experiments.

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MAG-T15

In-situ observations of bubble growth in basaltic, andesitic and rhyodacitic melts

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Bubble growth strongly affects the physical properties of degassing magmas and their eruption dynamics. Natural samples and products from quench experiments provide only a snapshot of the final state of volatile exsolution, leaving the processes occurring during its early stages unconstrained. In order to fill this gap, we present in-situ high-temperature observations of bubble growth in magmas of different compositions (basalt, andesite and rhyodacite) at 1100 to 1240 °C and 0.1 MPa (1 bar), obtained using a moissanite cell apparatus. Experiments show that heterogeneous nucleation of bubbles occurs in one single event and at very small degrees of supersaturation, due to the formation of crystal nuclei. Melt degassing is the driving mechanism of bubble growth at early stages, whereas coalescence becomes increasingly important as exsolution progresses. Ostwald ripening is less efficient and occurs only at late stages, if heterogeneous bubble size distributions (BSD) are achieved. The average bubble growth rate (G_R) ranges from $3.4 \cdot 10^{-6}$ to $5.2 \cdot 10^{-7}$ mm/s, with basalt and andesite showing faster growth rates than rhyodacite. The bubble number density (N_B) at nucleation ranges from $7.9 \cdot 10^4$ mm⁻³ to $1.8 \cdot 10^5$ mm⁻³ and decreases exponentially over time, because of bubble coalescence. The coalescence rate controls the evolutions of the BSD, with higher rates increasing the heterogeneity of BSDs by adding multiple modes to the distribution. In natural samples, such BSD's may be misinterpreted as resulting from several separate nucleation events. Incipient crystallization upon cooling of a magma may allow bubble nucleation already at very small degrees of supersaturation and could therefore be an important trigger for volatile release and explosive eruptions.

MAG-T16

The effect of alkalis and polymerization on the solubility of H₂O and CO₂ in alkali-rich silicate melts

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It is now well established that volatiles, such as H₂O and CO₂, play an important role in magmatic processes influencing physical and chemical properties of natural magmas. In order to have better knowledge on the role of volatiles, the effect of alkalis on the solubility of H₂O and CO₂ in alkali-rich silicate melts was investigated at 500 MPa and 1250°C in the systems with H₂O/(H₂O + CO₂) ratio varying from 0 to 1. Using a synthetic analogue of phono-tephritic magma from Alban Hills (AH1) as a base composition, the Na/(Na+K) ratio was varied from 0.28 (AH1) to 0.60 (AH2) and 0.85 (AH3) at roughly constant total alkali content. The obtained results were compared with the data for shoshonitic and latitic melts having similar total alkali content but different structural characteristics, e.g., NBO/T parameter (the ratio of Non-Bridging Oxygens over Tetrahedrally-coordinated cations), as those of the AH compositions.

Little variation was observed in H₂O solubility. The maximum CO₂ content in melts equilibrated with CO₂-rich fluids increases strongly with the NBO/T from 0.29 wt% for latite (NBO/T= 0.17) to 0.45 wt% for shoshonite (NBO/T= 0.38) to 0.90 wt% for AH2 (NBO/T=0.55). The highest CO₂ contents determined for AH3 and AH1 are 1.18 ± 0.05 wt% and 0.86 ± 0.12 wt%, respectively, indicating that Na is promoting carbonate incorporation stronger than potassium. An empirical equation is proposed to predict CO₂ solubility in various silicate melts as a function of the NBO/T, (Na + K)/ Σ cations and Na/(Na+K) parameters.

F. Vetere, F. Holtz, H. Behrens, R. Botcharnikov, S. Fanara (2014). The role of alkalis in the solubility of H₂O and CO₂ in silicate melts. Implication for phonotephritic magmas. *Contribution to Mineralogy and Petrology* 167: 1014

Magmatic petrology – from melt to rock

MAG-T17

Chaotic mixing – from lab to nature – revisiting a deep magma chamber

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Theoretical and experimental studies on mixing highlight the importance of stretching and stirring of fluid particles under chaotic advection enhancing mixing. In particular, a flow can be partitioned into regions of qualitatively different fluid motion: a) inner regular core regions; b) inner and outer recirculation regions and c) outer flow (Aref et al EPL 2014).

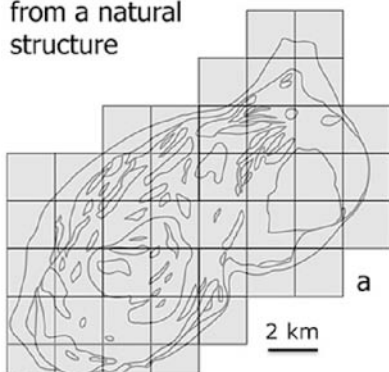
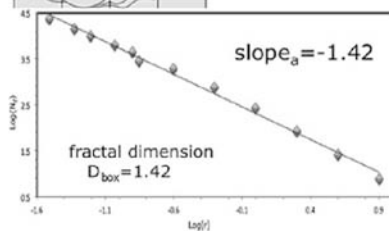
Recently the morphology of mixing patterns from chaotic mixing experiments with analogue and natural silicate melts (basalt and rhyolite) has been quantified by measuring fractal dimensions. A linear relationship could be derived between mixing time and morphological complexity (Morgavi et al JVGR 2013).

Here we focus on mixing between basalt and granite in a deep magma chamber, hence a plutonic environment. Mixing patterns, fractal dimensions and geochemical data from a 200 km² granitic pluton are summarized and compared to experimental results from chaotic mixing experiments with similar compositions. Different morphologic domains within the pluton reveal concentric fragmented and folded layers of granite in a gabbro-granite mixed matrix (recirculation regions). This is in contrast with two predominantly regular basaltic/gabbroic regions (regular core regions) (De Campos submitted to PAG). Fractal dimensions calculated from flow directions in the deep magma chamber are close to those measured for short mixing time experiments with natural melts (Figure 1).

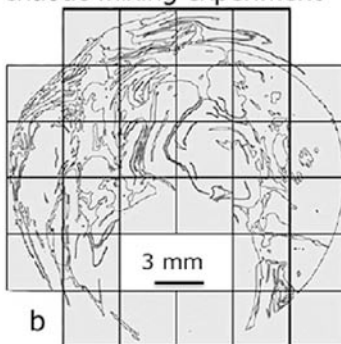
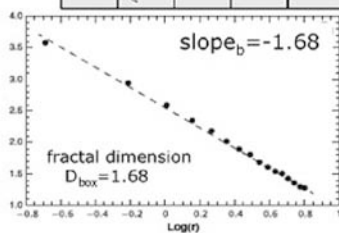
Coeval fractional crystallization, with no doubt, contributed to increase the complexity of the system. However, since flow and, therefore mixing, stops with temperature decrease, flow patterns must have been preserved, keeping the predominant morphology and composition from the moment when both contrasting magmas came together and froze-in. With further temperature decrease fractional crystallization took over and hybrid rocks were generated from the fractionation of magmas previously mixed at different proportions.

Magmatic petrology – from melt to rock

Flow lines
from a natural
structure



Flow lines from a
chaotic mixing experiment



MAG-T19

Ab initio simulation approach to study trace element partitioning between metal and silicate melts

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Trace element signatures are widely used to reconstruct magmatic processes that took place during the formation and evolution of the Earth. As the distribution of elements between different phases is governed by thermodynamics, element partition coefficients need to be known. However, their experimental determination is still challenging, especially at extreme conditions of pressure and temperature. First-principles computational methods have become very powerful recently and can provide new insight into the processes governing element partitioning.

We use such an atomistic modeling approach in order to understand the mechanisms by which trace elements are partitioned between metal and silicate melts. In the simulations, they are represented by a simple Fe melt and several $(\text{Mg,Fe})_2\text{SiO}_4$ melts with a varying Mg/Fe ratio. As typical trace elements, single Cr or Ni atoms are added to the systems.

Due to their predictive power, ab initio molecular dynamics (AIMD) simulations provide reliable structure models for the different melts, from which information about coordination environment, x-ray structure factors and further properties are derived. Simultaneously, AIMD gives access to thermodynamic properties, such as the equilibrium constants for the exchange of trace elements between metal and silicate melts.

First results with Ni as trace element show that in a silicate melt, Ni has strong similarities with Mg in terms of coordination number and nearest neighbor distance, differing clearly from Fe. In contrast to that, hardly any difference between Ni and Fe can be observed in a metal melt. Cr is expected to behave differently from the more siderophile Ni, which will translate to a different coordination environment. Finally, first estimates of the metal/silicate partitioning coefficients obtained from first-principles thermodynamic integration will be presented.

MAG-T20

Experimental constraints on REE-based slab thermometry

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The flux of elements from the slab into the mantle wedge is governed by the composition of the different subducted lithologies, the partitioning behaviour of trace elements and the subduction geotherm. It has been shown that the concentrations of elements such as K and REE depend primarily on T and are controlled by the solubility of accessory phases, such as phengite, monazite and allanite, in the melt [1, 2]. This T-concentration relationship has been used to derive a provisional Ce/H₂O geothermometer to determine the top slab T in subduction zones [3,4].

Here we report further results on allanite saturation in crystallisation experiments on a water over-saturated trace element-doped MORB composition at 3 to 5 GPa and 750-1000 °C. Together with previous results at 2.5 GPa and 750-900°C [2] the dataset now covers the full range of P-T conditions predicted for the slab below volcanic arcs.

All runs contain a typical eclogite residue of grt, cpx and rutile ±coesite that coexisted with a hydrous melt+fluid at run T. Allanite is observed up to ~900°C. With increasing P, D_{Na} cpx/melt increases and hence Na/K in the melt decreases. REE concentrations in the melts are similar to [2] up to P = 3.3 GPa. At P ≥ 3.6 GPa we observe increased REE concentrations in the melt by an order of magnitude. This jump in melt REE contents can be explained by the presence of a supercritical fluid by crossing the 2nd critical endpoint in the basalt-H₂O system. This is also supported by Si/Al systematics of the melts that increase when crossing from a melt to a supercritical state [5]. The excess H₂O then acts as an active solvent leading to increased REE solubilities. However, the overall T dependance of REE/H₂O is similar to previous results in sediment and basalt derived melts/fluids below and above the 2nd critical endpoint [1,2,3] when accounting for the physical state of the liquid. Thus, REE/H₂O of worldwide arc melts may well reflect magmatic conditions of the top slab below the volcanic arc with T ranging from ~750 to 950°C regardless if they are sediment or eclogite derived. In support the REE/H₂O of arc melts correlate with the thermal parameter Φ [4].

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Magmatic petrology – from melt to rock

MAG-T21

Big data in geochemistry – a global perspective of REE signatures in igneous rocks

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The fundamental hypothesis in geo/cosmochemistry that more data produce more answers lead to rapid data accumulation of hundred thousands of datasets over the past decades. While each new dataset adds to an improved picture of how Earth formed and evolved, insights from the entirety of the data are only rarely sought. Advances in computer power allows to access and analyse huge volumes of data using the concept of what became known as 'big data' analysis. In the light of these changes an additional fundamental hypothesis can be formulated: big data analyses produce new answers to geo/cosmochemical questions. Databases such as GEOROC or PetDB accumulate and systematise geochemical data. Yet, big data analysis using these databases to identify global geochemical patterns and signatures remain sparse.

This study tests the big data hypothesis by looking at REE of all igneous rocks compiled in the GEOROC database. The findings are a global negative Tm anomaly of -3.0% and a positive global Pr anomaly of +0.9% relative to the most recent REE solar system abundances, predominantly based on carbonaceous chondrites. Both terrestrial anomalies are not explained by current geochemical processes. Hence, these findings indicate a non-CI chondritic bulk silicate Earth composition of refractory elements and possible cosmochemical fractionations before Earth accretion. Bendel et al. (unpubl.) recently found a negative Tm anomaly of about -5% by studying >600 terrestrial samples. They used a different CI value for normalisation. Using the CI value Bendel et al. used, would also result in an -5% Tm anomaly. This is independent and excellent evidence for the validity of this big data approach. Further results are large negative Eu-anomalies in continental crust of more than -10%. These demonstrate prolonged magma residence times. In contrast, smaller, global negative Eu-anomalies of about -5% in oceanic crust indicate shorter magma residence times. Seafloor sediment recycling might be a local phenomenon as no global Ce-anomaly is found. These results provide a first glimpse of the potential of big data analysis in geo/cosmochemistry. Sophisticated tools to get new insights and a much better understanding of Earth and other planetary bodies can now be developed.

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Bendel et al. (unpublished)

MAG-P01

Mineral chemistry of chromian spinel in high-Cr podiform chromitites from Sabzevar ophiolite, NE Iran – implications for parental melt composition and geodynamic setting

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High-Cr podiform chromitites from Pahnestan and Pishkar-13 chromitite deposits, at Forumad massif, west of the Sabzevar ophiolite, NE Iran were investigated for determining host ophiolite origin. Results of 50 EPMA analyses from cores of the chromian spinel grains at the University of Barcelona, Spain, yield variable compositions with Cr# $[100 \times \text{Cr}/(\text{Cr} + \text{Al}) = 75\text{-}80]$ and Mg# $[100 \times \text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 58\text{-}76]$. The Al_2O_3 content varies in the range of 5.53-12.43 wt.%. Minor amounts of Ti (0.10-0.21 wt.% TiO_2), Mn (0.24-0.37 wt.% MnO), Ni (0.06-0.23 wt.% NiO), and V (<0.2 wt.% V_2O_3) were also determined. The studied spinels show both SSZ and ARC affinities [1] and fall within boninitic field [2] (Fig. 1-a,b). Al_2O_3 and TiO_2 contents of parent melt were calculated 8.10-11.60 and 0.22-0.32 wt.% respectively [3,4]. Degrees of fractional melting obtained 21- 23 for the chromitites source melt [5]. The data indicated that the chromitites at Sabzevar were precipitated from Mg-rich boninitic melt, probably in a forearc basin in which slab-derived fluids interacted with sub-lithospheric mantle wedge.

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Magmatic petrology – from melt to rock

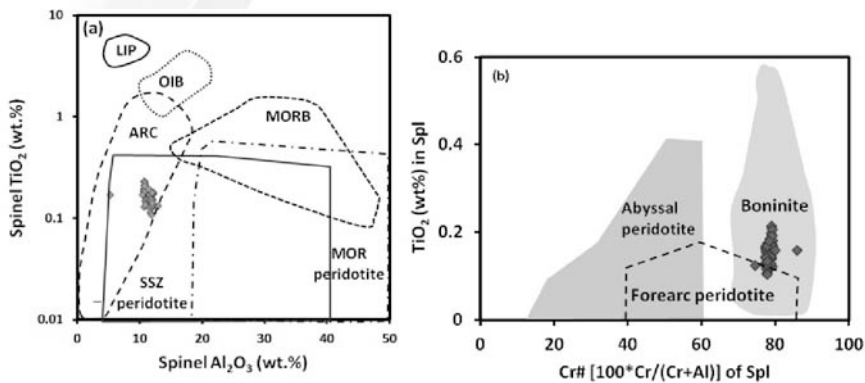


Figure 1: a,b- Compositional relationships in the studied chromitites.

MAG-P02

Mineral Paragenese und Mineralchemie der Büyük Yayla Obsidiane, İkizdere-Rize/NE-Türkei

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Auf der Hochalm Büyük Yayla, 25 km südlich von der Küstenstadt Rize im NO der Türkei, sind mächtige Obsidiane aufgeschlossen (Heide et al. 1996). In dieser Arbeit werden ihr Mineralinhalt und ihre chemische Zusammensetzung dargestellt.

Nach radiometrischen Altersdatierungen ($^{40}\text{K}/^{39}\text{Ar}$) liegt das Alter dieser Obsidiane zwischen $1,7 \pm 0,28$ und $2,00 \pm 0,24$ Ma (Hanedan-Nar, 2008). Makroskopisch lassen sich diese Obsidiane in a) einheitlich schwarze, b) schwarze mit rötlichen Schlieren, c) rötlich-braune, d) rötlich-bräunlich mit schwarzen Schlieren und e) breckzierte Typen unterscheiden.

Ihr Mineralinhalt besteht aus Feldspäten, Pyroxenen, Biotiten, Fe-Ti-Oxiden und Quarz; akzessorisch findet sich noch Zirkon, Apatit, Pyrotin, Kupferkies und Anhydrit. Feldspäte, Pyroxene, Biotite und Quarze treten sowohl als autogene Bildungen als auch als Restite auf.

Feldspäte: Dominierend sind die Plagioklase, der Rest Alkalifeldspäte. Die Plagioklase bestehen aus Oligoklas, etwas Andesin und sehr selten aus Albit, während die Alkalifeldspäte chemisch zw Na-K-Ca-Albit und Sanidin liegen.

Pyroxene: Eingetragen in das Ca-Mg-Fe-Diagramm zeigen die Pyroxene augitisch bis diopsidische Zusammensetzung. Oft bilden die sehr kleinen, autogenen Pyroxene kettenartige Reihen.

Fe-Ti-Oxide: In dem FeO-TiO₂-Fe₂O₃-Diagramm liegen die magnetitischen zw. Ulvospinell und Magnetit; die hämatitischen eher in der Nähe von Ilmenit. Ein winziger Teil zeigt Rutil-Zusammensetzung. Entmischte und nicht entmischte Fe-Ti-Oxide liegen in sehr enger Nachbarschaft. Die Entmischung basiert auf einer Aufheizung durch den Lavanachschub und der danach auftretenden Abkühlung.

Biotite: Die älteren Biotite sind etwas blasser als die jüngeren. In dem Al-Mg-Fe-Diagramm liegen sie zw. Phlogopit und Anit.

Literatur

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Magmatic petrology – from melt to rock

MAG-P03

Mantle-crust differentiation of chalcophile elements in the oceanic lithosphere – preliminary results

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The chalcophile elements, as associated with sulfides, are believed mainly from the study of ophiolites to be generally enriched in the upper mantle, but depleted by magmatic processes in the lower and upper ocean crust. However, studies of some orogenic lherzolites suggest a copper depletion of peridotites in relation to the primitive mantle, suggesting that a portion of the sulfides is melted during decompression and incorporated into the ascending magmas. The rarity of abyssal peridotites and the high degree of their alteration have not allowed these results to be verified *in situ* in the oceans.

Here, we present the first complete study of chalcophile elements based on a suite of rocks from an oceanic core complex (OCC), the Kane Megamullion at 22°30'N at the Mid-Atlantic Ridge. OCCs provide large exposures of mantle and lower crustal rocks on the seafloor on detachment fault footwalls at slow and ultraslow spreading ridges. The Kane Megamullion is one of the best sampled OCCs in the world [1], with 1342 rocks from 28 dredge sites and 14 dives [2]. We have made XRF, TD-MS and INAA analyses of 129 representative peridotites, gabbroic rocks, diabases and basalts. We monitored the influence of alteration in all magmatic samples. None show secondary enrichment by hydrothermal processes, as no sulfide veins were identified. Depletion by hydrothermal alteration is relatively small. We have established and taken into account a depletion factor based on comparison to samples with similar magmatic composition but differing degrees of alteration.

Magmatic petrology – from melt to rock

Our first results suggest a depletion of some peridotites in relation to the primitive mantle (28 ppm Cu; [3]). Dunites, troctolites and olivine gabbros are relatively enriched in chalcophile elements. The amount of sulfides decreases gradually with progressive differentiation, reaching a minimum in gabbro-norites and diabases. The highest bulk abundance of chalcophile elements in our sample suite was observed in dunites (up to ~ 300 ppm Cu in several samples) and a contact zone between residual peridotite and a mafic vein (294 ppm Cu). Plagioclase-bearing harzburgites, generally formed by late-stage melt impregnation in the mantle, are typically more enriched in Cu than unimpregnated residual peridotites. For these reasons, our initial results indicate sulfide melting during mantle melting, and their local precipitation in the mantle lithosphere due to late-stage melt impregnation.

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Magmatic petrology – from melt to rock

MAG-P04

Major, trace and rare earth elements distribution in magmatic rocks of the Bystrinskoe Au-Cu skarn-porphyry deposit (Eastern Transbaikalia, Russia) – metallogenic consequences

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Introduction: The large Bystrinskoe Au-Cu-Fe skarn-porphyry deposit in Eastern Transbaikalia, Russia, is constrained to the southern margin of the Mongolia-Okhotsk volcano-plutonic complex. The porphyry granite bodies (stocks and dikes) to which the deposit is related are made up of rocks of high-K calc-alkaline and shoshonite series. As the SiO₂ content of the porphyritic rocks increases from 52 to 68 wt %, their MgO concentrations remain high enough (4-9 wt %), and Mg# increases from 65 mol % in the mafic rocks to 75 mol % in acid ones.

Results: The rocks bear relatively low concentrations of Sr (50-300 ppm) low Y (2-11 ppm) and Yb (0.5-1.5 ppm) at elevated (La/Yb)_n ratios, which vary from 3 to 32. The petrochemistry and geochemistry of the rocks are closely similar to those of porphyritic rocks at the Shakhtama Mo-porphyry deposit. Both of the porphyry systems operated during the Mesozoic evolutionary episode of Transbaikalia: the K-Ar age is estimated at 167 ± 1.6 Ma for porphyritic rocks of the Shakhtama Complex (Berzina et al., 2013) and at 163 ± 3 Ma for phlogopite from skarn at the Bystrinskoe deposit. Porphyritic rocks from the Shakhtama deposits and rocks from the Bystrinskoe one show a decrease in the mantle-normalized elemental concentrations from LILE to LREE and MREE and general depletion in HFSE (Nb, Ta, and Ti) and HREE. Compared to the Shakhtama rocks, the rocks studied at the Bystrinskoe deposit are poorer in Sr and Y. In the Sr/Y vs. La/Yb diagram, these rocks plot within the field of adakites and island-arc calc-alkaline series and fall within the field of low-Si adakites in terms of MgO concentration (Martin et al, 2005), which suggests that the parental magmas were derived under transitional conditions. If these rocks at the Shakhtama deposit are postcollisional adakites (Berzina et al., 2013), then the transitional character of these roughly coeval rocks can be explained by their generation simultaneously with (or before) collision-related crustal thickening.

Conclusion. The relation of the Bystrinskoe deposit to adakites and adakite-like rocks could be one of the possible reasons for the high Cu and Au ore-forming potential of this skarn-porphyry system.

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MAG-P05

Partial melting effects and melt-peridotite interactions in the Pozanti-Karsanti ophiolite (eastern Taurides, Turkey)

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The Pozanti-Karsanti ophiolite, located in the eastern part of the Taurides (Turkey), consists of a mantle unit (peridotites) and an overlying crustal section, i.e. mafic cumulates and isotropic gabbros.

The mantle peridotite is built up of harzburgitic to dunitic rocks that are depleted in Al_2O_3 (0.11-1.01 wt.%) and CaO (0.10-1.07 wt.%) compared to the primitive mantle. Therefore these rocks represent a mantle residue from which various amounts of melt have been extracted. The low whole-rock Al- and Ca-values are consistent with the high Cr# [$= 100 \times \text{Cr} / (\text{Cr} + \text{Al})$] values of spinel that range from 44 to 70. These spinels generally have low TiO_2 (< 0.06% wt.%) concentrations, even spinels with high-Cr compositions in certain samples exhibit enrichments of up to 0.16 wt.% of TiO_2 . The whole-rock concentrations of chondrite-normalised rare earth elements (REEs) indicate depletion toward heavy to medium REEs. However, the entire mantle peridotite samples exhibit noticeable enrichment in light REEs and large-ion lithophile elements (LILEs) compared to medium REEs. The whole-rock heavy REE patterns of a few of the peridotite samples were comparable to the calculated melting curves representing various degrees of melting and are modelled by ~24-30% melting in the spinel stability field. However, a few of the samples are more depleted in medium REEs than heavy REEs. The patterns of heavy to medium REEs do not follow the melting lines produced by various degrees of melting in the spinel stability field. The heavy REE composition of these peridotite samples recommends that partial melting began in the garnet stability field and continued into the spinel stability field; they represent ~22-26% melting under various pressure conditions.

High anorthite (An) content of plagioclase as well as Nb depleted whole-rock composition of mafic cumulates and isotropic gabbros indicate furthermore that the crustal rocks of the Pozanti-Karsanti ophiolite formed from a melt that has been produced by melting of depleted source. This melt is thought to have enriched in light REE and fluid mobile elements that released from the subducting slab during the subduction of Neotethyan Ocean.

Therefore the Pozanti-Karsanti ophiolite displays a very complex crystallisation history compared to other ophiolites in the taurus mountains.

Magmatic petrology – from melt to rock

MAG-P06

Basalts and basanites of the Heldburger Gangschar, Thuringia

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The Heldburger Gangschar in the geographic center of Germany is part of the Miocene Central European Volcanic Province. It consists mostly of veins of mafic rocks extending in SSW-NNE direction and a few mafic diatremes, plus one single phonolite diatreme (Heldburg phonolite). Outcrops of the igneous products of this period are sparse. We present a petrographic overview of these mafic volcanic rocks from southern Thuringia, including findings of loose rocks from formerly known locations.

In general, the rock type is basanite or olivine-alkali-basalt. Phenocrysts of olivine and clinopyroxene are omnipresent. Igneous chromium spinel inclusions in olivine are absent in the observed specimens, pointing to some initial differentiation before the melts reached the surface level or to rather shallow melting depths. The basaltoids, although similar in their general appearance, show a very wide range in #Mg in olivine from 0.90 to 0.60, exceeding the previously known limits from this region at both ends. Ca p.f.u. in olivine increases from about zero at #Mg90 to about 0.01 at #Mg 70 and then stays at a plateau value.

The Heldburger Gangschar basaltoids show a large variety of interactions with mantle and crust derived wallrocks, e.g. olvine rims on orthopyroxene, magnetite rims on xenocrystic chromium spinel, diopside coronas around partially molten quartz grains. The clinopyroxene phenocrysts show clear evidence of partial equilibration and open system behaviour like opx dissolution lamellae, marginal dissolution and overgrowths, or internal disaggregation with formation of sieve textures.

Locally, felsic inclusions are found intermingled with mafic host melts that represent apatite-rich normally phonolitic compositions and seem to indicate local differentiation in sub-systems in addition to the Heldburg phonolite.

MAG-P07

Niobium minerals in the Heldburg phonolite, Thuringia

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Nb is geochemically enriched in highly evolved alkaline melts. We report a suite of Nb-rich minerals from the Heldburg phonolite, southern Thuringia, Germany. Texturally they appear to be either autocrysts from parts of this magmatic system different from the outcropping phonolite, of reaction products between these primary minerals and the phonolitic melt or of phenocrysts and groundmass phases formed from the phonolite melt.

Our documentation is based on electron beam microprobe chemistry and optical microscopy. Some mineral phases are non-ambiguously identified by these means, while other identifications remain doubtful. Some chemical compositions do not seem to fit with any approved mineral species.

The most widespread Nb mineral in the Heldburg phonolite is a late stage groundmass phase with the principal composition CaNbO_3 , pointing to the perovskite-group mineral latrappite. It is present as scattered grains in almost any thin section of this rock, but the grain diameters rarely exceed 1 μm . Among the larger Nb minerals (up to several 100 μm) the aeschynite group is prevalent. Crystals show sector zoning and belong to the nioboaeschynite subgroup. Other crystals with stoichiometry according to the aeschynite group have compositions that would suggest non-approved names like “Ti-vigezzite” or “Si-bearing Ti-vigezzite” and require further study.

Other Nb phases in the Heldburg phonolite with stoichiometry identical to established mineral systematics include members of the pyrochlore group (Fluorcalciopyrochlore), Na-dominated minerals with perovskite affinity (identical or polymorphic with Lueshit, Isolueshit, Paoloabibit, Natroniobit), or Columbite-(Mn). Some further minerals show element ratios not in accordance with any of the known Nb mineral groups. In some cases Nb minerals occur as intergrowths with other minerals uncommon for the host rock, such as magnetite-jacobsite solid solutions or bastnaesite-like phases, and with zircon.

There is strong evidence that the Nb minerals described here have formed within the Heldburg phonolite magmatic system (euhedral shape), but at least some of them were not stable anymore in contact with the phonolite melt at the time of volcanic eruption. It is to be answered from what kinds of melt the primary Nb-phases crystallized and where within the magmatic system this happened.

MAG-P08

Phonolites in the mantle?

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The Heldburg Phonolite, Thüringen, is well known for containing spinel lherzolite xenoliths and is thought to have originated from the upper mantle (Irving and Price, 1981). Thermobarometry of amphibole and clinopyroxene phenocrysts yielded P-T ranges of 4-10 kbar and 850-950°C indicating that the Heldburg phonolite must have originated from at least the lower crust by fractionation of a basanite parent melt (Grant et al, 2013). The Heldburg Phonolite is therefore an example of a “high-pressure” phonolite and the question of how phonolites could metasomatise the lower crust and upper mantle is explored here.

Highly fragmented spinel lherzolite and gabbro-norite xenoliths within the Heldburg Phonoliteeldburg phonolites have reacted with the melt to form rims of phlogopite + diopside around olivine and either amphibole + phlogopite or amphibole + diopside around orthopyroxene. These reaction rim assemblages have been recreated in piston cylinder experiments at 10-14 kbar and only form at temperatures of 900-950°C and high melt water contents (>4 wt.% H₂O). Reaction rim growth rates were measured over a range of conditions and were used to calculate residence times of olivine xenocrysts in the Heldburg Phonolite. Residence times were in the order of weeks to several months.

Upper mantle xenoliths from a range of locations contain hydrous veins of phlogopite + amphibole + diopside, yet the metasomatic agent has not been identified. We propose that percolative fractional crystallization of basanite melts in the upper mantle may locally lead to the production of phonolite melts. These will react with olivine and orthopyroxene dominated mafic rocks to form a metasomatic assemblage of phlogopite + amphibole + diopside. Residual glasses associated with hydrous veins have compositions that plot within or close to the phonolite phase field. Although subordinate to basanites, evolved melts may play an important role in alkali metasomatism.

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MAG-P09

The influence of Iron on Sulfur speciation in slab melts

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Sulfur (S) occurs in silicate melts as either sulfide (S^{2-}) or sulfate (S^{6+}) [1]. Spectroscopic studies revealed that S^{6+} is incorporated as SO_4^{2-} within the melt structure and S^{2-} as HS^-/H_2S and/or FeS depending on the iron (Fe) content of the melt. The ratio of Fe/S in the melt also has an influence on the S^{6+}/S^{2-} equilibrium as a function of the redox conditions in the system which is determined by the prevailing oxygen fugacity (fO_2). In Fe-free to Fe-poor systems (with Fe/S up to ~2.6) the S^{6+}/S^{2-} equilibrium is at ~1.5 log units lower fO_2 than observed for Fe-rich basaltic to andesitic systems [2]. This shift in the S^{6+}/S^{2-} equilibrium implicates a larger range of stability for SO_4^{2-} in Fe-poor melts and therefore a high potential of SO_4^{2-} in slab melts to oxidise the mantle wedge in subduction zones. However, a systematic shift of the S^{6+}/S^{2-} equilibrium with increasing Fe/S ratio has not been observed directly, yet. Here we present additional experimental results on S speciation in slab melts systematically doped with Fe in order to better understand the influence of Fe on S-speciation.

S-bearing hydrous glasses with a trondhjemitic model slab melt composition [3] and systematically varied Fe/S ratios ranging from Fe/S = 0 to 20 have been synthesised. The experiments have been performed at 3 GPa and 900 °C to 1000 °C in a Belt Apparatus at intrinsic fO_2 ranging from $fO_2 = QFM-1.5$ to QFM depending on run T and aH_2O in the melt. Preliminary Raman measurements indicate the existence of the intermediate sulfur species S_3^- in addition to SO_4^{2-} , HS^-/H_2S in the Fe-free glasses. Raman spectra also confirm that with increasing Fe/S additional Raman bands corresponding to Fe-S bonds occur, while the intensity of Raman bands related to H-S species, S_3^- and S^{6+} decreases. This confirms the preference of S to bond with Fe as S^{2-} in silicate melts at a constant $fO_2 \sim QFM$ as proposed by [2]. The presence of S_3^- in slab melts has interesting consequences on the S geochemistry and metal transport in subduction zones as S_3^- will enhance the release of sulfur from the FeS-bearing oceanic crust and should also exhibit a high affinity for Au and similar metals (Cu, Pt) [4].

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MAG-P10

Trace element partitioning between spinel and silicate melt – the effect of oxygen fugacity and spinel composition

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Spinel is a common accessory mineral that occurs in a variety of geological settings such as evolved basaltic magmas or chromitites. It may take up large amounts of certain trace elements such as HFSE or (redox sensitive) transition metals, but the trace element partitioning of these elements is not yet well constrained. Furthermore, (Cr)-spinel is often associated with economically important platinum group element (PGE) deposits. Therefore the behavior of PGE in a spinel-melt systems is of particular interest.

We present new partition coefficients between spinel and silicate melt for a range of trace elements (e.g., transition metals, high field strength elements (HFSE) and the platinum group elements Pt and Rh).

Experimental methods: Experiments were performed in an 1 atmosphere gas mixing furnace at temperatures between 1200 and 1430 °C and oxygen fugacities ranging from log -12 to log -0.7. Starting materials consist of glasses in the system (Cr₂O₃-FeO)-CaO-MgO-Al₂O₃-TiO₂-SiO₂ with trace elements added from standard solutions. The samples are suspended from a Pt or Pt-Rh wire in the furnace and equilibrated at the relevant temperatures and oxygen fugacities. Major elements were analysed by electron microprobe, and trace elements were analysed by Laser Ablation ICPMS. On one sample with high Pt and Rh concentration in the spinels, a TEM study was performed to investigate the presence of metallic (nano-) nuggets or platinum group element minerals as inclusions in the spinel.

Results: The Fe²⁺/Mg²⁺ ratio in spinel has little effect on trace element partitioning, but the concentration of Al³⁺, Fe³⁺ and Cr³⁺ appears to have a large effect on partitioning of Ti, Sc and the HFSE; although these elements are incompatible in all spinels, Cr and Fe³⁺ rich spinels generally have much higher partition coefficients than Al rich spinels. Partitioning of the multivalent elements V and Mo depends on fO₂, both D_V and D_{Mo} decrease with increasing fO₂.

Determining the partition coefficients of platinum group elements is complicated due to their tendency to form nano-scale nuggets in silicate melts, and possibly also in crystals. However, a TEM study for a high fO₂ sample shows no inclusions in spinel suggesting that the measured high concentrations (and high D's) in our experiments are correct. Partition coefficients for Pt and Rh appear to decrease with increasing FeO concentrations. D_{Rh} also appears to increase with increasing fO₂.

MAG-P11

The haplogranite system as a geobarometer for highly evolved melts – experimental investigations on the effect of Anorthite

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The determination of pressures in magmatic systems is a petrological key challenge. It is known that the position of the cotectic curves separating the primary fields of quartz and feldspar(s) in the haplogranite system is pressure dependent. The presence of normative anorthite (An, $\text{CaAl}_2\text{Si}_2\text{O}_8$) in the melt however will shift the position of the cotectic curves (e.g. James and Hamilton 1969). In this study we present experimental data on the effect of pressure on the position of the quartz-feldspar cotectic curves in rhyolitic systems with relevant Ca-, Fe- and Ti-contents.

Crystallization experiments in Fe-, Ca- and Ti-bearing rhyolitic systems have been performed at 200 MPa and 500 MPa in a temperature range of 790 to 1050°C to calibrate the positions of cotectic compositions in natural rhyolitic systems. The starting materials were pre-hydrated glasses with various proportions of Qz, Ab and Or components. Phase diagrams for both pressure levels are currently established for the following conditions: glass containing (A) 1.2 wt% H_2O , 7 wt% An, 2.5 wt% Fe and 0.4 wt% Ti (B) 3 wt% H_2O 3.5 wt% An, 1 wt% Fe and 0.2 wt% Ti.

Results show that the eutectic composition is shifted towards the Qz-Or sideline. This indicates that the approach proposed by Blundy and Cashman (2001) to account for the effect of An content on the position of the cotectic lines in the system Qz-Ab-Or is qualitatively correct, although the shift of the eutectic point is more pronounced than predicted by Blundy and Cashman (2001).

The Ca, Fe and Ti concentrations of the rhyolitic compositions were chosen so that the results can be applied to the Snake River Plain rhyolites. Using the compositions of glasses from selected eruptive products in which quartz and feldspar do co-exist, the preliminary experimental results are applied to constrain the pressure prevailing prior to eruption with particular attention to rhyolites collected from Kimberley Drill Core (project Hotspot). Magma storage conditions in the pressure range 250-400 MPa determined experimentally for the Indian Batt Rhyolite, Bruneau-Jarbidge eruptive center, are confirmed by the projection of the glass compositions in the Qz-Ab-Or system.

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MAG-P12

The late-stage evolution of basalts in the Bushveld Complex

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The Bushveld complex, a layered intrusion that covers ca. 65.000 km² in South Africa, is made up of a 7-9 km thick cumulate sequence containing major mineral resources. The upper 2 km of the intrusion (Upper Zone) is known for the abundance of Fe-Ti-V±P ore deposits. They form after the appearance of liquidus magnetite and ilmenite ± apatite in the crystallization sequence but the exact processes for their origin are still debated. Critical to bring new constraints to this issue is to get a better understanding of the evolution of late-stage residual liquids and the potential tapping of magma out of the main magma chamber.

We performed crystallization experiments on various estimates of parental magmas to the 'Upper Zone and Upper Main Zone' (UUMZ) of the Bushveld Complex. The base of this cumulate sequence is characterized by the occurrence of a 2-3 m thick layer of orthopyroxenite cumulate known as the 'Pyroxenite Marker'. It is considered to indicate the last influx of magma (ferrobasaltic composition) in the Bushveld magma chamber.

The main purpose of this project is to constrain phase equilibria and the liquid line of descent during the evolution from evolved basalt to rhyolite. We also aim at constraining the composition of the last replenishment after the Pyroxenite Marker. Experiments are run at 2 kbar on selected compositions proposed in the literature, varying essentially in SiO₂, CaO and FeO_{tot} contents. Liquidus temperatures for these compositions are in the range of 1190-1230°C (MELTS calculations (Ghiorso & Sack, 1995)).

The experimental data (particularly the pyroxene compositions and stability field) are compared with the continuous record of stratigraphic evolution in drill-cores (*Bierkraal* and *Bellevue*). The stability field of the pyroxenes is very sensitive to small compositional differences in the starting materials producing a variety of pyroxenes from orthopyroxene, pigeonite, sub-calcic augite to augite.

Experiments on more evolved compositions will be run in the near future and are expected to constrain the timing for the saturation of Fe-Ti oxides and apatite, which will be useful to understand the formation of Fe-Ti-V±P-rich layers and the very last stages of the liquid line of descent evolving to rhyolitic composition.

MAG-P13

Basic-granitic magma interaction in the dike complex (Western Sangilen)

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Two types of magmatism were occurred in Western Sangilen in Early Ordovician time: mantle and crustal. The results of mantle magmatism are formation of large basic intrusions (Bashkymugur, Bayankol, Erzin) and HT/LP metamorphism occurrence. Due to crustal magmatism a lot of A- and S- types granitoid massives were formed. The relationship between basic and acid magmatism was not established definitely in terms of time, geochemistry and petrology.

The presence of the synplutonic and mingling dikes containing both acid and basic parts indicates coexistence of contrasting composition magmas simultaneously.

Seventeen combined and synplutonic dikes on three areas of Western Sangilen (SE Tyva) were investigated.

According to the results of petrographic, geo- and petrochemical data some features and scales of basic-acid magmas interaction were recognized.

In the Erzin basic massif area mafic magma intruded autochthonous granitoids and caused its melting. Newly formed acid magma intruded already crystallized basic rock forming synplutonic dikes. The result of such kind of interaction is increasing of the amount of potassium and LIL elements in mafic rocks. The composition of the rock-forming minerals was not affected so we can suggest a minor minerals and intergranular mass changes.

Next two objects are synplutonic dikes in the Matut granite massif and combined, mingling dikes among metamorphic rocks. The composition of basic and acid parts is similar for both objects.

Synplutonic dikes intruded Matut granite massif show large (up to 1 m) interaction zones between acid and basic magmas. The composition of both whole rock and rock-forming minerals in granites were changed, diorite alkalinity increased, fine-grained amphibole rims on the contact formed.

Combined (mingling) dikes intruded host metamorphic rocks. They are formed by simultaneous injection of two melts of a contrast composition (basic and acid). Due to short time of interaction and quite small contact area the depth of interaction zone is about few centimeters. In the contact zone amount of water-bearing minerals decreases and composition of plagioclase changes.

The study allows to answer questions about the history of the region formation and to be a natural illustration for some theoretical mingling models.

Magmatic petrology – from melt to rock

MAG-P14

From Rock to Magma; Frictional Melting in the Conduit

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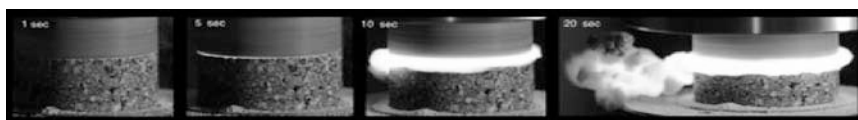
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The frequent, and as yet unpredictable, transition from effusive to explosive volcanic behaviour is common to active composite volcanoes, yet our understanding of the processes that control this evolution is poor. The rheology of magma, dictated by its composition, porosity and crystallinity, is integral to eruption behaviour and during ascent, magma behaves increasingly like a rock. The rock-like behaviour of magma on short timescales provides exceptionally dynamic conditions that favour strain localisation and failure. Seismicity released by this process can be mimicked by damage accumulation that releases acoustic signals on the laboratory scale, showing that the failure of magma is intrinsically strain-rate dependent.

This character aids the development of shear zones in the conduit, which rupture seismogenically, producing fault surfaces that control the last hundreds of meters of ascent by frictional slip. High-velocity rotary shear experiments demonstrate that at rock-rock interfaces, mechanical work induces comminution of asperities and heating which may induce melting and formation of pseudotachylyte. The viscosity of the melt, so generated, controls the subsequent lubrication or resistance to slip along the fault plane thanks to its non-Newtonian rheology. The silicate melt reveals a strong velocity-dependence and yields a tendency for extremely unstable slip thanks to its pivotal position with regard to the glass transition. This thermo-kinetic transition bestows the viscoelastic melt with the ability to either flow or fracture, with potentially drastic consequences for frictional slip dynamics.

In the conduit of dome-building volcanoes, the fracture and slip processes are further complicated; slip-rate along the conduit margin fluctuates. The shear-thinning frictional melt then acts as an important feedback mechanism on the slip plane, accentuating stick-slip cycles that bring the magma, step-wise, to the surface accompanied by characteristic repetitive seismic events. The bulk composition, mineralogy and glass content of the magma all influence frictional behaviour, which supersedes buoyancy as the controlling factor in magma ascent; hence it is of vital importance to recognise the frictional behaviour of volcanic rocks and magmas to understand the continuation of an eruption.



MOR-T01

Eclogite-facies metasomatism in the Monviso ophiolite (Italy) records long-range, channelized transport of fluids along the subduction shear zone

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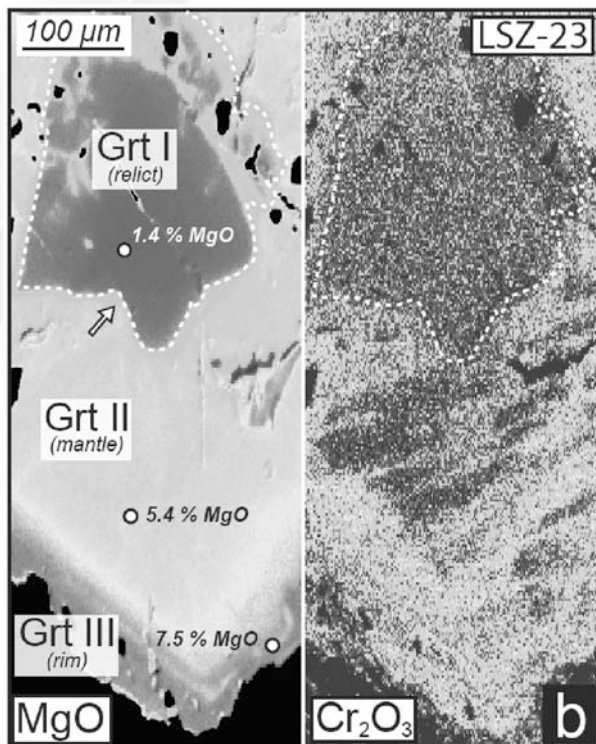
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The Monviso ophiolite Lago Superiore Unit (Western Alps; LSU) constitutes a well-preserved, almost continuous fragment of upper oceanic lithosphere subducted down to ca. 80 km (between 50 and 40 Ma) and later exhumed along the subduction interface. The LSU is made of eclogitized mafic crust (associated with minor calcschist lenses) overlying a metagabbroic body, with a km-thick serpentinite sole. This section is cut by two 10 to 100m thick eclogite-facies shear zones, found at the boundary between basalts and gabbros, and between gabbros and serpentinites (Lower Shear Zone: LSZ). Fragments of mylonitic gabbroic eclogites and marbles were dragged and dismembered within serpentinite schists along the LSZ during eclogite-facies deformation. Metasomatic rinds formed on these eclogite fragments at the contact with the surrounding antigorite schists during lawsonite-eclogite facies metamorphism testify to prominent fluid-rock interaction along with deformation. We present new petrological and geochemical data on hydrous eclogites (talc-, chlorite-, lawsonite- and phengite-bearing eclogites) and serpentinite-derived ultramafic schists from block rinds. Bulk-rock compositions, *in situ* LA-ICP-MS analysis and X-ray Cr/Mg maps of garnet demonstrate that these samples underwent significant Mg, Cr, Ni, $\pm$ Large Ion Lithophile Element enrichment and a marked depletion in Fe and V during eclogite-facies metasomatism. Ionprobe measurements of boron isotopic signature of phengite ($B=80\text{--}130\text{ }\mu\text{g/g}$; $d^{11}B = 0$ to $+7\text{‰}$), clinopyroxene and chlorite ($B_{11}B = -7$ to $+4\text{‰}$) and antigorite ($B=20\text{--}30\text{ }\mu\text{g/g}$; $d^{11}B = -4$ to 0‰) suggest that metasomatic block rinds formed during interaction with antigorite-derived fluids, probably related to antigorite breakdown. These compositional patterns point to a fluid-mediated element transfer along with deformation, originating from the surrounding serpentinite (with contributions from oceanic crust and/or sedimentary material). Antigorite breakdown, occurring 15-20 km deeper than the maximum depth reached by these eclogites, could have provided significant amounts of fluid promoting extensive fluid/rock interaction. We therefore hypothesize that the LSZ witnesses the existence of a highly anisotropic, subduction-parallel channelized fluid

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migration pathway within the subducted oceanic lithosphere under eclogite facies conditions, possibly in relation with transient unstable slip events rooted within LSZ serpentinites



MOR-T02

Jadeitite and jadeite-bearing rocks from the Rio San Juan Complex (RSJC), Dominican Republic – the impact of zircon

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Serpentinite mélanges in the RSJC host an array of tectonic blocks (blueschist, eclogite, orthogneiss, etc.) and a variety of quartz-free and quartz-bearing jadeitites and jadeite-rich rocks. Most jadeite-rich rocks occur as loose blocks or as boulders in river beds; however, quartz-bearing jadeitites also form layers or veins in lawsonite blueschists. This rock association is extremely rare and allows contact relationships between jadeitite and host rock to be studied. We have studied the geochronological, geochemical and oxygen isotope properties of zircon from a quartz-bearing jadeitite layer and its concordant host blueschist.

Zircon grains separated from the jadeitite layer are either unzoned or exhibit an irregular to pronounced oscillatory zoning pattern with both dark and bright domains under cathodoluminescence (CL). CL-dark zircon domains are in general oscillatory zoned and reveal an age of 117.1 ± 0.9 Ma (SHRIMP U/Pb) and a $\delta^{18}\text{O}(\text{Zrc})$ value of $5.4 \pm 0.4\text{‰}$ (IMS-1280). In contrast, the CL-bright zircon domains are younger (77.6 ± 1.3 Ma) and enriched in ^{18}O ($\delta^{18}\text{O}(\text{Zrc}) = 6.3 \pm 0.8\text{‰}$) compared to the CL-dark zircon domains. REE patterns of CL-dark and CL-bright domains differ significantly. Zircon grains from the jadeitite-hosting blueschist are texturally homogeneous and oscillatory or patchy zoned. They are slightly younger (113.6 ± 1.1 Ma) than the CL-dark zircon domains of the jadeitite layer, but possess, within error, an identical oxygen isotope composition ($\delta^{18}\text{O}(\text{Zrc}) = 5.6 \pm 0.6\text{‰}$).

The $\delta^{18}\text{O}$ values and geochemical patterns of both the zircon from the CL-dark zircon domains of the jadeitite layer and zircon separated from the blueschist are similar to values and patterns of igneous zircon from oceanic crust ($\delta^{18}\text{O}(\text{Zrn}) = 5.2 \pm 0.5\text{‰}$; Grimes et al., 2011, Contrib. Mineral. Petr. 161:13-33). Although jadeitites are often believed to have formed by direct crystallization from a HP aqueous fluid, in this example the CL-dark zircon domains are best interpreted to be igneous in origin, either representing remnants of a metasomatically altered protolith or xenocrysts. The CL-bright zircon domains in the jadeitite layer exhibit explicit geochemical features of metamorphic overgrowth and/or replacement and could either have formed contemporaneously with jadeite or reflect a later metamorphic event.

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MOR-T03

New age constraints for the development of the Münchberg Massif

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The Münchberg Massif is a classical area for the Variscan orogeny in Central Europe. It consists of an inverted nappe pile, with the Hangendseries (dominantly banded amphibolites with eclogite relicts and pegmatoids, representing decompression melts) at the top, underlain by the Liegendseries (metagranitoids), the Randamphibolite, the greenschist facies Prasinite-Phyllite-Series (including metagabbro), and the Randschieferseries (Paleozoic clastic sediments). Available age constraints indicate that HP metamorphism in the Hangendseries occurred near 395-380 Ma (Gebauer & Grünenfelder 1979, Stosch & Lugmair 1990), followed by deformation, nappe stacking, exhumation and cooling, continuing down to ~365 Ma (Kreuzer et al. 1989, Hammerschmidt & Franz 1992). Magmatic protolith ages as well as the stacking-related deformation history were up to now mainly enigmatic.

Here we present data for the magmatic protoliths for all series, based on zircon U-Pb LA-ICP-MS ages and crystallization and deformation ages based on Rb-Sr mineral isochrons for the pegmatoids, metagranitoids, and mylonitized metasediments. The main results are that the pegmatoids within the Hangendseries crystallized over a range of ~20 Ma from 400 to 380 Ma, confirming the previously determined age of HP metamorphism, and consistent with the known P-T-evolution (cf. Liebscher et al. 2007). The zircon U-Pb age spectrum for the banded amphibolites indicate a magmatic arc environment, active between ~700 Ma and ~480 Ma, an age pattern which is similarly seen in the orthogneisses of the Liegendserie. Both, the Randamphibolit and the metagabbro from the Prasinite-Phyllite Series yielded identical protolith crystallization ages near 400 Ma, suggesting that these units are the result of mafic magmatism in the same ocean basin. Metamorphic overprints, related to nappe stacking and tectonic transport, are recorded between 370 and 380 Ma (Liegend- and Hangendseries) and ~ 363 Ma (Prasinite-Phyllite Series).

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Metamorphic rocks – petrology, geochemistry, geochronology

MOR-T04

Evidence from the Acasta Gneisses for strongly depleted Hadean mantle components

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The isotope compositions of Earth's oldest rocks constrain its early crust-mantle differentiation history, as well as the proportions of juvenile and recycled components in Archean and Hadean crust [e.g., 1-4]. However, zircon populations used to monitor Hf isotopes can be biased by metamorphism, melting, weathering, and sedimentary transport. Hence, the degree of early mantle depletion remains poorly defined. To help resolve this issue, we investigated the Lu-Hf and Sm-Nd systematics of the Acasta Gneisses (NWT, Canada). Previous studies identified zircon grains from enriched sources [e.g., 1, 5-6], but do not directly trace the extent of mantle depletion. The rocks have also undergone several metamorphic episodes and some of the banded gneisses comprise multiple magmatic precursors of different age that have been juxtaposed by folding and shearing. Hence, it is debatable whether zircon ages should be used to calculate initial ϵNd values of rocks, and whether linear trends on Sm-Nd isochron diagrams represent meaningful geologic ages or mixing [7-10, 12-13]. We avoid some of these issues by targeting sets of genetically related samples, i.e., either rocks evolved from a single magmatic source or banded gneisses having layers that were isotopically re-equilibrated before 3.5 Ga. This approach revealed a series of gneiss layers that have been closed to Sm and Nd since 4.01 ± 0.06 Ga [11]. These samples yield ϵHf and ϵNd (4 Ga) of ca. +6 and +2, suggesting the long-term existence of a strongly depleted Hadean mantle source [11]. We are currently focusing on internal isochrons of individual layers to test whether the Sm-Nd and Lu-Hf systems have also remained closed on the mineral scale and to place constraints on the thermal history of these rocks.

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Metamorphic rocks – petrology, geochemistry, geochronology

MOR-T05

Ardennite-(V) within a high-*P/T* metamorphic conglomerate near Vitolište in the westernmost Vardar zone, Republic of Macedonia (FYROM)

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Ardennite with the general formula $^{VII}(Mn^{2+}, Ca, Mg)_2 ^{VI}(Mn^{2+})_2 ^{VI}[(Al, Fe^{3+})_2(Al)_2(Al, Mg, Mn^{3+}, Fe^{3+}, Cu^{2+})_2]^{IV}[(V^{5+}, As^{5+}, P, Si, Al)O_4](SiO_4)_2Si_3O_{10}(OH, O)_6$ typically occurs in quartz veins or in V- and/or As-enriched ferri-manganese metasediments metamorphosed at low to high pressures and temperatures of ~300 to 550 °C (Barresi et al. 2007). In the westernmost Vardar zone near Vitolište (Republic of Macedonia), a metamorphic Upper Cretaceous conglomerate contains former clasts of quartzite, quartz-muscovite schist, and reddish Mn-Fe-(V-As)-rich rocks. The latter show the paragenesis hematite + quartz + ardennite-(V) + epidote/piemontite + pyrophyllite + phengite + sudoite + cookeite + lawsonite + tourmaline + apatite. Furthermore, epidote contains inclusions of pumpellyite, titanite, albite, apatite and quartz. Many epidote grains are partially transformed to piemontite. The boundaries between clasts and matrix are blurred due to the effects of deformation and metamorphism.

Ardennite-(V) shows low contents of As (< 0.048 cpfu) and its composition essentially follows the exchange vector $(Si+Al+P)_{-1}V$, with V contents between 0.347 and 0.955 cpfu, P from 0.008 to 0.091 cpfu, Si from 0.015 to 0.469 cpfu and Al from 0 to 0.117 cpfu. Sudoite has the composition $^{VI}Al_{2.000}(^{IV}Al_{0.877-0.905}Si_{3.095-3.123}O_{10}(OH)_2(Mg_{1.770-1.884}Fe^{2+}_{0.131-0.165}Mn^{2+}_{0.046-0.065}Ti_{0.001-0.004}^{VI}Al_{0.904-0.961})(OH)_6$ and is often intergrown with potassic white mica that has relict phengitic cores (3.45-3.50 cpfu Si) rimmed by muscovite. Cookeite has the composition $^{VI}Al_{2.000}(Si_{3.098-3.121}^{IV}Al_{0.902-0.879}O_{10}(OH)_2(^{VI}Al_{1.851-1.872}Fe^{3+}_{0.031-0.045}Mn^{3+}_{0.011-0.012}Mg_{0.053-0.065}Ca_{0.017-0.023}Li_{1.000})(OH)_6$ and is often associated with pyrophyllite. Metamorphic *P-T* conditions can be estimated to 0.7-0.8 GPa and 320-350 °C.

The bulk-rock analysis of a boulder rich in ardennite-(V) shows 45 wt% SiO₂, 3.1 wt% TiO₂, 16.0 wt% Al₂O₃, 14.0 wt% Fe₂O₃, 7.4 wt% MnO, 2.2 wt% MgO, 2.0 wt% CaO, 0.1 wt% Na₂O, 0.3 wt% K₂O, 0.5 wt% P₂O₅ and 1.9 wt% V₂O₅. The Fe-Mn-V-rich gravel may represent intensively weathered detritus of an orthomagmatic V-bearing Fe-Ti oxide deposit.

Barresi et al. (2007) Eur J Mineral 19: 581-587

Metamorphic rocks – petrology, geochemistry, geochronology

MOR-P01

Gneisses and charnockites related with UHT metamorphism in Angara-Kan block (Siberian Craton, Russia)

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The Angara-Kan granulite-gneiss block (Yenisey Ridge) is one of the main basements uplift within the south-western margin of the Siberian Craton. Gneisses and charnockites related with UHT metamorphism have been discovered in the middle part of Angara-Kan block in the ore field of Kuzeevo gold deposit. They are represented by orthopyroxene and garnet-orthopyroxene gneisses containing assemblage Opx+Sill and charnockites with high-Al orthopyroxene. Granulites containing UHT assemblages were found. Mineral assemblages are: Opx-1 ($\text{Al}_2\text{O}_3=6,7-7,3$ wt. %) + Pl (An=40-43 %) + Kfs + Qtz + Ilm and Grt ($\text{Alm}_{54-56}\text{Py}_{37-38}\text{Grs}_4\text{Sp}_{54}$) + Opx-1 ($\text{Al}_2\text{O}_3=7,6-8,6$ wt. %) + Pl (An=38-41 %) + Kfs + Qtz + Ilm. Assemblage Opx+Sill is located along dislocation zones composed mostly of Ti-biotite (5.2 wt.% TiO_2), cordierite, magnetite and spinel. Orthopyroxene form intergrowth with sillimanite (Opx-2) and rims around biotite (Opx-3), both of them contain 5.5-6 wt. % Al_2O_3 . Charnockites consist of Qtz, Pl, Kfs (perthite) and Opx (Al_2O_3 8-9.4 wt.%). They also contain biotite-rich segregations with Opx+Sill assemblage. Formation of biotite-rich zones can be related with crystallization of partial melt on cooling stage. Crystallization of Crd and Opx-3 can occur at near isothermal decompression stage according to petrogenetic grid (Harley, 2008). On the basis of content of Al_2O_3 in orthopyroxene we suggest temperature of Opx-1 formation around 1000°C, Opx-2 and 3 - 870-900°C (Harley, Motoyoshi, 2000). This temperature correlates with estimates obtained by mineralogical geothermometers. Geobarometers show 7.9 - 10.5 kbar. This PT - data are in a good agreement with petrogenetic grid for KFMAS system (Harley, 2008).

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Metamorphic rocks – petrology, geochemistry, geochronology

MOR-P02

Metamorphic evolution of peridotites from the Schwarzwald: evidence from mineral trace element data and P-T pseudosections

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Peridotites occur as small, isolated lenses in migmatitic paragneisses of the Variscan Schwarzwald, Germany. We studied samples from four localities, i.e., one garnet-spinel peridotite from the Central Schwarzwald Gneiss Complex and three spinel peridotites from the Central and the Southern Schwarzwald Gneiss Complex. All samples are characterized by a medium to fine grained, massive texture, with relict porphyroblastic olivine (X_{Fo} : 0.89-0.90), orthopyroxene (X_{Mg} : 0.89-0.90), clinopyroxene (X_{Mg} : 0.93-0.94), spinel (X_{Mg} : 0.69-0.78), and occasionally chromite (X_{Mg} : 0.53-0.61), pargasitic amphibole (X_{Mg} : 0.88-0.93), and garnet (X_{Mg} : 0.73-0.74). Garnet is rimmed by an Opx-Cpx-Spl kelyphite. The relict porphyroblastic phases are surrounded by fine grained serpentine intergrown with minor chlorite.

High Sc/Zr-ratios and Mn-contents (>1200 ppm) of olivine indicate that all peridotites originate from the spinel-peridotite-field. A variable metasomatic overprint is reflected by high Li-contents of both olivine (1-9 ppm) and clinopyroxene (8-16 ppm), which are positively correlated with the modal amount of amphibole. Calculated pseudosections in the NCFMASH system suggest that the spinel-bearing peridotites equilibrated at pressures of 9.5-13.5 kbar, whereas the garnet-spinel peridotite formed at slightly higher pressures of 13.5-14.5 kbar. High temperatures of c. 980°C are estimated by the REE-in-two-pyroxene thermometer of Liang et al. (2013). Amphibolite facies re-equilibration at $P > 10$ kbar and temperatures of 695-745°C, as calculated from two-pyroxene-, Grt-Cpx, Grt-Opx-, and Ol-Spl-thermometry, affected all samples. The latter P-T data resemble those estimated by Kalt & Altherr (1996) for other peridotite occurrences in the Central Schwarzwald Gneiss Complex (i.e., 670-770°C, 14-18 kbar). Texturally late chlorite and serpentine formed at temperatures < 600°C, at still high pressures of > 10 kbar, suggesting that cooling was accompanied by only minor decompression.

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Metamorphic rocks – petrology, geochemistry, geochronology

MOR-P03

Petrologic and structural constraints on the late Variscan exhumation of lower crustal migmatitic gneisses of the Peterstal antiform (Central Schwarzwald, SW-Germany)

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The Central Schwarzwald Gneiss Complex (CSGC) is part of the Moldanubian Zone of the Variscan orogen. It originated during NW-SE convergence at c. 350-330 Ma, followed by extension and associated granite emplacement at c. 330-325 Ma (e.g. Krohe & Eisbacher, 1988). According to Kalt et al. (1994), HT-LP metamorphism (c. 730-780°C; 4-4.5 kbar) at c. 332 Ma affected the whole CSGC. Part of the paragneisses displays evidence for an earlier HP-granulite facies stage at ≥ 14 -18 kbar and 950-1010°C (Marschall et al., 2003).

The study area is located near Bad Peterstal. The migmatitic gneisses are regionally folded by the open, upright, and NNE-plunging Peterstal antiform. Main rock types are migmatitic Bt-Pl gneisses which are intercalated with minor Grt-Sil-Crd-bearing metapelites and rare amphibolite lenses. The observed mineral reaction history of the metapelites combined with geothermobarometry and calculated P-T pseudosections in the NCKFMASH-Ti system, point to a clockwise retrograde P-T evolution. Near-isothermal decompression from >11 kbar to 7-8 kbar at high temperatures of 800-900°C is evidenced by pseudomorphic replacement of kyanite (assemblage Ky-Fsp-Grt-Bt-Ilm-L) by sillimanite. These P-T estimates are substantiated by Grt-Bt and Ti-in-Bt thermometry, as well as GASP barometry. Subsequent cooling and decompression to 5-6 kbar and 600-700°C is reflected by the replacement of garnet by biotite (Grt-Bt-thermometry: 610-680°C). Mineral-melt interaction during cooling to subsolidus temperatures (<680°C) and further to c. 400°C, associated with decompression to 3-4 kbar, is indicated by the replacement of biotite by white mica and chlorite. This low-grade retrograde metamorphism is associated with extensive mylonitization of the rocks.

The observed retrograde metamorphic evolution of the paragneisses suggests late Variscan removal of mid- to upper crustal rocks and rapid exhumation of lower crustal gneisses. This exhumation was presumably triggered by updoming of the Peterstal antiform and concomitant detachment along shallow dipping top-to-E and top-to-W mylonitic to cataclastic shear zones on the limbs.

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Metamorphic rocks – petrology, geochemistry, geochronology

MOR-P04

Pressure-temperature evolution of a garnet-bearing metapelite from the northern Fichtelgebirge, Upper Palatinate

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A metapelite was studied, which was sampled 4 km north of the town of Selb. According to the geological map GMB Rehau 1:25000, this rock belongs to a Cambrian sequence. The metapelite contains mainly quartz, plagioclase, muscovite, chlorite, biotite, and several-mm sized garnet which is characterized by a foam structure in quartz with garnet plates forming an S in favourable sections. Such garnet porphyroblasts show a prograde concentric zonation from core to rim. Spessartine component decreases from 1 to 0.1 mol% and the pyrope component increases from 1 to 6 mol% towards the rim. Potassic mica shows a compositional range from 3.0-3.13 Si per formula unit. Staurolite formed at the margin of garnet and was found to be enclosed in rare andalusite. P-T pseudosections were calculated for the bulk-rock composition of the studied rock using the PERPLE_X computer software package, the metamorphic data set by Holland & Powell, solid-solution models for various mineral phases, and a haplogranitic melt model. The P-T pseudosections were contoured by various parameters such as the modal content of garnet and the pyrope content of this phase. From the pseudosections of the metapelite P-T conditions of 10 kbar and 520°C were derived for an early metamorphic stage which was followed by pressure release to 5.5 kbar at 550°C. The final metamorphic P-T conditions recorded by the studied rock are around 3.5 kbar and 580°C compatible with the presence of staurolite and andalusite and absence of melt. To understand the timing of this P-T evolution, U-Th-Pb dating was performed on monazite with the electron microprobe. A more or less continuous age spectrum between 270 and 360 Ma was obtained. At present, we tend to relate the late Devonian - early Carboniferous ages to the high-pressure metamorphism being the result of the collision of Laurussia and Gondwana. The subsequent exhumation might have occurred in the early to late Carboniferous. Afterwards, a contact metamorphism at 3.5 kbar and subsequent fluid-mediated processes occurred, triggered by the intrusion of granitic magmas nearby.

MOR-P05

Chemical composition of Ti-rich garnets as indicator for skarn zones from the contact aureole of Maronia pluton, western Thrace, Greece

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The Maronia skarn is located approximately 25 km west of Alexandroupolis in western Thrace, NE Greece. During the Tertiary, emplacement of a monzogabbroic intrusion into Mesozoic marbles of the Circum Rhodope Belt led to a unique melilitic skarn mineralisation.^[1]

We analysed the chemical composition of several garnet specimens (sampled over the entire contact zone between pluton and marble) by wavelength-dispersive X-ray spectrometry using a Cameca-SX 100 electron microprobe. Classification of skarn zones were done on the basis of associated mineral assemblages by field observations, macroscopic and microscopic studies. Even the chemical composition of garnet crystals points out the trend of skarn zonation. Identified skarn zones between the pluton and the marble are represented by following mineral assemblages:

(1) Cpx + Pl + Or + Ne + Ttn + Ap + Ti-Grt + Bt + Cal ± Wo ± Pct ± Tmp ± Ep ± Sdl

(2) Wo + Grs + Ti-Grt + Ves + Cal + Cpx + Phl ± Pct (± Ti-Zr-Cr-Grt)

(3) Cal + Wo + Grs + Mll + Ves + Prv ± Ti-Grt ± Cpx

The mineral chemistry of garnets corresponds to grossular-andradite solid solution series. Particularly noteworthy is the occurrence of Ti-Zr-Cr-rich garnet crystals which is possibly unique worldwide.^[2] In general, the chemical composition of Ti-rich garnets displays a decreasing Ti-content from monzogabbro to marble. Other crystals reveal zoning composed of an andradite-rich core surrounded by a grossular-rich rim (Fig. 1). This suggests that (i) the source of Ti is probably sphene, which is locally present as inclusion in garnet crystals, (ii) Ti has been transported by fluids from the pluton, and (iii) grossular is caused by the penetration of meteoric water.

Reaction of magmatic-hydrothermal fluids with the marbles resulted in extreme alkaline conditions and to crystallisation of the first known occurrences of nepheline (Ne) and sodalite (Sdl) in Greece.

Metamorphic rocks – petrology, geochemistry, geochronology

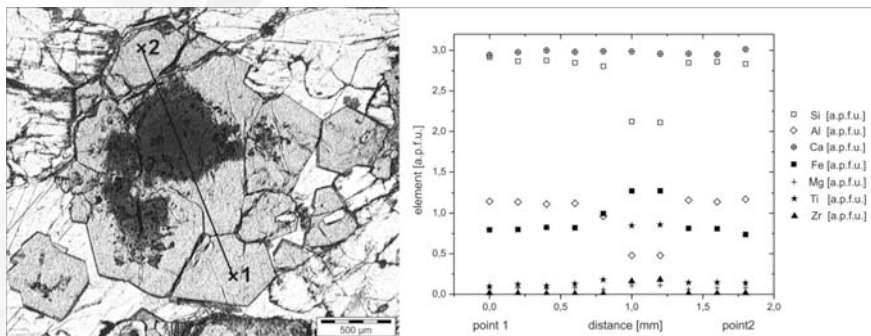


Fig. 1. Element distribution in a garnet crystal revealing higher Ti-, Zr- and Fe-contents and lower Si- and Al-contents in the core relative to the rim.

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²Katerinopoulou et al. (2009) A multi-analytical study of the crystal structure of unusual Ti-Zr-Cr-rich Andradite from the Maronia skarn, Rhodope massif, western Thrace, Greece. Miner Petrol, 95, 113-124

MOR-P06

Protolith determination of a metasedimentary series in the western Tauern Window

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Metamorphic rocks are the most important indicators for deciphering the evolution of an orogeny by determination of P-T conditions, time constraints and deformation conditions. However, the type of protolith may also contribute to a better understanding of the complete orogenic cycle. For meta-igneous rocks, this is well established, but for metasediments it is used less commonly.

Our study area is a classical, petrologically and in terms of geodynamic evolution well investigated area, the Pfitscher Joch in the Western Tauern Window. This unit was redefined by Veselá & Lammerer (2008) as the Pfitsch-Mörchner Basin and is a part of the Pennine nappe unit ('Untere Schieferhülle'), which represents the European basement during the Alpine orogeny. Likely during the Permian, sediments began to be deposited on this basement, which consists of Variscan granitoids ('Zentralgneis') and their Paleozoic country rocks. The post-Variscan, pre-Alpine sediments consist of conglomerates, a paleosol horizon (Barrientos & Selverstone 1987), clastic sediments, grading into quartzite with a conspicuous lazulite horizon (Morteani & Ackermann 1996) with crosscutting, but during Alpine metamorphism strongly folded and sheared tourmalinite veins, carbonate-rich sediments and marble. A striking feature of the whole area is the large-scale Greiner Shear Zone, a likely source of important fluid flow. Of special interest is a ~20 to 30 m thick series of tourmaline-feldspar-rich rocks with a gneissic appearance, interpreted as metavolcanics (Veselá & Lammerer 2008) intercalated in the metasediments. Here we present data based on detailed mapping, rock fabrics, mineral and whole rock chemistry with emphasis on tourmaline, B content and B isotopes. These data are consistent with the interpretation of the tourmaline-feldspar-rich rocks as metasediments.

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Meteorites and the early solar system – HED meteorites

MET-T01

Micro investigations of possible fluid-mineral interactions recorded in eucritic meteorites

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Eucrites are meteorites with basaltic compositions and textures that derive from the crust of a small differentiated asteroid, most probably 4-Vesta [1 and references therein]. These meteorites are generally assumed to be dry, because clear evidence for hydrous minerals such as in chondrites is lacking. The view of a dry asteroid 4-Vesta has been recently challenged by, e.g., the discovery of sub-curvilinear features on its surface [2] and high water contents of primitive melts [3]. Evidence for fluid-mineral interactions may be present in eucrites, but difficult to discern. Petrographic observations indicate that Fe enrichment veins in eucrites may be due to metasomatic overprints, but this is controversial [1, 4]. Here we present SEM-EBSD analyses of minerals in the eucrites Pasamonte and Juvinas to determine orientation relationships of clinopyroxenes across Fe-rich veins in order to distinguish contrasting theories. In case of a melt injection we may possibly see a change in orientation across this interface due to equilibration of the host with the melt. In contrast, a metasomatic or hydrous agent would not influence the crystal orientation and contacts should be very sharp [5]. In EBSD patterns across Fe enrichment veins in pyroxenes of Pasamonte and Juvinas, the orientation of the host diopside is the same on either side of the vein. The band contrast used as a measure of Kikuchi pattern quality is very high in these regions pointing to high crystallinity. The contact between the vein and the host diopside is sharp in acquired Euler orientation maps, which could support the fluid-mineral interaction model. However, a sharp interface made visible by EBSD does not necessarily imply a sharp contact on the atomic scale, as profiles can be below the spatial resolution of the technique. We will therefore also obtain high resolution mineralogical profiles across these interfaces by combined FIB-TEM analyses and results will be presented at the meeting.

Acknowledgements: We thank T. McCoy and the Smithsonian meteorite curation facility for making the Juvinas thin section 439-2 available.

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Meteorites and the early solar system – HED meteorites

MET-T02

Rare earth element signatures of meteoritic zircon

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Due to notable variations in bulk rock Zr concentrations among different meteorite classes the abundance of meteoritic zircon is highly variable. Despite this heterogeneity, crystalline zircon occurs as an accessory phase in lunar rocks, mesosiderites, and eucrites in particular, and rarely in some chondritic, Martian, and silicate-bearing IAB iron meteorites, as summarized in [1]. Similar to their variable abundances, the chemical characteristics of individual grains from various meteorite classes, i.e., lunar [2], eucrite [3-6], mesosiderite [7,8], Martian [9] and chondrite samples [7] are highly diverse with regard to their rare earth element (REE)- and other minor element abundances in particular. Chemical variations, i.e., in the overall REE abundances resulting in fractionated vs. flat REE patterns, and differences in the occurrence and magnitude of Ce- and Eu-anomalies are observed not only for zircon of distinct meteorite classes, but also for individual grains within single samples. However, with some exceptions, meteoritic zircon typically have superchondritic Zr/Hf values of 47 ± 8 (s.d., n=97; chondritic Zr/Hf = 32.9) with only rare exceptions, and exhibit fractionated REE patterns with a general depletion in LREE [1, and references therein]. Observed variations likely point to distinct formation conditions, (i) either due to variable chemical compositions of residual melt on a local scale, (ii) mixing of lithic fragments during impact processes since many samples are breccias, (iii) or resulted from thermal-metamorphic reactions. The degree of metamictization, co-crystallization with other REE-consuming phases such as phosphates, and elemental mobilization during impact-shock, if occurring at all, are probably of subordinate importance affecting the enrichments in LREE in particular [1,9].

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Meteorites and the early solar system – HED meteorites

MET-T03

Early dynamic mantle movements in young, semi-crystallized vesta

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Introduction: Petrologic and geochemical studies of diogenites offer various crystallization scenarios [1, 2] on the HED parent body. With their ultramafic composition, diogenites could either represent mantle residue after partial melting or constitute the product of fractional crystallization from molten magma, the latter occurring in magma chambers, multiple magma ponds or a larger scale magma ocean, or combinations of these scenarios. Structural analysis can reveal any post-crystallization deformation undergone by the diogenites, offering further constraints on dynamic processes occurring and conditions prevailing during cooling of the parent body. Our structural studies of olivine-rich diogenites indicate that the solidification of the HED parent body was not a static progression, but involved large-scale dynamic mantle movements, not unlike those experienced by the early Earth.

Methods: Structural analyses were performed on three olivine-rich diogenites: NWA 5784 (92% ol.), NWA 5480 (57% ol.) and MIL 07001 (13% ol.) applying electron backscatter diffraction (EBSD) to discover any lattice-preferred orientation (LPO) of the olivine crystals as indicator for the respective deformation mechanism. Numerical modeling [3] of the asteroidal solidification progression was performed based upon estimated Vestan parameters [3].

Results: The results confirm all three diogenites underwent post-crystallization, solid-state plastic deformation. For NWA 5480 and NWA 5784, this plastic deformation is clearly distinct from the axial compression [4] or shape-preferred orientation typically occurring in magma chambers or thick lava flows, ruling this deformation mechanism out. Numerical models [3] reveal a dynamically cooling asteroid with downwelling of dense, cool material at the base of the solidified lid into warmer softer material, dynamically inducing counter-upwelling of displaced lower-lying mantle. This model accommodates the temperature, strain and hydration constraints revealed by EBSD analysis.

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MET-T04

The lithophile trace elements in enstatite meteorites

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We report on trace element abundances from 50 enstatite meteorites including all the metamorphic types from EL3 to EL6, EH3 to EH6, impact melt breccias and impact melts, enstatite achondrites and aubrites. Our aim was first to evaluate the chemical diversity of these meteorites, and to constrain the behavior of lithophile trace element during the metamorphism of enstatite chondrites and during the genesis of aubrites. Part of our results has been recently published [1], but our new data allow a better look to the E4-E5 transition, and to aubrites. It is well known that most EL6 chondrites display unusual REE patterns displaying light REE depletions and often negative Eu anomalies (e.g., [2]). Such patterns, unusual for chondrites, are not restricted to EL types, but have been observed in an EH impact melt breccia (Galim-b), and in an EH impact melt (LAP 02225). They are probably related to the behavior of the sulfides (e.g., oldhamite) during impact, which are the main REE carriers in ECs (e.g., [3]).

We performed leaching experiments of a series of ECs in order to discuss the possible redistributions of lithophile elements between silicates and sulfides during EC metamorphism. Trace element abundances in silicate fractions strongly depend on the type of the rock (EH or EL, and metamorphic grade). For many elements, the sulfide contributions increase with the metamorphic grades. The trace element abundances of silicates are extremely variable. Negative Sm and Yb anomalies are observed in EL3-4 and EH3-4 residues, and are certainly the results of early nebular processes. Such anomalies are lacking in residues obtained with most metamorphosed EC, underlining the importance of trace element redistributions during metamorphism. In addition, EL6 silicates display distinctive positive Y anomalies that could be potentially ascribed to a less chalcophile behavior than Ho in the conditions that prevailed during EL metamorphism. We suggest that the trace element abundances in the silicate fractions can be used for classification purposes, even if the samples are strongly weathered finds. We will illustrate this point with some Saharan finds, Zacklodzie, and Happy Canyon. Itqiy is unique.

We analyzed 50 different fractions from 14 unpaired aubrites. Unsurprisingly, aubrites share some unusual chemical features with EC. For example, many aubritic pyroxenes display high $(Y/Ho)_n$ ratios. One of our Aubres samples exhibits a prominent Tb anomaly, which is probably the fingerprint of a sulfide phase. Furthermore, lithophile trace elements allow us to distinguish two distinct groups of aubrites, one with light REE-depleted pyroxenes and the other with light REE-depleted pyroxenes. The number of aubritic parent bodies is an open question.

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Meteorites and the early solar system – Chondrites

MET-T05

Metamorphism in the EH chondrite parent body recorded by minor elements in accessory olivine

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EH chondrite meteorites formed in a reducing part of the Solar Nebula and contain abundant metallic Fe and pyroxene stabilised by low $(\text{FeO}+\text{MgO})/\text{SiO}_2$. In unequilibrated EH3 chondrites, a range of oxidation states are in fact indicated by variable FeO in silicates. However, on approach to equilibrium during metamorphism, near complete reduction of Fe occurs along with production of silica by reduction and extraction of Fe from pyroxene. This results in consumption of olivine by petrologic type EH4/5 according to $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = \text{Mg}_2\text{Si}_2\text{O}_6$ and suggests that olivine in EH chondrites could be an indicator of metamorphic grade. Following previously suggested classification schemes, we have investigated olivine from eight EH3-4 chondrites by electron micro-probe analysis (A-881575, A-882059, ALHA-77295, EET87746, Sahara97079, Y-691, Y-74370, and Y-791790 from the National Institute of Polar Research, the Meteorite Working Group, and the Royal Belgian Institute of Natural Sciences). Average minor element contents of olivine are generally correlated across all meteorites. Olivine from A-882059, Y-74370 and Y-791790 are distinguished by much lower average concentrations of Fe, Cr and Ti and somewhat lower Ca, Al and Mn. Because new grain growth by dissolution-reprecipitation reactions is not possible due to consumption of olivine during metamorphism, concentration differences are likely to reflect pre-existing concentrations, or diffusion of cations through the olivine lattice. Results are consistent with diffusion of multivalent elements Fe, Cr and Ti to attain low equilibrium concentrations. Average Al contents are not well correlated with other elements, perhaps indicating slow diffusion of this tetrahedrally (rather than octahedrally) sited element. Minor elements in olivine therefore record the duration of metamorphism in the EH parent body, and we have found that Y-74370 and Y-791790 are among the most metamorphosed olivine-bearing EH chondrites.

MET-T06

Sulfide chemistry of enstatite chondrites – Identification of EH- and EL-subgroups?

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Electron microprobe analyses were performed on metal and sulfides (i.a., troilite, alabandite, keilite, and niningerite) of 44 enstatite chondrites [all petrologic types for both EL (29 samples) and EH chondrites (15 samples), except for EH6] to review if the major and minor element concentrations reveal correlations with petrologic type as previously suggested (e.g., [1,2], and references therein). Zhang et al. [1] reported, based on 17 E chondrites, that Ti and Cr contents in troilite, Si and Ni contents in kamacite, and the FeS content in alabandite and niningerite increase with petrologic type. However, the data of the present study could not confirm any of these trends. In agreement with [1], it appears that mineral chemistry cannot simply be correlated with the petrologic type in any form. Nonetheless, two different subgroups within both the EL and EH group can be distinguished based on troilite chemistry: Group I shows Ti concentrations from 0.03-1.84 wt% (EL) and 0.06-1.36 wt% (EH) and high Cr contents (mainly >2 wt%), while group II troilite mainly has Cr contents <2 wt% and a slightly narrower range in Ti 0.07-0.70 wt% (EH) and 0.23-0.90 wt% (EL). Samples of group I lack daubreelite and also show higher Fe contents in alabandite and niningerite (some of which are of keilite composition) than those of group II. These differences in sulfide chemistry could be either caused by different thermal evolutions or may indicate differences in accreted sulfide phases. Sub-solidus exsolution of daubreelite might explain its presence and the lower Cr in troilite of group II samples; however, as shown here, these observed chemical characteristics are independent of the petrologic type. Both scenarios might imply that these different groups derive from at least four different E chondrite parent lithologies (bodies?), two for each E chondrite subgroup. Even further parent lithologies are required regarding several anomalous E chondrites that neither fit into the EL nor the EH group [3-6], including LAP 032210 from this study.

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Meteorites and the early solar system – Chondrites

MET-T07

Elemental Complementarities in Rumuruti Chondrite NWA 753

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Complementary element concentrations in chondrules and matrix were reported in several carbonaceous chondrites [e.g., 1-4]. These suggest that chondrules and matrix formed from the same chemical reservoir. We extend this study to a very primitive type 3 fragment from the Rumuruti (R) chondrite NWA 753. Most of the 107 known R chondrites are highly oxidized breccias with 35-50 vol% chondrules, 42±11 vol% matrix, ~6 vol% opaque phases and

The studied fragment consists of ~30 vol% chondrules and chondrule fragments, ~10 vol% opaque phases and ~60vol% matrix. Relative to the bulk chondrite, the ten studied chondrules are enriched in MgO (36.8±3.7 wt%), SiO₂ (47.5±3.8 wt%), CaO (2.1±1.25 wt%) and TiO₂ (0.12 ±0.05 wt%) and depleted in FeO (10.3±2.8 wt%), Al₂O₃ (1.5±0.98 wt%) and MnO (0.3±0.18 wt%). The matrix has opposite concentrations, i.e. is enriched in FeO (33.5±2.2 wt%), Al₂O₃ (1.9±0.95 wt%) and MnO (0.34±0.04 wt%) and depleted in MgO (20.0±2.0 wt%), SiO₂ (34.1±1.2 wt%) CaO (0.58±0.43 wt%) and TiO₂ (0.05±0.03 wt%) relative to the bulk chondrite. Thermal metamorphism would equilibrate the meteorite components (e.g. olivine in chondrules and matrix) and lead to a loss of complementarity. It is more likely that different minerals were incorporated in different proportions in chondrules and matrix, e.g. during formation of chondrule precursor aggregates at high temperatures. High-T components such as olivine or perovskite would be preferentially incorporated in chondrules, while pyroxene and oxidised or hydrated minerals end up in the matrix.

The complementary relationships in R chondrites extend complementarity to another group of meteorites. Complementary relationships are probably a defining feature of all chondrites, but can primarily be observed in chondrites with a sufficient amount of matrix. Following the suggestions of [1-4], chondrules and matrix in R chondrites must have formed from a single chemical reservoir. Separate formation of both components and later mixing is unlikely. Models that comprehend the formation of chondrules and matrix in two different regions of the solar system can be discarded.

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Meteorites and the early solar system – Chondrites

MET-T08

Almost all chondrules in carbonaceous chondrites are zoned

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The past decades are marked by an increasingly better understanding of chondrule formation conditions, although pivotal constraints are still controversial. A particularly important and highly debated question is whether chondrules and matrix formed in the same or in different nebular regions. [1,2,3] point out that carbonaceous chondrites (CC) have CI chondritic ratios of non-volatile elements (e.g. Mg/Si, Fe/Si, Ca/Al), while chondrules and matrix have complementary element ratios. Most probably, chondrules and matrix incorporated different amounts of minerals and/or elements from the same parental reservoir; i.e. chondrules and matrix formed in the same reservoir.

Chondrule compositions are highly variable. Some of this variability may be produced during chondrule formation. [1,2,3,4] proposed that variable mineral contribution to chondrules and matrix produced their different composition. A series of studies demonstrated that chondrules probably acted as open systems [e.g. 5,6,7,8], i.e. a certain share of material was added late after the major chondrule fraction had crystallized by the interaction of a chondrule melt with the surrounding solar nebula, leading to chondrule zonation. We systematically study the occurrence, distribution and abundance of zoned chondrules. These have olivine in the core, pyroxene at the rim and occasionally silica at the rim.

We studied 80 chondrules in sections of 12 CC. Chondrules in all these meteorites except Mokoia have olivine at the core and a variably thick border zone consisting of pyroxene that poikilitically encloses olivine. This is the result of chondrule forsterite reacting with nebula SiO(g): $\text{Fo} + \text{SiO(g)} + 1/2 \text{O}_2 \rightarrow \text{En}$. The remaining SiO ended up in the matrix. Chondrules in almost all carbonaceous chondrites gained significant material from the surrounding nebula. This is independent evidence of the formation of chondrules and matrix in the same nebula region and demonstrates that chondrules behaved as open systems after their formation.

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Meteorites and the early solar system – Chondrites

MET-T09

Experimental study of oxygen isotope exchange between chondrule melt and water vapor

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We report on the results of time- and $f\text{O}_2$ -dependent oxygen isotope exchange experiments between a chondrule analogue melt and H_2O -rich gas phase, conducted to address the question of whether the oxygen isotope heterogeneity of chondrules [1] derives from the continuous exchange of a crystallizing melt with surrounding gas [2]. The experiments were performed at the temperature of 1500 °C, total pressure of 1 bar and different $f\text{O}_2$ in a vertical gas mixing furnace equipped with an H_2 - H_2O - N_2 gas mixing system using the loop technique. Equilibration of Fe-loop with silicate melt was used to check the oxygen fugacity.

Our results reveal that: 1) $f\text{O}_2$ in gas mixing furnace experiments can be well-controlled in the range down to IW-4 with a non-toxic H_2 - H_2O - N_2 mixture which is a suitable alternative for toxic CO - CO_2 mixtures for low $f\text{O}_2$ furnace experiments. 2) The oxygen isotope exchange between a silicate melt and the H_2 - H_2O - N_2 gas is proportional to the $f\text{O}_2$. Between IW-1.3 and IW-3.8 the exchange half-lives ($t_{1/2}$) varies from 70 to 230 minutes. 3) In a canonical solar nebula ($\log_{10} f\text{O}_2\text{-IW} \approx 6.9$, $P_{\text{tot}} = 10^{-3} - 10^{-6}$ bar) 50% exchange takes between 610 and 940 minutes ($\sim 10 - 16$ hrs).

However, the FeO content of chondrules is much higher than what is buffered by a nebular of solar composition. Higher $f\text{O}_2$ can be achieved by enrichment of a nebular compartment in dust relative to H_2 [3]. For dust-enriched systems ($P_{\text{tot}} = 10^{-3}$ bar), 50% exchange takes between 300 (800X dust enrichment, type-I chondrules) and 430 minutes (50X dust enrichment, type-II chondrules). This time-span agrees with the prediction that chondrules were heated to super liquidus temperatures for ≤ 7 hrs and were partially molten for some tens of hours in a shock wave model [4].

Therefore, our results demonstrate that the oxygen isotope composition of chondrules is expected to be the result of gas/melt partial exchange during chondrule forming events.

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Meteorites and the early solar system – Chondrites

MET-T10

Abundances of highly siderophile and chalcogen elements in the components of unequilibrated L chondrites

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Different classes of chondrites display resolvable differences in abundances and ratios of highly siderophile elements (HSE: Re, Au and platinum group elements). Because chondrites represent a mixture of, at least in some cases, genetically unrelated components (chondrules, Fe-Ni metal, fine-grained matrix, refractory and volatile enriched dark inclusions), study of the element abundances in the components is vital to understand the details of element fractionation by nebular, parent body or even terrestrial weathering processes. Here, we present HSE and chalcogen element (S, Se and Te) data of components of two unequilibrated L chondrites, Cenicerros (L3.4, fall) and QUE-97008 (L3.05, find).

Larger chondrules and sulfide grains were physically separated from these chondrites. Remaining material was crushed, separated into different size fractions, and each size fraction was divided into magnetic, slightly magnetic and nonmagnetic. Established isotope dilution and internal standardization techniques were used to obtain precise concentration data.

Variations and ratios of HSE and chalcogens (e.g. Re/Os, Pd/Ir, Se/Ir) indicate the existence of at least two different metal phases of different origin in magnetic, non-magnetic components and in chondrules. All magnetic components are enriched

(2-10 x CI chondrites) in HSE and show CI like relative abundances of refractory HSE (except Re as indicated by $^{187}\text{Os}/^{188}\text{Os}$). Rhenium in the magnetic fraction, is enriched relative to other refractory HSE (more strongly than in bulk L chondrites), either because of fractional condensation, a change in condensation behavior in non-solar gas compositions (e. g., during chondrule formation) or ancient parent-body alteration processes. In magnetic fractions, Se and S are depleted compared to the HSE, presumably during chondrule formation processes. Tellurium is depleted in all components (except Cenicerros M <50 μm) compared to other elements. The decoupling of Te from Se, S and the HSE in most components suggests that in L chondrites Te has a different volatility (and a variable geochemical affinity, sometimes more siderophile, sometimes chalcophile) than S and Se.

Meteorites and the early solar system – Chondrites

MET-T11

The mineralogy and metallography of a regolith particle returned from asteroid 25143 Itokawa

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In 2003 the Japan Aerospace Exploration Agency (JAXA) launched the Hayabusa spacecraft to rendezvous with the S-type near-Earth asteroid 25143 Itokawa. In 2005 the probe landed on the asteroid and collected regolith samples which were successfully returned to Earth in 2010. After NASA's Apollo missions to the Moon this was only the second time that samples were collected on the surface of an extraterrestrial body and brought back to Earth.

We received two samples of the typically <100 µm sized regolith particles collected. The particle RA-QD02-0115 had a size of 65 µm x 50 µm and was dominantly composed of olivine with abundant inclusions of Fe,Ni metal, troilite, chromite and merrillite. We sliced the particle into eight subsamples via the focused ion beam (FIB) method and extensively studied four of these samples by analytical transmission electron microscopy (TEM).

The mineral chemistry of olivine yielded a fayalite content of 29.8 ± 1.1 mol% and a molar Fe/Mn ratio of 57 ± 2 , both consistent with an equilibrated LL-type chondritic material, which was previously reported for other particles [1]. FIB slicing revealed abundant, mostly sub-µm sized voids within the particle.

The metal inclusions are often polyphase and consist predominantly of tetrataenite which is intergrown with taenite and kamacite, the latter being Co-rich (up to 6 at%). For the first time, we were able to detect the carbide haxonite, ideally Fe_{23}C_6 , in samples returned from 25143 Itokawa. Haxonite occurs as grains of up to 0.5 µm size and is associated with the metallic phases. The interface between haxonite and tetrataenite/taenite is semi-coherent and the cubic (base-)lattices share the same crystallographic orientations.

Haxonite has been described from unequilibrated type 3 ordinary chondrites, commonly in association with magnetite (carbide-magnetite assemblages, CMAs). These assemblages are interpreted to have formed from C-H-O-bearing, oxidizing fluids [2]. The high FeO content of olivine in RA-QD02-0115 and no detectable CaO suggest a petrologic type >3. The abundance of voids indicates the presence of a fluid during thermal metamorphism, but the absence of magnetite implies much more reducing conditions relative to type 3 CMAs.

[1] Nakamura et al. (2011), Science 333, 1113-1116.

[2] Krot et al. (1997), Geoch. Cosmoch. Acta 61, 219-237

MET-T12

Evidence for microimpacts in an olivine-dominated asteroidal dust particle returned by the Hayabusa space mission

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Hayabusa is the first sample return mission to an asteroid, aiming at understanding surface processes (space weathering, impacts) and constitution of regolith on a small primitive body (Itokawa asteroid). In the first international call for Hayabusa sample investigation we have received two precious olivine-dominated samples [1]: RA-QD02-0115 and RB-QD04-0042. Here we report analytical SEM and TEM investigations on grain RB-QD04-0042, providing clues to the impact history of Itokawa.

The olivine grain (40 x 50 µm) contains an intimate 10 µm wide intergrowth of FeNi alloy and iron sulfide on its surface. Furthermore a 6 µm diameter diopside inclusion emerged during FIB cutting.

TEM analyses of the FeNi alloy show a high Ni content of about 50 atom% and electron diffraction patterns reveal a face-centered cubic structure with superstructure reflections, both being compatible with tetrataenite [2]. Diffraction patterns of the iron sulfide attest to the stoichiometric iron sulfide troilite.

In terms of their defect microstructures, olivine contains locally a high density of [001] dislocations, while in other regions olivine is devoid of defects. Tetrataenite exhibits many mechanical microtwins and dislocations. Troilite contains some stacking faults with partial dislocations but is mainly characterized by a recrystallization texture with numerous subgrains. Diopside is basically defect-free.

In line with previous studies [3] the compositions of silicates and FeNi alloy point to an ordinary chondrite signature of Hayabusa dust. The majority of defects found in RB-QD04-0042 minerals are known to form by shock metamorphism, in particular the [001] dislocations in olivine and the microtwins in tetrataenite. The exclusive occurrence of defects on one side of the olivine indicates that the grain was affected by a micro-impact of a small (2-3 µm) particle.

Acknowledgments: Financial support was provided by the DFG (LA 830/14-1). We are grateful to JAXA for providing access to Hayabusa samples.

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Meteorites and the early solar system – Chondrites

MET-T13

Early formed chondrules in the Krymka (LL3.2) chondrite

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The formation process of chondrules, the major component of most chondritic meteorites, is still unknown and controversially discussed. The chondrule textures indicate that these former silicate melt droplets crystallized within minutes to a few days after their formation [1]. The predominant view is that all chondrules reached sphericity as independent droplets in space, crystallized and were already solidified at the time of chondrite accretion. However, it was recently shown by [2] that many unequilibrated ordinary chondrites (UOC's) contain lithic clasts consisting of mutually deformed chondrules, seemingly formed by the accretion of hot and viscously deformable chondrules. The parent rocks (termed "cluster chondrites") of these clasts obviously represent the earliest stages of chondrule agglomeration and possibly planetesimal accretion [2]. In order to test the above hypothesis we determined the crystallization ages of 9 chondrules from a single cluster chondrite clast in the Krymka (LL3.2) chondrite by applying the ^{26}Al - ^{26}Mg decay system using SIMS. We simultaneously measured the concentrations of the secondary ions ^{24}Mg , ^{25}Mg , ^{26}Mg , and ^{27}Al in multicollection mode using 4 Faraday cups in order to retrace the ^{26}Al concentrations in the chondrule melts. Our results show that the obtained ages for 8 chondrules are consistent with their crystallization at 0.44 ± 0.18 Ma after CAI formation, instantaneously followed by cluster chondrite accretion. One chondrule appears to be even older. These are the oldest ages for UOC chondrules published so far and for the first time date the accretion of a chondrite. Since the Krymka cluster chondrite is the first of its kind with known chondrule ages it is not clear whether these rocks generally consist of very old chondrules or if a suite of cluster chondrites exist with different formation ages. The accretion of hot and deformable chondrules very early in solar system history is a strong hint that chondrule formation and accretion of the first chondritic planetesimals were closely linked in time and space.

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MET-T14

Oxygen isotope systematics of CM chondrite calcite – constraints on aqueous alteration

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CM chondrites are regolith breccias consisting of variably altered fragments [1]. This is documented by minerals either modified by reaction with or directly precipitated from fluids (e.g., carbonates [2]). *In situ* ion microprobe (SIMS) oxygen isotope analyses of 84 calcite grains in CM chondrites Maribo (6 grains), Murchison (26), Cold Bokkeveld (23), Nogoya (19), and Banten (10) were obtained using the CRPG-Nancy CAMECA IMS 1270 and 1280 HR2 instruments to set constraints on aqueous alteration (fluid compositions, location, timing). All calcite grains analyzed in this study were distinguished from aragonite by micro-Raman-spectroscopy. Isotope analyses of these calcites combined with literature carbonate data [3-5] indicate a continuous change in oxygen isotope composition of the aqueous fluid. The results support the continuous fluid evolution model in a closed system [6,7] with certain carbonates tracking different precipitation events [3,4]. More primitive fluids have more positive $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ [3,4,6,7]. Hence, Maribo calcite (highest $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) is an early precipitate from a more primitive fluid, while Murchison, Cold Bokkeveld, Banten, and Nogoya calcite (lower $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) formed from a more evolved fluid, i.e., later on a relative time scale. Rough estimates of the fluid composition in equilibrium with the calcite grains (assuming a water temperature of 25°C, [8]) indicate a more ^{16}O -rich composition, clearly different from the initial CM water composition reported in [7]. This likely indicates that the calcite formed from a fluid that had changed its composition towards more ^{16}O -rich values due to reaction with anhydrous silicates. Based on preliminary examination of several distinct fragments in one Cold Bokkeveld thin section, calcite oxygen isotopy does not correlate with the degree of alteration of their host fragments, which could be indicative of pre-accretionary alteration.

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Meteorites and the early solar system – Chondrites

MET-T15

Noble gases in meteorites – What do they tell us about the (early) solar system?

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Because they are so rare in meteoritic matter, the elemental and isotopic compositions of noble gases are easily influenced by even minor contributions which would go unnoticed for other elements. This leads to an impressive variety of “noble gas components”, some of which are recognizable in bulk meteorite samples, others only in particular phases. Noble gases thus obviously have an enormous potential to decipher early (and later) solar system processes, but the multitude of components (the noble gas alphabet) and possibly involved processes also is responsible for the reputation of noble gas geo- and cosmochemistry “to non-practitioners to have much the air of the secret society and its dark art” (Ozima and Podosek, 2002). I will try to shed some light on this “dark art”, although it needs to be admitted that also for practitioners the subject remains very complex and even very fundamental relations between, e. g., the noble gas inventories in the sun, in planets and in meteorites, respectively, remain unclear. Some noble gas components and their carriers are clearly presolar, while for other components it is less clear where their isotopic and elemental identity was established. The presolar components had paved the way to identify and separate presolar grains such as nano-diamonds, SiC and graphite. Noble gas nuclides as daughter products of the radioactive decay of various short- and long-lived parent isotopes are widely used for chronological purposes. Noble gas isotopes produced by energetic particles from the galaxy or the sun also have chronological significance and in some cases may yield evidence for an early active phase of our sun, although the latter hypothesis is controversial. Noble gas analyses in tiny samples such as interplanetary dust particles or rare samples from, e. g., the surface of asteroid Itokawa require ever more sophisticated analytical techniques.

MET-T16

Clues to the formation of nanoscale alteration textures in the CM chondrites Murchison and Maribo

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Aqueous processes have altered many early solar system materials. Especially CI and CM chondrites have undergone aqueous alteration to various degrees [1-3]. Since all these chondrites are regolith breccias, it is still controversial where and when the alteration did occur [1,2]. In this study, textures of aqueous alteration in the two CM chondrites Maribo [4] and Murchison have been studied by FIB-TEM. In Murchison, an unusually Ni-poor tochilinite-cronstedtite-intergrowth (TCI) grain exhibits characteristic serpentine-brucite stacking sequences [e.g. 5]. However, within these TCI assemblages, lenses of magnetite occur. In Maribo, a total of five lamellae have been prepared from different aqueously-altered constituents, including so-called layered TCI (LTCl) assemblages (formerly “fishbone-tochilinite” [4]), and objects having LTCl-carbonate boundaries. Two distinct types of LTCl occur at the nanoscale: 1. Type-I LTCl is made of alternating tochilinite-rich and phyllosilicate-rich layers with thicknesses of a few hundred nanometers. 2. Type-II LTCl contains nanocrystals of magnetite, pentlandite and pyrrhotite, similar to the cosmic symplectite described in Acfer 094 [6], embedded in a very fine-grained groundmass.

The abundance of magnetite lenses within the TCI assemblages in Murchison might implicate magnetite-formation as an early stage-alteration product. Subsequently, TCI assemblages formed, replacing magnetite from the outside inwards. The precursor material of magnetite might be Fe-rich olivine or Fe that precipitated from a supersaturated aqueous solution. Type-I LTCl in Maribo may have formed through a sequence of tochilinite formation with subsequent phyllosilicate development along crystallographic dislocations with an increased Si-activity in the aqueous solution. Type-II LTCl might form as the result of either frictional heating during atmospheric entry or of more complex alteration-processes, probably prior to final parent-body formation.

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Meteorites and the early solar system – Chondrites

MET-T17

Reconstructing the thermal history of type II chondrules in the CO chondrite Kainsaz from chemical zoning in olivine and chromite

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Carbonaceous chondrites are a unique archive of the early history of the solar system and are affected to different degrees by thermal metamorphism on their parent bodies. We analyzed the chemical zoning of type II chondrule minerals in the CO3 chondrite Kainsaz using EMPA. Diffusion modeling was used to obtain information about the thermal history of the CO parent body.

We observe concentric but anisotropic zoning of Fe, Mg, Ca and Mn in olivine and concentric Fe-Mg zoning in chromite. To test if this zoning could have formed during chondrule crystallization, we used the MELTs program[1] to simulate the fractional crystallization of olivine and chromite from the chondrule melt.

The simulation predicts chromite crystallization temperatures consistent with the crystallization temperatures of 1300-1400°C obtained using olivine spinel thermometry [2]. The chemical zoning measured in olivine and chromite does not match the zoning patterns produced by fractional crystallization, however, since the compositions were modified after crystallization by diffusive exchange with the surroundings [3].

Therefore we simulated the olivine and chromite zoning with a one-dimensional diffusion model using $\Gamma = \int Ddt$ as a fitting parameter. The value of Γ quantifies the total extent of compositional change of the initial profiles by diffusive processes, which is directly related to the thermal history of the mineral.

Since all chromite crystals are in direct contact to olivine crystals, we used the temperature dependent Fe-Mg exchange between olivine and chromite [4] as boundary condition. Using these constraints, the chemical zoning observed in the chromite crystals can only be fitted assuming slow cooling, as expected during parent body metamorphism.

We modeled the thermal histories of parent bodies internally heated by ²⁶Al and derived a relation between Γ value and peak temperature for parent body metamorphism. Using this relation we estimate a metamorphic peak temperature of 765K from the Γ values obtained by diffusion modeling.

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MET-T18

Impact induced compaction of chondritic parent bodies and the initial porosity distribution of chondrites.

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Meteorites are fragments from recent collisions in the asteroid belt. The collision speed between two objects of the asteroid belt is given by the eccentricity and inclination of their respective Keplerian orbits. Typical values are on the order of a few km s⁻¹. In such a hyper-velocity collision, the smaller collision partner (projectile) is destroyed, whereas, depending on the mass ratio of the colliding objects, a crater on the larger body (target) is formed or it is entirely destroyed, too.

Especially meteorites that originate from unequilibrated parent bodies (<300 km in size) can provide important insights into the dynamics of chondrite formation and compaction. However, the last fragmentation process in which the meteorites are formed is extremely violent and changes the initial properties of the parent body, as the difference in porosity of carbonaceous chondrites and their parent bodies (C-type asteroids) show [1].

In order to quantify impact consolidation, we performed high-velocity impacts experiments into porous chondrite parent body analogs and measured the degree of compaction. To calculate the pressure, we adopted an impedance-matching algorithm. In our experiments, the volume filling factor ϕ (1- porosity) increases with increasing impact pressure with a power of 0.082 and reaches unity for pressures higher than 1 GPa [2]. Thus, we deduced the pressure range required to compact carbonaceous chondrites to their typical volume filling factors of $\phi = 0.6 - 0.9$ [4] to be between 2 and 200 MPa.

The experiments showed that the pressure in the target decreases with increasing depth as a function of projectile size. Therefore, the volume beneath the impact shows a variation in volume filling factor. The crater size and, thus, the ejected mass depend on the size of projectile and target as well as on the impact velocity [3]. However, not all of the compacted material is ejected by the impact; some compacted material remains on the parent body and changes its initial properties for further impacts.

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Meteorites and the early solar system – Chondrites

MET-T19

Modelling the thermal history of the parent body of Acapulco- and Lodran-like achondrites

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We apply our model of the thermal evolution of asteroids to the parent body of acapulcoites and lodranites. The model considers heating by radioactive isotopes, temperature- and porosity-dependent heat conduction, sintering, and melting, but not melt-migration. This model is compared to cooling histories inferred from thermochronological data and maximum metamorphic temperatures of A/L achondrites, and a genetic algorithm is applied to infer an optimised set of model parameters.

As a result, the parent body radius is determined to be ~270 km, the formation time ~1.66 Ma after CAI formation, and the average initial/surface temperature ~300 K, suggesting a formation of the acapulcoite-lodranite parent body in a hotter part of the accretion disk and at earlier time than the parent bodies of ordinary chondrites. The peak temperature in the core region seems to be sufficiently high for partial melting, but not for substantial differentiation. We argue that the body formed from a precursor material with a high matrix to chondrule ratio. The derived burial depth between 4 km (acapulcoites) and 8 km (lodranites) supports the assumption that all these meteorites were excavated from a small region of the parent body by a single impact event.

Meteorites and the early solar system – Achondrites and Isotopes

MET-T20

Disturbed Lu-Hf isotope systematics of achondrites – testing a new hypothesis

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The long-lived ^{176}Lu - ^{176}Hf decay system is a potentially precise chronometer, but when applied to meteorites, it often yields dates up to 300 Myr older than Pb-Pb. Irradiation by gamma [1] or cosmic rays [2] was suggested as the reason for this discrepancy, because it can accelerate ^{176}Lu decay thus rotating isochrons around their initial $^{176}\text{Hf}/^{177}\text{Hf}$ toward higher slopes. These irradiation mechanisms are untenable however because internal Lu-Hf isochrons with higher apparent ages [3, 4] have lower initial $^{176}\text{Hf}/^{177}\text{Hf}$ values, in disagreement with constant initial $^{176}\text{Hf}/^{177}\text{Hf}$ predicted by these models. Thus a different explanation is required for Lu-Hf dates that are too old.

Hot desert finds are often affected by terrestrial weathering as indicated by enrichments in Ba, Sr, U, and LREE with a typical crustal signature [5]. We hypothesize that Lu (a HREE) may also have been mobile during alteration and that terrestrial weathering can therefore potentially account for both the age discrepancy and the consistent patterns of scatter observed in the internal isochrons of both eucrites [4] and angrites [6].

We have now analyzed an ureilitic fragment of the Almahata Sitta meteorite, which is an observed fall from asteroid 2008 TC3 [7]. Owing to its short terrestrial residence time, it is an ideal sample to test our weathering hypothesis. Our first Lu-Hf data for pyroxene and bulk dust fractions define an errorchron corresponding to an age of 4598 ± 140 Ma. The high uncertainty on this date is caused by scatter of the individual points and the small overall spread in $^{176}\text{Lu}/^{177}\text{Hf}$ (0.01 to 0.04). Further isotope analyses of high-Lu/Hf phases (e.g., phosphates) should improve the precision and reveal whether the scatter among isochron points follows a pattern similar to that observed in other achondrites. To gain a better understanding of the relationship among different mineral phases and a possible terrestrial overprinting, detailed mineralogical investigations by SEM are also being performed.

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Meteorites and the early solar system – Achondrites and Isotopes

MET-T21

Isotopic variability of tantalum isotopes in early solar system materials

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Tantalum-180 is the rarest stable nuclide in the solar system and can only be formed at specific stellar environments. Therefore, the natural ratio of $^{180}\text{Ta}/^{181}\text{Ta}$ (ca. 0.00012) is very low and provides an analytical challenge for high precision isotope measurements. We present high-precision measurements performed using multicollector-ICPMS in a variety of natural samples to evaluate possible nucleosynthetic heterogeneities. Using a combination of 10^{10} and 10^{12} Ω Faraday amplifiers with jet interface we achieve a typical 2σ external reproducibility of ± 2.7 ϵ -units for samples of around 90 ng Ta that is mainly limited by counting statistics. Tantalum isotope ratios in various terrestrial samples are indistinguishable from an Alfa Aesar pure metal standard. Primitive carbonaceous meteorites were leached with 6N HCl, while the residues were digested in a table-top procedure and the leftover material was finally dissolved by using Parr Bombs. Several heavy elements exhibit r-/s-process related nucleosynthetic anomalies in the respective fractions. We found excesses of several ϵ -units in the $^{180}\text{Ta}/^{181}\text{Ta}$ ratio in table-top digested residues in Allende (CV3 chondrite) and NWA 3118 (CO3 chondrite). Possible processes causing differences in an isotope ratio of an element like Ta that only has two isotopes include mass dependent fractionation or nucleosynthetic heterogeneity. We prefer a model where the ^{180}Ta excesses are caused by insufficiently mixed material in the early solar system. Thus, the ^{180}Ta heterogeneity found for CV and CO chondrite components may be inherited from presolar material with distinct isotopic signatures.

Meteorites and the early solar system – Achondrites and Isotopes

MET-T22

Isotope anomalies of Hf and W in chondrite leachates and residues

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The stepwise dissolution of primitive chondritic meteorites allows to reveal nucleosynthetic anomalies that are otherwise hidden in the bulk rock mix. Here, we present for the first time combined Hf and W isotope data for acid leachates of several primitive chondrites, including some sufficiently precise analyses of p-process ¹⁷⁴Hf and ¹⁸⁰W.

First data reveal that most of the leachates and residues show anomalous s- and r-process Hf isotope patterns, consistent with the results of [1], whereas only one sample shows an apparent anomaly in ¹⁸³W, similar to the results of [2]. In terms of p-process isotopes, no resolvable anomaly in ¹⁷⁴Hf was found for any sample, whereas both positive and negative ¹⁸⁰W anomalies are resolved for most of the leachates and residues. The origin of the apparent decoupling between ¹⁷⁴Hf and ¹⁸⁰W possibly point towards different carrier phases for p-process Hf and W.

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Meteorites and the early solar system – Achondrites and Isotopes

MET-T23

High-precision measurements of p-process ^{190}Pt in weakly irradiated irons

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The first high-precision isotope analyses of p-process ^{190}Pt (0.014 %) in iron meteorites based on MC-ICPMS are presented. Predominantly irons with known low cosmic ray exposure ages (<100 Myr) were analysed in order to prevent neutron capture reactions that may have resulted from meteorite exposure to cosmic rays to obscure nucleosynthetic signatures. Preliminary data indicate that the abundance of ^{190}Pt in magmatic iron meteorites is indistinguishable from the terrestrial Alfa Aesar reference solution at the level of ~100 ppm. This observation strengthens the conclusions that isotope anomalies of ^{180}W in weakly irradiated irons are predominantly caused by ^{184}Os -decay (cf. Peters et al., 2014) rather than by heterogeneity of a nucleosynthetic p-process component in the solar nebula (cf. Schulz et al., 2013). Importantly, our improved analytical protocols furthermore allow significantly improved measurement precisions with respect to previous studies for the abundant Pt isotopes, e.g. a ca. fivefold better precision for $^{192}\text{Pt}/^{195}\text{Pt}$ (~20 ppm 2 σ) compared to Kruijer et al. (2013) is achieved. Our new, high-precision data tentatively suggest a deficit in s-process Pt for some irons.

Kruijer et al., EPSL 361 (2013): 162-172; Peters et al., EPSL 391 (2014): 69-7; Schulz EPSL 362 (2013): 246-257.

Meteorites and the early solar system – Achondrites and Isotopes

MET-T24

The importance of sulfur for the partitioning behaviour of the HSEs during Earth's accretion and differentiation

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The highly siderophile elements (HSEs - Os, Ir, Ru, Rh, Pt, Pd, Re, Au) were effectively removed from the Earth's mantle during the formation of the Earth's core. Previous metal-silicate partitioning experiments in S-free systems have shown that the HSE should have become strongly fractionated during metal-silicate equilibration. However, the HSEs are present in near-chondritic ratios in the Earth's mantle, giving rise to the "late-veneer"-hypothesis: After core formation was complete, oxidized, chondritic material delivered a small amount of HSE back to the mantle, establishing the observed HSE abundances. Over the past years it has been proposed that S was added during a late stage of accretion (e.g. the Moon forming impact), so that a sulfide melt could have been stable. This so-called "hadean matte" would have been removed in a final core-formation event, extracting the HSEs efficiently from the mantle.

In order to test the above hypothesis, we have performed a series of metal-silicate and sulfide-silicate partitioning experiments under high pressure-high temperature conditions. A molten peridotite was equilibrated with a range of compositions along the Fe-FeS binary (0 wt.% S - 36 wt.% S), doped with two of the HSEs (Pt, Pd, Ru or Ir) at a time (1-10 wt.% each). All experiments were performed in a multianvil-apparatus at 2100-2400 °C and 11-21 GPa using single crystal MgO capsules. Quenched silicate and metal or sulfide were analysed by electron microprobe for their major element concentrations while HSE abundances in the silicate were determined using LA-ICP-MS.

Overall, it can be observed that all HSEs become less siderophile with increasing S-concentration in the metal or sulfide. However, the least siderophile HSEs show only a small effect, while the more siderophile HSEs are strongly influenced. As a result, $D^{\text{metal-silicate}}$ of Pt, Pd, Ru and Ir converge with increasing S concentrations in the metal or sulfide phase. These results have important implications for our understanding of Earth's accretion and core formation history. An S-rich "hadean matte" segregating to the core would only result in a relatively small fractionation among the HSEs, better explaining the observed near-chondritic ratios of the HSEs in the Earth's mantle.

Meteorites and the early solar system – Achondrites and Isotopes

MET-T25

Geochemical constraints on the evolution of the Earth-Moon system

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The Earth and the Moon exhibit a unique pattern of refractory and volatile elements that permits valuable insight into early accretion, the giant impact event and late volatile addition. A remarkable similarity between the Earth and the Moon is the isotope composition of many refractory elements such as Ti [1] and Cr [2], whereas there are, for instance, small differences in the oxygen isotope composition [3]. Following the revision of the terrestrial Hf/W ratio [4], it is now known that the silicate Earth and the silicate Moon also overlap in their Hf/W [4,5], thereby explaining their nearly identical W isotope composition. Recently reported small ¹⁸²W excesses for lunar samples [6,7] may well be explained by slight differences in Hf/W between the Earth and the Moon within their present errors. Remarkable features of the silicate Earth and the Moon are their low Nb/Ta ratios (ca. 14 and 17, respectively [8]), limiting the amount of impactor material in the Moon to ca. 50%, in agreement with the most recent physical modelling results and oxygen isotope constraints [3]. The remarkably low Nb/Ta preserved in the Earth-Moon system may be a signature inherited from asteroidal precursors and indicates incomplete metal-silicate equilibration during accretion. A combination of recent experimental data for a number of volatile elements such as Pb [9,10] now supports models, where the Earth's inventory of highly volatile elements such as Pb is to > 90% supplied by a late veneer after the end of core formation. This mass balance is markedly different for more moderately volatiles like Rb, where only ca. 10% could have been added to account for the unique Rb/Pb ratio of the silicate Earth [10]. The Moon may therefore be a good analogue to a volatile depleted early Earth.

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MET-P01

Accessory Ca-phosphates in meteorites – distribution and composition

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The Ca-phosphates apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$) and merrillite ($\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$) are important accessory phases in numerous meteorite classes and exhibit diverse abundances and grain sizes. They are ideally suited for chronologic investigations, and as major carrier phases for halogens and REEs eligible to deduce degassing, fractionation processes, and fluid-rock-interactions in the early Solar System. However, their abundances, distribution and fractionation mechanisms within the early period of the Solar System have not yet been comprehensively constrained [1].

Despite their absence in some meteorites or meteorite groups, intensive search with SEM and EPMA technique at the University of Münster established a chemically and petrographically well-documented pool of 350 apatite and 279 merrillite grains covering different meteorite classes: H/L/LL ordinary (144 apatites / 156 merrillites), Rumuruti (2/2), and carbonaceous chondrites (30/-), acapulcoites (36/14), shergottites (14/7), ureilites (20/10), angrites (-/17), HEDs (49/44), iron (5/-), and stony iron meteorites (50/29). They feature a heterogeneous distribution among these groups with merrillite appearing slightly less frequent than apatite. Their grain size usually is within a range of 4-400 μm , but may reach up to 2 mm (e.g. in shergottites). Either one may be absent or limited to certain lithologies. Moreover their frequency of occurrence and sizes are increasing with the petrologic type of a chondritic sample.

If present, apatite basically controls the bulk halogen budget of a sample and therefore, the composition of its X-site with portions of Cl, F and OH is of particular interest. Selected apatite grains from four meteorite classes have been analyzed by EPMA so far determining their Cl and F contents, while OH had to be calculated by difference. Ordinary chondrites feature the highest Cl contents (up to 85% of the X-site), while eucrites and lunar samples show high F contents (up to 96%), both exhibiting OH contents of up to 40% [2,3]. Martian meteorites and ureilites do not show a particular preference for either endmember [3], but the latter exhibit lower OH contents.

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Meteorites and the early solar system

MET-P02

Synthesis of refractory metal nuggets (RMNs) and clues to the cooling rate of RMN bearing CAIs

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Introduction: Tiny refractory metal alloys/nuggets (RMNs) consisting of the highly refractory and siderophile elements (HSE) Re, Os, Ru, Ir, Mo, W and Pt as well as Fe and Ni are mainly observed inside Ca, Al-rich inclusions (CAIs) from chondritic meteorites (e.g. [1]). This association and the fact that both CAI minerals and refractory metals are predicted to condense first and simultaneously from a gas of solar composition (e.g. [2], [3]). This led several authors to assume that RMNs condensed directly from the solar nebula. However, due to their highly variable compositions deviating from the predictions, their formation mechanism remains unclear. Recently [4] found RMNs in cosmic spherules and proposed their formation by precipitation from a silicate liquid, which is supported by the formation of HSE micro nuggets in several experiments related to metal silicate segregation ([5]). We will present experimental evidence for a formation of RMNs by precipitation from CAI-Liquids.

Methods: In our approach, we synthesized a typical CAI type B1 composition, which was deposited together with the 9 metals in the same graphite capsule. The samples were heated in an induction furnace up to 1800 °C for several minutes under Ar-atmosphere at ~0.25 bar. After controlled quenching within several seconds or cooling over a period of a few minutes, the samples were recovered and analyzed by SEM.

Results: In our quenched materials, RMNs with highly variable compositions and appearances similar to meteoritic RMNs were found to be associated with perovskite, spinel and melilite. RMNs are absent in experiments cooled over a time interval of a few minutes. In conclusion, RMNs form by precipitation during cooling of CAI liquids within several seconds, much faster than previously assumed for CAIs.

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MET-P03

Partial melting of harzburgite in the Yurtuc meteorite of the HED series

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We investigated a sample from the Yurtuc howardite. It is comprised of a polymict breccia containing fragments of olivine, pyroxene, plagioclase, spinel, and quartz and millimeter sized clasts of harzburgitic composition. The harzburgites are comprised of orthopyroxene and less abundant olivine. In addition, fine-grained domains featuring graphic intergrowth of plagioclase, pyroxene, and Cr-rich spinel are present, which probably represent former melt pockets. The contacts between orthopyroxene and former melt pockets show complex geometry with intimate interfingering indicating partial melting of the pyroxene. In contrast, olivine does not seem to have been affected by melting. Both, pyroxene as well as olivine show secondary composition zoning towards the contacts with melt. Orthopyroxene shows a systematic decrease of the Mg content from about 1.45 a.p.f.u. in the grain interior to about 1.15 a.p.f.u. at the contact to the melt pockets and a concomitant increase in the Fe (0.58 to 0.68 a.p.f.u.), Ca (0.02 to 0.05 a.p.f.u.), Al (0.02 to 0.05 a.p.f.u.), Ti (0.002 to 0.012 a.p.f.u.), and Cr (0.009 to 0.015 a.p.f.u.) contents. Alteration trends are qualitatively similar but less strongly developed towards pyroxene-olivine interfaces. Along olivine-orthopyroxene contacts, olivine is replaced by a fine-grained orthopyroxene - Cr-spinel symplectite. The most conspicuous alteration phenomenon within the olivine is an increase in the Cr-content from 0.004 a.p.f.u. in the grain interior to 0.01 a.p.f.u. at the contact to the symplectite. The chemical alteration takes the form of diffusion fronts extending over about 10 to 30 micrometers into the orthopyroxene and olivine. Taking calibrations of Ti diffusion in orthopyroxene and of Cr-diffusion in olivine the time scale for the partial melting is estimated on the order of years to hundreds of years if alteration under constant temperature is assumed. Partial melting was thus related to an ephemeral thermal event most likely related to an impact on the HED mother body, which occurred under relatively oxidizing conditions as is indicated by the oxidation of Fe^{2+} to Fe^{3+} and supposedly of Cr^{2+} to Cr^{3+} associated with the formation of spinel + orthopyroxene symplectite from olivine.

Meteorites and the early solar system

MET-P04

Shock Classification of Martian Meteorites by Micro Raman Spectroscopy – clue for a better understanding of the magnetic signature and record

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We have investigated a further series of Martian meteorites by LASER Micro Raman Spectroscopy (LMRS). Main focus was on the plagioclase- maskelynite phases applying the Fritz et al 2005 [2,3] scheme for the shock classification of Martian meteorites. A second priority was on the iron-oxide/sulphide phases which carry the (paleo-) magnetic record but also very important information concerning the shock history of a specific Martian meteorite [4,5].

In [5] we have presented results of the following Martian and obtained the following range of peak shock pressures: Dho 378 (and M12, unofficial pair) - > 50GPa (recrystallized), KG 002 40-45GPa, Los Angeles 001/002 40-45GPa, NWA 2800 40-45GPa, NWA 5789 <5-14GPa, Tissint 40-45GPa, NWA 4797 >50GPa (recrystallized), NWA 6342 > 50GPa (re- crystallized), NWA 7032 >50GPa (recrystallized), NWA 7320 40-45 GPa.

In our studies we have included a set of samples (terrestrial equivalents such as plagioclase and maskelynite, and some preinvestigated Martian meteorites [2,3]) as a calibration measure in order to reproduce earlier published results.

Meteorites and the early solar system

Sample	Type	Peak Shock	Plagioclase Structure
JaH 479	Basaltic S.	26-40 GPa	Maskelynite
NWA 2975	Basaltic S.	26-40 GPa	Maskelynite
NWA 5990	Basaltic S.	40-45 GPa	Maskelynite
NWA 6162	Basaltic S.	26-40 GPa	Maskelynite
NWA 6963	Basaltic S.	26-40 GPa	Maskelynite
NWA 2990	Ol.-Phyric S.	26-40 GPa	Maskelynite
NWA 4468	Poikilitic S.	26-40 GPa	Maskelynite
YM 000097	Poikilitic S.	40-45 GPa	Maskelynite
Plagioclase	Basalt/Terceira	Unshocked	Plagioclase
Plagioclase	Basalt/Iceland	Unshocked	Plagioclase
Maskelynite	Popigai Crater Russia	S5-6	Maskelynite Terrestrial

Tab.1.: Summary of the new results on a set of shergottites (S.), and terrestrial plagioclase/maskelynite samples. The second plagioclase is very fresh material from the 2010 eruption of the Eyjafjallajökull volcano as it was sampled during the eruption.

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Meteorites and the early solar system

MET-P05

Raman Spectroscopy on Terrestrial and Meteoritical Natural Glasses

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Introduction: In the case of the Exomars programme, to be launched 2016-2018, Raman Spectroscopy is foreseen as an instrumental payload component.

LASER Micro Raman Spectroscopy

The main advantages of LMRS can be briefly summarized as follows:

- *Repeatable and rapid mineralogical analyses, fully non-destructive*
- *Applicable on non-prepared rough surfaces and small particles*
- *Resolution to micron sized individual grains*
- *Discrimination of polytypes/polymorphs (eg carbon or organic phases)*
- *Quick mapping of large areas, and due to the sharpness of the Raman features detection of (very) low concentration phases in complex mixtures or absorbing matrices*

However, basic precondition for a successful application of LMRS on planetary or asteroidal surfaces is testing the sensitivity and applicability in the laboratory and trying to simulate space conditions. A second major task must be establishing and extending existing LMRS databases on space materials and terrestrial equivalents.

Results: The Raman spectra of all investigated natural silica-rich (extra-) terrestrial glasses are characterized by the following typical features:

- Generally quite noisy signal showing more or less high background
- High fluorescence background at higher wave numbers (from about 1000 1/cm)
- Two broad bands centred around 450-600 1/cm and 850-1100 1/cm

The high fluorescence background is an indicator of the high degree of amorphization. The positions and detailed shape of the two broad bands is different for the various types of natural glasses reflecting (i) Si-O-Si bonding differences, (ii) SiO₄ ring arrangements and (iii) lattice disorder. Additionally, sharp Raman bands are observed in some glasses, eg fulgurites or impactites, at higher wave numbers.

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MET-P06

New Results on mineralogy, Raman Spectroscopy and magnetic signature of the Chelyabinsk meteorite

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The atmospheric explosion and fall of the (later) Chelyabinsk meteorite of 15th February 2013 was the most extraordinary event of its kind within the last 100 years. Numerous fragments in kg - size or less of the meteorite have been collected in the meantime. The Chelyabinsk meteorite was classified as LL 5 ordinary chondrite (S4 and W0) (MetBull 2014).

In our contribution we will present results of our investigations on the mineralogy and phase composition, and the magnetic signature of the meteorite. One important focus of Raman spectroscopy was on the shock classification (plagioclase-glass-maskelynite transformation) and the high pressure phases within the shock melt veins.

Samples: for our investigations we used several up to 3cm sized individuals whereby the fusion crust is partly missing. A polished thick (PS) and a thin section (PTS) were also available for our purposes. Both black and white lithologies could be analyzed including several melt veins of mm sized thicknesses.

Methods: Quantitative chemical data of the observed phases in Chelyabinsk LL 5 chondrite have been obtained by Electron Microprobe Analysis (EMPA) using a Cameca SX100 system operated at 15KeV. All analyses were performed on a PS. Raman spectroscopy was also performed on non prepared surfaces which has the advantage of avoiding any cutting or preparation effects. A Horiba Xplora Integrated confocal LASER micro Raman system was used for our studies (mostly the 532/638 nm LASERs). Magnifications were between 100 and 1000x (LD) with acquisition times of 3-5 sec and accumulation numbers of 2-5.

The following phases could be identified so far, more details will be given in our contribution (poster): olivine, (ortho-) pyroxene, plagioclase, (Mg, Al) chromite, kamacite, taenite, (Cr) troilite, Na-merrillite, whitlockite, apatite, calcite. In addition, in the shock melt veins, a number of high-pressure phases could be observed.

Rare plagioclase grains showed typical plagioclase Raman patterns indicating a low-shock degree (S 1-2).

The magnetic signature is dominated by soft magnetic kamacite which does not carry a stable (paleo-) magnetic information. The role of other magnetic phases such as chromite which sometimes might record strong magnetization components at low temperatures (space conditions) is currently under investigation.

(1) Chelyabinsk meteorite, in MetBull 2014.

Meteorites and the early solar system

MET-P07

Fractionation of major elements, chalcogens and highly siderophile elements in components of the unequilibrated L-chondrite QUE 97008

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Bulk rocks of chondrites are often used in geochronological studies that apply short-lived decay systems. However, because chondrites are often mixtures of genetically unrelated material (e. g. chondrules, inclusions), a detailed understanding of the origin and processing history of the components is required for meaningful age interpretations.

Here we report data for abundances of major and minor elements, S, Se, Te (chalcogens) and the highly siderophile elements (HSE) in components of the unequilibrated ordinary chondrite QUE 97008 (L 3.05). The goal of this work was to distinguish genetically unrelated material in this chondrite by study of the variations of siderophile, lithophile and chalcophile elements. The components have been separated by grain size fraction and magnetism and were digested in conc. HNO₃ + conc. HCl (2:1) in a high-pressure asher. Isotope dilution, external and internal calibration techniques were applied. Covariations of lithophile, siderophile and chalcophile major, minor and trace elements determined in the same aliquot were used to constrain the effect of imperfect or artificial separation of silicates and sulfides from metal.

Variations and ratios of some HSE and chalcogens (e.g. Re/Os, Pd/Ir, Se/Ir) indicate the existence of at least two different metal phases of different origin in magnetic (fractionated ratios) and non-magnetic components (CI like), respectively. The metal in non- and slightly-magnetic components likely condensed in different environments compared to the main metal+sulfide assemblage in QUE 97008. With the exception of Re, Pd and Au, the HSE in magnetic fractions display only little fractionation compared to CI-chondrites. Depletion of the chalcogens in magnetic components compared to the HSE and CI-chondrites indicates volatility-controlled loss of these elements, presumably during chondrule formation. Tellurium in all components is more depleted compared to HSE and Se and S, which suggests that in this chondrite, Te has a different volatility than S and Se. Variations of the HSE and chalcogens and their ratios do not support an origin of these compositions by solid metal-liquid metal partitioning.

MET-P08

Infrared spectra of meteoritic analogs to protoplanetary disk material

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Protoplanetary disks are the places where planetary systems form around other stars. It is possible that the processes occurring there are similar to those in the solar nebula and that the precursor dust particles in these protoplanetary disks are similar to those constituting primitive meteorites in our solar system.

The infrared emission of warm dust in protoplanetary disks around luminous young stars has been observed and spectroscopically analyzed in high signal-to-noise by the Spitzer Space Telescope Infrared Spectrograph (IRS). The assignment of spectroscopic features to the presence of certain minerals is, however, not yet complete, partially due to incomplete knowledge of the infrared spectra of relevant minerals from laboratory studies.

We have performed infrared spectroscopy of different parts of primitive meteorites such as CAIs and chondrules. We compare these spectra with those of constituent minerals (olivine, clino- and orthopyroxenes, melilite, nepheline) in order to assign individual spectroscopic features. In addition, we demonstrate how these spectra can be compared to astronomical spectra of protoplanetary disks.

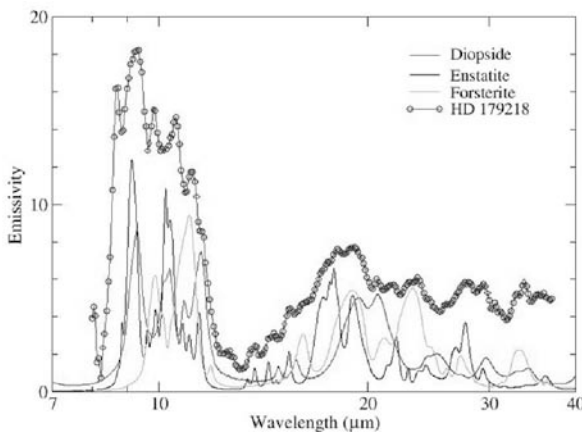


Fig. 1: Infrared emission spectrum of the protoplanetary disk of the star HD 179218 (Juhász et al. 2010) compared to the infrared absorption of an olivine, an ortho- and a clinopyroxene. The astronomical spectrum has been processed by subtraction of the

stellar spectrum and by division through a 150 K Planck function, in order to derive the dust emissivity

Meteorites and the early solar system

MET-P09

Mid-Infrared absorption spectra of five meteorites – comparison with observed spectra obtained by vega-type stars

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Original molecular cloud dust and solid grains condensed in a protoplanetary disk (PPD) remained in meteorites. These dust grains are essential source of planet formation since the chemical composition of the grains survived in solar nebula is responsible for the composition of the planets. It has been conceivable that the formation of the terrestrial planets occurs in high metallicity environments where the dust grains are abundant¹. Still the formation and evolution processes of dust grains are not well understood yet. Scientists endeavor to elucidate how dust grains have undergone chemical and physical metamorphosis and evolved during the chemical transformation, and moreover, how they play a role in the process of planet formation in PPDs. Meteorites have great possibilities to pin down the properties and processing history of the dust grains and the mechanisms of planet formation.

Astronomers are observing the emission of warm dust from some evolved planetary systems (Vega-type stars) in the infrared (IR) region by space-borne telescopes and that IR spectra bear information on the mineralogy of the interplanetary dust in these systems. Thus we report herein the medium effect free laboratory absorption spectra² of five different meteorites (Allende, NWA4759, Capot Rey, NWA869, NWA3318) compared with observed spectra of Vega-type stars. The measured absorption spectra clearly show very abundant minerals, esp. crystalline silicate, in each meteorite. What is to be noted that the peak position of 23 μm , which is attributed by translational motions of metal cations³ of olivine system, is located at longer wavelength (NWA4759: 23.6 & 24.8 μm ; Allende: 24.6 μm) than the band of forsterite which is observed in PPDs. This peak shift indicates that olivine in these meteorites has higher Fe content. As compared with HD69830, the translation peak of Allende sits at much longer wavelength (24.6 μm) than HD69830 (23.9 μm) due to the higher Fe content (Fo50)⁴ than olivine dust grains in the debris disk. This amount of Fe in silicate system may help us to understand the chemical pathway for further dust grain evolution to planet formation.

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MIC-T01

Abandoning rate constants – from rate spectra to overall dissolution rates

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Many natural processes and technical applications require our ability to provide a reliable prediction of crystal surface reactivity. However, this reactivity is not a material constant. Instead, intrinsic variability of this important parameter has been experimentally demonstrated [1]. Consequently, both, single rate constants and surface area normalization are problematic for the explanation and prediction of surface-controlled reactions.

As an alternative approach, the concept of rate spectra has been recently introduced [2]. This concept includes and quantifies the individual contributions to the overall rate and, thus, analyzes heterogeneous surface reactivity. Rate spectra are used to evaluate rate distribution data that are based on direct surface analysis using data collected by, e.g., atomic force microscopy or vertical scanning interferometry. Material flux maps are calculated from a minimum of two consecutive topographic maps and then used to analyze rate contributions [3].

While typically these maps are measured in the laboratory, we apply in this study results from kinetic Monte Carlo (KMC) simulations. In this approach, we utilize temporal sequences of KMC results of crystal dissolution. The heterogeneity of surface rates causes shape differences of rate spectra. The advantage of this approach is that KMC results can be used to analyze systematically the influence of specific reaction sites and their contributions to the resulting rate spectrum and, ultimately, the overall reaction rate.

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MIC-T02

Crystallographic controls on the intrinsic rate of aragonite dissolution

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Recent work shows complex differences in the stability of crystallographic faces of orthorhombic, aragonite-type carbonates as a function of pH. For example, under acid conditions, (100) and (130) faces stabilize at the expense of (110), (010), and (001) faces, changes that are apparently driven by relatively weak differences in the geometry of protonation on various faces [1]. It is unclear how these patterns may relate to the single rhombohedral carbonates (e.g., calcite, magnesite), where dissolution and growth kinetics are strong functions of defect geometry, and the overall control of dissolution rate is most closely related to step interactions and kink site densities on the common cleavage surface (104). In calcite, these interactions are controlled by basic energetic differences in the attachment or detachment penalties at specific sites [2]; under low pH conditions, magnesite surfaces show strong changes in step geometry and kink distribution [3]. In addition, most of the dissolution rate data for aragonite have been collected using powdered materials [e.g., 4], with the attendant difficulty in the expression of absolute rates with respect to the crystal surface [5]. In this context, we present preliminary data of aragonite dissolution on various crystal faces as a function of pH, collected using a vertical scanning interferometer equipped with a quasi in situ environmental cell [6]. The specific goal of this work is understand how the transition to acidic regimes influences the intrinsic rate (in the context of statistical distributions [5]) observed on the various crystallographic faces of aragonite, and how these changes may differ from those observed in rhombohedral carbonates such as calcite.

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MIC-T03

Kinetic Monte Carlo simulations: Predicting the unpredictable?

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There is a growing need to predict the behavior of geochemical systems, most acutely at the intersection between natural and industrial environments (e.g., Fukushima Daiichi, Deepwater Horizon). This is hardly an alarmist statement, given the deterioration of public infrastructure in developed countries, the large costs of system failures, water quality, energy, and waste management. Such catastrophes will occur with increasing frequency. It is thus essential that earth science develops a core competency in prediction of complex systems and the quantitative assessment of risk. Much of our current approach assumes that predictability is simply a matter of adequate parameterization of simple governing equations.

As an illustration, consider the difficulties of predicting dissolution-precipitation. Our understanding is that of a simple feedback loop: the nucleation and growth of the product driving undersaturation with respect to the reactant. However, this chemical model requires a key physical and dimensional constraint, i.e. how porosity (and thus permeability) is maintained as reactive interfaces propagate. For even a rudimentary prediction of such a system, a multidimensional chemical and physical model is mandatory. One approach is kinetic Monte Carlo modeling, incorporating the heterogeneous distribution of reactive sites, the complex variation of rates with respect to equilibria [e.g., 1], and how this distribution couples to nucleation and growth. As case examples, we discuss kinetic Monte Carlo modeling results of quartz, calcite, and phyllosilicate dissolution [2] in the context of equilibrium constraints provided by the stepwave model [3] and a conceptual framework of statistical rate distributions [4]. This integrated approach offers exciting new insight into predicting natural geochemical systems.

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Microstructures, textures and interfaces of minerals

MIC-T04

Architecture of biomaterials – morphologic versus crystallographic hierarchy

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Mytilus edulis prismatic calcite and nacre layers exhibit a crystallographic structural hierarchy which differs substantially from the morphologic hierarchy. This makes biomaterials fundamentally different from classical crystalline materials. Morphologic building units are defined by their surrounding organic matrix membranes, e.g. calcite fibers or nacre tablets. The crystallographic building units are defined by crystallographic co-orientation. EBSD quantitatively shows how crystallographic co-orientation propagates across matrix membranes to form highly co-oriented low-mosaic composite-crystal grains, i.e. calcite fiber bundles with an internal mosaic spread of 0.5° full-width-at-half-maximum (FWHM) or nacre towergrains with an internal mosaic spread of 2° FWHM. These low-mosaic composite crystals form much larger composite-crystal supergrains, which exhibit a high mosaicity due to misorientations of their constituting calcite fiber bundles or nacre towergrains. For the aragonite layer these supergrains nucleate in one of three aragonite {110} twin orientations; as a consequence the nacre layer exhibits a twin-domain structure, i.e. the boundaries of adjacent supergrains exhibit a high probability for misorientations around the aragonite c-axis with an angle near 63.8° . Within the supergrains, the constituting towergrains exhibit a high probability for misorientations around the aragonite a-axis with a geometric mean misorientation angle of 10.6° . The calcite layer is composed of a single composite-crystal supergrain on at least the sub-millimeter length scale. Mutual misorientations of adjacent fiber bundles within the calcite supergrain are mainly around the calcite c-axis with a geometric mean misorientation angle of 9.4° . The frequency distribution for the occurrence of misorientation angles within supergrains reflects the ability of the organism to maintain homoepitaxial crystallization over a certain length scale. This probability density is distributed log-normally which can be described by a geometric mean and a multiplicative standard deviation. Hence, those parameters are suggested as a numeric measure for the biologic control over crystallographic texture.

MIC-T05

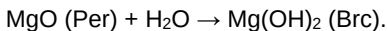
Kinetics of periclase hydration at 200 MPa and temperatures ranging from 350°C to 620°C

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During the retrograde stages of metamorphism and during fluid-rock interaction hydration of anhydrous minerals may occur, which potentially has effects on the physical rock properties and rheological behavior. To understand the feedback between hydration and rock properties, it is important to know the corresponding reaction rates.

We choose the MgO-H₂O model system using a geometrically well-defined starting configuration to investigate the hydration of periclase (MgO) producing brucite (Mg(OH)₂) according to the reaction



To this end, dedicated hydration experiments were done using millimeter-sized single crystals of periclase cubes with surfaces oriented parallel to (001) which were exposed to distilled water at temperatures of 350°C to 620°C and 200 MPa hydrostatic pressure using rapid-quench autoclaves. Run durations were between 5 and 40 minutes. In all experiments a layer of brucite was formed on the surfaces of the periclase. Time series experiments revealed a constant propagation rate of the hydration front indicating a linear rate law. At fixed time, the overall growth rate increased from 350°C to 530°C and decreased towards higher temperatures, and finally vanished at about 630°C where equilibrium was attained between periclase, brucite and H₂O. Interface reaction control is inferred from the linear growth behavior and the overall kinetics is described by a single phenomenological parameter referred to as the mobility of the reaction interface relating reaction front velocity to reaction affinity. The temperature dependence of the interface mobility can be described by an Arrhenius relation with a pre-exponential factor of $8.07 \times 10^{-13} \text{ m}^4/\text{sJ}$ and an activation energy of $E_A = 55 \text{ kJ/mol}$.

MIC-T06

Interface geometry and topotactic relations of oriented TiO₂ inclusions in a garnet host crystal

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Combined U-stage, electron backscatter diffraction (EBSD) and TEM-investigations of fine-grained acicular rutile inclusions in coarse-grained metapelite garnet led to the conclusion that the host lattice controls the interface geometry, grain shape, developed crystal faces, shape preferred orientation and crystallographic preferred orientation of the inclusions (Proyer et al, 2013).

U-stage data showed that rutile grains with high aspect ratio have their long axes mainly parallel to Grt $\langle 111 \rangle$ and subordinately parallel to Grt $\langle 100 \rangle$. According to EBSD and TEM data the phase boundaries follow low-indexed garnet planes, as the interface segments are predominantly parallel to Grt $\{110\}$ and subordinately parallel to Grt $\{100\}$ for acicular grains. Isometric rutile grains also developed phase boundary segments parallel to Grt $\{112\}$.

Contrasting with the grain geometry and SPO of the inclusions, which follow low-indexed garnet directions or planes, the crystallographic orientation of rutile yielded a complex though still systematic pattern. There are no unique orientation relations between low indexed rutile and garnet planes, and phase boundaries in TEM seem to be incoherent. However, EBSD data of 213 rutile inclusions showed that Rt c-axes are arranged along cones around Grt $\langle 111 \rangle$ forming clusters at 12 positions along these cones. Each cluster has a fixed Rt a-axes orientation with respect to the corresponding Grt $[111]$ direction. A second subordinate Rt-population has c-axes parallel to Grt $\langle 111 \rangle$ and one of their a-axes parallel to one of the Grt $\langle 110 \rangle$ directions. Despite of the complexity we demonstrate a systematic correspondence of the inclusion and host lattices. The host control on both the interface geometry and crystallographic orientation of the inclusions points to their genesis as precipitates within or at the surface of the host crystal. Intragranular precipitation of Rt-needles requires the formation of new phase boundaries with energetically favorable geometry. Considering the high aspect ratio of Rt, surface forces play a minor role in the formation of this host-inclusion microstructure which is rather controlled by the thermodynamic driving force, the mechanical host lattice properties and diffusion required for TiO₂ accumulation.

Proyer et al (2013) Contrib. Min. Pet. 166, 211-234

MIC-T07

Enhanced diffusion rates adjacent to healed cracks – effects on re-equilibration of submicron inclusions in host garnet

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Microstructures defined by mineral inclusions in Permian meta-pegmatite garnets from the Koralpe (Eastern Alps, Austria) reveal mechanisms linking inclusion re-equilibration to host mineral deformation. Sampled Fe-Mn garnets contain abundant submicron-sized inclusions (1 μm - 2 nm $\varnothing$). This Permian magmatic assemblage was affected by eclogite facies metamorphism and deformation during the Cretaceous eo-Alpine event.

Trails of coarser inclusions (1-10 μm $\varnothing$) crosscut the garnet and are flanked by 10-100 μm wide 'bleaching zones' characterized by the absence of $\leq 1\mu\text{m}$ sized inclusions in optical and SE images. Their microstructural characteristics indicate that trails formed at sites of healed brittle cracks. FEG-microprobe data show that trails and bleaching zones *can* form isochemically, though some trails show non-isochemical coarsening. No change is ever observed in garnet major element composition.

Cross correlation EBSD reveals subtle garnet lattice rotation spatially correlated with bleaching zones. Rotation around consistent misorientation axes increases gradually to a maximum of 0.1-0.45° at trail centers. Targeted TEM foils confirm higher dislocation density within bleaching zones, though absolute dislocation density is still low.

Inclusion coarsening was facilitated by locally enhanced diffusion rates in garnet near healed brittle cracks. The preferred mechanism for this is increased dislocation density near former cracks. In this case the dislocations are interpreted as a plastic wake originating from crystal plastic deformation at the crack tip. Faster diffusion could instead be due to increased volatile content of the garnet in bleaching zones introduced while cracks were open. However, this theory requires a more complex explanation for the presence of dislocations, such as strain localization in garnet domains with reduced nanoinclusion content. Transient internal surfaces in a host can influence inclusion re-equilibration by altering local diffusion rates in the lattice adjacent to them.

Microstructures, textures and interfaces of minerals

MIC-T08

Myrmekite formation in the Weinsberg granite (South Bohemian Batholith) – localized interface processes and microstructure evolution

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We report on myrmekites from the Weinsberg granite of the Moldanubian zone of Upper Austria. Petrographic evidence clearly testifies to the replacement nature of the myrmekites, which formed rims on mega crystals of pre-existing perthitic alkali feldspar preferably at the contacts to primary magmatic plagioclase at around 500°C. Myrmekite formation was metasomatic on the scale of the myrmekite domains. Sodium and calcium were added and potassium was removed from the reaction site, whereas silicon and aluminum appear to have been conserved across the reaction front. More or less continuous quartz layers at the supposed original contacts between magmatic alkali feldspar and plagioclase suggest that a corona type microstructure was formed initially and the typical vermicular quartz-plagioclase intergrowth of the myrmekite only took over during later stages of reaction. Three myrmekite domains with successively decreasing grain sizes can be discerned with the youngest, most fine-grained portions of the myrmekite being in direct contact with the alkali feldspar. In the most fine-grained myrmekite domains a composition zoning is observed within the plagioclase showing a systematic increase of the anorthite content towards the quartz vermiculae.

The evolution of the myrmekite microstructure and the plagioclase composition zoning of the myrmekite matrix are qualitatively explained by a thermodynamic model of discontinuous precipitation, which accounts for chemical segregation by diffusion within the reaction front and the propagation of the reaction front with intrinsic finite mobility as potentially rate limiting processes. Constraints on the underlying reaction rates are derived from the preserved microstructure and chemical pattern. Heterogeneous distribution of grain-internal deformation in the myrmekite is interpreted as a growth feature related to different transformation strain at segments of the myrmekite reaction front, where quartz and plagioclase are formed.

MIC-P01

Almandine – synthesis, crystal chemistry, defects and physical properties

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Almandine, ideal end-member formula $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, was synthesized at high pressures and temperatures under different f_{O_2} conditions with different starting materials. The reaction products were characterized using a number of experimental techniques in order to obtain a better understanding of the precise chemical and physical properties of almandine. The nature of possible defects, such as the Frenkel, Schottky and site-disorder type, the role of minor additional components, especially Fe^{3+} and OH^- , and the presence of solid-phase inclusions were investigated.

Almandine in both polycrystalline and in single-crystal form was obtained in the synthesis experiments. Hydrothermal experiments yielded almandine single crystals from roughly 5 microns in size up to approximately one millimeter and which show varying physical properties. Fine-grained polycrystalline almandine in the form of compact pellets, with individual grain sizes mostly less than about 15 microns, was obtained from water-free syntheses made in graphite capsules. The synthetic crystals were investigated using X-ray powder diffraction, electron microprobe and TEM analysis, and using ^{57}Fe Mössbauer and IR single-crystal spectroscopy. BSE photos on different polycrystalline almandines, synthesized without water, show a variety of fine inclusions and unreacted starting material. TEM results show certain nanosized, 100 nm to less than 10 nm, magnetite inclusions in some synthetic almandines, similar to those observed in natural almandine crystals. A room temperature FTIR single-crystal spectrum of a hydrothermally grown almandine shows two broad OH-stretching bands at 3613 cm^{-1} and approximately 3490 cm^{-1} both of which split into more bands at 77 K. ^{57}Fe Mössbauer measurements show small but various amounts of Fe^{3+} in octahedral coordination for many synthetic almandines and whose concentration depends on the synthesis experiment.

Various possible local defects in almandine are analyzed using Kröger-Vink notation with regard to probable minor exsolution phases that have been observed in synthetic as well as in natural crystals. These phases are mainly, but not only, magnetite (spinel), rutile and ilmenite. The crystal-chemistry and physical properties of almandine are analyzed in terms of various possible model defects.

Microstructures, textures and interfaces of minerals

MIC-P02

Element partitioning at a propagating reaction interface – growth of spinel in the MgO-Al₂O₃ system, experiment and thermodynamic model

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The formation of magnesio-aluminate spinel was investigated experimentally at 1350°C and ambient pressure using a uniaxial creep apparatus (Jeřábek et al 2014). Single crystal periclase and corundum machined to quadrilateral prisms (3 by 3 by 5 mm) with their (0001)_{cor} and (100)_{per} faces polished were put into contact. Assemblies were annealed at 1350°C for run durations of 5 to 160 hours. A dead load of 0.26 kN was applied to ensure good mechanical contact. A continuous layer of spinel formed along the periclase-corundum contact, which successively grew in thickness. The boundary between two microstructurally and texturally distinct domains within the spinel layer coincides with the position of inert Pt markers indicating that spinel grew at proportions 1/3 into the directions of periclase and corundum, respectively, which is compatible with interdiffusion of 2 Al³⁺ versus 3 Mg²⁺. The spinel shows a systematic, close to linear variation in composition across the layer, with the mole fraction of Al₂O₃ in spinel, X_{Al}^{sp} , being higher at the spinel-corundum interface than at the spinel-periclase interface. Irrespective of the run duration $X_{Al}^{sp} = 0.66$ corresponding to local equilibrium at the spinel-periclase interface. In contrast, the X_{Al}^{sp} at the spinel-corundum interface successively increases with run duration from $X_{Al}^{sp} = 0.67$ after 5 hours to $X_{Al}^{sp} = 0.69$ after 160 hours run duration successively approaching local equilibrium, which is at $X_{Al}^{sp} = 0.70$ at the conditions of the experiments.

A thermodynamic model accounting for free energy dissipation due to interdiffusion of Al³⁺ and Mg²⁺ as well as by the interface reactions at the spinel-periclase and the spinel-corundum interfaces was formulated that predicts the system evolution from the known free energy landscape and the kinetic parameters describing diffusion of Al³⁺ and Mg²⁺ as well as the mobilities of the two reaction interfaces. It is found that, after nucleation has occurred, reaction rim growth is interface reaction controlled during the early growth stages and becomes diffusion controlled later on. Deviations from local element partitioning are predicted for the interface reaction controlled growth stages, which tend to diminish when the system passes into the diffusion controlled kinetic regime. The experimentally observed deviations from Al/Mg equilibrium partitioning at the spinel-corundum interface thus reflect the finite mobility of this reaction interface at the conditions of the experiment.

Jeřábek et al (2014) Am. Journ. Sci, 314, DOI 10.2475/05.2014.00

Microstructures, textures and interfaces of minerals

Microstructures, textures and interfaces of minerals

MIC-P03

Internal Microstructures and Breakdown of Garnet from Moldanubian Granulites (Gföhl Unit, Dunkelsteinerwald, Lower Austria)

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Some conspicuous symplectite bearing granulite facies rocks from the Moldanubian Gföhl Unit in Lower Austria show an unusual bulk composition with very high Mg, Ca contents and 14 mole% normative corundum. They contain garnet ($X_{\text{Pyr}} > 0.5$), clinopyroxene (X_{Mg} : 14 mole%; X_{CaTs} : 0.3), pargasitic hornblende (X_{Mg} : 17 mole%), and plagioclase ($X_{\text{An}} > 0.8$). The primary microstructure is granular and well equilibrated.

Garnets of about 2cm size are common. Often they are resorbed and thus significantly smaller. The garnets show internal deformation. The lattice orientations of the different domains show non coaxial strain around a common rotation axis approximately parallel to [211]. From crystal orientation imaging incipient polygonalization of garnet during crystal plastic deformation under high grade metamorphic conditions is inferred.

Along garnet margins and within cracks, various replacement symplectites were formed comprising distinct assemblages among orthopyroxene, spinel, anorthite, Al-rich amphibole, tschermakitic diopside, sapphirine and corundum. Symplectite formation was probably induced by decompression. The last peak metamorphic conditions of the Gföhl Unit has been estimated in previous studies with pressures and temperatures around resp. 8-11 kbar and 700-800°C. The rocks then experienced isothermal decompression followed by isobaric cooling around 5-6 kbar [1]. The temperature during the formation of the symplectites has been estimated using Grt-Opx-thermometry and resulted in values of approx. 750°C for the pressure-range of 5-6 kbar, indicating essentially isothermal decompression.

Towards the interface with the Opx+Spl+Pl-symplectite garnet shows secondary diffusional zoning, which can be used for geospeedometry modelling. This zoning is characterized by increasing Fe and decreasing Mg towards the garnet rim. Diffusion modelling yields a time interval for symplectite formation of about 1000 years, dating thus an ephemeral episode during decompression within the geological time frame. Preservation of the delicate symplectite microstructures and the lack of penetrative deformation are consistent with isobaric cooling at 5-6 kbar suggested earlier.

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Microstructures, textures and interfaces of minerals

MIC-P04

The most frequent interfaces between olivine crystals

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Properties of polycrystalline materials are strongly controlled by the internal interface (grain boundary - gb) network, because the properties of gb's strongly differ from those of the crystal lattice. Any gb has a minimum of five degrees of freedom in orientation space: three to specify the axis and angle of misorientation (disorientation) between the two adjacent grains and two to describe the plane of the gb in the coordinates of the two crystals. Although the misorientation is often used to characterize gb networks, recent studies on metals and ceramics showed that the gb planes are much more significant for gb properties. Here, we determined the gb plane distribution of polycrystalline forsterite.

We used electron backscatter diffraction, EBSD, to detect over 2.100.000 data points and about 135.000 gb segments (traces).

We used the EDAX® (TSL) OIM software for mapping. Gb line segments were extracted and the resulting data set was evaluated with algorithms developed at Carnegie Mellon University, Pittsburgh, adapted specifically to allow for the evaluation of orthorhombic crystal symmetry. Using this approach, a full characterization of the gb character distribution, GB CD, defined as the relative areas of gb's of different types, distinguished by their five degrees of freedom (Rohrer, 2007) has been obtained.

The gb planes showed a preference for low index planes, which is in agreement with recent findings on other materials (e.g. MgO, TiO₂ etc.). Furthermore, it is in agreement with previously determined surface energies (e.g. Gurmani et al., 2011). In contrast to (Faul and Fitz Gerald, 1999) we did not observe a higher amount of grains with 60° misorientations.

From our measurements, we conclude that surface energy minimization probably occurs by faceting the gb planes to obtain as much area as possible of low-index surfaces that are also the low energy surfaces on single crystals. The gb area distribution therefore resembles the stereographic projection of an idiomorphic single crystal.

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MIC-P05

Behavior of Fe during dissolution-precipitation reactions

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We summarize observations on the grain boundary and the reaction front between experimentally and naturally grown titanite on rutile and kyanite on corundum during a dissolution-precipitation reaction. The experiments were carried out in the systems $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-HCl-H}_2\text{O}$ and $\text{TiO}_2\text{-SiO}_2\text{-(Al}_2\text{O}_3\text{)-CaO-NaCl-H}_2\text{O}$ ($\pm\text{CaF}_2$) in cold-seal and piston cylinder experiments, using natural or synthetic rutile resp. corundum crystals, with a NaCl- or HCl-bearing fluid as starting materials at conditions similar to the natural occurrences. Elements between the separated external sources and the mineral to be dissolved (corundum or rutile) are transported in the fluid and availability is controlled by the permeability of the reaction corona. Natural examples come from (partly retrograded) eclogite and granulite terranes (Münchberg area, NE Bavaria; Tromsø eclogite; Mysore, India). Two reaction fronts develop, one around corundum or rutile, and one between the reaction corona and the rock matrix. Here we focus on the phenomena of the reaction front of the dissolved crystal, and of the distribution of non-essential trace elements released from corundum resp. rutile, such as Fe, Cr, Nb, Zr and Hf.

The phase boundary around rutile in natural examples is characterized by a 200 nm wide zone of strong Fe-enrichment. The Fe-concentration is not connected to the presence of an Fe-mineral such as ilmenite inclusions in rutile at the reaction front; where an ilmenite lamella ends at the reaction rim, the concentration of Fe in the adjoining titanite and in the phase boundary is the same as in other areas. The phase boundary in a natural sample has an internal structure, with a partly amorphous and a partly crystalline zone, possibly with secondary(?) chlorite as the main constituent. The Fe-content in rutile decreases strongly near to the reaction front, and also the titanite crystal has its lowest Fe-contents near to the front. In contrast, HFSE in rutile increase strongly toward the front. Between natural corundum and kyanite, we observed Fe-enriched layers at the grain boundary of the corundum host and kyanite corona minerals. In experiments, we found that Fe in the corundum crystal is systematically leached in an up to 40 μm wide zone, which is enriched in Si.

Microstructures, textures and interfaces of minerals

MIC-P06

Computertomografische Vergleichsstudien rezenter Korallen und eisenzeitlicher Korallenzier

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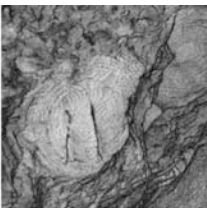
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Nach aktueller Datenlage sind die insbesondere für eisenzeitliche weiße Fibeldekors verwendeten Materialien rezente Korallen, aber auch fossile Korallen und z.B. Nummulitenkalke. Zur Charakterisierung des Ursprunges des im Forschungsmittelpunkt stehenden korallinen Dekors sind systematische materialwissenschaftliche und taxonomische Studien notwendig. Hierzu werden neben Korallenzier unterschiedliche rezente sowie fossile Korallenskelette zerstörungsfrei mittels der 3D-Mikro-Röntgen-Tomographie (3D- μ XCT) analysiert. Die Auflösungen im μ m-Bereich erlauben die Unterscheidung von auch innerhalb eines Objekts auftretenden verschiedenen Korallenarten, von Bohrwurminkrustationen und Silifizierungen sowie von Veränderungen wie die Phasenumwandlung von Aragonit zu Kalzit, die z.B. durch Langzeiteinflüsse von meteorischen Wässern erfolgen.

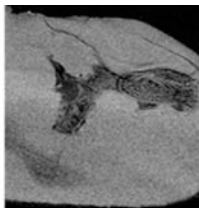
Die derzeitigen Ergebnisse verifizieren den 3D-taxonomischen Ansatz und sollen eine Eingrenzung der für die Korallenzier verwendeten Skelette auf wenige Spezies ermöglichen, wobei für rezente Arten der mediterrane Raum und für fossile Arten der baltischen Raum angenommen werden kann. In ausgewählter Korallenzier konnten neben korallinen Fossilien z.B. auch Nummuliten festgestellt werden.

Grundlegende chemische und physikalische Daten, die die computertomografische Charakterisierung komplettieren, wurden ebenfalls zerstörungsfrei zu Pigmenten (Raman-Spektroskopie) sowie zu Karbonatphasen und deren Mg-Gehalten (XRD) und zur Oberflächenmorphologie (SEM) erfasst.

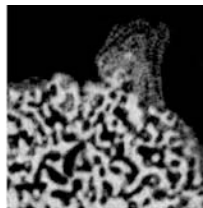
Aus systematischen sowie aus Anwendungsgründen werden zoologisch taxonomische Beurteilungen in die Studien einbezogen.



CT: Nummulitenkalk (Eozän u.a. in Geschieben Norddeutschlands)



CT: Fossiles Relikt in Fibel-besatz (Kleinkorbetha, Mitteldeutschland)



CT: Südsee-Koralle mit heller Aragonitkoralle und Aufwachsung von roter Kalzitkoralle

MIC-P07

Deformation fabrics at the transition from spinel to garnet Iherzolite in the CMAS system

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The fabrics of metamorphic rocks display abundant evidence that deviatoric stresses influence mineral reactions. Nevertheless, the influence of concurrent plastic deformation on phase transitions has received relatively little attention in the literature. In this project, we are investigating the reaction of clinopyroxene + orthopyroxene + spinel to garnet + olivine in the CMAS system under shear conditions and compare it with static phase transformation experiments. Starting materials were produced from glasses of the appropriate composition in piston cylinder experiments at 1 GPa and 1000°C for up to 10 days in order to increase grain size. The resulting samples show grain sizes of about 5-15 μm for all phases. Samples were then deformed in a 6-axis multi-anvil press (Manthilake et al., 2012) in the garnet stability field at 1100°C and 2.5 GPa to 30% pure shear at strain rates between 5×10^{-5} and $5 \times 10^{-6} \text{ sec}^{-1}$.

Preliminary results show that the production of garnet is significantly higher in the deformed samples (up to a factor of 2 to 3) than in the statically annealed reference sample indicating that deviatoric stresses enhance the reaction rate. Also faster strain rates (higher stresses) appear to promote garnet growth. Quantitative analysis of the changing phase proportions however are complicated by chemical gradients between phases due to the sluggish kinetics of the reaction. The deformed samples showed extremely homogeneous strain distribution and only weak development of CPO in olivine and clinopyroxene, indicating that deformation likely occurred by diffusion-assisted grain boundary sliding. Newly formed garnet grains at the phase boundaries between spinel and pyroxene have a grain size up to 10 μm and form larger ($> 200 \mu\text{m}$) domains of equal orientation both in the statically and dynamically reacted samples. In the deformed samples the orientation domains additionally show continuous orientation dispersion around the intermediate fabric axis, indicating that orientations change continuously with progressive deformation similar to the growth of porphyroblastic snowball garnets (e.g. Robyr et al., 2014).

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PHY-T01

Strength of (Mg,Fe)O Ferropericlasite and the Fate of Subducting Slabs in Earth's Lower Mantle

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The properties of the lower mantle, Earth's largest shell by volume, largely impact global geodynamic processes. (Mg,Fe)O ferropericlasite is the second most abundant mineral phase in Earth's lower mantle and may play a key role for the deformation behavior of the lower mantle and for generating seismic anisotropy (1). Particularly in large strain regions of Earth's mantle, bulk mantle deformation may be controlled by strain rate partitioning into ferropericlasite, which is thought to be the rheologically weakest mantle phase (2).

Here, we present results from synchrotron radial x-ray diffraction measurements on (Mg_{0.9}Fe_{0.1})O and (Mg_{0.8}Fe_{0.2})O carried out at the Advanced Light Source (Lawrence Berkeley National Laboratory) up to 100 GPa. We find evidence for a marked increase of yield strength from 30 to 70 GPa, making ferropericlasite 3-4 times stronger in the lowermost mantle than predicted previously. In large strain regions of Earth's lower mantle, such as around subducting slabs, the strength increase will limit strain rate partitioning into ferropericlasite, thereby locally increasing mantle viscosity. We will discuss the impact of the strength increase on the fate of subducting slabs.

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PHY-T02

Atomistic modelling of dislocations in MgSiO_3 perovskite

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The heat transfer from the mantle results from convection, involving plastic flow of high pressure phases in the solid state. The plasticity of $(\text{Mg,Fe,Al})(\text{Si,Al})\text{O}_3$ perovskite, the main constituent of the lower mantle, is therefore crucial to understand the Earth's dynamic. Its deformation occurs at very low strain rate (from 10^{-12} to 10^{-16} s^{-1}), and under extreme pressure and temperature conditions (from 30 to 140 GPa, 500 to 4000°C), which are challenging to reach experimentally.

The recent progress in the modelling of materials behaviour, which until now have been mostly used on metals, are applied here on MgSiO_3 perovskite (Mg-Pv), by means of dislocation modelling at the atomic scale. This work is an attempt to understand the plasticity of Mg-Pv, by being the first step of a multi-scale modelling of its deformation.

MgSiO_3 perovskite has an orthorhombic structure, described within the $Pbnm$ space group. Orthorhombic distortions from the ideal perovskite structure are enhanced by pressure. We model dislocations with $[100]$ and $[010]$ Burgers vectors, which correspond to the shortest lattice parameters. Dislocation cores are relaxed in molecular statics calculations at various pressures, using classical rigid-ion pairwise potential. The determination of the dislocations resistance to glide indicates that $[100](010)$ and $[010](100)$ are the easiest slip systems in Mg-Pv, in the full pressure range of the mantle.

To assess the mobility of dislocations under the action of stress and thermal activation, we rely on i) Nudged elastic band calculations to evaluate the lattice friction and ii) calculations of the nucleation energy of kinks on a dislocation line. Both quantities being useful to introduce the effect of temperature on dislocation glide. From the dislocation mobility, a first expression of the strain rate produced by dislocation glide can be calculated.

PHY-T03

Modelling of dislocation mobility in transition zone minerals

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Solid-state convection in the transition zone of the Earth's mantle is controlled at the microscopic scale by plastic deformation of wadsleyite and ringwoodite. These consecutive high-pressure polymorphs of olivine are considered to be the dominant phases in the boundary separating the upper from the lower mantle, a region over which the viscosity is thought to increase rapidly.

Here, we study crystal defects in these high-pressure polymorphs using computational material science. This is a promising approach to identify and describe the strain producing crystal defects responsible for plastic flow in extreme conditions of the deep Earth. In this study we focus on dislocations which are usually considered as the most efficient defects contributing to intracrystalline deformation. The Peierls-Nabarro-Galerkin (PNG) model is used to predict the dislocation structures and fundamental properties of both Mg_2SiO_4 high-pressure polymorphs integrating the non-elastic nature of dislocations from atomic scale DFT based calculations.

The onset of dislocation mobility at high finite mantle temperatures is related to thermally activated nucleation and propagation of kink-pairs under deviatoric stress. A mobility law is derived by constructing a kink-pair nucleation model parametrized by the PNG-results. The original contribution of the present work is to elaborate this model for dissociated dislocations as they occur in wadsleyite and ringwoodite. This allows us to predict the critical activation enthalpy inherent to kink-pair nucleation required to overcome lattice friction. The model suggests the possibility of different kink-pair mechanisms for dissociated dislocations to exist as a function of stress controlling the rate of glide. The effective glide velocity is exponentially related to the critical kink-pair nucleation enthalpy which leads to the first estimates of transition zone viscosities due to the onset of glide. Evaluating the athermal temperatures reveals the rate controlling character of dislocation glide in this mantle boundary region.

These are the first quantifications bridging the fundamental properties of defects in complex transition zone silicates and a potential deformation process active in the Earth's interior.

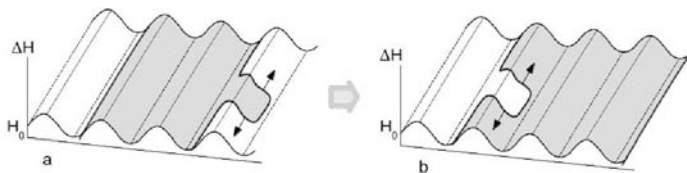


Fig 1. Example of a kink-pair nucleation mechanism. a) Nucleation on the leading partial of a dissociated dislocation over the energy barrier associated to lattice friction. b) Nucleation of the trailing partial after propagation of the first kink-pair.

PHY-T04

Temperature dependence of [100](010) and [001](010) dislocation mobilities in natural olivine

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Olivine is the most abundant mineral in the upper mantle, and its rheological properties are keys to understand the mantle dynamics. Knowledge of dominance of slip systems can be used to assess flow pattern in the mantle combining with observation of seismic anisotropy. The open question is what a determinant of a dominant slip system is. The dominant slip system is usually determined from deformation experiments. However, the deformation experiments may lead to misinterpretations due to the extremely large stress applied to the sample in comparison with the stress conditions in the earth's interior. In order to avoid these problems, dislocation recovery experiment was conducted in this study, in which dislocation mobility is measured under quasi-hydrostatic conditions. The mobilities of dislocations formed by the [100](010) and [001](010) slips were measured as a function of temperature at ambient pressure, in order to examine whether temperature is a key parameter for the dominant slip system. The activation energies are found to be 420 ± 120 kJ/mol and 390 ± 80 kJ/mol for the [100](010) and [001](010) dislocations respectively. Our result suggests that temperature is not a determinant of a dominant slip system. The similarity between these activation energies and that of Si self-diffusion (410 ± 30 kJ/mol) suggests that Si diffusion controls dislocation motion under low stress conditions. On the other hand, the higher activation energy acquired by deformation experiments (~ 500 kJ/mol) compared with this study indicated that the deformation mechanism in the deformation experiments may be different from that of dislocation motion under low stress conditions.

Mineral physics and the deep Earth's interior

PHY-T05

Melting relations in the system $\text{CaCO}_3\text{-MgCO}_3$ at 6 GPa

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Buob et al. (2006) performed sub- and super-solidus experiments in the system $\text{CaCO}_3\text{-MgCO}_3$, using the multi-anvil press at 6 GPa and at high temperatures. In comparison to the low pressure experiments by Byrnes & Wyllie (1981) and Irving & Wyllie (1975) in the system $\text{CaCO}_3\text{-MgCO}_3$, Buob et al. (2006) showed how higher pressures have a large impact on the topology of the phase diagram. However, more data are needed to fully understand the phase relations, especially on the Mg-rich side of the phase diagram at 6 GPa. Buob et al. (2006) reported tremendous quenching problems, which made the determination of the phase relations at the Mg-rich side of the phase diagram at 6 GPa impossible. As a consequence the phase relations are only plotted schematically in their Fig. 3. Furthermore the melting point of magnesite at 6 GPa is controversially reported. Buob et al. (2006) estimate it as 1650 °C based on experiments of Irving & Wyllie (1975), while Shatskiy et al. (2014) propose 1900 °C based on experiments of Katsura & Ito (1990).

To avoid quenching problems we investigate the super-solidus phase relation of the Mg-rich side of the phase diagram, using a rotating multi-anvil press. This allows us to grow big crystals and to separate them from the melt at 6 GPa shortly before quenching. The recovered capsule with the run product were cut into two halves and one half was polished for electron microprobe analyses. To determine the melting point of magnesite two approaches were applied: first the falling sphere method (Baker 2004) and second in-situ differential thermal analysis in the multi-anvil press (Fukui et al. 2000). So far the first results indicate a shape of the corresponding phase diagram that is completely different to the estimate of Buob et al. (2006) with the melt composition being much more Mg-rich.

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PHY-T06

Nano-inclusions in milky diamonds from Juina, a super deep source

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Investigations of diamonds from super deep sources enable to explore mantle processes down to the transition zone and even the lower mantle [e.g. 1-7]. To better understand the origin of these specific diamonds it is essential to get information on the nature of the medium from which they crystallize and on the conditions prevailing during their formation. We performed a combined nano Synchrotron X-Ray Fluorescence (nano-SXRF) and Transmission Electron Microscopy (TEM) study on nano-inclusions of a unique set of milky diamonds from alluvial deposits in Rio Soriso, Juina area, Brazil. The Focused Ion Beam (FIB) technique was applied to prepare TEM slices at the GFZ Potsdam. The investigated Juina diamonds contain several thousand of nano-inclusions with a size range between 30 and 200 nm. Especially the smaller ones exhibit well-developed octahedral crystal faces. Nano-SXRF mapping provide the trace element distribution across millions of the nano-inclusions. Only a few seem to contain element concentrations above detection limit. TEM bright field and dark field images shows stress halos around each nano-inclusion which indicates trapped solids or fluids. EELS studies of individual nano-inclusions show the expected C K-edge at 288 eV for sp^3 hybridized carbon together with a distinct pre-peak at 283 eV which may result from sp^2 -bonds. A few EELS measurements reveal the N K-edge at 401 eV. The presence of high amounts of N may explain the rarity of measurable element concentrations during nano-SXRF studies since light elements like N are not detectable with this method. Detected Moiré pattern indicate a solid phase in some of the inclusions. Most likely, a subset of nano-inclusions consists either of N_2 or NH_3 .

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Mineral physics and the deep Earth's interior

PHY-P01

Theoretical prediction of new CaAl_2O_4 high-pressure super dense phase

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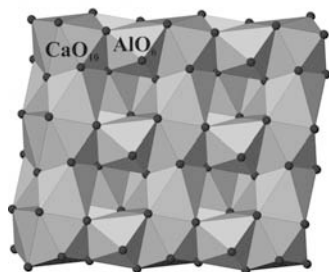
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²IGMR of NAS of Ukraine, Physics of mineral substance, Kiev, Ukraine

The aim of this work was to summarize the observed and simulated structure types of CaAl_2O_4 and theoretically analyze with the help of *ab-initio* (QE code [1]) and atomistic techniques (GULP code [2] using self-developed interatomic potential set [3]) their ability to be probable candidates for lower mantle conditions. Changes in crystal structure geometry, interatomic distances, phase densities and elastic properties of four CaAl_2O_4 structures under investigation (two «marokite-like» structures, «layer» structure, described firstly in [4] and new hypothetical one) were determined in 0-200 GPa pressure range. Both simulation methods predicted the appearance of unknown yet super-dense CaAl_2O_4 modification, based on « $\alpha\text{-PbO}_2$ » motive. This structure refers to the space group $P2_1/n$. Results of semi-empirical and *ab-initio* calculations are correlated with each other but differ in the details. For example, from the results of *ab-initio* calculations new predicted phase becomes the densest modification at $P=170$ GPa, whereas atomistic calculations predicted this value equal to 150 GPa. In the optimized structure the coordination of Al can be described as distorted octahedra with a range of Al-O distances from 1.72 to 1.98 Å (at $P=200$ GPa). Note, that the 7-th oxygen is only slightly farther (2.28 Å). Ca atoms are situated in distorted 10-vertex oxygen polyhedra with Ca-O distances from 1.96 to 2.49 Å (fig. 1). Bulk modulus of this structure is much smaller in magnitude than those of marokite-like phases, so this structure has a much larger compressibility allowance.

Thus two independent calculation methods predict the appearance of unknown yet super-dense modification of the simple CaAl_2O_4 chemical composition, which can accumulates Ca and Al atoms at Earth's lower mantle pressures. The existence of this phase can be verified experimentally at high pressures.

This study was supported by the RFBR (№№ projects 12-05-00809, 12-05-00983). Computer simulations were performed on the SKIF MSU supercomputer.



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Linkage of CaO_{10} polyhedral and AlO_6 octahedral in super dense CaAl_2O_4 structure.

PHY-P02

Atomistic modeling of dislocations with [100] Burgers vector in MgSiO₃ post-perovskite

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The recently discovered MgSiO₃ post-perovskite phase (*Cmcm*) is only stable at high pressure and temperature conditions corresponding to the lowermost ~150km of the mantle (the D" layer). The unusual for the high-pressure phases layer-like structure of the post-perovskite may be responsible for the observed seismic anisotropy of the D" layer. However, mechanical properties, information about dislocations and their behaviour under stress are not well known still. This work represents a theoretical study of the post-perovskite within the semi-empirical approach using the Buckingham interatomic potential parameters previously derived by [3].

To describe the energy cost incurred as a result of a shift and to deduce the most favorable slip systems, the GSF excess energies are calculated at 120 GPa. The lowest energy barrier as well as the smallest values of the ideal shear stress (ISS), are related to the slip systems with the smallest [100] Burgers vector ($b=2.521$ Å) and to the slip system [001](010) with the glide plane cutting only Mg-O bonds. Good agreement with the *ab-initio* results [4] verifies the accuracy of the chosen interatomic potential model [3].

The C-lattice of the post-perovskite results in four potential Burgers vectors: [100], [010], [001] and $\frac{1}{2}$ [011]. Taking into account the results of GSF calculations, the [100] Burgers vector was chosen as the most promising to test first. After structural relaxation, two possible locations of the stable [100] screw dislocation were revealed. Both dislocations have pure screw cores spreading in {011}. The observed geometry of the dislocation core spreading (Fig. 1) suggests the [100](010) slip system as the most probable. Indeed, the evaluated Peierls stress for the [100](001) slip system is more than ten times bigger than for [100](010).

Modeling of [100] edge dislocations is in progress.

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Mineral physics and the deep Earth's interior

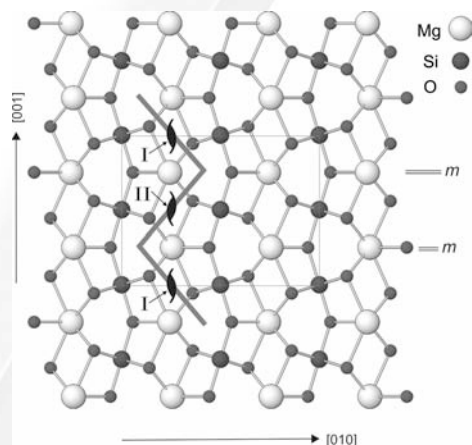


Fig.1. The observed spreading of the [100] screw dislocation cores in MgSiO_3 post-perovskite

PHY-P03

Stability and structure of $\text{Mg}_2\text{Fe}_2\text{O}_5$ at high P-T conditions

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Most parts of the deep upper mantle and transition zone are characterized by the presence of spinel-structured phases that can incorporate Fe^{3+} and Fe^{2+} in their structure. More recently, a new oxide structure with M_4O_5 stoichiometry has been discovered [1, 2], opening the possibility for an additional Fe^{3+} -bearing phase in transition zone mineral assemblages. In addition, the potential stability of the Mg analog to Fe_4O_5 , (i.e. $\text{Mg}_2\text{Fe}_2\text{O}_5$) could have implications for the phase relations of magnesioferrite-rich spinel (MgFe_2O_4).

To determine whether $\text{Mg}_2\text{Fe}_2\text{O}_5$ may be a stable phase under mantle conditions, we performed high-pressure multi anvil experiments at pressures between 8 and 23 GPa and temperatures of 1100-1550 °C. The starting materials were stoichiometric mixtures of MgO and Fe_2O_3 or pre-synthesized MgFe_2O_4 . A high $f\text{O}_2$ was achieved by addition of PtO_2 powder to the sample. Run products were analyzed by electron microprobe and powder X-ray diffraction. Our experiments demonstrate that the $\text{Mg}_2\text{Fe}_2\text{O}_5$ end-member composition becomes stable between 14 and 18 GPa at 1300°C. The lower pressure stable assemblage is MgO + Fe_2O_3 .

$\text{Mg}_2\text{Fe}_2\text{O}_5$ is isostructural with Fe_4O_5 and has cell parameters: $a = 2.8887(2)$ Å, $b = 9.7273(8)$ Å, $c = 12.5495(10)$ Å and a volume of $352.63(3)$ Å³. Single-crystal structural refinements of this phase reveals that Mg is present in all structural sites, although it preferentially occupies the large prismatic M3 and the “wüstite-like” M1 octahedral sites. The substitution of Mg into the Fe_4O_5 structure gives rise to a more regular M1 octahedral site and it affects the coordination of the M2 site by reducing significantly the difference between the longest M2-O2 bond distance and the other relatively shorter bonds. Thus the coordination of M2 becomes more similar to an octahedral coordination instead of pyramid with rectangular base as in Fe_4O_5 and CaFe_3O_5 [4].

Additional experiments with MgFe_2O_4 compositions reveal that the spinel-phase breaks down to

$\text{Mg}_2\text{Fe}_2\text{O}_5 + \text{Fe}_2\text{O}_3$ at 15 GPa and 1550°C indicating that the phase relations of MgFe_2O_4 must be more complicated than those proposed by [3].

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Mineral physics and the deep Earth's interior

PHY-P04

Structural properties of carbonate-silicate melts in the system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2$ – incorporation of trace elements investigated by Extended X-ray Absorption Fine Structure Spectroscopy

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Carbonatitic volcanism generally occurs within intraplate settings often associated with continental rifting. The only active carbonatitic volcanism is observed at the Oldoinyo Lengai, Tanzania, generating carbonatites in close association with phonolites and nephelinites¹. Although the processes of carbonatite genesis remain unclear, there is strong evidence that carbonate-bearing melts play a crucial role during mantle-melting, for diamond formation and as metasomatic agents. Carbonate melts show unique properties such as extraordinary low melt viscosities and densities, exceptional high surface tensions and electrical conductivities as well as distinct geochemical affinities to a wide range of trace elements². To understand their chemical and physical behaviour as well as the processes operating in the deep Earth, it is fundamental to elucidate the structural properties of carbonate-bearing melts. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a versatile tool for investigating the short- to medium-range structural properties of melts and glasses in an element specific way. This study aims at unravelling the influence of carbonate concentration on the structural incorporation of geochemically important trace elements such as Y, Sr and Rb in silicate melts with varying carbonate concentration in the system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2$. In this contribution, the structure of (carbonate-bearing) silicate melts is investigated on glass samples quenched from high temperature and pressure. EXAFS measurements were conducted at the synchrotron facility beamlines SAMBA (SOLEIL) and BM23 (ESRF) in fluorescence mode. Information derived on the trace elements' local structure will be used to develop a structural model for carbonate-silicate melts. Ultimately, the project will contribute to gain insight into the structural control on chemical fractionation processes in carbonate-bearing magmatic systems in the deep Earth.

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PHY-P05

Pressure-induced structural phase transition of Pb-lawsonite

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Lawsonite-type compounds $A^{2+}B^{3+}_2[(OH)_2[Si_2O_7] \cdot H_2O$ ($A = Ca, Sr, Pb, Ba$; $B = Al, Mn$) are hydrous sorosilicates with structurally bound OH^- groups and H_2O molecules. Lawsonite ($CaAl_2$) has a relatively high density (3.09 g/cm^3) and is stable within a broad p-T field [1, 2]. Because of the high water content lawsonite is considered a potential carrier of H_2O into the deep Earth [3, 4].

Pb-lawsonite end-member was synthesised in a piston cylinder press at 4 GPa and 600 °C at GFZ Potsdam. Pressure-dependent Raman spectra of the synthetic Pb-lawsonite powder were acquired at the GFZ Potsdam in diamond anvil cells up to 16 GPa using two different pressure-transmitting media (NaCl, Argon).

According to [2 and 5] Ca-lawsonite shows a clear and reversible structural transition to a high-pressure modification in the region of 8.5-11 GPa and there are indications for another pressure-induced transition at 4 GPa. The first transition occurs through the shearing of $(010)_{\text{ortho}}$ planes containing AlO_6 octahedral chains in the $[100]_{\text{ortho}}$ direction [2].

Analyses of p-dependent Raman-spectra let us to the conclusion that Pb-lawsonite transforms to a high-pressure modification also at about 11 GPa despite the different space group of Pb-lawsonite compared to Ca-lawsonite. The Pb-lawsonite Raman spectra show a well pronounced discontinuity at 11 GPa in the Raman shift of the Si-O-Si symmetric stretching band at 667 cm^{-1} (RT, ambient pressure). In an attenuated form this discontinuity can also be seen in the shift of the Si-O-Si bending vibration at 446 cm^{-1} as well as in the bandwidth behaviour, determined with autocorrelation analysis of the spectral region between 630 cm^{-1} and 1150 cm^{-1} . This region contains mainly symmetric and antisymmetric stretching vibrations of Si-O-Si and SiO_3 units.

Moreover, band shifts and autocorrelation analysis indicate a weak discontinuity at around 3 GPa.

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PHY-P06

In situ X-ray diffraction investigations of goethite (FeO(OH)) and groutite (MnO(OH)) at high pressures and temperatures

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The P - V - T behavior of goethite (FeO(OH)) and its Mn-analogue groutite (MnO(OH)) has been determined under high pressures and high temperatures up to 7.5 GPa and 500 °C using a MAX 80 cubic anvil high-pressure apparatus (DESY, HASYLAB, Hamburg, Doris III, Beamline F.2.1). Several experimental runs were carried out for both minerals, first compressing the samples at room temperature and then heating them until a breakdown reaction occurred. For FeO(OH) other P - T paths were chosen as well. The samples were mixed with vaseline to ensure hydrostatic pressure transmitting conditions, NaCl served as an internal standard for pressure calibration. Energy dispersive diffraction patterns were collected at a fixed 2θ angle ($\theta \approx 4.52^\circ$). At pressures > 7.1 GPa and temperatures > 310 °C respectively $P > 6.3$ GPa and $T > 350$ °C the transformation goethite - ϵ -FeO(OH) was observed. The transformation pressure is slightly lower than reported by [1]. Between 400 °C and 450 °C the sample dehydrated to hematite. By fitting a Birch-Murnaghan EOS to the data, the bulk modulus of goethite was determined as 112.26 ± 2.26 GPa, ($K' = 4$), $V_{T,0} = 138.79 \pm 0.10 \text{ \AA}^3 \cdot \exp \left[\left((0.497 \pm 0.103) \times 10^{-4} dT \right) \right]$, $(\partial K_T / \partial T)_P = -0.033 \pm 0.020 \text{ GPa K}^{-1}$. The V_0 value is in very good agreement to the value from the literature [2]. Our value for K supports [3] and disagrees with [4]. The obtained bulk modulus for ϵ -FeO(OH), $K = 143.4 \pm 14.9$ GPa, $V_0 = 66.18 \pm 0.15 \text{ \AA}^3$, ($K' = 4$), is in accordance with literature values [4], [5]. Groutite is more compressible than goethite. For the Mn-analogue we obtained $K = 87.26 \pm 3.4$ GPa, $V_0 = 139.76 \pm 0.14 \text{ \AA}^3$, ($K' = 4$).

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CRY-T01

P-T-X controls on K and Na incorporation in dravitic tourmaline

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Potassium is commonly considered incompatible in tourmaline $[XY_3Z_6(T_6O_{18})(BO_3)_3V_3W]$ and typically found in trace concentrations at the [9]-coordinated X-site. However, K concentrations as high as 0.58 K pfu have been found in otherwise dravitic tourmaline from the (ultra) high-pressure rocks of the Kokchetav Massif, Kazakhstan (Shimizu and Ogasawara, 2005), and recently we synthesized tourmaline with up to 0.71 K pfu at 4.0 GPa and 700°C (Berryman et al., 2014), raising the question of the influence of pressure on tourmaline's ability to incorporate K into its structure. To investigate the effect of pressure, fluid composition, and temperature on the relative incorporation of Na and K at the X-site, we synthesized dravitic tourmaline in the $MgO-Al_2O_3-B_2O_3-SiO_2-KCl-NaCl-H_2O$ system from an oxide mixture and excess fluid at a range of conditions: 0.2 - 4.0 GPa, 500 - 700°C, and variable fluid composition. Analysis of the synthesized tourmaline by electron microprobe (EMP) and transmission electron microscopy (TEM) shows that the incorporation of K at the X-site increases with pressure, temperature, and KCl concentration in the fluid; a maximum of 0.71 K pfu (leaving 0.29 X-sites pfu vacant) was incorporated in K-dravite synthesized at 4.0 GPa from a 4.67 *m* KCl, Na-free fluid. In contrast, Na incorporation depends predominately on fluid composition rather than pressure; dravite with the highest-measured Na content of 0.96 Na pfu was synthesized at the lowest pressure investigated (0.2 GPa) from a 4.11 *m* NaCl and 1.24 *m* KCl fluid. In addition, increasing temperature is slightly negatively correlated with Na incorporation. Comparison of our results to K-dravite from the Kokchetav Massif suggests that the latter formed in a K-rich, Na-poor environment at ultrahigh metamorphic grade, in or near the diamond-stability field.

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CRY-T02

Al-Mg disorder and tetrahedrally coordinated B in synthetic K- and Mg-rich tourmaline

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The tourmaline mineral group is chemically one of the most complicated groups of silicate minerals, with the general formula $X Y_3 Z_6 [T_6O_{18}] (BO_3)_3 V_3 W$. In natural Mg-rich tourmalines the X site is usually occupied by Na, Mg is predominantly found at the Y site, Al at the Z site, Si at the tetrahedral (T) site, and B in a trigonally coordinated site. Recently, Berryman et al. (2014) synthesized Mg-rich tourmaline in the $MgO-Al_2O_3-B_2O_3-SiO_2-KCl-NaCl-H_2O$ system with up to ~0.7 apfu K at 4.0 GPa and 700°C. From one of these synthetic tourmaline crystals (size ~20 µm in length), a single crystal structure refinement was performed. As a first step, the quality of the crystal was checked with a KAPPA APEX II CCD single-crystal X-ray diffractometer. The same crystal was subsequently measured with a STOE StadiVARI four-circle goniometer with a Dectris PILATUS 300K pixel detector. The results of the refinement show that the $\langle Y-O \rangle$ and $\langle Z-O \rangle$ distances are ~2.01(1) and ~1.93(1) Å, respectively. This can only be explained by significant disorder of Mg and Al between the two 6-coordinated sites (Y and Z site). Surprisingly, a significant amount (~0.6(1) apfu) of tetrahedrally coordinated B was identified for the first time in a Mg-rich tourmaline. A similar substitution of Si by B was already observed in Al-rich tourmalines by different authors (e.g., Ertl et al., 1997; 2012). These results show that significant amounts of B at the T site cannot be excluded in natural and synthetic Mg-rich tourmalines.

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CRY-T03

Temperature-induced $P2_1/c$ to $C2/c$ phase transition in radiation damaged titanite

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In titanite (endmember composition CaTiSiO_5) actinides like U and Th can occur as natural constituents of the crystal structure. After a period of time the long-range ordered crystal structure is destroyed by self-radiation damage resulting from α -decay events of the radiogenic impurities. [1]

We present our results of recent in situ temperature-dependent Raman spectroscopic measurements of two partially amorphous (metamict) titanite samples with accumulated radiation doses $\sim 1.2 \times 10^{18}$ α -events/g (E2335) and $\sim 2.2 \times 10^{18}$ α -events/g (M28696) and amorphous fractions of 0.24 and 0.5, respectively. They provide evidence for a thermally induced transformation analogous to the phase transition $P2_1/c \leftrightarrow C2/c$, which is characteristic of endmember titanite. Quantitative analysis of the temperature evolution of the wavenumbers and widths of Raman-active vibrations in both partially amorphous titanites reveals an anomaly near 500 K which is consistent with the $P2_1/c \leftrightarrow C2/c$ phase-transition temperature of titanite close to its endmember composition. The structural transformation near 500 K is observed by Raman spectroscopy even in heavily radiation-damaged and chemically inhomogeneous titanite (M28696). The microstructure of the samples consists of coexisting amorphous and crystalline domains, with the $P2_1/c$ to $C2/c$ phase-transition occurring in the latter. [2]

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CRY-T04

Investigating the annealing dependency of Al/Si distribution in Eifel sanidine

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Sanidine is the monoclinic high-T modification of K-rich alkalifeldspars. Annealing at $T > 900^{\circ}\text{C}$ usually causes disordering of Al/Si distribution at the two non-equivalent tetrahedral sites, but it is supposedly possible to disorder samples of sanidine from Volkesfeld/Eifel at notably lower temperatures and shorter times [1]. To investigate this behavior and compare various approaches to obtain the Al/Si distribution, samples from different Eifel locations and Madagascar have been studied. Al/Si order was determined by direct and indirect methods.

Neutron powder diffraction experiments were executed at Fine Resolution Neutron Powder Diffractometer E9, single crystal neutron diffraction at 4-circle Diffractometer E5 and diffuse neutron scattering experiments at Flat-Cone Diffractometer E2, all located at the Berlin Research Reactor BERII. The Al/Si distribution was determined directly, refining site occupancies by applying Rietveld analysis to powder diffraction data and XTAL for single crystal data. This approach is inapplicable when using X-ray data, due to similar atomic form factors of Al^{3+} and Si^{4+} , thus indirect methods [2,3] were applied. X-ray powder diffraction was performed at Helmholtz Centre Berlin, single crystal X-ray diffraction at Ruhr-University Bochum. The obtained data was processed using Rietveld refinement and ShelXL software respectively.

It was possible to verify a dependency of decreasing Al/Si order on increasing annealing times and temperatures. We observed different results from direct and indirect methods, regardless whether samples were untreated or annealed. A stronger change of Al/Si distribution during annealing was revealed applying direct determination. Surprisingly we couldn't observe any difference in annealing behaviour of sanidine from Eifel and Madagascar, suggesting the Al/Si distribution is not the origin of the optical anomalies observed in sanidine from Volkesfeld.

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CRY-T05

Structural processes during zeolite collapse and comparison with melt quenched glass

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Zeolite crystals are characterized by an open crystal structure comprising large cages formed by $[\text{SiO}_4]$ - and $[\text{AlO}_4]$ -tetrahedra, hosting different cations such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} or even larger molecules like H_2O . Upon heat or pressure treatment the crystal structure collapses to the amorphous state before recrystallizing to a denser crystal structure.

We will present Raman- and IR spectroscopic data showing the structural collapse of

(Na, K)-LSX zeolite collapse. Additional thermal analysis and in-situ high temperature XRD are providing kinetic information on the collapse process.

The properties of the amorphous state achieved through the zeolite collapse will be compared to a normal melt quenched glass of the same chemical composition. Regarding the existence of an *ideal glass*, this is of major scientific interest.

CRY-T06

First crystal-structure descriptions of natural mullite and a related mineral termed “sillimullite”

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Synthetic mullite represents one of the most prominent ceramic materials due to its outstanding properties, such as high temperature stability in harsh atmospheres, its low thermal conductivity, and especially the favorable creep behavior and the low thermal expansion, the latter causing a very favorable thermal shock behavior. The mineral mullite occurs only rarely in nature because of its high temperature - low pressure formation conditions. The first occurrence of natural mullite from the Isle of Mull (Western Scotland) was mentioned in a footnote by Bowen and Greig (1924). The crystal structure of the natural mullite is closely related to its synthetic counterpart but has not been described yet due to its fibrous morphology with thin needles preventing accurate structure refinements with diffraction data. Here, we describe the crystal structure of natural mullite found in the Eifel area (Germany) having a more isometric habit suitable for single-crystal X-ray diffraction studies.

A new mineral from the Eifel area intermediate between sillimanite and mullite, named “sillimullite”, was studied by electron microprobe analyses and single-crystal X-ray diffraction methods. The chemical compositions derived from microprobe investigations and crystal-structure refinements are $\text{Al}_{7.84}\text{Fe}_{0.18}\text{Ti}_{0.03}\text{Mg}_{0.03}\text{Si}_{3.92}\text{O}_{19.96}$ and $\text{Al}_{8.28}\text{Fe}_{0.20}\text{Si}_{3.52}\text{O}_{19.76}$, respectively. The first composition is close to a stoichiometric sillimanite (with Fe, Ti, and Mg incorporated) and the second composition is between sillimanite and mullite. The discrepancy between the two compositions is assumed to be caused by nano-scaled exsolution of amorphous SiO_2 from a phase of sillimanite composition which is beyond the resolution of the microprobe, while the diffraction data are not affected by the presence of SiO_2 . Sillimullite crystallizes in the orthorhombic space group $Pnam$ with $a = 7.5127(4) \text{ \AA}$, $b = 7.6823(4) \text{ \AA}$, $c = 5.785(3) \text{ \AA}$, $V = 333.88(4) \text{ \AA}^3$, $Z = 1$. It has a complete Si/Al ordering like sillimanite but with neighboring double chains of SiO_4 and AlO_4 tetrahedra having an offset of $\frac{1}{2}$ parallel c relative to each other causing - in the usual setting with $a < b$ - the change of the space-group setting from $Pbnm$ (sillimanite) to $Pnam$. Therefore, the crystal studied here can be considered to represent a new mineral intermediate between sillimanite and mullite, designated as sillimullite.

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CRY-T07

New insights into the crystal structures of uranyl sulfate minerals

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Uranyl sulfate minerals and compounds are important products after weathering of uraninite (Plášil 2014). During past few years several new uranyl sulfates were discovered, providing us new insights into the complex crystal chemistry of these minerals. U^{6+} forms in solid state most frequently two triple axial U-O bonds, resulting in formation of a uranyl ion, $[UO_2]^{2+}$. This, in turn, can further be coordinated in the equatorial plane by four, five or six ligands, leading to a square, pentagonal, or hexagonal bipyramidal coordination, respectively. The geometrical characteristics for these coordinations have been reviewed in detail by Burns et al. (1997) and Burns (2005), giving the typical bond lengths for the distinct coordination geometries. In general, the strong directional anisotropy of bond distribution observed in the typical uranyl coordination geometries favors the formation of low-dimensional structures, consisting of 2D - layer, or 1D - chain structures of U-oxide bonds, with a strong prevalence of layered structures. Topologies of the structural units of U^{6+} minerals and compounds can be represented by corresponding graphs (Burns 2005), in order to simplify and classify them. A bond-valce approach (Hawthorne and Schindler 2008; Schindler and Hawthorne 2008) give us also a predictive besides explanatory power, which can help us in better understanding the stereochemstry of interstitial complexes in uranyl oxyalts, which are crucial for their thermodynamic stability. Here, such approach is discussed with regard to the recently discovered new uranyl sulfate minerals.

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CRY-P01

Synthesis and structure of a new crystalline silicic acid:

Hydrated H-Apophyllite, $\text{H}_{16}\text{Si}_{16}\text{O}_{40} \cdot 8 \text{H}_2\text{O}$

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Crystalline silicic acids are layered silicates prepared by acid leaching of alkaline and alkaline earth layer silicates. Synthetic materials as well as minerals have been used as parent materials, e.g. Apophyllite, Magadiite, $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$, etc. The ion exchange of Na^+ , Ca^{2+} , etc. against H^+ leads to silicic acids like H-Magadiite or Disilicic Acid I. The crystal structures of most crystalline silicic acids, including the one of H-Apophyllite [1] remained, however, unsolved due to severe structural disorder. So far, the structures of only three silicic acids have been solved: H-LDS [2], H-RUB-18 [3] and Disilicic Acid I [4].

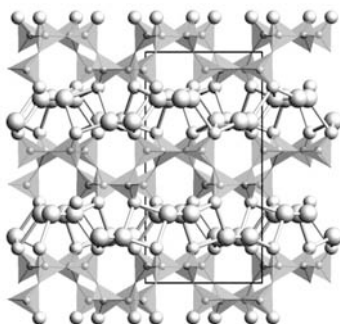
Hydrated H-Apophyllite, was synthesized at 0°C by leaching a natural Apophyllite crystal $\text{KCa}_4[\text{Si}_8\text{O}_{20}(\text{OH}/\text{F})] \cdot 8 \text{H}_2\text{O}$, in a large surplus of 1.2 M hydrochloric acid. TG/DTA, NMR and FTIR spectroscopy confirmed that Hydr. H-Apophyllite is a hydrous layer silicate. The XRD powder pattern was indexed in tetragonal symmetry (P4/ncc) with $a_0 = 8.8 \text{ \AA}$ and $c_0 = 14.6 \text{ \AA}$. The crystal structure was solved by model building; a subsequent Rietveld refinement converged to $R_{\text{Bragg}} = 0.033$ and $\chi^2 = 1.3$ confirming the structure model. Hydr. H-Apophyllite contains silicate monolayers of the same topology as present in Apophyllite. The silicate layer is constructed from interconnected 4-rings forming a puckered layer. A sheet of hydrogen bonded water molecules is intercalated between the silicate layers. There are strong hydrogen bonds between the terminal OH groups of the silicate layers and adjacent water molecules ($d(\text{O} \dots \text{O}) = 2.6 \text{ \AA}$). These layered building blocks are interconnected by a multitude of weak hydrogen bonds ($d(\text{O} \dots \text{O}) \approx 3.15 \text{ \AA}$).

Hydr. H-Apophyllite decays at room temp. within one day to a product of low crystallinity.

References

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The Figure shows the structure of Hydr. H-Apophyllite projected on (100). Tetrahedra represent the silicate layers, spheres represent water molecules (large) and terminal OH groups (medium sized).



CRY-P02

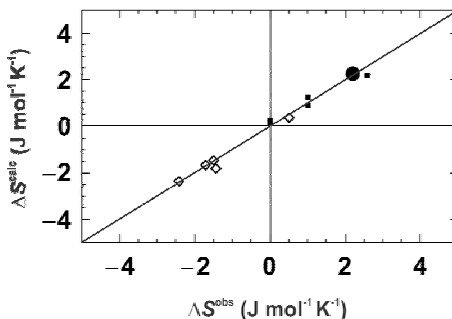
The vibrational entropy of solid solutions

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The excess vibrational entropy, defined as the deviation of the vibrational entropy from the linear combination of their end-member values, is found to depend on bond length changes that occur with compositional variations [1]. The bond length changes depend itself on the elasticity of the substitution polyhedron in the end member structure in a way that the elastically stiffer substitution polyhedron forces the softer one to fit to its size [2, 3]. In cases where the smaller substitution polyhedron is elastically softer, its bond lengths are expected to be strongly enlarged by the stiffer and larger substitution polyhedron resulting in positive excess heat capacities and correspondingly positive excess vibrational entropies. On the other hand, if the larger polyhedron is elastically softer, its bond lengths are forced by the stiffer and smaller substitution polyhedron to become shorter and may result in negative vibrational excess entropies. Based on an empirical relationship that uses the differences of end member volumes and bulk moduli, the maximum excess vibrational entropy is estimated. This ΔV vs. ΔK approach has been applied to binary alloys [3, 4], silicate solid solutions [2, 5] and the NaCl-KCl binary [6]. A comparison of calculated and calorimetrically determined excess vibrational entropies of these binaries is compiled in the figure below. Binary alloys (*open symbols*) are often characterised by negative excess vibrational entropies, whereas solid solutions consisting of anion and cation sublattices often show positive excess vibrational entropies (*closed symbols*). The reason for this different behaviour is discussed.

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CRY-P03

Crystal structures and isotypism of the iron arsenate kamarizaite and the iron phosphate tinticite

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The first determination of the crystal structure of triclinic $\text{Fe}_3^{3+}(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ from the Le Mazet vein, Échassières, France, based on single-crystal data, led to a study on the correct crystallographical description of tinticite $[\text{Fe}_3^{3+}(\text{PO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}]$ and its arsenate analogue kamarizaite $[\text{Fe}_3^{3+}(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}]$. For tinticite, orthorhombic, monoclinic and triclinic symmetries were reported in contradictory articles [1-5], and a “disordered”, triclinic structure model was proposed, based on powder pattern decomposition [4]. For kamarizaite, orthorhombic symmetry was reported [6]. The structure determination of the Le Mazet material [MoK α , 293 K, SHELX-97, $R(F) = 2.91\%$; all H atoms detected] gave space group $P-1$ (no. 2), with $a = 7.671(2)$, $b = 8.040(2)$, $c = 10.180(2)$ Å, $\alpha = 68.31(3)^\circ$, $\beta = 75.35(3)^\circ$, $\gamma = 63.52(3)^\circ$, $V = 519.3(2)$ Å³, $Z = 1$. Based on this structure model, Rietveld analyses of tinticite from Bruguers, Spain, and self-collected kamarizaite from Lavrion, Greece (type locality), provided clear evidence that both the published model for tinticite [4] and the reported orthorhombic symmetry for kamarizaite [6] are not consistent with these new findings. Refined unit-cell parameters of the Bruguers tinticite are $a = 7.646(2)$, $b = 7.962(2)$, $c = 9.998(2)$ Å, $\alpha = 67.87(2)^\circ$, $\beta = 76.06(2)^\circ$, $\gamma = 64.06(2)^\circ$, $V = 504.9(2)$ Å³ [$R_{\text{wp}} = 7.07$, $R_{\text{wp}}' = 13.14\%$, $\text{GOF} = 1.82$]. The Lavrion kamarizaite has $a = 7.705(1)$, $b = 8.089(1)$, $c = 10.216(1)$ Å, $\alpha = 68.30(1)^\circ$, $\beta = 75.33(1)^\circ$, $\gamma = 63.53(1)^\circ$, $V = 526.6(1)$ Å³ [$R_{\text{wp}} = 5.66$, $R_{\text{wp}}' = 8.53\%$, $\text{GOF} = 1.42$]. Our results prove kamarizaite and tinticite to be triclinic and isotypic. The common atomic arrangement is characterised by three unique Fe sites, two unique As/P sites, 14 O and nine H sites. The topology features zig-zag chains along [1-10] of edge-sharing FeO_6 dimers corner-linked by a third FeO_6 octahedron. The chains are corner-linked by the $(\text{As/P})\text{O}_4$ tetrahedra into a 3D framework additionally strengthened by medium-strong to weak H-bonding.

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CRY-P04

Crystal structure of $\text{Cu}_{10}(\text{AsO}_4)_4(\text{SO}_4)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$, a new copper arsenate-sulphate mineral closely related to leogangite

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A greenish to blue-green, new secondary copper arsenate-sulphate mineral, visually indistinguishable from leogangite, $\text{Cu}_{10}(\text{AsO}_4)_4(\text{SO}_4)(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ [1-3], was found as bladed crystals with a lancet-shaped outline and vitreous lustre on samples collected from dumps of Bronze-age copper mining in the Brunnkendlgraben, Schwarzeleotal, Tyrol, Austria.

Single-crystal and powder X-ray diffraction studies combined with chemical analyses showed the mineral to be a new species with the formula $\text{Cu}_{10}(\text{AsO}_4)_4(\text{SO}_4)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$. The crystal structure was solved and refined in space group $P2_1$ (no. 4)

[MoK α , 293 K, SHELX-97, $R(F) = 4.2\%$, Flack parameter 0.024(15)]. Refined single-crystal cell parameters are: $a = 10.756(2)$, $b = 12.292(2)$, $c = 12.131(2)$ Å, $\beta = 92.89(3)^\circ$, $V = 1601.8(5)$ Å³. A comparison with leogangite [$C2/c$; $a = 21.770(7)$,

$b = 12.327(4)$, $c = 10.720(3)$ Å, $\beta = 92.85(1)^\circ$, $V = 2873(2)$ Å³] reveals that $c_{\text{new mineral}} \sim 0.5a_{\text{leogangite}}$, the other two cell edges and the monoclinic angle being nearly identical.

All atoms are in general positions. A thick heteropolyhedral sheet parallel to (001) is built of distorted $\text{Cu}(\text{O}, \text{OH}, \text{H}_2\text{O})_{5-6}$ polyhedra and AsO_4 tetrahedra sharing edges and corners. This sheet is nearly identical to that in leogangite, but contains four more H_2O ligands. The single SO_4 tetrahedron is located in the interlayer space. In the new mineral, it is attached to the heteropolyhedral sheet only via one corner, whereas in leogangite it is connected to two adjacent sheets via all its four corners. The interlayer space also hosts four H-bonded water molecules.

A calculated powder diffraction pattern fits very well that of pale blue-green crusts, consisting of tiny, lancet-shaped crystals, found on dumps of another Tyrolean locality (Graschberg near Thierbach, Wildschönau) [4]. Thus, the new mineral may be more widespread.

Further work is underway to determine all physico-chemical properties of the new species.

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CRY-P05

Al-Mg and Al-Fe disorder in metamorphic tourmaline

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The tourmaline mineral group is chemically one of the most complicated groups of silicate minerals, with the general formula $X Y_3 Z_6 [T_6O_{18}] (BO_3)_3 V_3 W$. Metamorphic tourmalines in metasedimentary rocks belong to the dravite-schorl series. The *X* site is usually occupied by Na, the *Y* site is in dravite predominantly occupied by Mg and in schorl by Fe^{2+} , Al occupies the *Z* site, and Si the *T* site. Dravite from Plankogel Complex, which is a lithostratigraphic element within the Austroalpine Unit, was formed at temperatures ≤ 600 °C. The *Y* site of this dravite is occupied by $\sim(Mg_{2.5}Al_{0.5})$ while the *Z* site is occupied by $\sim(Al_{5.6}Mg_{0.4})$ (Pertlik et al, 2003). Tourmalines from the Bunte Series, Lower Austria, formed at temperatures of ≥ 700 °C, have a Mg occupancy in the range ~ 0.9 - 1.3 apfu Mg at the *Y* site and ~ 1.1 - 1.2 apfu Mg at the *Z* site (Ertl et al., 2003; 2008; unpubl. data). Heating experiments showed, that the Fe-Al disorder between the *Y* and *Z* site significantly increases at temperatures of 700-750 °C (e.g., Ertl et al., 2012; unpubl. data). A lot of new data have been acquired within the last 15 years. Hence, we can conclude that Al-Mg as well as Al-Fe disorder between the 6-coordinated *Y* and *Z* sites in tourmaline generally significantly increases at temperatures ≥ 700 °C. This important conclusion is another step for using tourmaline as geothermometer.

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CRY-P06

Recrystallisation study of radiation damaged titanite and pyrochlore

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Minerals with radiation damage show a structural pattern of crystalline, quasi amorphous and fully disordered clusters. Those clusters are the result of alpha decay processes of incorporated uranium and thorium in the minerals. Structural damages and their behaviour as a function of thermal annealing is of great interest for material sciences, for instance for the better understanding of embedding materials of actinides from radioactive waste. Previously discussed embedding materials include titanite and pyrochlore ceramics. In nature, such minerals can occur in the metamict state. [1], [2]

The analysis of pyrochlores and titanites exposed to different radiation doses on annealing using X-ray diffraction (XRD) gives insight into their recrystallisation behaviour. ²⁹Si magic angle spinning nuclear magnetic resonance (NMR) spectroscopy of damaged titanite is used to characterise local structural changes. Since XRD is sensitive to long range order and ²⁹Si NMR to the Si vicinity, both methods are well complementary. [3]

Recrystallisation temperatures are sensitive to crystal chemistry, structural topology and disorder phenomena; hence pyrochlores differ considerably in partly crystalline and completely XRD amorphous pyrochlores and from titanite. ²⁹Si NMR signals of heavily metamict titanite decrease in full width at half maximum upon annealing, indicating restructuring in the direct Si vicinity.

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CRY-P07

The correction of beam-shadowing effects due to partially filled sample holders in Bragg-Brentano experiments

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In Bragg-Brentano powder X-ray diffraction, incompletely filled sample holders result in an error in sample height leading to a constant shift of diffraction peaks in 2θ that can be corrected for with most Rietveld programs. At low diffraction angles sample-height effects also have a significant influence on the intensities of the observed diffraction peaks due to shadowing of the beam by the rim of the sample holder. If reflections are observed at low diffraction angles and if errors in sample height cannot be avoided, e.g. due to experimental requirements, serious reductions of diffracted intensities or even complete absence of reflections have to be expected at low 2θ .

The correction algorithm presented in equations 1-4 allows for the correction of these effects, which especially should be considered for materials with diffraction peaks in the low 2θ range (e.g. zeolites and clay minerals). The developed correction algorithm (eq. 1-4) was successfully verified using a series of zeolite A measurements with defined shifts in sample height (Figure 1).

$$I_{\text{tot}} = I_{\text{obs}} F_s \text{ (eq. 1)}$$

with

$$F_s = (\gamma'_1 + \gamma'_2)/(\gamma'_2 + \gamma'_4) \text{ (eq. 2)}$$

$$\gamma'_{1/2} = \arctan((\sin\theta I_s)/(2 R \pm \cos\theta I_s)) \text{ (eq. 3)}$$

$$\gamma'_4 = \theta - \arctan((2 R \sin\theta (d + R \sin\theta))/(2 R^2 \cos\theta \sin\theta + R I_s \sin\theta - 2 d R \cos\theta - d I_s)) \text{ (eq. 4)}$$

R is the radius of the goniometer, d the shift in sample height, and I_s the length of the sample in direction of the beam.

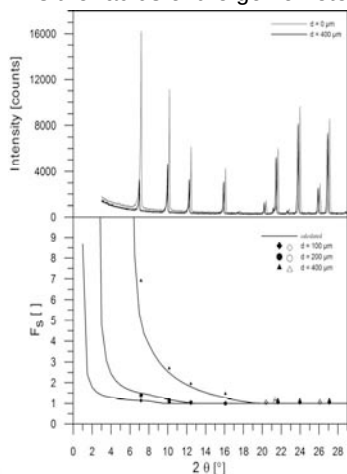


Figure 1: Top: Low 2θ part of diffraction patterns of zeolite A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27 \text{H}_2\text{O}$) for the same lot prepared with different sample preparations (height shifts of 0 μm and 400 μm). Bottom: Observed and calculated correction factors to be applied to the intensities of the samples with lowered surface to match the intensities of the sample with perfect surface height. The symbols represent samples with surfaces deliberately lowered by 100 μm (squares), 200 μm (circles), and 400 μm (triangles), respectively. Open symbols are shown for weaker reflections.

CRY-P08

Crystal-chemical characterization of ammonium exchanged zeolites

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Zeolites belong to the most important classes of materials with main applications as catalysts, e.g., in oil refinery, adsorbents and as ion exchangers, e.g., for the softening of water with a production of more than 1 million metric tons per year just as an additive to laundry detergents. NH₄ zeolites, where the ammonium ion represents the charge-compensating cation, play an important role as precursor materials in the production of H-zeolites. The hydrogen zeolites in turn represent the actual catalysts with their protons acting as Brønsted acids. Here, we present first results on ammonium-exchanged zeolites within the framework of a project studying the mechanisms of deammoniation processes in zeolites to produce the H-forms acting as catalysts. First results are obtained for the natural minerals willhendersonite and merlinoite and synthetic zeolite A.

Single crystals of willhendersonite (ideally $\text{KCaAl}_3\text{Si}_3\text{O}_{12} \cdot 5\text{H}_2\text{O}$) were ammonium exchanged in a 0.5 molar NH₄Cl solution at 20 °C. Ammonia was added to increase the pH of the solution to 9.5, thus avoiding dissolution of the crystals in an acidic environment. The lattice parameters of the triclinic willhendersonite changed from $a=9.2010(3)$ Å, $b=9.2138(3)$ Å, $c=9.4930(3)$ Å, $\alpha=92.365(1)^\circ$, $\beta=92.704(1)^\circ$, $\gamma=90.066(1)^\circ$ to $a=9.210(1)$ Å, $b=9.223(1)$ Å, $c=9.518(1)$ Å, $\alpha=92.850(2)^\circ$, $\beta=92.659(2)^\circ$, $\gamma=90.046(2)^\circ$. EDX analyses showed that all K was exchanged by NH₄. The crystal structure was refined to $R1 = 4.4\%$ yielding a structure model with NH₄ close to the initial K sites.

Similar experiments were performed with merlinoite (ideally $(\text{K},\text{Na},\text{Ca}_{0.5})_{10}\text{Al}_{10}\text{Si}_{22}\text{O}_{64} \cdot 20\text{H}_2\text{O}$) single crystals in an ammonium nitrate solution. EDX analysis showed that essentially all K was exchanged by NH₄. Lattice parameters in space group *Immm* changed from $a=14.192(1)$ Å, $b=14.213(1)$ Å, $c=9.952(1)$ Å to $14.233(1)$ Å, $14.235(1)$ Å, $9.947(1)$ Å. Single-crystal structure refinements are in progress. The exchanged merlinoite is compared with an NH₄ containing merlinoite mineral.

Further on, single crystals and powder samples of synthetic zeolite A (ideally $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$) were NH₄ exchanged and investigated by X-ray diffraction methods at room temperature. In addition, a series of samples with different K/NH₄ ratios was produced by partial exchange. Thermal analyses showed that the zeolite decomposes already at rather low temperatures when about 10% of the Na is replaced by NH₄.

CRY-P09

Structural phase transitions of $\text{Cu}_2(\text{OH})_3\text{Cl}$

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The structure of paratacamite, a trigonal polymorph of $\text{Cu}_2(\text{OH})_3\text{Cl}$, was described by Fleet in 1975. It has since been established that, at ambient temperatures, trigonal symmetry in $\text{Cu}_2(\text{OH})_3\text{Cl}$ has to be stabilized by Zn, Co, Ni or Mg partially substituting for Cu. Herbertsmithite, $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, forms the end-member compound of Zn substitution in $\text{Cu}_2(\text{OH})_3\text{Cl}$. The mineral has attracted much attention for its unusual ground state properties, enabled by geometric frustration of antiferromagnetic ordering on the undistorted, two dimensional Cu-sublattice. Here we report the stabilization of trigonal symmetry in an almost pure $\text{Cu}_2(\text{OH})_3\text{Cl}$ by increasing temperature. The zone centre phase transition from the triclinically distorted anatacamite structure to the R-3 symmetry of paratacamite occurs close to 360K. A subsequent zone boundary phase transition to the herbertsmithite aristotype structure in space group R-3m is observed close to 400K. The latter phase transition had previously been reported for a Zn-stabilized paratacamite, where it occurs in a temperature interval between 353 and 393K (Welch et al., 2014).

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CRY-P10

A new calcium arsenate mineral, $\text{Ca}_3(\text{AsO}_4)_2 \cdot \sim 5.9\text{H}_2\text{O}$, and its crystal structure

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Several arsenates with the stoichiometry $\text{Ca}_3(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 2, 3, 4, 5, 8, 10, 11$) were reported to occur as stable or metastable phases in the system $\text{CaO-As}_2\text{O}_5\text{-H}_2\text{O}$

[1-5], including the mineral species rauenthalite ($n = 10$) and phanouxite ($n = 11$). A new mineral with the formula $\text{Ca}_3(\text{AsO}_4)_2 \cdot \sim 5.9\text{H}_2\text{O}$ was detected on a sample of limonite-coated baryte from the Clara mine, Black Forest, Germany. It forms small tufts of pearly white, subparallel laths, visually very similar to rauenthalite or phanouxite.

The crystal structure of the mineral was determined from intensity data collected from a tiny crystal fragment [$\text{MoK}\alpha$, 293 K, SHELX-97, $R(F) = 6.2\%$]. Two further datasets obtained from crystals twinned by non-merohedry confirmed the structure model, but resulted in higher R -values ($\sim 12\%$) due to the close overlap of reflections from the two twin individuals.

The space group is $P-1$ (no. 2). The refined unit cell, $a = 6.705(1)$, $b = 13.609(3)$, $c = 14.105(3)$ Å, $\alpha = 81.67(3)^\circ$, $\beta = 89.38(3)^\circ$, $\gamma = 76.49(3)^\circ$, $V = 1237.9(4)$ Å³ ($Z = 2$), is somewhat similar to that of mcnearite, $\text{NaCa}_5(\text{AsO}_4)(\text{HAsO}_4)_4 \cdot 4\text{H}_2\text{O}$ ($a = 13.50$, $b = 14.10$, $c = 6.95$ Å, $\alpha = 90^\circ$, $\beta = 92^\circ$, $\gamma = 119^\circ$) [6], the structure of which is unknown.

The asymmetric unit contains six Ca, four As, ~ 27.8 O and ~ 23.6 H atoms. The atomic arrangement is characterised by corner- and edge-sharing $\text{Ca}(\text{O}, \text{H}_2\text{O})_{6-8}$ polyhedra corner- and edge-linked by AsO_4 tetrahedra [$\text{As-O} = 1.660(5) - 1.704(5)$ Å] into heteropolyhedral slabs parallel to (001). Adjacent slabs are connected by two edge-sharing $\text{Ca}(\text{O}, \text{H}_2\text{O})_7$ polyhedra. Channels along [100] and [010] host three, somewhat disordered and only H-bonded H_2O molecules (with refined occupancies ~ 1.0 , ~ 1.0 and ~ 0.8). Thus, the structural formula may be written as $\text{Ca}_6(\text{H}_2\text{O})_9(\text{AsO}_4)_4 \cdot \sim 2.8\text{H}_2\text{O}$.

Comparisons with the crystal structures of related minerals and compounds will be drawn.

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Mineralogical museums and collections

MUS-T01

Digitalisierung der Gesteinsdünnschliffsammlung an der TU Bergakademie Freiberg

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Innerhalb des durch die DFG geförderten Projektes „Aufbau eines webbasierten Systems zur Erschließung, Digitalisierung und Visualisierung der Dünnschliffsammlung an der TU Bergakademie Freiberg“, einem Teilprojekt aus dem Bündelantrag „Geo- und montanwissenschaftliche Sammlungen in Freiberg und Dresden“ im Rahmen der Ausschreibung „Erschließung und Digitalisierung von objektbezogenen wissenschaftlichen Sammlungen“, werden Dünnschliffe digitalisiert, in einer relationalen Datenbank erfasst und der Öffentlichkeit über das Internet zugänglich gemacht.

Die Sammlung der Gesteinsdünnschliffe enthält ungefähr 45.000 Objekte mit weltweit verschiedenster Herkunft und ist von historischer Bedeutung, da sie auf eine Vielzahl von Wissenschaftlern zurückgeht und die ersten Objekte aus der zweiten Hälfte des 19. Jahrhunderts datieren. Die Vorgehensweise der digitalen Erfassung aller zur Verfügung stehenden Daten wird durch einen Workflow beschrieben. Im Zentrum steht die Erstellung von hochaufgelösten Mikro-Panorama-Aufnahmen. Diese werden mithilfe eines Polarisationsmikroskops sowohl mit polarisiertem Licht als auch mit gekreuzten Polarisatoren aufgenommen. Die so erzeugten Einzelbilder werden über die Software AxioVision Rel. 4.8 der Firma ZEISS zusammengesetzt. Im Weiteren werden die zum Dünnschliff zugehörigen Dokumente, wie zum Beispiel Karteikarten, eingescannt, damit die historischen Aufzeichnungen auch visuell zur Verfügung stehen.

Damit die digitalisierten Daten zukünftig wissenschaftlich genutzt werden können, erfolgt in Kooperation mit der Senckenberg Gesellschaft für Naturforschung Frankfurt die Entwicklung eines Datenbanksystems. Dafür wird die Software SeSam_neo auf die Anwendung im Bereich der Geowissenschaften angepasst. Ebenso sind die Tiefenerschließung der erfassten Dünnschliffe, sowie eine Recherche der logistischen, geographischen und genetischen Verknüpfung zu anderen Objekten in den Geowissenschaftlichen Sammlungen vorgesehen.

MUS-T02

Die Smaragdsammlung Wolfram Schäfer in der Mineralogischen Staatssammlung München

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Der Münchner Physiker Wolfram Schäfer hat sein ganzes Sammlerleben dem Edelstein Smaragd gewidmet. Dabei interessierten ihn geschliffene Steine wenig, sein ganzes Interesse galt den Ausbildungen und den Vorkommen dieser Mineralvarietät. Besonders wichtig war ihm, möglichst viele der weltweiten Smaragdorkommen persönlich kennenzulernen und sie zu besammeln. Dabei waren ihm nicht nur die optisch schönen Kristallstufen wichtig, er legte besonderen Wert auch auf lagerstättenkundlich aussagekräftige Handstücke und Belege möglichst aller Paragenese-Mineralien.

Seine Sammelleidenschaft begann - natürlich - im nahegelegenen Habachtal mit dem Smaragdbau an der Leckbachscharte, aber bald führten ihn seine Reisen auch zu den Smaragdlagerstätten in Kolumbien, Brasilien, Norwegen und Namibia. Gerne ergriff er die Gelegenheit, bei einer Umstrukturierung seiner Firma frühzeitig seinen Arbeitsplatz frei zu machen. Er nutzte die freie Zeit, am Department für Geo- und Umweltwissenschaften der LMU München, ein Studium der Mineralogie aufzunehmen, das er 2002 mit dem Diplom abschloss. Der Titel seiner Diplomarbeit ist „Geologische, mineralogische und geochemische Untersuchungen an zwei Smaragdorkommen in der Neuhof-Formation, SW-Namibia“.

2014 hat Wolfram Schäfer seine gesamte Sammlung, die neben den Smaragden auch noch Stufen anderer Edelstein-Mineralien, wie z.B. Topas, Rubin, Saphir, Diamant enthielt, der Mineralogischen Staatssammlung geschenkt. Zusammen mit der Smaragd-Lagerstätten-Forschungssammlung von Dr. Günther Grundmann, die von der TU München an die Staatssammlung gelangt ist, und den zahlreichen russischen Smaragdstufen aus der Leuchtenberg-Sammlung besitzt die Mineralogische Staatssammlung damit die wissenschaftlich bedeutendste Smaragd-Lagerstätten-Forschungssammlung in Deutschland.

Mineralogical museums and collections

MUS-T03

The Mineralogical Society of Jena and Count Vargas Bedemar

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Eighteen Years after the foundation of the mineral collection in Jena Johann Georg Lenz (1745-1832), first Professor for Mineralogy at the university of Jena, founded the first geoscientific society, so called "Die Societaet für die gesammte Mineralogie zu Jena". Lenz as the founder and director of the society intended to work together with a president and there should be named ordinary, extraordinary and correspondent members.

During the following 88 years about 2500 persons got a diploma of membership and at least more than 3000 persons (professionals like R.J. Hauy, M. v. Flurl, A.G. Werner, A. Bruce, Maria Paulowna - daughter of tsar Paul I, H. Struve and J. H. L. Pansner contacted the Jenaer society. Once they got a member normally they sent minerals, rocks and fossils and also literature and maps from all over the world to Jena.

What about the presidents of the society? The first one, Domokos Teleki, a young Hungarian nobleman, died already in his second year as acting president. He was followed by Prince Dimitrij Gallitzin, a former Russian diplomat who donated his huge and spectacular private collection in 1802 to the Society in Jena. Shortly after his death he was followed by Johann Wolfgang von Goethe (1799-1832) as the 3rd president. Goethe used his popularity to get in contact to many people interested in mineralogy. So he got in correspondence to Carl Friedrich August Grosse who called himself since 1809 Count Vargas Bedemar. Grosse was born 1768 in Magdeburg/Germany, studied Literature in Göttingen and Halle; during his whole life he was interested in mineralogy and geology. He published a few books, mainly during his stay in Italy from 1792 to 1809. Because of some political affairs he had to leave Italy and went to Denmark. There he got in contact to the King and other persons of the government. He went on excursions through the northern part of Europe. For many years he had been in charge for the mining interests of the Danish government and member of the Danish Society for the Advancement of Science. During this time Goethe supported Bedemar (already been an extraordinary member) to get vicepresident of the "Mineralogische Societaet in Jena" in 1820. Vargas Bedemar sent many suites of minerals, amongst others lots of zeolites, to Jena. And he followed Goethe as president and held this job till he died in Copenhagen in 1847.

MUS-P01

Collections of Crystal Models at TU Berlin

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Since 1770, the foundation of the Bergakademie Berlin (mining academy), teaching collections have been indispensable for the education of geoscientists at the successor organisation: Technische Universität Berlin. Crystal models have been an integral part of mineralogical teaching until today: nothing better than a wooden model of an octahedron to understand cubic symmetries, to get a feeling for mirror planes and rotation axes.

Thus, the collections at TU Berlin are housing today app. 3500 models of crystals, mainly of natural occurring minerals - a treasure only few universities worldwide are able to provide. Most of these models are 4-6 cm in size, made of pear wood or maple wood, a minority made of gypsum.

A main and precious collection consists of 675 different models made of maple wood, crafted by the company of Dr. A. KRANTZ in Berlin and Bonn, mainly after models constructed by Gustav ROSE (1798-1873). ROSE studied in Berlin under the renowned Prof. Christian Samuel WEISS (1780-1856, who first introduced crystallographic axes) and later became professor of mineralogy at Bergakademie and University of Berlin. Another one consists of 743 different crystal models made of pear wood, after Paul GROTH 1880, who studied mineralogy and crystallography among others in Berlin under Gustav Rose and became docent at the Bergakademie Berlin (1871-1872).

Several other collections of wooden models are kept at TU Berlin, one with engraved letters KTH (Königlich Technische Hochschule, predecessor of TU Berlin, 1879-1916), even one of black-and-white-symmetries. Few models are made of gypsum, after Prof. F.X.Zippe (1791-1863), Prague/Vienna. Further important teaching collections contain wooden models up to 20 cm and pasteboard models about 30 cm in size.

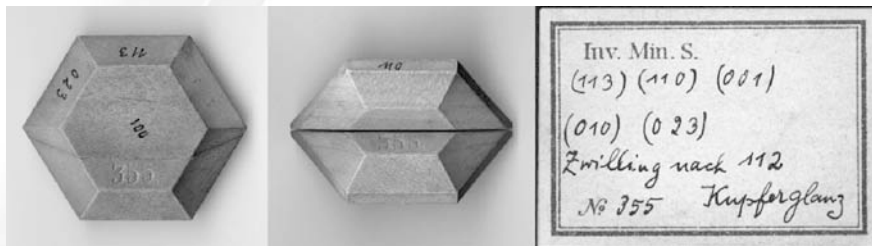
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Mineralogical museums and collections



Model of Chalcocite, "series of 675", 1862, maple wood, 4.5 cm, rotatable twin (112).

- a. single crystal position
- b. twin position.
- c. original label of BergakademieBerlin.

MUS-P02

A remarkable Paragenesis of Antimony-Sulfosalts from Southern Spain

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In the abandoned mine Mina Casualidad near Almeria, Spain, the authors discovered a remarkable ore enrichment with a great variety of antimony-sulfosalts.

Main ore mineral in the mine is a Zn-rich and silver-poor antimony-fahlore which is found in small veinlets and impregnations in a pyritiferous mica schist. Main gangue minerals are barite and an iron-rich dolomite.

A younger paragenesis on clefts and as impregnations in the mica schist yielded antimony-dominated sulfosalt minerals in a great variety. Most frequent minerals are fülöppite and plagionite, followed by semseyite, zinkenite, veenite, twinnite, robinsonite, heteromorphite, bournonite, launayite and moeloite. Silver-rich parts of the veinlets contained miargyrite, andorite, ramdohrite and argentite.

Jordanite and geocronite have both been found in the sulfosalt paragenesis. The As-rich jordanite is more frequent than the Sb-rich geocronite. EMPA measurements showed a complete solid solution between both minerals in the samples from Mina Casualidad. A miscibility gap between both as postulated by Bryzgalov et al. (2011) could not be found. The same authors described the not IMA-approved mineral "schulzite" from Darasun as a Sb-rich geocronite. This is in contradiction to the investigations of Birnie et al. (1976) who showed that the maximum Sb/As ratio is 2:1 and that the structure doesn't allow the integration of more Sb-atoms.

During our investigation of the jordanite-geocronite solid solution using material from Mina Casualidad sometimes higher Sb-contents than 2:1 were found. Careful investigations of that material always showed that these analyses came from extremely fine grained mixtures of galenite and veenite. This leads to the assumption that the "schulzite" material investigated by Bryzgalov et al. similarly is a galenite/veenite mixture.

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Mineralogical museums and collections

MUS-P03

„Natur und Kunst, sie scheinen sich zu fliehen; und haben sich, eh man es denkt, gefunden“

Gemeinsame Veranstaltungen des Museums Reich der Kristalle mit Münchner Kunstmuseen

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Im Kunst- und Museumsareal München entstehen aktuell neue und fachübergreifende Zusammenarbeiten zwischen den Museen. So hat das Museum Reich der Kristalle München mit der Alten Pinakothek München ein Kinderprojekt zum Thema „Ein römischer Kalkofen“ angeboten. Die Kinder hatten dadurch die Chance Kunst und Naturwissenschaft an einem Tag kennen zu lernen und in Einklang zu bringen. So sollten die kleinen Besucher zuerst das Gemälde »Ein römischer Kalkofen« des Malers Sébastien Bourdon genau beschreiben und sich überlegen, wie denn die Leute im alten Rom Kalk gebrannt haben und ob das Gemälde der Wirklichkeit entspricht. Anschließend wurde im Museum Reich der Kristalle demonstriert, wie man Kalk brennt. Dabei wurde auf die chemischen Prozesse die beim Kalkbrennen ablaufen eingegangen. Zudem lernten die Kinder unterschiedliche Kalksteine und Calcitkristalle makroskopisch und mikroskopisch kennen.

Eine weitere fachübergreifende museale Zusammenarbeit stellt der Austausch von Kunstwerken und Mineralen dar. In diesem Zusammenhang hat das Museum Reich der Kristalle eine große Amethyst-Stufe an das Museum für Abgüsse Klassischer Bildwerke ausgeliehen. Im Gegenzug bekam das Reich der Kristalle Kunstobjekte zur Symmetrie-Ausstellung, die im Jahr der Kristallographie in der neuen Sonderausstellung präsentiert wurden.

MUS-P04

Die Minerale in der Äußeren-Kennzeichen-Sammlung von Abraham Gottlob Werner

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Abraham Gottlob Werner (1749-1817) veröffentlichte 1774 das Buch „Von den äußerlichen Kennzeichen der Fossilien“¹. Die in diesem Buch beschriebene analytische Herangehensweise, Minerale anhand äußerer Kennzeichen zu bestimmen, ist noch heute gültig.

Ab 1775 war Werner als Lehrer der Bergbaukunst und Mineralogie und als Inspektor an der Bergakademie Freiberg tätig. Um seinen Studenten und ihn besuchenden Fachleuten die äußeren Kennzeichen der Minerale an charakteristischen Belegen demonstrieren zu können, legte er hier eine Äußere-Kennzeichen-Sammlung an. Für die Präsentation im Werner-Museum der Bergakademie ergänzt und abgeschlossen umfasste diese Sammlung im Jahr 1823 652 „Fossilien“, 253 Porzellantafeln mit Farbaufstrich aus Meißeiner Porzellan und 562 Kristallmodelle. Die Objekte sind bis heute annähernd vollständig erhalten und geben einen authentischen Einblick in Werners Kennzeichenlehre, s. Abb.

Im Rahmen des DFG-Projektes „Aufbau eines webbasierten Systems zur Erschließung, Digitalisierung und Visualisierung des Bestandes der historischen mineralogischen Kennzeichensammlung von Abraham Gottlob Werner an der TU Bergakademie Freiberg“ wird diese Sammlung bearbeitet. Der Tagungsbeitrag stellt die Minerale der Sammlung in ihrem Kontext und den entwickelten Workflow der Digitalisierung vor.

¹ Abraham Gottlob Werner. Von den äußerlichen Kennzeichen der Fossilien. Leipzig 1774.

² Carl Gustav Adalbert von Weissenbach: Wernersches Museum Abtheilung 3., Aeussere Kennzeichen-Sammlung. 1823; TU Bergakademie Freiberg, Universitätsbibliothek, Sign. XVII 702.

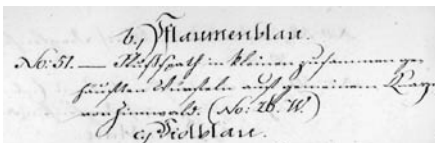
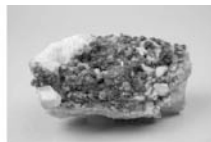
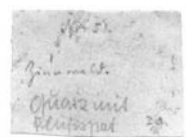


Abb.: Katalogeintrag von 1823² „Pflaumenblau“ mit der dazugehörigen Fluoritstufe (Zinnwald, 9,7 cm x 5,5 cm x 5,5 cm) und Etikett (Albin Weisbach, 19. Jh.).

Mineralogical museums and collections

MUS-P05

Pilot project – further development of SeSam_neo providing a new collection management system for the Geoscientific Collections at the TU Bergakademie Freiberg

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Three parts of the Geoscientific Collections at the TU Bergakademie Freiberg, i.e., the Thin-Section Collection, the Fossil Fuel Geology Collection and the Mineralogical Collection of External Characteristics of A.G. Werner, have been selected for web-based digitization within a DFG-funded pilot project. After a first testing phase, advantages and disadvantages of the different consulted management collection systems were weighed up, and finally SeSam_neo was chosen albeit further development is needed for its geoscientific adjustment. Specific thesauri basing on the mineralogical, petrographical, palaeontological and stratigraphical standard systems of classification (e.g., Strunz & Nickel 2001, Le Maitre 2008, Fettes & Desmons 2011, GTS 2012) will be integrated. These allow the description of objects using modern established standards supplemented by original and historically important determinations, characterizations and remarks. Another feature to implicate and to display the historical relevance of the Freiberg Geoscientific Collections is the integration of a locality-time thesaurus reflecting the changes in administration units over time. Missing geographical coordinates and imprecise or uncertain locality descriptions will be approached by retrospective georeferencing. Currently, a preliminary model for the database structure was defined. The applicability of the developed database prototype has to be checked and proven for the three mentioned sub-collections. Their unification considering and maintaining the diversity and heterogeneity of organization still requires some effort. The aim of this project is to make the Freiberg Geoscientific Collections available via internet, and also to use the enhanced SeSam_neo system for other geoscientific collections (e.g., the Dresden Petrographical Collections).

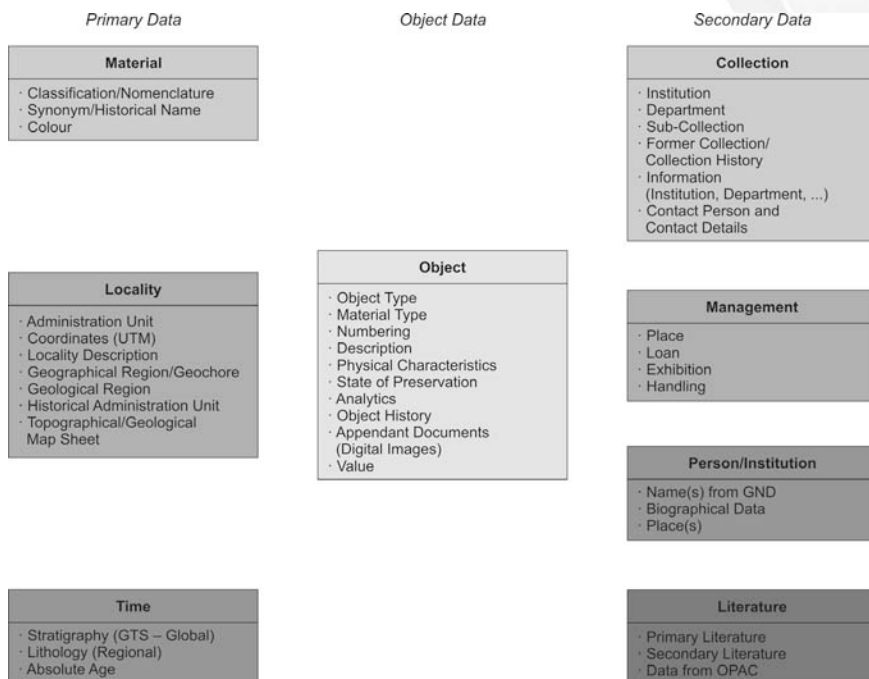
Mineralogical museums and collections

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Database organization scheme of SeSam_neo's geoscientific modul.

FLU-T01

First-principles study of Zr and Hf speciation in supercritical aqueous fluids

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Cation complexation in solution is a key parameter for understanding the controlling mechanism of fluid-rock interaction and the solubility of minerals in hydrothermal fluids. However, investigations of the molecular structure of geological fluids are challenging as the structure of the fluid depends strongly on pressure, temperature and chemical composition. Furthermore, these changes are instantaneous, i.e. the high P-T structure is not quenchable. A promising approach to identify and quantify cation speciation in solutions is to combine in-situ spectroscopy at high pressures and temperatures (e.g. Raman or x-ray absorption spectroscopy) with first-principles modeling techniques.

Here, we study the complexation of the high field-strength elements Zr and Hf in supercritical aqueous solutions using first-principles molecular dynamics simulations. While pressure and temperature are kept constant at about 1 GPa and 1000 K, the fluid composition is varied between pure water, NaOH and HCl solution. Both Zr and Hf prefer an octahedral coordination environment composed of mixed OH, Cl and H₂O ligands. For each complex, theoretical x-ray absorption (XANES) spectra are computed for a number of snapshots from the molecular dynamics trajectories and compared to experimental XANES spectra [1]. A very good agreement between experimental and theoretical spectra is obtained for the chloride solutions containing predominant complexes of $[(\text{Zr,Hf})\text{Cl}_4(\text{Cl,OH})(\text{H}_2\text{O})]$. The agreement is less satisfactory for Zr/Hf monomer complexes in NaOH fluids, which suggests the formation of larger oligomeric Zr/Hf species in the fluid.

[1] Wilke et al. (2012) Earth Planet. Sci. Lett. 349-350, 15-25

FLU-T02**The behaviour of Cl and Br during water-rock interaction and its implications for the halogen budget of basement brines - an experimental study on rocks from the Schwarzwald, SW Germany**M. Burisch¹, M. Marks², G. Markl¹¹*Universität Tübingen, Petrology, Tübingen, Germany*

Deep crustal, highly saline basement brines (with salinities up to 26 wt.% NaCl equivalent) are a global phenomenon and invariably characterized by Cl as the predominant anion and low Cl/Br ratios (below 288) in contrast to bicarbonate-dominated fluids with higher Cl/Br ratios (above 1000) typical of shallower crustal levels. Those fluids are invoked to play an important role in ore forming processes since the high chlorinity enhances base metal solubility drastically. However the processes causing these high salinities and the source of Cl are insufficiently constrained and poorly understood.

We performed leaching experiments at 25°C and 275°C (at 1.4 kbar) on typical Variscan crystalline basement rocks (granite and gneiss) and their mineral separates (feldspar, quartz and mica) in ultrapure water using two grain size fractions (0.063-0.125 and 2-4 mm) and variable fluid/rock ratios for a maximum duration of 31 days. Additionally, the precursor rock material was carefully characterized by major and trace element analyses (XRF and pyrohydrolysis) and fluid inclusion petrography.

Based on our data we present a new hypothesis involving fluid modification along migration paths within the crystalline basement, as a key factor for the genesis of highly saline, Cl-dominated basement brines. We show that the mode of alteration of the fluid chemistry during water-rock interaction strongly depends on grain size of the rock: smaller grain size results in higher Na/Ca, lower Na/Cl ratios and vastly higher chlorinity (by a factor of up to 13.5) of the resulting fluid.

Br is released instantaneously by easily soluble phases associated with felsic rock components. In contrast a significant smaller proportion of the rock's Cl budget is accessible as easily soluble phases. Therefore Cl/Br ratios of basement brines, typically below the Cl/Br ratio of their host rocks seem to be an effect of transient alteration processes. Although we do not fully understand the underlying mechanism, this implies that cataclastic deformation in the upper crust causing a grain size decrease has a large impact on the fluid's halogen budget and therefore fluid migration along such cataclastic zones may explain the high Cl and Br concentrations observed in basement brines without the need of an external halogen source.

FLU-T03

Temporal evolution of mid-ocean ridge vent fluid chemistry – an experimental study

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Submarine hydrothermalism along mid-ocean ridges (MOR) governs energy and mass fluxes from Earth's interior into the oceans. Recent investigations revealed high element discharge at the brittle deformed slow and ultra-slow spreading Mid-Atlantic Ridge (MAR) [1]. This points towards that seawater access to unaltered rocks along juvenile fault systems may create high fluid and high element fluxes, leading to extensive rare earth element (REE) and metal mobilization at high temperatures as observed at 5°S MAR [2].

However, estimations on total mass transfer between oceanic lithosphere and oceans have large uncertainties, in particular with respect to early-stage hydrothermalism with its obviously high impact on total element discharge and ore deposit formation.

In order to decipher the temporal evolution of high-temperature MOR vent fluid chemistry we started a systematic time resolved study of gabbro mineral grains reacting with natural seawater at 425°C, 400 and 1000 bar, at water-to-rock mass ratios (w/r) from 0.5 to 10, and run durations from 3 to 720 hours. Fluid products were sampled either (1) ex situ or (2) in situ at experimental temperature and pressure conditions.

According to [3] heated seawater became a very reactive phase by generation of $\text{HCl}_{(\text{aq})}$ from seawater Mg-chloride with $\text{pH}(25^\circ\text{C}, 1 \text{ bar}) = 1.7$ prior to significant interaction with gabbro. Note that the starting seawater had a $\text{pH}(25^\circ\text{C}, 1 \text{ bar}) = 7.8$. Fluid element concentrations increased with increasing w/r. Most fluid element concentrations as well as REE fluid pattern were not affected by quench effects. Furthermore, the results of this study give evidence that strong Eu-anomalies as known from many MOR hydrothermal vent fluids world-wide are generated by REE sorption onto, and/or incorporation into, secondary mineral phases rather than solely by complexation in the fluid.

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FLU-T04**New Insight on Lithium and Boron isotope fractionation during serpentinization derived from batch reaction investigations**C. Hansen¹, A. Meixner^{1,2}, S. Kasemann^{1,2}, W. Bach^{1,2}¹*University of Bremen, Department of Geoscience (FB5), Bremen, Germany*²*MARUM Zentrum für Marine Umweltwissenschaften, Bremen, Germany*

Serpentinization is a key process within the geochemical cycling between seawater and oceanic lithosphere as well as in suprasubduction zones. Promising potential tracers for the associated low T alteration, hydration- and dehydration mass transfer processes are the elements Li and B. During the serpentinization of peridotites by interaction with seawater, B tends to be greatly enriched, whereas Li is more likely partially leached from the rock. When serpentine minerals break down during slab subduction, the fluid mobile elements are rereleased, transferred into the mantle wedge and can ultimately be traced all the way up into the products of arc volcanism. The mass transfer driven by fluid-rock interaction is accompanied by characteristic Li and B isotope fractionation. A precise quantification of this fractionation is essential for using Li and B isotopes as tracer of these processes. Many different factors have to be taken into consideration and in particular, empirical fractionation coefficients have not yet been determined for the serpentinization processes.

We conducted multiple batch experiments (100 °C, 200 °C; 400 bar) reacting fresh olivine (5g; Fo₉₀) with seawater-like fluids (75 ml, 3.2 wt.% NaCl) which were adjusted in composition with respect to Li (0.2, 0.5 µg/ml) and B (10 µg/ml). We use Dickson-type reactors, consisting of collapsible 100-mL Ti-capped gold reaction vessels housed in steel autoclaves. The apparatus permits the concomitant retrieval of small volumes of fluids, which were analyzed for pH, major and minor elemental concentration (ICP MS) and Li and B isotope ratios (MC ICP-MS). The data provide information on the reaction progress and the ongoing isotope fractionation. Preceding and subsequent analyses of solid reaction educts and products via TG/DSC, SEM, XRD, AGFM and MC ICP-MS facilitate a comprehensive quantification of the serpentinization reactions. First results suggest a reaction turnover of about 70% after 224 days for the run at 200 °C and a distinctive B fractionation into solid mineral phases ($[B]_{\text{Fluid}(\text{start-final})} = -3.9 \text{ µg/ml}$; $\Delta^{11}\text{B}_{\text{Fluid}(\text{s-f})} = +1.5 \text{ ‰}$). The 100°C experiment yielded a very low extent of serpentinization (5-10%), but still distinct B uptake ($[B]_{\text{Fluid}(\text{s-f})} = -1.1 \text{ µg/ml}$) and even greater isotope fractionation ($\Delta^{11}\text{B}_{\text{Fluid}(\text{s-f})} = +2.13 \text{ ‰}$).

FLU-T05

The behavior of H₂ and CO₂ in siliciclastic reservoirs during energy/hydrogen storage

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The R&D lighthouse project H2STORE comprises six subprojects, which are conducted by the Institute of Geosciences of the FSU Jena, the Clausthal University of Technology and the Geosciences Research Centre (GFZ) Helmholtz Center Potsdam and investigates the impact of chemical energy storage in siliciclastic reservoir rocks. Thus large scale underground storage of energy in depleted oil-/gas fields or saline aquifers as hydrogen or in combination with CO₂-injection (power to gas technology - P2G) can be a most important part within the “Energiewende” program of the German Government. First fundamental studies on H₂ and its reaction with siliciclastic rocks were done almost 30 years ago by e.g. Foh et al. (1979) and Carden & Paterson (1979). However this research almost ceased and is most recently reactivated by some industrial and academic projects in the framework of a potential energy supply by renewable sources.

One of these projects is H2STORE, which investigates the impact of injected H₂ and H₂-CO₂ mixtures on potential reservoir sandstones at different temperature and pressure conditions. Thereby the behavior of distinct mineralogical assemblages, formation fluid compositions, microbiological populations, and hydrocarbon species (present as residuals in depleted HC-reservoirs) and their effects on the petrophysical/geohydraulic properties of the sandstones are regarded. To evaluate these processes laboratory experiments with petrophysical, mineralogical and microbiological focuses are conducted at reservoir conditions.

The main emphasis of the work performed at the IGW-Jena is the fate of porefilling cements and porerimming coatings exposed to migrating fluids (H₂) and their relationship to the petrophysical/geohydraulic rock attitude. This knowledge on chemical dissolution and physical detachment processes of the minerals, which might be induced by H₂ exposure, is essential to evaluate the capability of a H₂ underground injection into reservoir sandstones and its potential impact on reservoir quality and the corrosion of the technical equipment.

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FLU-T06**Multi-phase carbonate precipitates in the CO₂ reservoir at the Ketzin pilot site – CO₂-induced trapping mechanism or drilling artefact?**S. Bock¹, C. Höschel², M. Nowak³, H.- J. Förster⁴, R. Gaupp¹¹*Friedrich-Schiller-University Jena, Institute of Geosciences, Jena, Germany*²*Technische Universität München, Lehrstuhl für Bodenkunde, Freising, Germany*³*Max-Planck Institute of Biochemistry, Biochemical Processes, Jena, Germany*⁴*Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Potsdam, Germany*

In this ongoing study we aim to prove the occurrence of mineral trapping as result of CO₂ storage on the short time scale of four years. Short term effects of CO₂ on a porous siliciclastic reservoir were studied at the CO₂ Ketzin pilot site, which offered the possibility to study probable CO₂-induced mineralization processes on field scale.

The CO₂ Ketzin pilot site is situated in the Northeast German Basin, 30 kilometers west of Berlin. The subsurface contains Paleozoic to Cenozoic rocks in the setting of a halokinetic-formed anticlinal structure. Two saline aquifers of the Upper Triassic Stuttgart Formation in depths of 630 to 650 m and 660 to 665 m were chosen for a four-year injection test of CO₂. This reservoir is covered by a >165-m-thick caprock system of massive mudstones, which prevent leakage. The reservoir rocks were characterized by core material recovered before injection in 2007 and by core material recovered in 2012 after injection of 64,000 tons of CO₂.

Comparison of cores recovered before and after four years of injection revealed minor amounts of newly formed carbonate (micrometer size), but no changes in general mineralogical rock composition. It appears that these single and multiphase carbonates formed as consequence of the interaction between rock, saline formation water and injected CO₂ and thus indicate mineral trapping. Chemical investigations revealed siderite and calcite, enriched in Ba, Sr, Na and Cl concentration in contrast to diagenetic-formed dolomite. This proves precipitation in a highly saline environment.

However, this carbonate precipitation can also result from the highly alkaline, K₂CO₃ based drill mud, which was used to recover the cores. To prove mineral trapping, isotopic analyses ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of the precipitates were performed by Secondary Ion Mass Spectrometry at micro to nano-scale (NanoSIMS). The results with respect to isotopic fractionation processes will be compared to the isotopic signatures of the injected CO₂, the formation fluid prior and after CO₂ injection and the drill mud. Due to different fractionation processes during the formation from each of these sources, carbonates formed as a result of mineral trapping should be identifiable by their isotopic composition.

FLU-T07

Vein mineralizations in Mesozoic sediments – archives of fluid-evolution in the Thuringian basin (Germany)

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Vein mineralizations were studied in samples of Mesozoic sediments in the Thuringian basin (Germany) from natural outcrops, road cuts, quarries and drill cores in order to characterize paleo-fluid systems. Most veins are restricted to WNW-ESE trending fault systems. The mineralizations comprise carbonates (calcite, dolomite, siderite, ankerite), additional sulfates (gypsum, celestine, barite), and rare sulfides. Methods applied comprise bulk rock analyses (petrography, XRD, XRF, ICP-MS), mineral analyses (EPMA, LA-ICP-MS) and isotope studies (O, H, C, S, Sr).

First $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analyses of calcite mineralizations reveal differences between veins within Triassic and Jurassic sediments. Within the Lower Muschelkalk two types can be distinguished: Type I ($\delta^{13}\text{C}_{\text{(V-PDB)}}$: 2 to 3 ‰, $\delta^{18}\text{O}_{\text{(V-PDB)}}$: -7 to -10 ‰) is as high in $\delta^{18}\text{O}$ as the carbonatic host rocks; Type II is lower in $\delta^{13}\text{C}$ (-5 to -8 ‰). Comparing the analyses with published data from Hudson (1977) and Schwinn & Markl (2005) in the systems $\delta^{13}\text{C}_{\text{(V-PDB)}}$ vs. $\delta^{18}\text{O}_{\text{(V-SMOV)}}$ the Type I calcites exhibit marine values indicating precipitation from intra-formational fluid transport.

On the contrary, Type II calcites from veins in the Jurassic, Muschelkalk and Buntsandstein fall on a mixing line between Type I calcite and Paleozoic limestones (Schwinn & Markl 2005) with increasingly lower $\delta^{13}\text{C}_{\text{(V-PDB)}}$ with increasing stratigraphic depth. The Type II calcites in veins indicate extra-formational ascending paleo-fluid transport in the Thuringian basin.

Initial $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ isotope analyses of gypsum and baryte mineralizations indicate that isotope ratios of vein fillings are comparable to those of the vein-related host rocks of the Keuper and Zechstein, respectively. These data indicate precipitation of vein sulfates from intra-formational paleo-fluids only.

First high resolution in situ-Sr- isotope analyses also reveal host-rock related differences between veins occurring in different stratigraphic horizons of Triassic and Permian sediments, respectively.

The present study is part of INFLUINS, a BMBF-funded project bundle, which is dedicated to the comprehensive description and understanding of the fluid systems within the Thuringian basin in time and space.

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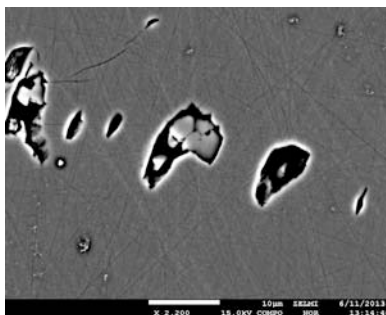
FLU-T08**Incorporation of quartz into corundum via aqueous fluids: experimental and natural examples**D. Schultze¹, G. Franz¹¹*Technische Universität Berlin, Mineralogie Petrologie, Berlin, Germany*

The metastable assemblage of quartz+corundum well inside the thermodynamic stability fields of all three Al_2SiO_5 polymorphs has been reported from many experimental setups (e.g. Harlov & Milke 2002, Roy & Osborn 1954, Roy & Roy 1954) and natural samples (Kihle et al. 2010). The latter are generally interpreted as indicator for high p-T metamorphism (inside Crn+Coe stability field) of the correspondent rock, preserved at lower p-T conditions due to the absence of water. In experiments at water saturation nucleation of Al_2SiO_5 is however reported only at conditions at around 20 kbar and 1200°C, whereas coexisting Qz and Crn precipitates can be observed over a broad range of more moderate conditions. Not only is the formation of Al_2SiO_5 kinetically inhibited (Harlov & Milke 2002), solubility of Al_2SiO_5 in aqueous fluids is higher than that of Crn and Qz (Manning 2007).

We investigated the interaction of Crn with aqueous fluids of varying pH and saturated in silica in different experimental setups at kyanite and sillimanite stability. The results demonstrate that silica can be incorporated into the corundum lattice together with water during the beginning dissolution of corundum. Quartz forms solid mineral inclusions in corundum instead of reacting with corundum to Al_2SiO_5 (Fig.1).

These experimental products and new natural assemblages of assumed moderate p-T formation conditions (< 600°C, 5 kbar) were analysed using electron microprobe and transmission electron microscopy in order to get detailed insight into the ongoing mechanisms during the experiments and to determine whether or not the natural examples could display comparable fluid-solid interaction processes.

Fig.1 Quartz grains growing in a fluid trail crosscutting a corundum grain after experimental treatment in silica saturated aqueous fluid (500°C, 5kbar)



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FLU-T09

Changes in tourmaline trace element geochemistry during magmatic fractionation and hydrothermal ore deposition

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The Cu-Sn-W deposits in the SW England ore field of Cornwall are related to the Variscan granitic magmatism and to the accompanying greisen and hydrothermal veins. To understand the formation of these deposits in detail, one has to understand distribution of Cu, Sn and W between various phases (melt, solids, fluid, and gas) during melt fractionation and fluid exsolution as well as during precipitation. Tourmaline is a perfect recorder of these processes as it is the only mineral present during all these stages in abundant quantities. Incorporating trace elements like Cu, Sn and W into its structure, tourmaline will shed light on the enrichment and precipitation of these important metals.

Hence, this project aims for the first time to investigate tourmaline trace element geochemistry from orthomagmatic rocks via pegmatites, aplites and exoskarns, greisen to hydrothermal veins of different stages in the well-investigated area of Cornwall in SW England.

Tourmaline from all geological settings related to the Variscan magmatism was sampled to cover all crystallization and mineralization stages. The variety of different textures and color zonings of tourmaline has been analyzed by EMPA. The major elements show a range between different Fe²⁺ and Mg²⁺ end-members like dravite and schorl, feruvite and uvite as well as foitite and magnesio-foitite and with different W site allocation each end-member occurs as oxy, hydroxyl and fluor phase as well. The distribution of Ca and Ti in the sector zoned tourmaline will provide an empirical geothermometer, which will be augmented by heating-freezing and LA-ICP-MS measurements of fluid inclusions. The trace elements in tourmaline analyzed by LA-ICP-MS reflect the composition of the fluid they precipitate from. These changes carry information about when and where the economically important elements entered the system and under which conditions they were precipitated as ore mineralization. Ultimately, this project will also contribute to establishing the trace element geochemistry of tourmaline as an exploration tool.

FLU-T10**Structural incorporation of W⁶⁺ into hematite and goethite and its bearing on hydrothermal and supergene Fe ores**S. Kreißl¹, R. Bolanz², J. Göttlicher³, R. Steininger³, G. Markl¹¹*Eberhard Karls Universität, Mathematisch-Naturwissenschaftliche Fakultät, Fachbereich Geowissenschaften, Tübingen, Germany*²*Friedrich-Schiller-University, Institute of Geosciences, Jena, Germany*³*Karlsruhe Institute of Technology, ANKA Synchrotron Radiation Facility, Karlsruhe, Germany*

The most common Fe³⁺-(oxi)hydroxides, *hematite* (α -Fe₂O₃; hem) and *goethite* (α -FeOOH; goe), form under various pH, Eh and T conditions in near-surface environments. While hem forms as primary mineral in hydrothermal processes, goe and hem are the most important secondary mineral phases during the supergene oxidation of primary Fe²⁺ minerals like siderite (FeCO₃). During the latter, hem and goe act as geochemical sinks for metals and toxic elements, released during weathering of ore deposits. This may work either by adsorption or by structural incorporation. Unlike adsorption, the incorporation into the crystal structure guarantees a long-time storage and so maybe records the hydrothermal evolution at supergene stage.

In this study, we investigated the chemical signature of major and minor elements in botryoidal hem/goe sequences ("glaskopf") from natural secondary Fe- and Mn-ores (Schwarzwald Ore District, SW-Germany). The main focus was on tungsten (W), where we also used X-ray absorption spectroscopy (XAS) to determine the structure of the W species.

A comparison of the EXAFS spectra and various W-phase models shows, that W actually resides in both Fe-(oxi)hydroxide structures, rather than forming a separate phase. In hem W is incorporated by an isomorphous exchange of two Fe³⁺ by one W⁶⁺, whereas goe incorporated W⁶⁺ by oxygen deprotonation for charge balance. W L₃ and L₁ XANES spectra indicate distorted WO₆ octahedra in both, the hem and goe structures.

W, As, Si, Al and P contents show similar and also reversed systematic fluctuations in the zoned mineral textures. This mainly depends on the mineralogy of the samples as well as the evolution of the equilibrated fluid at their formation. The samples show higher W concentrations in hem compared to goe. The difference in affinity of W to hem/goe may be related to the different formation mechanisms of hem/goe from their (here W-doped) precursor phase ferrihydrite.

W contents are elevated at deposits hosted by granites or orthogneisses. Some W is also found in sandstone-hosted ores which are, however, related to major fault zones. We think that granitic rocks are the major source of W in continental basement and that along major fault zones, fluids (which govern the formation of the secondary Fe phases) can percolate more deeply and thereby mobilize W from deeper level rocks.

FLU-T11

Ferrous minerals in banded iron formation from Hamersley Range, Australia – Are they primary or diagenetic?

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Banded iron formations (BIFs) are sedimentary rocks which occurred in a large time span during the Precambrian. They are distributed world-wide and typically constitute of alternating silica-rich and iron-rich bands. The mechanism of deposition is still debated because the original mineralogy is probably always overprinted by diagenesis, metamorphism or alteration. Common models involve oxidation of ferrous iron in the water column as well as partial reduction of iron oxides under anoxic conditions after deposition or during diagenesis. Alternatively, the direct formation of Fe-rich silicates from a ferruginous ocean has been suggested [1, 2].

BIFs from the Hamersley Region in West Australia only show a low-grade overprint with a mineralogy dominated by chert, siderite, ankerite, stilpnomelane and pyrite. A sample from this location was characterized by a combination of X-ray diffraction, evolved gas analysis as well as optical and scanning electron microscopy. The chert-rich layers (50-100 μm) contain a small amount microcrystalline stilpnomelane needles. Notably, pure and dense stilpnomelane layers permeating the sample in 20-50 μm bands are frequently observed as well. Siderite-rich layers (50-200 μm) with subhedral to euhedral grains are sometimes associated with pyrite and common surrounded in a chert matrix.

The formation of stilpnomelane under anoxic conditions has been examined using thermodynamic calculation. The influences of temperature and further geochemical parameters (pH, $a[\text{Fe}^{2+}]$, $a[\text{SO}_4^{2-}]$, $a[\text{SiO}_{2(\text{aq})}]$) have been tested. Amorphous silica and amorphous $\text{Fe}(\text{OH})_3$ were used as a precursor for chert for hematite, respectively. Stilpnomelane was precipitated as a simplified Fe-Si-O-OH gel as suggested by [2], furthermore pyrite, siderite and magnetite were taken into account.

The suggest model ($a[\text{SiO}_{2(\text{aq})}]=10^{-2.7}$, $f[\text{CO}_2]=10^{-0.2}$) shows that stilpnomelane-like phases are thermodynamically favored between 27-37 °C, at higher temperatures siderite is stable. At lower temperatures, chert and stilpnomelane can form together. The model suggests that ferrous BIFs can realized under anoxic conditions from a supply of hydrothermal ferrous iron.

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FLU-T12**Zoned supergene mineral associations formed during weathering of galena – mineralogical description and hydrogeochemical modeling**M. Keim¹, G. Markl¹¹*Universität Tübingen, Mathematisch-Naturwissenschaftliche Fakultät, FB Geowissenschaften, Tuebingen, Germany*

If galena (PbS) is exposed to near-surface conditions, supergene alteration produces thermodynamically more stable secondary lead phases. In this work we investigated 41 thin-sections of weathered galena and adjacent country rock. We identified cerussite (PbCO₃), anglesite (PbSO₄) and pyromorphite group minerals (PyGM) (pyromorphite Pb₅(PO₄)₃Cl, mimetite Pb₅(AsO₄)₃Cl and vanadinite Pb₅(VO₄)₃Cl) as secondary lead phases formed in a spatially well-ordered zoning texture around the preexisting/relic galena. Cerussite and anglesite occur either as in situ replacement of galena and/or as euhedral crystals in cavities. The PyGM are either located as a thin crust at the margin of the former/relic galena or as infiltration products in the host rock/gangue. During progressive weathering anglesite typically disappears first, with proceeding evolution cerussite dissolves and finally only the highly insoluble PyGM persist as a perimorphose.

In order to explain the observed textures a thermodynamic model for supergene galena weathering was created using PHREEQC. It implies variable physiochemical conditions relevant for the formation of secondary lead minerals. The modeling shows that over the whole relevant pH-range, PyGM are the most stable lead phases, precipitating at very low ion activities. This explains their textural position. Whether cerussite or anglesite forms depends mainly on the pH-value of the supergene fluids. Furthermore, calculated solubility diagrams show that anglesite is under most surface conditions the most soluble phase, followed by cerussite and PyGM. This again reflects the microscopic observations. Our models also show the influence of temperature, different CO₂-partial-pressures and/or mineral reactions on the formation and stability of secondary lead phases.

As a further step, the duration of formation of a natural mm-thick pyromorphite crust was calculated using natural phosphate fluxes from Kaiser et al. (2003). The calculation indicates that mm-thick pyromorphite crusts can be formed in geological short time periods of a few hundred years, which is in agreement to observations in old mines.

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FLU-T13

Formation of colloidal multilayers on nanostructured crystal surfaces-an experimental approach

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The formation of colloidal multilayers on nanostructured crystal surfaces is important for a multitude of technical and natural processes, such as diagenetic reactions or membrane fouling. Surface topography variations at the submicron scale are able to control nanoparticles and colloids [1]. In our study, we focus on the formation of multilayers in an aqueous system at the water-crystal interface with respect to DLVO-theory [1, 2]. We used silica particles and three different types of nanostructured SiO₂-surfaces, to get a systematical insight into the layer formation. The surfaces were structured using photolithographic treatment onto silicon wafers, which were then oxidized by peroxomonosulfuric acid. Out of this procedure we received blank wafers and wafers with pillars of heights of 50 nm and 500 nm; the space between the single pillars is 1000 nm. The experiments were performed in a flow cell (Fig. 1). An aqueous suspension of nonfunctionalized silica colloids (POSTNOVA, d=0.8 µm) was set to a slight alkaline pH, to ensure a zeta potential >70 mV between the particles as well as the particle-surface interface. This system serves as an analog for, e.g. silicate particles and collector surfaces. After preparation the suspension was led in intervals of 50 ml through the flow cell with a flow velocity of 0.7 ml/min by using a syringe pump. After the reaction intervals, the cell was rinsed with a solution of the same pH as the suspension to remove any residual, nonattached particles out of the flow cell. Vertical scanning interferometry (VSI) was applied. This method allows for the analysis large fields-of-view at high spatial resolution and, thus, for the quantitative understanding of heterogeneous surface evolution [1]. Using this approach we want to answer the question, whether the multilayer formation is governed by layer-by-layer deposition or by the lateral and vertical growth of single islands of particles.

First data suggest, that the formation of the initial layer will preferably take place by the growth of islands followed by further layer-by-layer deposition to form multilayers.

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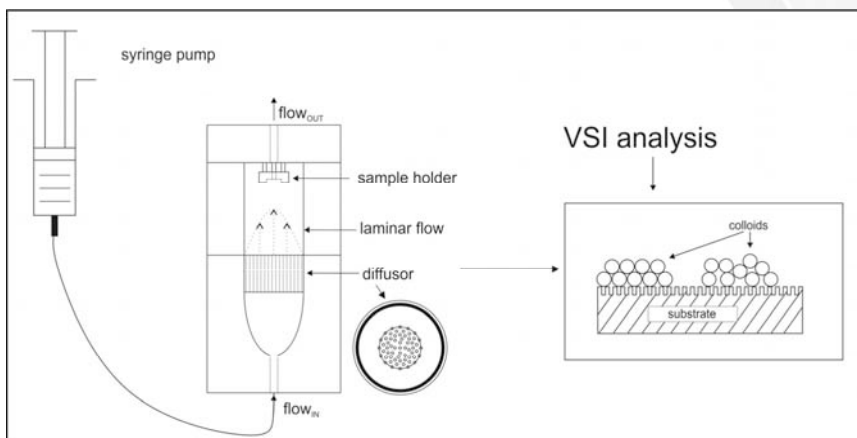


Figure 1: Workflow and cell design

FLU-T14

Dissolution of polycrystalline material analyzed by the rate spectra concept

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Many environmentally and technically important crystalline materials require our ability to predict their dissolution kinetics. An example is the dissolution of UO_2 pellets from spent nuclear fuel material. Thus far, the application of the new *rate spectra concept* [1] has showed how rate modes may contribute to the overall rate of dissolution of a single crystal surface [2]. The existence of such modes underscore that a single mean value is insufficient to describe properly the surface reaction rate and its variability.

Now, the application of polycrystalline material adds significant complexity to the problem, such as density of grain boundaries and variation of grain orientations. Here we focus on the analysis of dissolution kinetics and their variability of polycrystalline material. We hypothesize that specific modes of the rate spectra will dominate the overall reaction rates. Here we study marble samples showing well-defined variability in grain size and orientation. We utilize an experimental setup that has been previously used for the analysis of calcite single crystal dissolution kinetics [3] and allows thus for a direct comparison with these previous studies.

We analyze the material flux from the surface of well-characterized marble samples in long-term experiments. Characterization includes grain boundary density and crystallographic orientation. Interferometry measurements generate surface topography maps using a quasi in situ environmental cell [4]. This approach allows for a direct and large field-of-view analysis. In this study, we focus on the impact of density of grain boundaries on material flux. Here we utilize endmembers of populations of crystallographic orientation to show its impact on the variability of reaction rates.

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FLU-T15**Fluid infiltration and pseudomorphs formation during the replacement of garnet and pyroxene in the Caledonides of western Norway**

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The Precambrian granulite facies rocks of Lindås Nappe, Bergen Arcs, Caledonides of W.Norway are partially hydrated at amphibolites and eclogite facies conditions. The Lindås Nappe outcrop over an area of ca 1000 km² where relict granulite facies lenses make up only ca 10%. At Hillandsvatnet, garnetite displays sharp hydration fronts across which the granulite facies assemblage composed of garnet (60%) and clinopyroxene (40%) is replaced by an amphibolite facies mineralogy defined by chlorite, epidote and amphiboles. This setting allows us to assess the mechanism of fluid transport through an initially low permeability rock and how this induces changes of texture and element transport.

There is no visible porosity within the garnets and clinopyroxenes but all new minerals formed are porous. This replacement of garnet and clinopyroxene is pseudomorphic so that the grain shapes of the garnet and clinopyroxene are preserved even if when they are completely replaced.

This requires that the reactive fluids must pass through the solid crystal grains and this can be achieved by an interface coupled dissolution-precipitation mechanism. Porosity generation is a key feature of this mechanism (Putnis and Austrheim 2012). Putnis et al. 2007 and Xia et al. 2009 have shown that even in pseudomorphic reactions where the molar volume increases, porosity may still be generated by the reaction. This is fundamental in understanding the element mobility and the mass transfer in a low permeability rock. The textural evolution during the replacement of garnet and pyroxene in our rock sample conforms to that expected by a coupled dissolution-precipitation mechanism.

FLU-T16

The replacement of Celestine (SrSO_4) by Strontianite (SrCO_3) studied *in situ* by Raman spectroscopy

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The replacement of celestine (SrSO_4) by strontianite (SrCO_3) has extensively been studied over the past decades. Strontium carbonate is a very important industrial reagent and the replacement of celestine by strontianite in a carbonate solution represents one route to obtain strontianite. We have started to investigate this system as a model reaction to study the mineral replacement mechanism and the behavior of oxygen isotopes at solid-fluid reaction interfaces. Raman spectroscopy provides a powerful tool to *in situ* monitor the reaction kinetics, but also to study the behavior of oxygen isotopes at reaction interfaces and in the fluid. Raman measurements of isotopically enriched compounds have revealed that oxo-anion groups perform localized vibrations with distinct frequencies, reflecting the oxygen-based isotopologues of the oxo-anion molecule. The relative intensities of these bands are proportional to the isotopologue fractions in the molecule species, which allows the precise quantification of its isotope composition.

First information about the replacement kinetics was obtained by real time, *in situ* Raman spectroscopy using isotopically natural solutions. Measurements were carried out in a closed system consisting of an in-house-made Teflon[®] fluid cell with an internal heating system. The fluid cell was filled with a 1M Na_2CO_3 solution and an equimolar amount of celestine powder with grain sizes between 63 and 125 μm . The experimental temperatures were 35°C, 40°C, 45°C, and 50°C. At the start of the experiments the aqueous $\nu_1(\text{CO}_3)$ band could be observed at 1065 cm^{-1} that lost intensity over the course of the reaction. Complementary the aqueous sulfate $\nu_1(\text{SO}_4)$ band at 981 cm^{-1} grows in intensity. From the relative changes between these bands we derived the reaction rates and the activation energy. Future experiments will then be carried out with ^{18}O -labelled solution, which will allow studying the oxygen isotope exchange between carbonate and sulfate in solution, while celestine is being replaced by strontianite. In the next step, the replacement reaction front movement and the behavior of oxygen isotopes will directly be studied *in situ*, spatially resolved, and in real-time by Raman spectroscopy using a special reaction cell.

FLU-T17**Behavior of Sr and Y during apatite replacement – insights from Hydrothermal Diamond Anvil Cell experiments**

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Apatite [Ca₅(PO₄)₃ (F,OH,Cl)] is a major host of halogens in many magmatic and metamorphic rocks and can incorporate large amounts of rare earth elements (REE) and other trace elements (Y, Na, Si, Mn, U, Sr). Apatite is also formed in hydrothermal environments and its composition is sensitive to changes in the fluid composition. Here, we present an experimental study to investigate the behavior of Y (as a proxy for REE) and Sr during reactions of Y and Sr-bearing single crystal Cl-Apatite with hydrothermal KOH and NaF solutions at 300-600°C and crustal pressures.

Experiments were performed using a hydrothermal diamond anvil cell (HDAC) at DESY in Hamburg. The Y and Sr-rich Cl-apatite starting material reacts with the hydrothermal fluids via a coupled dissolution-precipitation process. During replacement of synthetic Cl-Apatites (which contain ca. 1000 ppm Sr and Y each) the two trace elements are effectively mobilized from the apatite. Sr and Y concentrations of the fluid are measured using time-resolved SR-μXRF at Beamline L (DORISIII). The Sr and Y concentrations of the fluid vary strongly as a function of overall amount of fluid present, the composition (KOH or NaF) of the experimental fluid, and temperature. All three factors seem to control the dissolution of starting material apatite, the subsequent release of Sr and Y into the fluid as well as the precipitation of new apatite which incorporates some of the Sr and Y from the fluid. The interaction of REE-rich apatite with hydrothermal fluids is a viable process leading to mobilization of large amounts of REE which could be relevant to ore genesis processes.

FLU-T18

Fluid composition effects on the experimental replacement of Carrara marble by apatite

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Mineral replacement reactions that produce pseudomorphs have been explained as a coupled dissolution - reprecipitation process (Putnis, 2009). The solid-fluid interaction, the different textural effects, the generation of porosity, epitaxy, and the persistence of external morphology make these processes highly interesting not only in the study of metasomatic and metamorphic geology but also in the field of materials sciences.

Calcium carbonates are readily replaced by apatite, making it an attractive model for the study of such processes. In this study, it was used to explore reaction rates, porosity structures, and textural effects of such replacement by changing the composition and concentration of the fluid used for reaction.

Small Carrara marble cubes (almost pure in CaCO_3) of around 2 mm³ were treated in hydrothermal reaction vessels at 200°C using phosphate bearing solutions with and without the presence of different ions: chlorine, fluorine and magnesium.

Mounted and polished cross sections of the reacted samples were examined by scanning electron microscopy and electron microprobe analysis to determine the extent of replacement, the textural evolution and the composition of the product phases. Mineral phases could be identified by Raman spectroscopy. Results show that changes in the chemistry of the fluid seem to influence the evolution of the reaction front: whether it is more effective through the grain boundaries towards the centre of the grains, or through the developing porous structures towards the centre of the rock. Moreover, the micro-porosity of the replaced product also shows significant dependence on the solution composition, varying from being very heterogeneous to a more uniform micro-porosity distribution as observed in this study.

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FLU-T19**Experimental alteration of bone in acidic solutions**

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Understanding the fossilization process in bones during diagenesis is essential for the reliable application of geochemical proxies as well as for the reconstruction of the paleobiology and paleoenvironment of vertebrates. To investigate the fossilization process of modern bones, in particular the uptake of rare earth elements (REE), in vitro alteration experiments were performed. In addition, the recrystallization and crystallinity changes of bioapatite during experimental alteration were studied with the aim to understand the mechanism of bone alteration.

For this purpose cubes (2 x 2 x 2 mm) of modern ostrich bone were placed in 1 ml ¹⁸O-spiked (23.77 at.-% ¹⁸O) multi-element HNO₃ solution with a pH of 0.4. Subsequently, the samples were artificially altered under six different temperature conditions (90° - 190°C) for two weeks. Backscatter electron images display concentric alteration rims, whose width is decreasing with increasing reaction temperature. XRD and Raman spectroscopic analyses reveal the formation of monetite (CaHPO₄) and whewellite (Ca(C₂O₄)·H₂O) in the altered bone specimens. LA-ICP-MS analyses further reveal a major uptake of REE in these rims and a fractionation of REEs in the bone during alteration. The uptake of REEs was confirmed by complementary ICP-MS analyses of the experimental solutions, showing that REE-uptake by the bone increases with increasing reaction temperature. To determine the degree of bone dissolution and/or formation of authigenic phosphate minerals the concentrations of the major elements Ca and P in the experimental solutions were also analysed. Ca is enriched in the solutions at all temperatures, whereas the P content in the solution decreases continuously with increasing temperature. This indicates that more apatite is dissolved at lower than at higher temperatures. Oxygen isotope analyses of the phosphate group of the bone apatite from the 90°C and 190°C experiments display strong ¹⁸O-enrichment with $\delta^{18}\text{O}_{\text{PO}_4}$ values of over 7800‰ throughout the bone cube. In all experimental solutions trace elements such as Al, Ba, Fe, Mn, Pb and U are depleted with respect to the starting concentrations. This indicates that these elements are scavenged from the solution during bone alteration.

FLU-T20

New Insight in the coupled dissolution and precipitation of aragonite and calcite

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Aragonite is a mineral found in many different geologically and biologically relevant systems, making it a very abundant calcium carbonate polymorph. Since aragonite is unstable under standard pressure and temperature, the coupled dissolution of aragonite and subsequent precipitation of calcite is a rapid process which has been studied in former experiments using isotopic attenuation methods [1].

However, direct imaging of the proposed heterogeneous calcite nucleation on the aragonite surface is very difficult and therefore extremely rare [e.g. 1]. Since the mechanism of epitaxial nucleation should be crucial for a coupled dissolution and precipitation [2], a detailed visual monitoring of the alteration of aragonite surfaces during coupled dissolution-precipitation experiments could be very helpful in understanding the aragonite-calcite transition in detail.

In this study we use vertical scanning interferometry (VSI) to directly observe the alteration of aragonite surfaces in coupled dissolution and precipitation experiments in flow cell reactors. VSI has been a valuable tool to receive high resolution images of larger field of views compared to atomic force microscopy [3]. Due to the ability of the VSI method to focus on a particular crystal face we can investigate the influence of the facial orientation on the previously proposed epitaxial nucleation. Such detailed knowledge about the mechanism of coupled dissolution and precipitation in the aragonite - calcite system could possibly lead to new insight into the quantitative prediction of aragonite replacement reactions in natural systems. By obtaining quantitative information about the behavior of different crystal face orientations of aragonite during substitution, a precise statement about the kinetics for the transformation of a single aragonite crystal to calcite could be possible.

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FLU-T21**A real-time, *in situ* Raman spectroscopic study on borosilicate glass corrosion**C. Lenting¹, T. Geisler¹¹Uni Bonn, Steinmann-Institut für Geologie, Mineralogie und Paläontologie, Bonn, Germany

Current knowledge on the silicate glass corrosion mechanism and its kinetics is based on either observations made on naturally or experimentally altered glasses. In both cases, characterisation of formerly hydrous reaction products is performed *ex situ* after a drying process. Combining a newly designed fluid cell with a confocal Raman spectrometer made it possible, for the first time, to monitor the advance of a corrosion front into borosilicate glass *in situ*, spatially resolved, and in real-time. Such real-time, *in situ* Raman spectroscopic measurements could be ground-breaking for our understanding of properties controlling the corrosion process within bulk solution, reaction rim, and at the reaction interface.

First results of an *in situ* and real-time experiment with a ternary borosilicate glass at an initial pH of 1 and 70°C for about 10 days revealed the development of a several micrometer thick and increasingly polymerised silica rim as corrosion product that is directly deposited from solution after congruent glass dissolution rather than being formed by *in situ* restructuring of an alkali-leached residual glass, as currently publicized. Furthermore, the occurrence of a water-rich interfacial layer was observed during glass corrosion for the first time. Future experiments will be carried out with a special fluid cell that allows the addition of isotope tracers (D, ¹⁸O) during a running experiment. Any re-equilibration of the silica and the transport of water through the reaction rim could then be monitored by isotope frequency shifts of certain Raman bands, which will give further spatially-resolved insights into the dynamics of the corrosion process of borosilicate glasses.

FLU-T22

Pattern Formation during the alteration of glasses – insights from experimental studies and modelling

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Altered zones of archaeological glasses often show intriguing banding patterns in backscattered electron images, reflecting chemical and/or structural variations. We report the results of static glass corrosion experiments with different silicate glasses, which also revealed chemical and structural banding patterns inside silica-based corrosion zones. Pattern formation thus originates by self-organization and does not necessarily need external forces like seasonal weather changes as previously suggested. Furthermore, these patterns cannot be explained by existing glass corrosion models that are based on diffusion-controlled solid state reactions. However, they can nicely be explained by a model that assumes congruent dissolution of the glass network, which is coupled to the reprecipitation of amorphous silica at an inwardly moving reaction interface. The feedback necessary for pattern formation is given by a competition between the kinetics of the transport of chemical species through the silica corrosion layer and the coupled dissolution-reprecipitation reactions at the interface. First attempts were made to model the interface coupled dissolution-precipitation process in order to reproduce pattern formation. A program based on the finite element method was implemented in VB.Net, which was coupled to the geochemical code PHREEQC (Parkhurst & Appelo 1999). Additionally, a numeric solution was taken into account and implemented as lattice box model. The following assumptions were made: The glass composed of silicon, cation A, and cation B dissolves congruently. Silicon will be directly precipitated as amorphous silica in the same box in which the glass is dissolved. Cation A speeds up the dissolution and diffuses slowly, whereas cation B leads to a decrease of the dissolution rate and diffuses fast. This is a reasonable assumption as it is known that, for example, small amounts of dissolved sodium or boron have a strong influence on the solution pH, which, in turn, controls the glass dissolution rate. Moreover both cations have the possibility to precipitate as component of the amorphous silica gel. With these assumptions our model is able to reproduce chemical patterns inside the corrosion rim.

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FLU-P01**Zur Mineralogie des Eisenerzvorkommens von Kakopetros, Chania-Kreta (Griechenland)**G. Alevizos¹, N. Katzagiannakis¹, A. Stratakis¹¹*Technical University of Crete, Mineral Resources Engineering, Chania, Greece*

Zahlreiche Eisenerzvorkommen treten in vielen Regionen Kretas auf, insbesondere in den Präfekturen von Chania und Rethymno, West-Kreta. Die Eisenerzvorkommen treten innerhalb der Phyllit-Quarzit-Serie (PQS) auf, die eine tektonische Einheit der Phyllit-Decke Kretas darstellt. In West-Kreta ist die PQS zwischen der Tripali- im Liegenden und der Tripolitza-Einheit im Hangenden eingeschaltet. Die PQS besteht hauptsächlich aus Phylliten und Quarziten, sowie Metakonglomeraten, Marmoren, Kalkphylliten und Metabasalten.

Das Eisenerzvorkommen liegt in der Nähe des Ortes Kakopetros, 40 km südwestlich von Chania und wurde gelegentlich wirtschaftlich ausgenutzt. Das Erz kommt in Form eines Lagers in einer Kontaktzone zwischen den Phylliten-Quarziten der Hochdruck/Tieftemperatur metamorphen PQS und den überliegenden Kalksteinen, vor.

Die Phyllite und Quarzite sind innerhalb der Kontaktzone intensiv zerrüttet und brecciert. Sie sind von Eisenreichenlösungen stark imprägniert, die in Form von Limonit (Goethit) ausgefällt worden sind. Die Eisenerze setzen sich hauptsächlich aus Goethit, Quarz und Kryptomelan zusammen. In untergeordneten Mengen treten Muskovit, Lepidokrokot und Hämatit auf. Die Eisenvererzung erscheint vorwiegend in Form von Goethit und seltener als Lepidokrokot, unter Verdrängung des Bindemittels der Phyllite und Quarzite. Hämatit tritt sporadisch in den Eisenerzen auf und ist meist sekundär durch Dehydratation des Goethits entstanden. Gelegentlich ist die Eisenvererzung mit einer Manganmineralisation verknüpft. Als Manganmineral wurde Kryptomelan identifiziert. Goethit und Kryptomelan bilden oft rhythmisch, konzentrisch, gebänderte Texturen, entlang von Spalten und Hohlräumen. Die Abscheidung von Fe und Mn auf den Korngrenzen der Phyllit und Quarzit Bestandteile, die bei der Änderung des Redoxpotentials stattfindet, beruht ausschließlich auf die Löslichkeit und Migrierfähigkeit dieser beiden Übergangsmetalle.

Aus der erzmikroskopischen Untersuchung der einzelnen Mineralen und ihrer Verdrängungsverhältnisse, sowie ihrer Texturen, stellt man weiter fest, daß es sich um eine epigenetische Ausfällung von sekundären Eisen- und Manganmineralen aus Verwitterungslösungen handelt, die zu einer intensiven Vererzung in den Phylliten und Quarziten geführt hat.

FLU-P02

Time resolved alteration of gabbro in high-temperature hydrothermal systems – an experimental study

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Recent investigations suggest that about 50 percent of hydrothermal alteration of oceanic crust occurs along the slow and ultra-slow spreading Mid-Atlantic Ridge (MAR) [1]. It is evident that high-temperature hydrothermalism along the MAR creates high fluid and high element fluxes from the lithosphere to the ocean [1, 2] in particular at early stages [3].

Thermodynamic and kinetic modelling of water-rock interaction under the high pressure and high temperature conditions of this type of submarine hydrothermalism in great water depths is difficult because of the special physical properties of these systems. Moreover, quantitative evaluation of water-rock interaction processes based on the geochemistry of natural samples requires reliable thermodynamic and kinetic data that in particular for these systems are not available.

In order to unravel the temporal evolution and the impact of early-stage hydrothermalism on the alteration of mafic oceanic lithosphere we started a systematic experimental study using natural seawater reacting with oceanic gabbro at 425°C, 400 and 1000 bar at variable water-to-rock mass ratios, and variable run duration. Both parameters simulate varying fluid fluxes.

Our results show that hydrothermal alteration of gabbro by seawater at high pressure and temperature conditions is a very rapid process. Anhydrite and major masses of secondary MgOH-bearing mineral phases, mainly as smectites, form within a few hours. Amphiboles were extensively formed after a few days followed by talc. The high impact on early-stage hydrothermalism on mass transfer between seawater and mafic oceanic lithosphere is evident from the intense alteration of gabbro by seawater even only within the duration of a few hours.

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FLU-P03**The formation of the rare earth mineral parisite in emerald bearing carbonate veins of Muzo/Colombia**J. Artel¹, U. Altenberger¹, C. Günter¹, J. Fernandez Lamus²¹*University of Potsdam, Institute of Earth and Environmental Science, Potsdam, Germany*²*Universidad Nacional, Departamento de Geociencia, Bogota, Colombia*

The area of the Eastern Cordillera of Colombia is well known for its emeralds. Occasionally, the rare earth (REE) mineral parisite ($\text{Ca}(\text{Ce}, \text{La})_2(\text{CO}_3)_3\text{F}_2$) occurs as single, euhedral grains. The host of parisite and other minerals like pyrite, emeralds and albite are carbonate-dominated veins formed by sodium-rich brines of non-magmatic sources. The wall rocks of these veins consist of low-grade metamorphic black shales of Cretaceous age. The calcite-dominated veins, of probably Tertiary age, are controlled by strong and localized deformation. The present study focuses on “single-grain parisites”. Electron microscopy, electron microprobe and ICP analyses reveal a more complex growth history of parisite single crystals.

The parisite crystallization is initiated after the tectonically enhanced formation of the calcite veins. “Crack - seal” processes control in part vein mineralization. Parisite growth starts by nucleation of several grains until coalescence and equilibrium fabrics are reached. These grains form the center of the later “single grains”. The further evolution of parisite is controlled by lamellar growth, syn- to post-tectonic to the calcite fibers formed during “crack - seal” dominated widening of the vein(s). The lamellae are grown pseudomorphically after calcite fibers. Locally, lamellae of bastnaesite grew. Dissolved calcite fibers leave behind needle-shaped cavities.

The stepwise growth of chemically heterogeneous parisite indicates variations in the physical conditions and composition of the fluid supply. The needle shaped calcite inclusions parallel to the lamellar section of the parisite crystal reveals the importance of “crack - seal” processes during the opening of the veins. Whereas elements like sodium, calcium and fluorine were supplied from the saline brines, chemical profiles in the wall rocks indicate that, in addition to chromium and vanadium, the rare earth elements were originated from the black shales.

FLU-P04

Contributions to the formation of accessory minerals in the emerald deposits of Muzo/Colombia

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Colombia is famous for its emeralds. They originate in the Eastern Cordillera, particularly in two zones on the eastern and western flank, northwest and northeast from Bogotá. The samples that have been studied are from Muzo. The Muzo mine belongs to the western zone and is one of the most profitable emerald mines worldwide.

Colombian emerald deposits are explained by hydrothermal origin without any influence of magmatic processes. Hydrothermal fluids penetrated tectonically strained Cretaceous black shales. This provoked a leaching of remarkable amounts of Be, Cr, V and rare earth elements among other elements from the black shales. Those were able to interact with the sodium-rich hydrothermal fluids. As a consequence the black shales suffered strong sodium-metasomatism and emeralds as well as various accessories crystallized in veins.

The present study suggests, that in cases where beryllium is not provided by leaching of the black shales, a greenish vanadium-bearing mica crystallizes. Albite is the most abundant accessory mineral; it replaces the black shales metasomatically. Nearly completely albitized black shales adjacent to emerald-bearing veins are the consequence. Apatite is characterized by high concentrations in fluorine. It appears in veins associated with albite and - if present - greenish mica and pyrite. Pyrite occurs as a primary mineral in the black shale, as well as a secondary mineral, probably due to a local thermochemical reduction of sulfates to sulfides and high concentrations of Fe. Secondary crystallized pyrite sporadically carries small quantities of chalcopyrite and sphalerite. Sphalerite is rich in Cd. Although rutile occurs primarily in the wall rocks, rutile is formed during the formation of emeralds, too. In addition, euhedral xenotime with high concentrations of Er, Gd and Yb crystallizes, simultaneous to albite. New monazite probably crystallizes in the albitized black shales, too.

Albite, i.e. sodium-rich fluids, forms the first pulse of vein-forming minerals. F-apatite, V-rich mica, emerald, rutile and pyrite (with inclusions of chalcopyrite and sphalerite), as well as xenotime, follow during and after the albite crystallization.

FLU-P05**Molecular structure of Na(OH) solutions at high P and T – insights from in-situ Raman spectroscopy and ab initio molecular dynamics simulations**

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Fluids are very important agents in metamorphic and igneous processes. They transport matter and catalyze mineral reactions. Various studies [1] suggest that it is crucial to study the physical properties of alkaline fluids under high pressure (P) and temperature (T) conditions. While aqueous solutions of Na (OH) under ambient conditions are already understood well [2] much less is known about the structure of these fluids under extreme P-T-conditions.

Here, we investigate different aqueous solutions of sodium hydroxide contained in a hydrothermal diamond anvil cell by in-situ Raman spectroscopy from ambient conditions up to 1.4 GPa and 700 °C. The spectra are analysed by peak fitting. In addition, they are interpreted with the help of ab initio molecular dynamics simulations. The simulations are set up to resemble the experimental conditions. This allows a direct comparison of vibrational spectra extracted from the simulations with the measured Raman spectra.

The combined experimental and computational study provides new insights in how the molecular structure of Na(OH) solutions changes with Na(OH) content, P and T. Potential implications of our results on more complex geological fluids will be discussed.

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ENV-T01

Unique algae bacteria mineral assemblages in a highly metal-contaminated stream

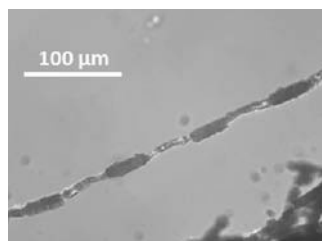
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Highly metal-contaminated, slightly acidic (~pH 6.0) underground water emerges in a former German uranium mining district (Ronneburg, Germany). Recently, massive upwelling formed small streams and iron-rich terraces along grassland down to the drainage creek. These streams are characterized by high abundances of iron oxidizing bacteria and conspicuous greenish and brownish filamentous algae during the summer months that show iron mineral incrustations. Since these algae have not been characterized, the aim of this study was to elucidate (a) if the algae are colonized by iron oxidizing microorganisms, (b) the spatial arrangement of microbial constituents, and (c) the type of iron minerals and their location on the algal surfaces. Observation of algae by confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) revealed that filamentous microalgae are encrusted with iron mineral precipitates that are colonized by bacterial cells. Mineral precipitates are distributed in a regular but discontinuous pattern on the surface of the algal filaments (Fig.). Fourier transform infrared spectroscopy (FTIR), inductively coupled plasma mass spectroscopy (ICP-MS) and Raman spectroscopy data indicated that ferrihydrite was the major constituent of iron mineral precipitates on algae. Amplicon pyro-sequencing targeting 16S rRNA genes and quantitative PCR assays employing specific primers for different groups of iron oxidizing bacteria revealed that *Gallionella*-related iron oxidizing bacteria were dominantly colonizing algae. *Gallionella* seem to not only preferably colonize algal surfaces but also may cause formation of ferrihydrite. The site specific colonization of *Gallionella* and accumulation of ferrihydrite on algae were likely induced by the algal physiological activity and its morphology. We suggest that *Gallionella* might use extracellular polysaccharides to adhere to algal surfaces and accelerate iron oxidation which is present in high concentrations in the stream water.



ENV-T02

***Mesorhizobium australicum* mediates low pH Mn(II) oxidation leading to the formation of bixbyite**

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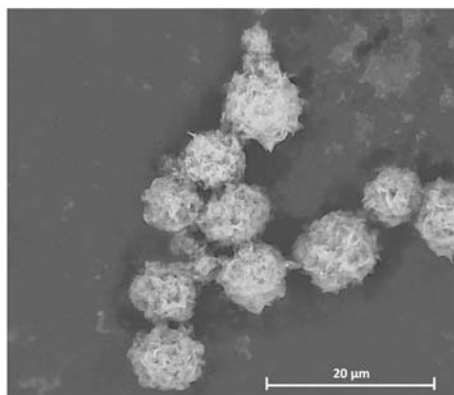
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Mn oxides are strong oxidants and adsorbents that contribute substantially to control the distributions and bioavailability of cations. Especially, Mn oxide minerals present in acidic environments are practical and ecological significant for natural attenuation and pollution remediation. Majority Mn oxide minerals were believed to be initiated by manganese oxidizing microorganisms (Tebo et al., 2005). Despite birnessite and todorokite were assumed to be the most predominant biogenic Mn oxides (Webb et al., 2005), it was shown that Mn(III), known as a transient before, was the major Mn species in suboxic zones of the Black Sea (Trouwborst et al., 2006) and sediment porewater (Madison et al., 2013). Here, for the first time, we demonstrate the formation of Mn(III) oxides at low pH by *Mesorhizobium australicum* strain T-G1 that was isolated from an acidic, heavy metals contaminated former uranium mining district, Ronneburg, Thüringen, Germany. We further elucidated that T-G1 might utilize a binary strategy which includes multicopper oxidase and super oxides to oxidize Mn(II) directly and indirectly to Mn(III) according to pH conditions and growth phases.

Figure 1: Scanning electron microscope image of Mn(III) oxides mediated by *Mesorhizobium australicum* T-G1 at pH 5.5



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ENV-T03

Characterization of biogenic Mn oxides produced by Mn(II)-oxidizing bacilli isolated from a Mn oxide-rich soil layer

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Naturally occurring Mn oxides are ubiquitous in the environment and most are produced via the microbial oxidation of Mn(II). These so called biogenic Mn oxides are extremely efficient oxidants and sorbents, and as such they control the mobility of trace metals and impact on the flow of electrons and the cycling of carbon in the subsurface. To better understand the formation of biogenic Mn oxides and their role in element cycling, we have studied Mn oxide-rich soil layers at the former uranium mining site, Ronneburg, Germany. Here, soil geochemistry is unfavorable for abiotic Mn oxide formation due to the acidic pH; this combined with low carbon contents and high heavy metal loads, which also challenges microbial activity. Despite these conditions, Mn oxide-rich soil layers at the study site were rich in poorly crystalline Mn(III/IV) oxides most closely resembling the abiotic phyllomanganate δ -MnO₂. We have identified and isolated *Bacillus* sp. GH_P2_28 and *Brevibacillus* sp. GH_P2_27, able to produce biogenic Mn oxides in axenic cultures. Our products were characterised by electron microscopy and synchrotron spectroscopy techniques. In agreement with previous studies on biogenic Mn oxides, we identified very poorly crystalline δ -MnO₂-like products. Mn oxide encrusted bacteria showed unique morphological and mineralogical features specific to each strain, including an enrichment of Mn(III) in *Brevibacillus* sp.. In light of our work, it appears that Mn(II)-oxidizing bacteria (MOB) are able to catalyse Mn(II) oxidation, and that species-specific mechanisms prevail.

ENV-T04

Mineralogical investigation of a geogenic Tl-As contamination near Buus (Switzerland)

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We are investigating the composition of a naturally contaminated agricultural land near the village Buus in the Swiss Jura Mountains range. The site is called *Erzmatt*, located on dolomitic and lacustrine limestone, hosting a small, intensively weathered ore deposit, and known since historical times for its barrenness (Truninger, 1922; Suter, 1915). Already Truninger (1922) attributed the barrenness and the agricultural problems to soil pollution by arsenic. We confirmed this suspicion with ICP-OES/MS measurements and determined an average amount of arsenic in a depth between 0-140 cm of 5463 mg kg⁻¹. The concentration of As increases with depth, up to a maximum at a depth between 70-90 cm of 22765 mg kg⁻¹. Intriguingly, the thallium concentration in the soil averages at 2229 mg kg⁻¹. The maximal level of thallium reaches 12800 mg kg⁻¹ in a depth of 60 cm. In our current work, we focus on the determination of the secondary Tl and As minerals and their crystal structures. This interest stems from the assumption that these minerals fix or potentially release these elements, hence are the clues of the elemental mobility and distribution in contaminated soils. Powder X-ray diffraction (P-XRD) and wave-dispersive electron microprobe (WDX-EMP) analyses revealed minute fragments of primary pyrite, and sphalerite. In some samples, we also detected native copper. The ore body contains commonly barite-pharmacosiderite, scorodite, and arseniosiderite, together with X-ray amorphous hydrous ferric oxides (HFO) and goethite. Due to the overlap of the X-ray emission lines of Pb, S, Tl, and Mo in the EMP spectra, a manual fitting was done to discriminate the elements. Although primary Tl minerals were not found, some samples contain the secondary Tl mineral avicennite. Due to its paucity and fine-grained state, this mineral was not detected in the P-XRD data. With precession electron diffraction, we positively identified avicennite by *ab initio* solution of its structure with a cubic cell, space group *Ia-3*, and a cell parameter of $a = 10.5803 \text{ \AA}$, $Z = 16$, in agreement with previous data for Tl₂O₃ (Otto, 1993).

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Minerals in the environment – from geo- to biosphere

ENV-T05

Rare earth element patterns – process indicators in the biogeosphere

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Due to high mobile concentrations, acidic areas such as former mining sites are suitable environments to study rare earth elements (REE, La-Lu) in solids, water and biota (SWB). Normalization to a respective standard results in REE patterns that allow for approaching processes within these complex systems. To study REE in the SWB systems, the remediated basement area of a former U leaching heap near Ronneburg/Germany has been investigated in a case study for 10 years. The groundwater REE pattern at this site features an enrichment of middle REE (MREE), which recently has been discussed to be the result of preferential release from pyrite and complexation with a metastable S-species [1]. Depending on the hydrochemical conditions, formation and dissolution of secondary phases can alter the REE pattern in solution. At the study site, heavy REE (HREE) enriched Al-phases - formed in a channel collecting metal-rich seepage water - were analyzed. Further, the interaction of acidic groundwater and Mn-oxides to which Ce is associated in higher extent is considered to cause a positive Ce-anomaly observed in the groundwater [2]. As indicated, formation and transformation of Fe-phases have a comparatively low impact on the REE pattern in solution.

Site-specific MREE enrichment or the Ce-anomaly can be tracked into biomass. In pot experiments, the bioavailable REE pattern from the mining-impacted soil is maintained in aerial plant biomass of three different grasses and sunflower whereas specifically light REE and/or HREE are translocated into aerial biomass. REE patterns further indicate that the impact of grasses on the rhizosphere is similar to each other, but different from sunflower. Fungi like *Lactarius pubescens* can mobilize REE associated to soil fractions inaccessible for plants, and are able to accumulate them preferentially in the pileipellis and gills of their fruiting bodies. This indicates different mechanisms in different taxa, which needs to be taken into account when considering ecotoxicological potentials of metals. REE can serve to understand such differential mechanisms in different kingdoms like plants and fungi, or different plant taxa like monocotyl and dicotyl plants families.

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ENV-T06

Mineralogy and microbial diversity in As-rich waste dumps

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Weathered sulphides are a rich source of secondary minerals of which ferric arsenates occur abundantly {Felix: rare minerals do not occur abundantly. That is a paradox}. The geochemistry and chemical stability of the arsenates are the subject of many research fields, due to the severe impact of arsenic on the environment. The microbial impact on such habitats is of great interest as well. Here, we study biogeochemical changes upon microbial impact on arsenate minerals from the Medieval waste dumps in the Kaňk deposit, Kutná Hora (Czech Republic), and two historical mines from Rotgülden-Salzbürger Land (Austria) and Chyžné (Slovakia).

The minerals occur as olive-green, yellow or brown nodules or crust precipitations. Optical microscopy shows anhedral, fine-grained, nanocrystalline or amorphous phases trapped in the interstices of subhedral quartz and feldspars gangue minerals, depicting a strongly altered environment. In X-ray diffraction, scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), with sulphates; gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and hydroniumjarosite [$(\text{H}_3\text{O})\text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$], are common in all three localities. The ferric arsenates comprise zýkaite [$\text{Fe}_4(\text{AsO}_4)_3(\text{SO}_4)(\text{OH}) \cdot 15\text{H}_2\text{O}$], bukovskýite [$\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 9\text{H}_2\text{O}$] and kaňkite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$). The scanning electron microscope images show the arsenate morphology as prismatic, acicular or botryoidal crystals in the fine-grained clay-rich matrices. The arsenic is highly mobile, and scatters widely in other mineral phases, and is enriched in the gel phases. The amorphous gels predict the paragenesis of the Fe-rich secondary minerals, through element partitioning in the inhomogeneous mass.

The microbial diversity was assessed by cultivation to study the microbial community functions and ecological relevance, and to obtain strains for study of physiological features. Generally, the arsenic-rich secondary mineral assemblages had low microbial prevalence ($\text{cfu} < 2 \cdot 10^5$). A higher microbial diversity was obtained from complex media (Standard 1 agar) as compared to minimal media (modified Minimal agar media), with majority of the pure strains being aerobic or facultative anaerobic. Many strains were able to excrete siderophores, while tolerating 5 mM to 1000 mM arsenate. Only a few nitrate reducers were found. The 16S rDNA sequences were dominated by actinobacterial (*Bacillus* sp. and *Microbacterium* sp.) and proteobacterial (*Acidovorax* sp. and *Achromobacter* sp.) strains.

Minerals in the environment – from geo- to biosphere

ENV-T07

Former U mining provides an excellent study site for supergene Mn mineralization under acidic conditions

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Extensive uranium mining in the former German Democratic Republic (GDR) in eastern Thuringia and Saxony took place during the period of 1946-1990. During mining activities pelitic sediments rich in organic carbon and uranium were processed and exposed to oxygen. Subsequent pyrite oxidation and acidic leaching lead to partial contamination of the area with heavy metals and acid mine drainage (AMD) even despite of remediation efforts. One of those areas is the former heap Gessen (Ronneburg, Germany) where the residual contamination can be found 10 m under the base of the former heap containing partly permeable drainage channels. In such a system a rapid but locally restricted mineralization of Mn and Fe oxides takes place under acidic conditions despite remediation efforts. The secondary minerals occur as colored layers close to the shallow aquifer in glacial sediments and could be identified as birnessite and todorokite as Mn phases and goethite as the Fe phase. As a consequence of geologically fast formation the supergene mineralization provides a cost efficient contribution to remediation (natural attenuation) strategies of substrates residually contaminated with heavy metals (e.g. Cd, Co, Ni, Zn).

For examination of the fast formation of the supergene mineralization under acidic conditions a special designed lysimeter approach was developed since Mn oxides are not known to be thermodynamically stable under these conditions. The predominant phases observed in the field: Mg phase (evaporative salts), Fe phase (goethite), Mn phase (Mn-oxides/ hydroxides) and Al phase could be formed in the lysimeter experiment due to capillary rise of contaminated groundwater. Additionally, a microbe mineral interaction for the Mn phase is hereby likely since Mn-oxides occur in the lysimeter next to organic material and microbes and as physicochemical conditions do not favor the formation of solid Mn phases. Both, reactive interfaces between groundwater and sediment and also microbes are believed to retrieve higher redox potentials leading to thermodynamically stable Mn oxides even under acidic conditions.

ENV-T08

Extracellular Biomineralization processes in carbonate benthic foraminifera and cyanobacteria

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Since the 1960s, benthic foraminifera have been shown to be sensitive to heavy metals pollution. According to the fairly large body of literature today available, these unicellular organism producing Ca carbonate shells are known to respond to heavy metals pollution by a modification of the assemblages, shell deformity, and bioerosional processes (1 and references therein, 2). It is commonly accepted that low Mg foraminifera are extracellular biologically controlled mineralization, while high Mg foraminifera are intracellular biologically controlled mineralization (3). Actually, Science and Technology allow us to unravel mineralogical speciation of trace elements in foraminifera shells and molecular processes genetically encoded that rule mineralogical speciation. This work is aimed to investigate by XAS analysis the Zn speciation in low Mg and high Mg benthic foraminifera shells sampled in heavy metals polluted areas from Sardinia (Italy).

Analysis of Zn edge XAS spectra indicates that Zn coordinative environment is different in low Mg (*Elphidium*) and high Mg (*Quinqueloculina*). In *Elphidium* specimens, Zn forms an independent phase, hydrozincite $[\text{Zn}_5(\text{CO}_3)_2\text{OH}_6]$. In high Mg (*Quinqueloculina*) samples, however, Zn is either substituting Ca ions, or is adsorbed onto calcite nanocrystals surfaces. Low Mg and high Mg foraminifera are extracellular and intracellular biomineralization, respectively. This implies significative differences in the physiology and molecular functioning of ionic pumps that are genetically encoded. The speciation and effective bioavailability of Zn in the investigated shells, thus, depends on the biomineralization mechanism. The high Mg *Quinqueloculina* seems to have not selective molecular tools for Zn transport within the cell. However, the low-Mg *Elphidium* seems to have a natural defense against Zn pollution, that consists in a molecular capability to precipitate Zn as an independent phase located within the carbonate shell. This capability is common to other unicellular organisms, cyanobacteria *Scytonema* sp., that survive in Zn extreme polluted waters by precipitating hydrozincite extracellular biomineralization.

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Minerals in the environment – from geo- to biosphere

ENV-T09

Mineralogical changes of asbestos fibers in human lungs

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Asbestos has been banned in many countries because of its carcinogenic potential. Despite this, many states continue to mine, export and process mineral fibers. In this study, we address the mineralogical changes that result from the interaction of asbestos with human lung tissue by comparing the mineral fibers in the original fiber cement roof panels (Eternit) with those in a diseased ex-eternit worker.

The cement roof panel was characterized by powder X-ray diffraction (PXRD), scanning (SEM) and transmission electron microscopy (TEM). PXRD data reveal the typical components of Portland cement (mainly alite, belite, celite and ettringite). Both SEM and TEM observations show an intimate intergrowth between fibers and the cement components. The matrix consists of amorphous and crystalline components. Chrysotile fibers are well preserved, exhibiting the typical hollow-cone morphology. Despite the industrial processing Energy dispersive X-ray microanalysis (EDX) of isolated fibers suggests an unmodified chemistry compared to the raw material.

The second sample was removed from the lung of a deceased Eternit-worker. Chrysotile were characterized using TEM after removal of the organic component. The fibers are partially amorphized and show an increased sensitivity to the electron beam. Organic residues has been hardly identified in contact with the fibers and any of them, have been found incorporated into organic clusters. In contrast, amphibole fibers are still well crystalline and do not show any significant changes.

Further investigations will concentrate on the characterization of mineral fibers without removing the organic matrix. For this purpose the sample will be embedded into epoxy and cut by ultramicrotomy, allowing to directly study the mineralogical changes in the organic environment.

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ENV-T10

Kinetics of olivine dissolution in the presence of *Synechococcus* sp. cyanobacteria biomass in partially closed batch reactors

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This study quantified the effects of active and dead *Synechococcus* sp. cyanobacteria on olivine dissolution rates. Experiments were performed for a maximum time of 450 hrs. For the first 100 hrs in presence of metabolizing bacteria an alkaline pH (9.5 - 10.5) were determined for 0.001 and 0.01 M Na⁺. A near neutral pH of 8.2 was recorded for 0.1 M Na⁺. This value correlates with that of dead cyanobacteria, suggesting a decrease in metabolic activity due to salt-stress. At 100 hrs, active cyanobacteria bio-reactors showed a decrease in pH from 10 to 8.2, which remained constant until the end of the experiments. A control growth experiment in the absence of olivine powder showed a sustained alkaline pH ranging between 9.5 to 10.5 for at least 330 hrs. This suggests a toxic effect of olivine on cyanobacteria metabolic activity. Total alkalinity in the presence of cyanobacteria biomass and natural olivine ranged from 0.6 to 1.2 mM compared to a maximum of 0.6 mM under inorganic conditions. This implies a greater buffering capacity of the cyanobacteria surface which is able to increase the alkalinity. Mg concentrations with cyanobacteria at 0.001 and 0.01 M Na⁺ were lower than under inorganic conditions, suggesting the interaction of biomass with dissolved Mg or the formation of biofilms on olivine. The alkaline pH of 8.2 ± 0.1 and 8.2 ± 0.4 detected in reactors containing cyanobacteria may indicate the enhancement of the hydrolysis mechanism of olivine dissolution contributing to a decrease in Mg. Active cyanobacteria shifted the pH to values of 9.5 and 10.5 during the first 100 hrs. Inoculation of dead cyanobacteria bio-reactors with active biomass at 330 hrs recorded a pH increase to 10.3 and 10.5 for 0.001 and 0.01 M Na⁺. With active bacteria the R_{OL} values ranged from -11.4 to -11.7 and were in good agreement with those resulting from the hydrolysis mechanism of olivine dissolution at alkaline conditions. At pH values of 8.2 ± 0.1 and 8.2 ± 0.4 in reactors with active and dead cyanobacteria, R_{OL} were in the order of -10.9 to -11.4. These values suggested a lower dissolution rate than that generated through surface protonation mechanisms for inorganic conditions. Furthermore, this may imply a shift in olivine dissolution mechanisms, from mineral surface protonation to hydrolysis, in the presence of cyanobacteria biomass.

ENV-T11

Akaganéite and schwertmannite – spectral properties and geochemical implications of their presence on Mars

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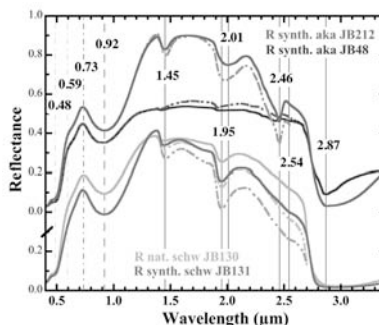
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The ferric oxyhydroxide minerals akaganéite and schwertmannite are associated with acidic environments and iron alteration on Earth and may be present on Mars as well. These minerals have a tunnel structure and are crystallographically related. Their extended visible region reflectance spectra include a broad Fe³⁺ electronic transition centered near 0.92 μm , a reflectance maximum near 0.73 μm and a shoulder near 0.59 μm . The near-infrared (NIR) reflectance spectra of these minerals are dominated by broad overtones and combinations of the H₂O vibration features near 1.44-1.48 and 1.98-2.07 μm (~ 6750 - 6950 and 4830 - 5210 cm^{-1}) in akaganéite spectra and near 1.44-1.48 and 1.95-2.00 μm (~ 6750 - 6950 and 5005 - 5190 cm^{-1}) in schwertmannite spectra. Additional bands due to OH vibrational overtones and combination bands occur near 1.42 μm (~ 7040 cm^{-1}) and 2.46 μm (4070 cm^{-1}) in akaganéite spectra. A strong and broad band is observed near 2.8-3.1 μm (~ 3300 - 3600 cm^{-1}) in reflectance and transmittance spectra of akaganéite and schwertmannite due to overlapping OH and H₂O stretching vibrations. H₂O bending vibrations occur near 1620 cm^{-1} (~ 6.17 μm) in akaganéite spectra and near 1630 cm^{-1} (~ 6.13 μm) in schwertmannite spectra with additional bands at lower frequencies due to constrained H₂O molecules. OH bending vibrations occur near 650 and 850 cm^{-1} (~ 15.4 and 11.8 μm) in akaganéite spectra and near 700 cm^{-1} (~ 14.3 μm) in schwertmannite spectra. Sulfate vibrations are observed for schwertmannite as a ν_3 triplet at 1118, 1057 and 1038 cm^{-1} (~ 8.9 , 9.5 , and 9.6 μm), ν_1 at 982 cm^{-1} (~ 10.2 μm), ν_4 near 690 cm^{-1} (~ 14.5 μm) and ν_2 at 608 cm^{-1} (~ 16.5 μm). Fe-O bonds occur near 410-470 cm^{-1} (μm) for akaganéite and schwertmannite. Both minerals readily adsorb H₂O molecules from the environment and incorporate them into the tunnels. If akaganéite and schwertmannite were present on the surface of Mars they could enable transport of H₂O from the near-surface to the atmosphere as the partial pressure of H₂O varies diurnally.

Figure 1 VNIR spectra of akaganéite and schwertmannite under ambient (dashed) and dehydrated (solid) conditions.



ENV-T12

Air pollution on the eve of Chinese Spring Festive 2008 in Beijing

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More than thousand tons of fireworks and firecrackers were launched and set off on the eve of Chinese Spring Festive 2008 in mega city Beijing. Beyond the custom driving away “ghost”, from reunion dinner to over midnight, the amount of particulate matter ($<10\text{ }\mu\text{m}$) in air reached a level of $207\mu\text{g}/\text{m}^3$ and the “smell” of gunpowder strongly impacted on human beings and merged into their respiratory tracts and lungs. The “taste” of air on the eve was analyzed by means of X-ray diffraction, high-energy polarized energy-dispersive X-ray fluorescence spectrometry and scanning electron microscope. Phase analysis for particulate matter ($<10\text{ }\mu\text{m}$) reveals that potassium chloride, potassium sulfate, ammonium chloride, sulfate hydrate and quartz were the main phases instead of carbonates, silicates, clays, sulfates as well as ammonium chloride in the normal case in winter. By comparing the reactants of gunpowder and firework-powder with their products, 10 Reactions are proposed to describe the comprehensive explosive processes of firecracker and firework in the atmosphere on the eve of Spring Festive. Chemical composition analysis indicates that the concentrations of sodium, magnesium, aluminum, potassium, sulphur and chloride in the eve air were 4.6, 8.8, 7.5, 8.5, 3.3 and 5.3 times of the normal case in winter, respectively. This kind of air “taste” easily causes cough and breathing trouble and even diseases in respiratory tracts and lungs.

Minerals in the environment – from geo- to biosphere

ENV-P01

Arsenical acid mine drainage with colossal arsenic concentration from Jáchymov in Czech Republic – mineralogy, geochemistry, microbiology

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Extreme arsenical acid mine drainage (a-AMD) developed by weathering of native arsenic in a sulfide-poor environment (with sparse proustite, Ag_3AsS_3 , and rare pyrite, FeS_2 , argentopyrite, AgFe_2S_3 , and arsenopyrite, FeAsS) on the 10th level of the Svornost mine in Jáchymov (Czech Republic). The a-AMD is characterized by very high As concentration (80,000-130,000 mg/L) in the liquid phase and pH close to 0. Therefore, a-AMD is the ultimate end-member of arsenical pollution and may be locally encountered at sites with similar primary mineralogy. The secondary mineral that identifies such environments is kaatialaite $[\text{Fe}^{3+}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}]$; in the presence of U, rare and unusual sulfates and arsenates of U^{4+} běhounekite $[\text{U}^{4+}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$ (Plášil *et al.*, 2011) and arsenates štěpíte $[\text{U}^{4+}(\text{AsO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ (Plášil *et al.*, 2013a) and vysokýite $[\text{U}^{4+}[\text{AsO}_2(\text{OH})_2]_4 \cdot 4\text{H}_2\text{O}]$ (Plášil *et al.*, 2013b) are formed. Another rare phase able to store acidity is a uranyl arsenate $[(\text{H}_3\text{O})^+_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}]$. Many of these minerals are able to store acidity (i.e., H^+ ions) in their crystal structures. We were able to isolate microorganisms on oligotrophic media with pH ~1.5 supplemented with up to 30 mM As(III). Colonies with different morphologies were observed. These microorganisms were adapted to highly oligotrophic conditions which disabled them for long-term under laboratory maintenance. The extremely low cell densities and low microbial biomass did not allow gaining sufficient amounts of DNA for downstream PCR amplification and clone library construction. The combination of extremely acidic conditions, high arsenic concentrations, high Rn concentration in the air, lack of light, and low amount of available organic nutrients make this environment unfavorable for intensive microbial colonization but our first results show that certain microorganisms are capable to adapt even to these harsh conditions.

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ENV-P02

Elemental composition of detrital magnetite from the upper Yangtze River sediments – implication for the provenance discrimination

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Magnetite as one of the typomorphic minerals, its crystal textures and chemical finger prints carry unique significance in the provenance discrimination of sediment. In this study, we applied the petrographic and electron probe microanalysis of 804 detrital magnetite grains to distinguish the sediment provenance between the mainstream and major tributaries of the upper Yangtze River drainage basin. Most of the detrital magnetite grains in the upper Yangtze River are homogeneous, except for a few of grains are derived from the mafic plutonic/volcanic and felsic volcanic parent rocks. Chemical analysis shows that elemental composition of the magnetite grains exhibits pronounced variations in the different tributaries and reaches of the mainstream. Elemental composition of the magnetite grains in the mainstreams reflects the contributions of major tributaries sediment. Based on chemical fingerprint, we suggest that the different elemental compositions of the magnetite grains are controlled by the various parent-rock types, the sediment contributions closely related to the tectonics, climate and erosion of parent rocks within the different drainage basins. Detrital magnetite grains of the upper Jinshajiang are primarily derived from sources composed of felsic plutonic and intermediate volcanic rocks, cropping out in the SE Tibetan Plateau. The widely distributed Emeishan basalts and Panxi layered ultrabasic-basic rocks are the major contributors to the sands of the lower Jinshajiang sediments because of the significant increase of the magnetite grains characterized by high concentrations of Ti, Mg, Cr, Al and Mn. The multi-sources and larger catchment containing all kinds of parent rocks collectively govern the chemical composition of the magnetite grains and sediment sources in the Chuanjiang basin, which result in the mixing of material and homogenization of chemical characteristics of magnetite grains. The derivations of magnetite grains of tributaries are directly depended upon various parent rocks distributed in their basins. In general, the detrital magnetite grains achieved better utility to the provenance discrimination of sediments in the upper Yangtze River drainage basins.

Minerals in the environment – from geo- to biosphere

ENV-P03

Clay minerals in Zhoulao core sediments since late Cenozoic, Jiangnan Plain, Central China: implication for the time of modern Yangtze River's formation

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In this study we applied clay mineralogy to trace the sediment provenance in Jiangnan Plain, the middle reach of the Yangtze River, and tried to provide useful information on the evolvement of the Yangtze River. We tested the relative content of clay minerals in the sediments from Zhoulao core, the depocenter of the Jiangnan plain, discussed the characteristics and provenance of clay minerals, and compared the climatic characteristics reflected by clay minerals in Zhoulao core sediments with $\delta^{18}\text{O}$ in ODP Site 1146 and 677. The results showed that the clay mineral compositions of Zhoulao core sediments have four kinds: illite, smectite, chlorite and kaolinite. The variation of the relative content of clay minerals showed the core was divided into two phases: phase I (145 m~300m) and phase II (4 m~145m). In phase I: The relative content of illite was comparatively low and the relative content of smectite was comparatively high; In phase II: The relative content of illite had increasing trend gradually and the relative content of smectite had decreasing trend gradually. Throughout the whole core, the relative content of kaolinite and chlorite didn't show obvious regular pattern. Climatic change was the main influencing factor on the characteristics of clay minerals in phase I of Zhoulao core; the change of the sedimentary source was the main factor in phase II. The time of provenance change was about 1.63 Ma B.P., that was also the time of the modern Yangtze River's formation.

ENV-P04

Microbial impact on calcite precipitation

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The carbon cycle is an important natural process which involves the exchange of carbon between different reservoirs such as atmosphere and biosphere. The metabolic activity of organisms and the cycle of organic carbon affect the flux of atmospheric CO₂ in form of carbonates. The precipitation of carbonates are influenced by changes of the milieu. These mechanisms are both controlled by geogenic processes and bacterial activity.

In this study, bacteria isolated from limestone were analyzed for their ability to form carbonates. Therefore, samples were taken in the Thuringian Basin, which is surrounded by layers of Muschelkalk. The bacteria were isolated from groundwater, rock samples, as well as soil formed on Middle and the Lower Muschelkalk. The bacterial strains were cultivated on calcium containing media to study their ability to form carbonates. Most bacterial strains were able to form crystals through calcification. By applying SEM, surface structures as well as the microbial impact on the crystals were observed. Crystal morphologies varied broadly, and microbial cells were visualized on the crystals. The present minerals were identified to be carbonates using EDX and XRD. Additionally, the biomineralization was dependent on water content, calcium salts supplied and temperature. Thus, we can provide evidence for environmental and microbial impact on the naturally occurring processes effecting the formation of carbonate mineral phases.

ENV-P05

Quantifying the kinetics of olivine dissolution in partially closed and closed batch reactor systems

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This study quantified the rates of olivine dissolution under constant air injection, in partially closed batch reactors and in control closed batch reactors (in the absence of air flow), in the presence of 4 grams olivine, and 0, 0.001 and 0.01 M NaNO₃. Experiments were performed for 40440 and 36048 minutes in partially closed and closed reactors respectively. Under constant air injection, solution pH ranged from 6.8 and 7.3 for all conditions at the start of the experiments, to 7.5 and 7.8 at 40440 minutes. In the absence of air flow, an alkaline pH of 9.6 to 9.3 was observed for 36048 minutes. This pH difference is attributed to the constant buffering the solution through the formation of dissolved carbonate species (H₂CO₃/HCO₃⁻). The alkaline pH, measured in the presence of olivine, implied a mechanism of pH control caused the presence of Si(OH)₄ species from the mineral surface. This effect was suggested by a drop to near neutral pH of the same aliquots, upon filtration of the olivine through a N₂ degassed filter. A decrease in total alkalinity was measured for experiments under constant air injection, as a function of increasing NaNO₃, suggesting a mechanism of Na⁺/CO₃²⁻ interaction involved in the enhancement of olivine dissolution rates through proton/Mg exchange. In the absence of air flow, the total alkalinity reached a maximum of 0.25 mM, compared to 0.9 mM with air flow at 0.01 M NaNO₃. Magnesium concentration increased in the presence of NaNO₃ and permanently dissolving CO₂ in partially closed batch reactors. This strongly suggests a key role of Na⁺ (coupled to CO₂ dissolution) for enhancing olivine dissolution. Mg/Si ratios for all conditions showed incongruent olivine dissolution, suggesting a combination of two dissolution mechanisms at alkaline and near neutral pH values, in closed and partially closed batch reactors. The rate of olivine dissolution (R_{OL}) was calculated as a function of mineral surface area and forsterite equilibrium solution parameters. In the presence of constant air injection, highest log R_{OL} values range from -11 to -10.7 at the acidic to near neutral conditions (pH = 6.8 to 7.2). Slower dissolution rates, with log R_{OL} values of -11.5 to -11.4 were determined for experiments in the absence of air flow at alkaline pH values (9.6 to 9.8). Constant air injection (i.e. constant dissolution of CO₂ at atmospheric pressure) in the presence of Na⁺ has proven effective for enhancing olivine dissolution.

ENV-P06

Geosphere-Biosphere processes between mine waste, water and *Phragmites australis* at San Giorgio river (SW Sardinia, Italy)

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Activity at the Iglesias mining district (Sardinia SW, Italy) ceased about twenty years ago, after centuries of intense exploitation of base metal sulphides, calamine and barite ores. On June 2012, a joint campaign between the University of Cagliari and the United States Geological Survey (USGS) was carried out to apply hydrologic tracer techniques (Kimball 2002; Bencala et al, 2011) to San Giorgio river (close to Iglesias town). This method allows one to measure metal load for a number of river sections that are synoptically sampled. Then the water discharge evolution and the synoptical measure of metal load can be seen along the whole river. Tracer work was carried out sampling 19 sections along the river plus 9 tributaries. Based on the water chemistry, the Rio San Giorgio was divided into 3 groups, which differ for the concentration of SO_4^{2-} , which is inversely correlated with HCO_3^- . The water discharge increased from 17.4 L/s to 36.7 L/s along the river. The load of Zn shows an abrupt peak of 6 kg/day after receiving tributaries from mine wastes. Then, it decreases. In this work, we proof that the intense riverbed vegetation increases the hyporheic exchange flow by 2-3 times with respect to non vegetated systems. Besides this hydrologic effect, the processes of interaction between riverbed and *Phragmites australis* (geo-biosphere interaction) are likely to play a substantial role in the abatement of heavy metals load. Bulk quantification and investigation of microscopic processes of heavy metal adsorption through surfaces of *Phragmites australis* roots are ongoing. Our preliminary data from Scanning Transmission X-rays microscopy and X-rays Absorption Spectroscopy indicate that Zn seems to occur associated with Si and Al in an external rim at the root epidermis.

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ENV-P07

Geogenic arsenic enrichment in Upper Permian and Lower Triassic sedimentary rocks of Thuringia, Germany

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The average concentration of the trace element arsenic in the Phanerozoic rocks in Germany ranges from 5 to 12 $\mu\text{g/g}$ for different lithologies. However, arsenic concentrations can be several times elevated in certain sedimentary lithologies such as pelites and even more so in coal beds and their seams.

In the present study, we investigated all sequences of the Lower Triassic and Upper Permian formations with their different lithologies (sandstones, mudstones, evaporites, volcanic ash layers, coal beds) in order to identify relevant sedimentary carriers of arsenic. Motivation for this study is the fact that the aquifer systems of the Lower Triassic formation are locally important sources of drinking water and affected by elevated arsenic concentrations. Data from the water wells in north-western Thuringia show arsenic concentrations above the WHO limit value for drinking water (10 $\mu\text{g/L}$). The regional distribution as well as lack of secondary vein mineralizations or anthropogenic sources within this area point to a geogenic, strata bound source of arsenic.

Geochemical analyses on sedimentary rock samples from selected drill cores and outcrops in Thuringia show elevated arsenic contents of $>50 \mu\text{g/g}$, especially in the carbonaceous sediment sections as well as in the gray-green claystones. Mineral phases that incorporate arsenic in the Upper Permian coal beds seem to be sulfides, whereas arsenic seems to be bound to clay minerals in the Lower Triassic sedimentary rocks of lacustrine origin. Further aim of the study is to identify the processes and conditions under which arsenic is mobilized from the relevant mineral phases and transferred into the groundwater.

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ENV-P08

The fate of As⁵⁺ during the thermal transformation of As-bearing rhomboclase to (H₃O)Fe(SO₄)₂

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In arid regions, affected by acid mine drainage (AMD), the toxic element arsenic is often associated with iron sulfates like rhomboclase ((H₅O₂)Fe³⁺(SO₄)₂ × 2H₂O) [1]. Rhomboclase (Rhc) can further dehydrate to (H₃O)Fe³⁺(SO₄)₂ [2], a compound likely to be formed over time in arid regions with high annual temperatures. Since rhomboclase can incorporate significant amounts of As (0.87 wt.%) [1], this study is dedicated to the structural incorporation of As⁵⁺ into Rhc and its dehydration product (H₃O)Fe³⁺(SO₄)₂.

Rhc was synthesized by dissolving 1 g of Fe³⁺₂(SO₄)₃ × H₂O in 2 mL of As₂O₅ solutions with varying As-concentrations (molar As/Fe ratios of 0, 0.25, 0.5, 0.75, and 1.0), adding 2 mL concentrated sulfuric acid, and drying the solutions in crystallizing dishes at 303 K for 72 h. After crystallization, Rhc was separated from the remaining solution, dried and sealed tightly. The association of As with Rhc was checked by scanning electron microscopy with a Zeiss ULTRA Plus in energy dispersive mode. Purity and thermal decomposition of Rhc was determined with a Bruker D8 powder X-ray diffractometer (XRD) using Cu-Kα radiation. The samples were placed in an Anton Parr heating chamber and analyzed *in situ* during thermal transformation from 25 to 100 °C.

Rhc, synthesized in the presence of As, incorporated 0, 0.6, 3.7, 6.8, and 7.4 wt.% As, with respect to the molar As⁵⁺/Fe³⁺ starting ratios of 0, 0.25, 0.5, 0.75, and 1.0. With increasing As-concentrations, the unit-cell parameter *b* increased from 18.299 Å to 18.319 Å, indicating the structural incorporation of As into Rhc. No indicators for other crystalline or amorphous phases could be determined by XRD. For all As-concentrations, Rhc dehydrated to (H₃O)Fe³⁺(SO₄)₂ at a temperature of >80 °C with no further intermediate phases. Subsequently, As concentrations in Rhc and (H₃O)Fe³⁺(SO₄)₂ will precisely be determined by inductively coupled plasma mass spectrometry (ICP-MS). As-oxidation state and modes of structural incorporation will be investigated by X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS).

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ENV-P09

Carbon and Oxygen isotope signature of hydrozincite biomineralization in Zn-Pb mine (South-West Sardinia, Italy)

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Weathering of unmined mineral deposits, alteration zones, and mined areas generally add heavy metals to waterways. In the near-neutral stream of southwestern Sardinia (Italy), mine-drainage chemistry produces a large amount of Zn in the Rio Naracauli creek. The mineral hydrozincite $[\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]$ precipitates from Rio Naracauli creek according to a biologically mediated process decreasing dramatically the concentrations of Zn and other metals. Rio Naracauli hydrozincite, a monoclinic carbonate of Zn with T-O-T structure, is made of nanocrystals producing mesocrystals of platelet shape encrusting cyanobacteria sheaths forming globules of various diameters. The precipitation of bio-hydrozincite is controlled by photosynthetic microbial community specifically filamentous cyanobacterium (*Scytonema* sp.) and microalgae (*Chlorella* sp.). This bio-mineralization is extracellular controlled and is mainly formed from late spring to early summer.

Although Zn comes from the solution (Wanty et al. 2013), carbonate ions can be produced either by bacteria and algae photosynthesis or/and directly from the solution. Here, we report preliminary results of isotopic carbon and oxygen compositions to discriminate the possible main carbon source used to build this bio-mineral. The analysis of several specimens collected in the Rio Naracauli creek indicates that, irrespective of water temperature, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values decrease from -2.94 to -5.0 and -3.44 to -4.68 respectively, during the April - August seasonal sampling periods. On the same sampling period we do not find a clear linear relation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the downstream distance of 1 km. The different seasonal isotopic signature however is maybe related to the recognized changing in size and morphology of hydrozincite globules. *In vivo* experiments are presently under way to identify how water and biomass contribute to the hydrozincite $\delta^{13}\text{C}$ signature.

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ENV-P10

X-ray powder diffraction versus sequential chemical extraction – a new combined method for exacting mineralogical speciation of sulphidic mining wastes

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Determination of the exact mineralogical composition of an unknown rock or a mineral sample has always been a big challenge for scientists. The X-ray powder diffraction (XRPD) is an efficient method for this purpose. In case of altered and not well-crystallized rocks, the efficiency of this method sometimes dramatically decreases and the detection limit may rise by a few percent, which is not acceptable. This is a typical problem for oxidized or just oxidizing sulphidic samples, where acid rock drainage (ARD) takes place. The produced secondary minerals are poorly crystallized or even amorphous.

Sequential chemical extraction (SCE) was originally developed to determine the heavy metal concentration in soils, but quickly became a frequently used method in other fields of geosciences and an exact method for chemical speciation, characterization of heavy and base metal mobility from minerals, rocks, soil material or mining wastes.

This paper introduces how the X-ray powder diffraction and the sequential chemical extraction can complement each other. Both methods have their own limitations, but using them as a combined method, scientists can increase the efficiency of determination of the mineralogical composition. A further aim of this present study is to show the applicability of the combined method for altered sulphidic mine waste materials.

Modern techniques for mineralogical research

MOD-T01

X-ray diffraction in the lab – benefits and perspectives using large 2-dimensional detectors and X-ray optics

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The progress in development of 2-dimensional X-ray detectors as well as X-ray optics during the last decade nowadays makes these components also affordable for common X-ray labs, thus opening completely new opportunities for the users (1). The possibility to gain fast insight into material properties, as well as more demonstrative ways of teaching X-ray diffraction to students are among the advantages.

The combination of modern focussing X-ray optics even with standard sealed tube systems now gives the chance to generate spotsizes below 100µm with intensities which are by magnitudes higher compared to commonly used collimator based systems. Due to this unique advantage, fast locally resolved phase mappings even of uneven samples are possible within a few minutes without time consuming sample preparation (2).

Large 2-dimensional detectors allow to cover several 10° of 2Θ and ψ with one measurement. Combining these detectors with the above mentioned X-ray optics (μ -XRD²) enables for the first time direct and local insights into crystallinity, texture, and phase content of the analyzed samples. As an additional advantage of such a combination measurement times down to a few seconds have to be mentioned. Suddenly monitoring of fast temperature dependend processes during heating or cooling experiments becomes feasible, as no time consuming moving of the detector is impeding. By integration of a differential thermal analysis (DTA) system in such an X-ray diffraction set-up (μ -XRD²), a plurality of material properties can be measurd at one glance, such as structural changes and energy changes during the heating or cooling of the sample (3).

In teaching X-ray diffraction in a common X-ray lab, many factors influencing the shapes of X-ray diffraction patterns can no be visualized more easily. For example sample preparation effects which influence the crystallite size can as well be shown as influences of texture or differences between single crystal patterns compared to powder patterns...

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MOD-T02

Coupling a 5kN Bending Jig with a Microdiffractometer – an In Situ Study of Phase Transformations in Zirconia under Tensile Stress

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Yttria stabilized Zirconia ceramics exhibit a combination of excellent mechanical properties, which make them a promising material for tribological applications with high loads. Their high toughness of up to $15 \text{ MPa} \cdot \text{m}^{0.5}$ is achieved through a transformation toughening mechanism based on the tetragonal-to-monoclinic phase transformation in the stress field surrounding cracks. The increase in unit cell volume accompanied with this transformation results in the formation of compressive stresses around the crack tips and consequently increases the fracture toughness.

However, this phase transformation can also occur as an extended phenomenon at the surface during wear with mechanical and/or chemical interaction at low temperatures and thereby become a part of the degradation by tribological processes. Despite some studies on the subject, the role of external stresses is still poorly examined. Therefore a new experimental set-up has been devised, which enables in situ studies of phase transformation under stress by X-ray diffraction (XRD) and Raman spectroscopy. Together these methods are capable to monitor the processes at and below the surface.

In our presentation we will introduce a our test rig, which incorporates for the first time a bending module (Kammrath & Weiss GmbH) placed inside a Bruker D8 Discover μ -XRD²-diffractometer coupled with a μ -Raman spectrometer. The bending module provides loads up to 5 kN and allows in situ measurements on the tensile face of a zirconia bending bar. Bending can be conducted in both 3-point and 4-point geometry, enabling experiments with or without a stress gradient in the measured sample area. Focusing X-ray optics facilitate a high spatial resolution with high X-ray intensities. Owing to the large 2D-detector covering 40° 2Theta and Psi, direct insights in stress induced textural changes are possible and measurement times are as short as a few seconds. For the first time this gives the opportunity of direct insights into time dependent structural changes during loading or unloading. Additionally, Raman spectroscopy is conducted at the same sample position by a Raman spectrometer-head mounted inside the XRD machine.

Modern techniques for mineralogical research

MOD-T03

High-Speed PIXE – a new tool for Automated Mineralogy using a Color X-Ray Camera

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Methods of automated mineralogy form the analytical backbone of geometallurgy. Most of them exploit the combined imaging and analytical capabilities of optical and scanning electron microscopes. Typical results are „phase maps“ either derived from the distribution of major elements or determined directly. The effective application of such methods for strategic metals which are won as by-products from other metal ores or secondary raw materials is handicapped by the restricted possibilities to determine the spatial distribution of such trace elements like In, Ga, Ge or the rare earth elements (REE). The recently commissioned High-Speed PIXE (Particle Induced X-Ray Emission) setup at the Helmholtz-Institute Freiberg for Resource Technologies will overcome these limitations by using the advantages of PIXE over traditional electron beam based methods like the better peak-background ratio.

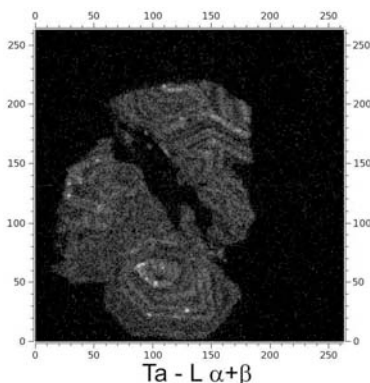
We use the SLcam[®] Colour X-ray Camera - a novel pnCCD pixel detector (264×264=69696 pixel) combined with a polycapillary X-ray optics (Scharf et al., 2011) as detector for element specific X-ray radiation. This design allows us the simultaneous determination of trace element distributions on a 12 × 12 mm² area with a lateral resolution better than 100 µm. First results of geometallurgical applications of this method are presented.

References

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Figure

Elemental distribution map of Ta (La+ Lblines) in cassiterite (Erzgebirge)



MOD-T04

Quantitative chemical analysis of carbon and oxygen in molten Fe-rich alloy by analytical transmission electron microscopy

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Carbon dissolved in metal is likely to strongly affect metal-silicate partitioning of siderophile elements, such as Co, Ni, V, Cr, Si, and O, between molten Fe-rich alloy and silicate melt in a laser-heated diamond anvil cell (LHDAC). The source of such carbon is the chemical reaction between the sample and the diamond anvils. In order to determine reliable metal-silicate partition coefficients, corrections must be made based on the concentration of carbon in the metal. Unfortunately carbon is extremely difficult to analyse quantitatively using transmission electron microscopy (TEM), due to various sources of hydrocarbon contamination during sample preparation and in the TEM. The analysis of oxygen contents is also important for evaluating the metal-silicate partitioning of this element.

Here we report a procedure to evaluate carbon and oxygen contents in focused ion beam (FIB) prepared TEM lamellae from LHDAC samples. The FIB lamellae were cleaned by a plasma cleaning system prior to TEM analysis. We calibrated ratios of partial cross-sections of carbon and oxygen against iron in electron energy-loss spectroscopy (EELS) analysis in a TEM operating at 200 kV under an oil-free vacuum system. The advantage is to enable the quantitative chemical analysis of carbon and oxygen dissolved in the molten Fe-rich alloy, combined with energy dispersive X-ray spectroscopy (EDXS) of the other heavier elements. Preliminary results indicate 3-7 at% carbon and 16-29 at% oxygen in Fe-rich alloys recovered from 43-100 GPa and 3700-5500 K as evaluated by EELS, together with metal-silicate partitioning by EDXS. We are planning to cross-check the obtained carbon contents with the other established analytical techniques (e.g., Nano-SIMS).

MOD-T05

Method development for the LEAP and TEM characterization of (Ba,Ra)SO₄ solid solutions on the atomic level

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The formation and stability of the (Ba,Ra)SO₄ solid solution has been considered in recent safety cases for the geological disposal of spent nuclear fuel. The uptake of Ra into barite was observed in experimental studies [1, 2]. Previously, we followed a close-to-equilibrium approach and carried out ToF-SIMS analysis of the solid indicating the mostly homogeneous uptake of Ra in amounts predicted by thermodynamics [3]. During the evolution of the experiments, kinetic effects, e.g. entrapment, were observed. After 2 - 3 years experiments reached thermodynamic equilibrium with a mostly homogeneous Ra distribution in the solid. Samples of the solids over the course of experiments [3] are available for analysis. However, for a detailed description of the Ra uptake and recrystallization process, nano-analytical methods need to be established as further spatial resolution is wanted.

The laser-assisted atom probe tomography (LEAP) is a powerful tool for chemical analysis on the atomic level. Previous atom probe models were restricted to electrically or thermally conductive samples. Now, many possibilities for the analysis of minerals are open. Here, we present a method development for characterization of barite by LEAP and TEM. With this method the barite particles before the start of the experiments [3] were analyzed. Later, this method will be applied to the characterization of the (Ba,Ra)SO₄ sampled during the course of the experiments.

The main focus of the analyses is set to the detection of inhomogeneities in the primary particles before the experiments that influence the evolution of Ra uptake with time. Investigated characteristics are porosity, crystal structure and chemical composition. First results of the LEAP analyses as well as the TEM characterizations of the barite particles before the experiments will be presented. They suggest an inhomogeneous, layered distribution of lighter elements, e.g. Na and H₂O, within the crystal volume. The LEAP results are supported by TEM characterization. The possible influence of these inhomogeneities on the uptake of Ra into barite will be discussed.

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MOD-T06

Phase Analysis by Optical Cathodoluminescence Microscopy (CLM) in refractory materials.

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The investigation of worn modern refractory materials is a complex task due to the diversity of phases and multicomponential materials with varying grain sizes up to the mm-range reacting with corrosive slags and melts. Optical cathodoluminescence microscopy (CLM) is a powerful method for fast sample characterization with distinct advantages over conventional optical microscopy. The strong luminescence color of many phases encountered in refractories makes CLM a perfect tool to resolve grain zoning or to identify reaction zones at the slag/refractory interface.

In our study we are dealing with the corrosion of partially (PSZ) or fully stabilized zirconia (FSZ) in blast furnace slags and other siliceous melts. Due to the dissolution of the stabilizing agent into the melt, a transformation from partially stabilized tetragonal or fully stabilized cubic zirconia into the monoclinic modification occurs. In addition to the analysis of zirconia materials after service time in the metallurgical industry some tests with Y-PSZ and Y-FSZ crucibles and various slags have been done to gain a better understanding of the processes taking place during operation conditions.

The phase transformation zone from cubic or tetragonal ZrO_2 to monoclinic ZrO_2 due to slag exposure can be analyzed using cathodoluminescence microscopy. Baddeleyite and its synthetic equivalent monoclinic zirconia are well known for their bright blue luminescence color whereas tetragonal and cubic ZrO_2 hardly show any luminescence. This obvious difference makes cathodoluminescence microscopy a powerful mapping tool to follow zirconia phase differentiation.

We present examples for CLM based analysis on refractory-melt interaction with focus on zirconia transformation. We demonstrate the power of combining CLM as a path finding method with subsequent phase (Raman spectroscopy, $\mu\text{-XRD}^2$) and chemical analyses (WDS).

MOD-T07

Mineral-Water interaction in Callovo-Oxfordian clay rock probed by broadband dielectric spectroscopy

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Safety solutions of management for all radioactive waste in order to protect the present and future generations from the waste risks is an essential need. The French National Radioactive Waste Management Agency (ANDRA) is in charge of long-term management of radioactive waste produced in France. ANDRA has been systematically studied the possibility of implementing an underground repository for high-level and long-lived waste in the underground laboratory in Bure/France (Meuse district, eastern Paris Basin). The geological formation under consideration consists of a 130 m thick clay rock layer (Callovo-Oxfordian - COx clay rock) located at a depth of 500 m.

The absolute water content is a key state parameter for monitoring and prediction of Thermal-Hydraulic-Mechanical-Chemical and Radiological processes in nuclear waste repositories since it drives radioactivity confinement. Broadband high frequency (HF) electromagnetic (EM) measurement techniques offer useful tools for quantitative estimation of the absolute amount and binding state of water as well as for probing of interfacial processes due to mineral-water interactions in porous media. Against this background, the dielectric relaxation behavior of a set of clay-rock samples were studied with broadband dielectric spectroscopy at frequencies from 1 MHz to 10 GHz in a water saturation range from 0.16 to nearly saturation. The experimental determined EM properties were decomposed in the underlying dielectric relaxation processed based on a generalized fractional relaxation model with three relaxation processes: (i) a high frequency water process with relaxation times τ between 6 and 11 ps and two interface processes which are related to interactions between the aqueous pore solution and mineral particles such as (ii) adsorbed/hydrated water relaxation superimposed by counter ion relaxation with τ between 7.6 ns and 20.8 ns as well as (iii) Maxwell-Wagner effects with $\tau > 100$ ns. Moreover, the EM properties were modeled based on a thermodynamic approach which allows the quantification of Gibbs-energy of free/interfacial water relaxation as well as a coupling to the electrical conductivity contribution in the aqueous pore solution. The results clearly indicate the potential of broadband HF-EM techniques for quantitative characterization of physico-chemical state parameters in underground repositories in clay formations.

MOD-P01

Roughness parameter distributions as tool to monitor topography changes at mineral surfaces

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Elementary processes like crystal growth, mineral dissolution and adsorption are of utmost importance for numerous geological and technical issues. An incomplete, but significant list of relevant fields may include the immobilization of pollutants by adsorption or coprecipitation, rock alteration (including soil formation and acid-mine drainage), carbon sequestration, corrosion and scale formation as well as diagenetic and metamorphic processes (e.g. [1]).

Surface area, surface topography and their evolution during reactions at the mineral-water interface are governed by the rates as well as the reaction mechanisms prevailing at reactive sites of the mineral surfaces. Thus, mineral surface area is far from being a constant although it is commonly used in this way (e.g. by BET measurements on starting material) to normalize dissolution rates.

Recent methodologies of measuring surface topography at mesoscopic length scales (e.g. confocal microscopy, interferometric methods) allow to link surface topography and, thus, surface roughness with reactivity and probably reaction mechanisms. Surface roughness parameters are statistical values and intrinsically depend for heterogeneous surfaces on the applied area and on the resolution of the imaging technique. By varying the measuring field on a given surface and a systematic evaluation of all parts of the surface a roughness parameter distribution is received.

This contribution demonstrates that roughness parameter distributions calculated from topography data of processed and reacted pyrrhotite surfaces (measured by confocal microscopy) are virtually insensitive to the chosen part of a reacted area while surface roughness parameters calculated for the entire surface are highly variable. Thus, roughness parameter distributions give truly robust results without any bias of choosing areas thought to be “representative” for a surface. This finding also permits to only take a limited number of topography measurements if the characteristic features of a surface are smaller than the field of view of the applied technique. It further allows to monitor the evolution of the surface topography (and thus reactivity) in a statistically robust way.

[1] Putnis & Ruiz-Agudo (eds.) (2013) *The Mineral-Water Interface*, Elements, Vol. 9(3).

MOD-P02

Quantification and verification of mineral phase content of iron: rich brown coal fly ash by Rietveld-method

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The iron - rich brown coal fly ash of the Lower Lusatia is characterized by high SiO_2 (36-44 %) and Fe_2O_3 contents (15-20 %). Contents of CaO (16-22 %) and Al_2O_3 (8-13 %) are moderate. To identify the individual mineral phases, X-ray diffractometry were used on material, obtained by selective solution experiments. Quartz, brownmillerite, magnesioferrite, hematite, anhydrite, periclase, melilite, diopside, merwinite, larnite, mullite, free lime, microcline and apatite were identified. These filter ashes have a high content of amorphous phase, which is characterized by a distinctive amorphous hump. The mineral phases of the fly ash were refined by Rietveld-method and the amounts of mineral contents were determined quantitatively. The amorphous content was determined by the internal standard method. To verify the quantified mineral content, the fly ashes were mixed with increasing amounts of the identified mineral phases. The mixed samples were measured in turn, refined with Rietveld-method and quantified. To verify the amorphous phase glass powder was intermixed with the fly ash (Fig.1). If possible the ascending peak shape areas of standalone peaks of single crystalline phases were used to proof the verification of these phases.

11 of the main phase contents were verified. Generally, the verified values are in accordance to the quantified amounts without intermixing. In cases of the high amorphous content and the high amount of quartz the verified content corresponds with minimal differences (0,1-0,2%) to the quantified content. Mineral phases with low quantified content (<10%) shows little differences (0,1-0,9%) to the verified content (Fig.2).

Modern techniques for mineralogical research

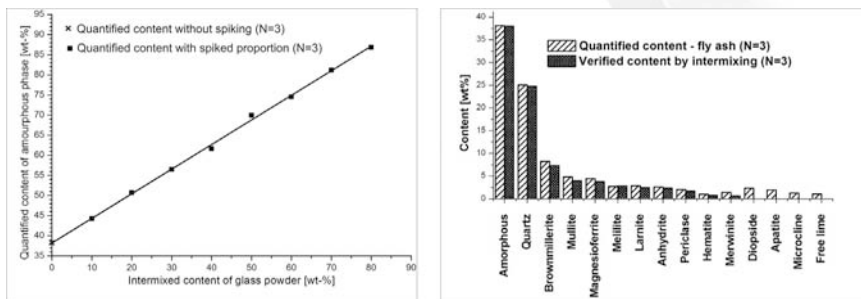


Fig.1: Regression line of quantified content of amorphous phase in BFA mixed with an increasing amount of glass powder.

Fig.2: Comparison of mineral phase content and verified amount of phase by mixing.

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Colin R. Ward, David French [2006]: Determination of glass content and estimation of glass composition in fly ash using quantitative X-ray diffractometry. Fuel 85 (2006) 2268-2277

Modern techniques for mineralogical research

MOD-P03

Challenges in the fully automated sample preparation of mineral raw materials and industrial process products for XRF and XRD analysis

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Fully automated sample preparation system of pellets for XRF and XRD analysis was investigated. Ten different sample materials (four iron ores and two iron pellets, iron sinter and slags) were considered. The tests were realized with the prototype of a new *Centaurus (Version 2)* by FLSmith. Investigations were performed to characterize the parameters necessary for the automated sample preparation of the different materials (grinding parameters, press force, press time, number of dispensed grinding additive, material input). Furthermore, the new equipment was tested on process stability and cross-contamination when switching the material.

After recipe parameters were defined for the different sample materials, a grinding parameter test was realized to determine the influence of grinding time and grinding speed on the XRF and XRD analysis results. Tests on reproducibility of sample preparation and cross-contamination were carried out on selected samples. To test the reproducibility of the sample preparation a series of ten analysis pellets was prepared for one of the iron ores, one of the iron sinters and one of the slags. A reproducible sample preparation was proven by the XRF and XRD measurements. The values for the determined oxides and minerals fluctuate around the averaged value inside the 3 sigma range (Figure 1A). For testing the cross-contamination five iron ore samples, five raw meal samples, five iron ore samples, five raw meal samples ... for a total of four rounds (in total 40 samples) were prepared. The cross-contamination is characterized by the carry-over of iron oxide (Fe_2O_3) to the raw meal. The investigations showed a remarkable carry-over of Fe_2O_3 to raw meal for the first two samples out of five (Figure 1B).

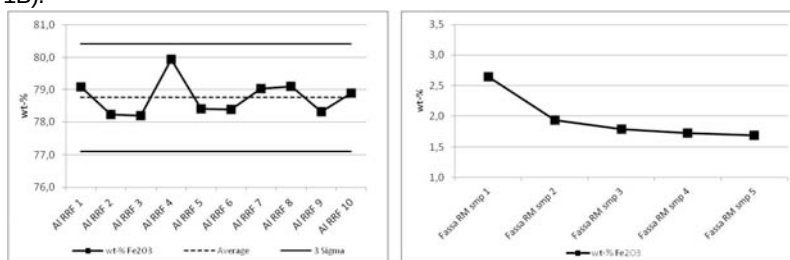


Figure 1: Selected XRF results for the test with iron ore. A: Reproducibility test. Fe_2O_3 content in the iron ore sample. Shown are the measured values and the calculated average and 3 sigma range. B: Carry-over of Fe_2O_3 from iron ore into raw meal.

MOD-P04

New perspectives for lower mantle reaction mechanism research using modern X-ray sources

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Chemical composition of the Earth's mantle phases have a major effect on their stabilities and consequently on their reactions. Especially concerning light elements and trace elements, compositions of phases in the lower mantle remain basically unknown because the phases are not accessible and cannot be studied directly. In order to better learn about reactions of mantle phases, related redistribution processes of elements and the resulting properties of the mantle, mantle phases have been studied by in-situ methods.

Within the past years, laser-heated diamond anvil cells have been combined with synchrotron radiation induced methods to study chemical reactions by in-situ x-ray fluorescence analysis and combined x-ray diffraction (XRD) (Petitgirard et al., 2012). Synchrotron radiation provides sufficiently small spot sizes, hard x-rays and a high sensitivity. Chemical and structural information were obtained at temperatures of up to 4200 K and pressures up to 130 GPa. First time-resolved measurements have been made with the objective to follow reaction mechanisms. For XRD, a time-resolution of msec could be achieved by single shot pulsed laser heating (Goncharov et al., 2011), while for in-situ XRF studies, the time-resolution is currently limited to the sec regime. It is either limited by detector speed or sensitivity or both.

An alternative method to study reactions of lower mantle phases are laser-driven shock and ramp compression experiments. The samples are generally pumped with an long-pulse optical laser and then probed with an x-ray source at a delayed period. Combined with x-ray free electron lasers as a probe beam, these experiments offer the unique possibility to study reactions at a rate of up to MHz due to the x-ray timing structure and the increased number of photons. The High Energy Density science instrument at the European XFEL (HED) will provide unique possibilities for research at extreme states of matter. The instrument is one of the six baseline instruments at the European XFEL and will start user operation in the second half 2017.

Modern techniques for mineralogical research

In this presentation, we will show results from in-situ experiments at conditions in the lower mantle at currently available sources and discuss the perspectives to study reaction mechanisms at such conditions at the upcoming HED instrument.

Gorcharov et al., 2011, Journal of Applied Physics, 111(112609):1-6.

Petitgirard et al., 2012, Review of Scientific Instruments, 8:013904-5.

MOD-P05

Low-temperature and high-temperature infrared properties of spinel and corundum and their application to stardust spectra

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In infrared spectra of the dust shells around pulsating red giant stars, emission bands at 13 μ m and 32 μ m wavelength are detected. These infrared bands probably originate from vibrations in refractory aluminum oxides such as *corundum* or *spinel*. Both corundum and spinel have been discovered in meteorites in form of presolar grains and CAIs (Calcium-Aluminum-rich inclusions). Since they are among the first minerals that condense in the outflows of evolved stars, these oxides may serve as “seeds” for the formation of other, more abundant stardust minerals such as silicates (e.g. forsterite and enstatite). Until very recently, the infrared spectra of minerals that were used for the comparison with astronomical data were based on *room-temperature measurements*. However, none of the template spectra reproduced the astronomical features at for the 13 and 32 μ m satisfactorily. Given that the temperature of a material directly influences the IR active modes of minerals, the position and shape of their small particle spectra will also change with the temperature. Thus, comparing astronomical spectra with only room temperature spectra doesn't make sense if we aim at more detailed description of the minerals in space.

We have measured the mid-infrared reflectance spectra of synthetic spinel and corundum in a temperature range of 10K to 928K. Subsequently, we fitted the data with a four-parameter, semi-quantum model in order to derive the refraction (n) and the absorption (k) indices of these materials. From both n and k, we have calculated *small particle spectra of spinel and corundum* - for different grain shapes - and compared these spectra with dust emission spectra of pulsating red giant stars, focussing on the above mentioned features at 13 and 32 μ m. Thereby, we were able to set stronger constraints on the possible temperatures and grain shapes of corundum and spinel grains in circumstellar shells, assuming that one of these minerals is indeed the “carrier” of the 13 μ m and 32 μ m emission bands.

MOD-P06

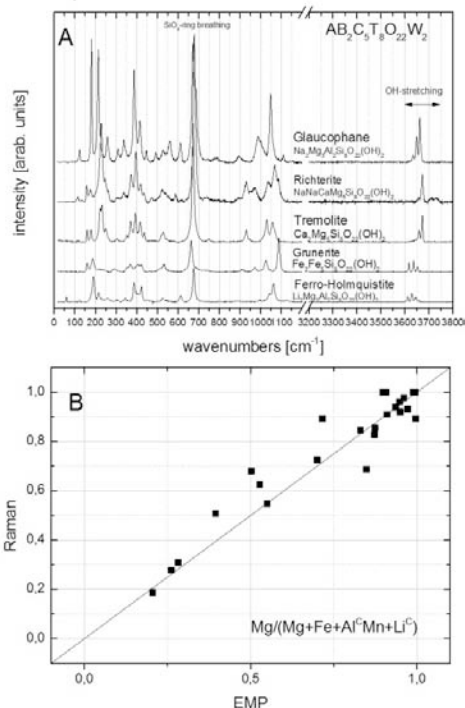
Crystal chemistry of amphiboles studied by Raman spectroscopy

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Amphiboles are complex hydrous silicates that are of great significance in geoscience, e.g. for geothermobarometric applications, as well as in material and environmental science. Amphiboles have several non-tetrahedral crystallographic positions that can be occupied by various cations and at the same time, a certain element can enter the amphibole structure at different crystallographic sites. This hinders the crystallochemical determination based only on the electron microprobe analysis. Extensive infrared spectroscopic studies have shown that the O-H bond stretching mode is sensitive to the chemistry of the adjacent non-tetrahedral positions. Raman spectroscopy offers a non-destructive, preparation-free alternative, however there are only few studies on this topic. In this work we study qualitatively and quantitatively the site occupancy of the non-tetrahedral positions on the basis of Raman peaks originating from OH-stretching modes.

Fig.1 A: Representative Raman spectra of main amphibole subgroups. B: Mg/(Mg+Fe) ratio determined by Raman intensities vs results from electron microprobe analysis.



MOD-P07

Quantitative estimation of radiation-induced defect accumulation in zircon (ZrSiO_4) – a REE^{3+} photoluminescence and Raman spectroscopic approach

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We present first results of a comparative study addressing effects of radiation-induced damage in two types of sample, namely, (i) natural zircon that has experienced long-term self-irradiation due to the radioactive decay of trace-U and -Th, and (ii) samples irradiated with heavy ions. The objective is to provide REE^{3+} laser-induced photoluminescence (PL) and Raman spectroscopic estimates of irradiation-induced damage for zircon samples of unknown geothermal history.

The full-width-at-half-maximum (FWHM) of certain PL sublevel bands of trace REE^{3+} , and the $\nu_3[\text{SiO}_4]$ Raman band, are used to estimate the radiation damage present. Complementary to results of [1], it has been found that the FWHMs of REE^{3+} -related PL bands relate closely to the effective time-integrated α -dose of well-characterised natural zircon samples. Hence, PL of REE^{3+} may be used for the quantitative estimation of radiation damage, in addition to the already well-established Raman-based approach.

Further, we compare naturally radiation-damaged zircon with ion-irradiated material. For this purpose, well-crystalline, gem-quality zircon from Ratanakiri (Cambodia) was annealed, and thin foils (1.5 μm thickness) - prepared with the focused ion beam (FIB) technique - were irradiated with Au-ions (Fig. 1).

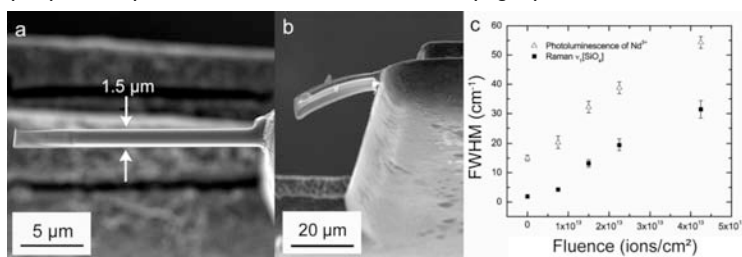


Fig.1 Zircon irradiation with Au ions: Lamellae were prepared with the FIB technique (a) and irradiated. Radiation damage causes volume swelling (b) and an increase of spectroscopic band widths (c). The FWHM of the PL emission of trace Nd^{3+} ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$) and the Raman $\nu_3[\text{SiO}_4]$ mode were found to be well suitable to estimate the radiation damage created.

Funding by the Austrian Science Fund (FWF) through project P24448-N19, and University of Vienna Doctorate School IK052 is gratefully acknowledged.

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MOD-P08

A new Procedure for Trace Element Analysis of Fluid Inclusions with UV-fs-LA-ICP-MS and its Application on Tin Granites

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To get new insights into the process of metal enrichment in crustal fluids, LA-ICP-MS analyses of both, fluid inclusions from ore deposits and of synthetic inclusions from HP/HT experiments are the method of choice. The opening of fluid inclusions during LA-ICP-MS analysis is crucial, since sample material can get lost due to splashing out of the ablation pit or by leakage through cracks in the host mineral.^[1] We have developed a new analytical setup for the determination of trace element concentrations in fluid inclusions by UV-fs-LA-ICP-MS.^[2] Laser ablation was performed at a low temperature of -40°C with frozen inclusions by using a modified heating-freezing stage as the ablation cell. With this method it was possible to successfully analyse 53 of 55 frozen synthetic NaCl-H₂O fluid inclusions in quartz, covering a size range between 8µm and 25µm down to a depth of 50µm. Trace element analyses were performed with a fast scanning magnetic sector field ICP-MS. The lower limits of detection for fluid inclusion analysis vary from 0.1µg/g (for ²⁰⁹Bi) to 10µg/g (for ³⁹K). The typical analytical uncertainty, based on the reproducibility of experimentally synthesized fluid inclusions, ranges between 10% and 30% (1RSD), depending on the element and respective concentration level. The here presented method is a highly efficient tool for the determination of accurate trace element data on low concentration levels (~50µg/g) in small fluid inclusions with a high success rate of > 90%.

First trace element data from natural fluid inclusions of two different tin granites, 1) the Land's End Granite (Cornwall, UK) and 2) the Schellerhau Granite Complex (Erzgebirge), acquired with this new freezing technique will be presented.

[1] Pettke et al. (2012), Ore Geol. Rev. 44, 10. [2] Albrecht et al. (2014), J. Anal. At. Spectrom, advance article. [3] Heinrich et al. (2003), Geochim. Cosmochim. Acta, 67, 3473.

MOD-P09

Einsatz eines Versuchsplanungsprogramms zur Optimierung der technischen Eigenschaften von Deponiestabilisaten aus calciumreichen Braunkohlenfilteraschen

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Deponiestabilisate aus calciumreicher Braunkohlenfilterasche und REA-Wasser sind komplexe Phasengemische mit hohen Gehalten amorpher Bestandteile. Sie zeigen trotz vergleichbarer chemischer und mineralogischer Zusammensetzung der Ausgangsstoffe oft unterschiedliche technische Eigenschaften. Über die Ursache ist bisher wenig bekannt [1].

Untersuchungen zum quantitativen Phasenbestandes von 80 Stabilisaten zeigen, dass die Druckfestigkeit im Wesentlichen von der Korngröße der Ausgangsstoffe und dem Verhältnis der reaktiven Bestandteile (C₂S, C₃A, Anhydrit, Yeelimite, Freikalk, amorphe Phasen) der Braunkohlenfilteraschen abhängt. Demnach werden hohe Druckfestigkeiten erreicht, wenn die Korngröße der Braunkohlenfilterasche durch Zugabe von Wirbelschichtasche erniedrigt wird und bei der Hydratation so viel Calcium, Aluminium und Sulfat freigesetzt wird, dass eine optimale Ettringitkristallisation einsetzen kann. Überschüssiges Calcium und Sulfat führt zur Entstehung von Nebenphasen (Gips, Portlandit), welche die Druckfestigkeit der Stabilisate negativ beeinflussen.

Mit Hilfe statistischer Versuchsplanung (STAVEX) wird untersucht, ob sich im System der Braunkohlenfilteraschen die Einflussgrößen so kombinieren lassen, dass gleichbleibend hohe Druckfestigkeiten bei niedrigen Wasserdurchlässigkeiten erreicht werden. Nach Auswertung der Ergebnisse soll die bestmögliche Kombination der Faktoren gefunden werden, mit der optimale technische Eigenschaften [2] für Stabilisate aus Braunkohlenfilteraschen erzielt werden.

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Modern techniques for mineralogical research

MOD-P10

New perspectives of synchrotron radiation based techniques for mineralogical research at ANKA

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Mineralogical research may benefit from the development of new analytical techniques at synchrotron radiation sources. Here, we briefly give an overview of developments, recently made or tested at the synchrotron radiation source ANKA of the Karlsruhe Institute of Technology. A hydrothermal cell has been designed for in situ X-ray diffraction up to 200 °C and 16 bar. It has been applied so far to track reactions of calcium silicate hydrate phases during the production of the novel cement Celitement that is being developed at the KIT. This sample cell might also be suited for example to investigate low temperature low pressure hydrothermal ore mineral formation. For X-ray absorption spectroscopy (XAS) a full field mode has been setup that enable parallel detection of several thousands of X-ray absorption spectra in transmission (XANES radiography) at the SUL-X and XAS beamlines [1]. Applications in mineralogy can be, e.g., chemical species mapping in soil or petrological thin sections to discover red-ox gradients, provided that the chemical element of interest is in the percent concentration range and sample thickness is optimized for X-ray transmission. Spatial resolution as low as 1.5 µm x 1.5 µm is theoretical possible. A high energy resolution X-ray emission spectrometer has been installed at the INE-Beamline. This instrument enables new insights into the electronic structure with focus on actinides and their homologues that facilitate better understanding of the migration behavior of such elements in a nuclear waste repository [2]

With the development of a Color X-ray Camera (CXC, SLcam, IfG Berlin) parallel detection of X-ray fluorescence emission (full field X-ray fluorescence microimaging) becomes reality. The CXC has been successfully used at the ANKA FLUO beamline to discover vanished paints on a Phoenician ivory object by detecting traces of chemical elements of the former pigments providing essential information for the assessment of the original appearance of the object. [3].

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T01

Cadmium isotope fractionation during evaporation and re-condensation

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Studies of volatile metal stable isotope fractionations, e.g. in meteorites or volcanic samples, can place constraints on evaporation and condensation processes. However, the isotope fractionation observed in experiments is typically much smaller than predicted by Grahams law and isotope effects related to condensation are barely studied experimentally.

To obtain a better understanding of related isotope fractionation effects, combined evaporation/condensation experiments were conducted under atmospheric pressure at variable fO_2 in air and CO-CO₂. Anorthite-Diopside glass doped with 17 volatile elements was prepared and molten in a gas-mixing muffle tube furnace. Silicate melt residues from evaporation were repeatedly sampled and then analyzed for volatile element loss and Cd isotope fractionation by single- and multiple-collector ICP-MS. The distribution of volatile elements that recondensed along Al₂O₃ plates placed within the furnace tube was analyzed using an XRF scanner. Cadmium leached from these condensation plates was analyzed for its isotope composition.

A moderate suppression of Cd isotope fractionation is observed for the evaporation into air, while Cd isotope fractionation related to the more rapid Cd depletion under reduced conditions in CO-CO₂ was suppressed much stronger. Cadmium condensed at slightly higher temperatures in air than in CO-CO₂. As expected from kinetic theory, light isotopes are enriched in the condensates relative to the vapor. Hence the light Cd isotopes are enriched at the hotter regions closer to the melt surface.

Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T02

Terrestrial and Lunar Constraints on the Composition of the Earth's Late Veneer

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Osmium isotopic data, highly siderophile element (HSE) and S-Se-Te concentration data on fertile peridotites from the earth's mantle [1-7] and recent experimental studies on metal-silicate partitioning [8] are broadly consistent with late addition of chondritic material to the earth's mantle after core formation ('late veneer'). HSE/S ratios and CI chondrite like S/Se and Se/Te of the bulk silicate earth (BSE) suggest that the late veneer was rich in volatiles and, in terms of its depletion in volatile elements similar to CM carbonaceous chondrites [7]. However, ratios of Ru and Pd relative to other HSE in the BSE are suprachondritic and Os isotopic data and Rh/Ir show values similar to ordinary or enstatite chondrites, rather than carbonaceous chondrites. In order to explain these discrepancies, the following testable hypotheses have been proposed: (1) The earth's mantle contains residual amounts of Ru and Pd from metal-silicate segregation that were mixed with late accreted material [7, 9]. (2) The late veneer was predominantly comprised of carbonaceous chondrite like material with a minor proportion of differentiated metal representing fragments of cores of planetesimals [10]. (3) The late veneer had a volatile element composition similar to carbonaceous chondrites, but slightly different refractory HSE ratios, owing to fractionation processes in the solar nebula [7]. Evidence from HSE, Se and Te abundances in ancient lunar impact rocks will be presented that may favor (3).

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T03

Lunar ^{182}W and the origin of the Moon

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The most widely accepted model for the origin of the Moon involves a giant impact hitting the proto-Earth near the end of Earth's main accretion phase. Essential constraints on lunar origin are provided by the similar O, Ti and W isotope compositions of the Earth and Moon, suggesting that the Moon predominantly consists of material derived from the proto-Earth's mantle [1-3]. The most recent simulations of the Moon-forming impact are consistent with this [4-6]. As ^{182}W is the decay product of now-extinct ^{182}Hf , the similar $^{182}\text{W}/^{184}\text{W}$ ratios of the bulk silicate Earth (BSE) and Moon are particularly important. The $^{182}\text{W}/^{184}\text{W}$ of the bulk silicate portion of a planetary body mainly depends on the timescale and conditions of core formation, so that it is very unlikely that two distinct bodies have identical W isotope compositions. If the Moon contains a large fraction of impactor mantle material it would, therefore, be expected to have a $^{182}\text{W}/^{184}\text{W}$ different from that of the BSE. Here we present new high-precision $^{182}\text{W}/^{184}\text{W}$ analyses of KREEP-rich lunar samples determined by MC-ICPMS to help constrain the age and origin of the Moon. Superimposed neutron capture-induced $^{182}\text{W}/^{184}\text{W}$ shifts were quantified through Hf isotope analyses on the same samples [7]. Our results demonstrate that the Moon shows an excess in ^{182}W of ~25 ppm relative to the present-day bulk silicate Earth. The small ^{182}W excess of the Moon is in good agreement with elevated $^{182}\text{W}/^{184}\text{W}$ in some Archean samples [8], suggesting that the Moon exhibits the same $^{182}\text{W}/^{184}\text{W}$ as the BSE before addition of the late veneer. This similarity is unlikely to be coincidental, but provides important constraints on lunar origin. Either the Moon almost entirely derived from (pre-late veneer) terrestrial mantle material, or the impactor mantle, impactor core and proto-Earth's mantle mixed very efficiently during the giant Moon-forming impact. In either case, the W isotope data are best accounted for if the Moon formed 'late', that is, more than 50 Ma after solar system formation.

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T04

Highly siderophile elements in Apollo 16 impact melt rocks: constraints on late accreted material in the earth-moon system

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Early work on ancient lunar impact rocks from the Apollo landing sites has shown that significant quantities of highly siderophile elements (HSE) were added to the lunar crust after core formation and magma ocean crystallization [1]. Most of the HSE in the lunar crust were supplied during the basin forming impact events (>3.8 Ga). Because of low intrinsic abundances of the HSE in lunar crustal rocks, the HSE budget of lunar impact melt rocks is dominated by the composition of the impactors. Hence, the compositional record of ancient lunar impact rocks provides constraints on the composition and timing of the impact flux to the earth and moon, with important implications for the inner solar system dynamics and the late accretion history of the terrestrial planets [2]. This information may also hold the key to understand the observed excess abundance of HSE in the earth's mantle and the slight deviation of some HSE ratios from chondritic ratios [3-5].

New results of an ongoing study on HSE abundances in ancient lunar impact melt rocks from the Apollo 16 landing site, using isotope dilution methods combined with $^{187}\text{Os}/^{188}\text{Os}$ data as a time-integrated measure of the Re/Os ratio highlight similarities and differences of Apollo 16 impact rocks to differentiated and undifferentiated meteorite groups. Most Apollo 16 impact melt rocks display strongly fractionated HSE patterns and suprachondritic $^{187}\text{Os}/^{188}\text{Os}$, similar to data on some iron meteorite groups. In detail, we note differences in the ratios of some refractory HSE that cannot be explained by the fractionation processes in asteroidal cores. In contrast, granulitic impactites at the Apollo 16 site display chondritic to slightly volatile-depleted compositions [4]. Similarly, ancient impact rocks from other Apollo sites lie in-between these mixing end members [4-6]. We will discuss the implications of these observations for the late accretion of primitive objects and fragments of differentiated planetesimals and their composition on the early lunar and terrestrial surface.

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T05

A depleted mantle origin for Hadean protoliths of the Acasta Gneisses

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The existence and persistence of depleted Hadean mantle domains that formed during Earth's early crust-mantle differentiation is controversial [e.g., 1-4]. The ¹⁴⁷Sm-¹⁴³Nd and ¹⁷⁶Lu-¹⁷⁶Hf systematics of ancient rocks provide a potent tool for addressing this topic and complement U-Pb(-Lu-Hf) studies on zircons [e.g., 1, 3, 4]. These systems can 1) date the last isotopic equilibration within or among rocks by isochrons, and 2) provide initial isotope ratios that constrain the persistence of enriched or depleted silicate domains.

Previous zircon [e.g., 5-7] and some whole rock studies [8, 9] on the Acasta Gneisses found no evidence for depleted Hadean mantle. In contrast, we reported a ca. 4.0 Ga Sm-Nd isochron of contiguous gneiss layers that yields an $\epsilon_{\text{Nd}_{4\text{ Ga}}}$ of $\sim +2$ and associated $\epsilon_{\text{Hf}_{4\text{ Ga}}}$ of up to $+6$ [10]. We report new Sm-Nd-Lu-Hf data from additional locations of the same rock unit. Also, zircon grains from two previously analyzed layers were analyzed for Lu-Hf (solution MC-IPCMS) and U-Pb (LA-ICP-MS) systematics and imaged using CL.

The new Sm-Nd data scatter around a 4.0 Ga trend (MSWD = 13) consistent with the previously determined 4.0 Ga isochron [10]. Two new samples from one location lie on this isochron (MSWD_{combined} = 1.5). Low-pressure digestions of previously analyzed layers [10] yield a Lu-Hf errorchron of ca. 3.9 Ga. Solution Lu-Hf data for zircons identify multiple populations within a given layer. Many grains are partially metamict and exhibit complex zoning and fluid-induced recrystallization. Overgrowths dated at 3.8 Ga (Pb-Pb) imply that inherited cores are > 3.8 Ga, consistent with earlier reports [e.g., 6, 8].

We think partial digestion of inherited zircon — metamict, thus dissolved in low-pressure digestions — scatters the Lu-Hf rock data. However, the Sm-Nd data imply a last metamorphic equilibration of the rock unit at ca. 4.0 Ga, requiring ≥ 4 Ga igneous precursors derived from a depleted mantle [10].

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T06

Geochemistry and Petrology of 3.8 Ga Archaean peridotites from southern West Greenland

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The Eoarchean Itsaq gneiss complex (IGC) of southern West Greenland comprises ultramafic and mafic units embedded in tonalitic-trondhjemitic and granodioritic gneisses that have been proposed to represent remnants of Eoarchean mantle and cumulate associations with ages of >3.7 Ga (Friend et al. 2002). In order to gain new insights into the evolution and isotopic composition of the Eoarchean mantle, several samples from three different localities in southern West Greenland were analysed. The sampled localities included dunites and harzburgites from the region south of the Isua Supracrustal belt, within the southern gneisses, and isolated exposures south of Nuuk. Most samples contain fresh olivine, pyroxene, and spinel, with variable degree of alteration. In an Al/Si versus Mg/Si diagram, the studied peridotites fall on the mantle depletion trend similar to younger peridotites. ICP-MS trace element analyses, carried out at Kiel University, reveal near chondritic REE abundances in the harzburgite and dunite samples. The chondrite normalized REE element patterns of the best preserved peridotites from the Isua region are less LREE-depleted (La_N/Yb_N from 0.31 to 0.60) than most modern peridotites and show small negative Eu anomalies in some cases. The Zr/Nb ratios of those peridotites range from 0.52 to 2.0. Furthermore, most samples are enriched in W compared to similarly incompatible elements (W/Th from 1.77 to 87.7), either due to mantle metasomatism or due to secondary alteration. First MC-ICP-MS analyses revealed predominantly positive $\epsilon_{Hf}(3.85)$ from +16 to -1.2 and $\epsilon_{Nd}(3.85)$ from +8.7 to -0.8. Measured $^{176}Lu/^{177}Hf$ range from 0.01 to 0.09. Altogether, these results suggest the existence of old (>3.8 Ga) mantle domains, with a long term depletion history, as documented for the Isua greenstone belt, e.g., by Hoffmann et al. (2010).

Friend, C.R.L., Bennett, V.C., Nutman, A.P. (2002) Abyssal peridotites >3800 Ma from southern West Greenland: Field relationships, petrography, geochronology, whole-rock and mineral chemistry of dunite and harzburgite inclusions in the Itsaq Gneiss Complex: Contributions to Mineralogy and Petrology, 143, 71-92.

Hoffmann, J.E., Münker, C., Polat A., König, S., Mezger, K., Rosing, M.T., (2010). Highly depleted Hadean mantle reservoirs in the sources of early Archaean arc-like rocks, Isua, SWGreenland. *Geochimica et Cosmochimica* 74 (24), 7236-7260.

Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T07

Tourmaline B-isotopes as tracers of fluid sources in silicified zones of the Barberton Greenstone Belt, South Africa

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Many Mesoarchaeon greenstone belts contain pervasively silicified volcano-sedimentary sequences. Silicification is often regarded as a result of fluid circulation in shallow sub-seafloor convection cells, but other fluid sources such as submarine vent systems are also discussed. In this study we used the Potsdam 1280 SIMS to determine B-isotope ratios in hydrothermal tourmalines from silicified zones in the Barberton Greenstone Belt. We use these data to discriminate between seafloor alteration and other fluid sources.

The 6 samples studied include silicified komatiites and cherty metasedimentary rocks from the Mendon Formation. The silicified komatiites locally preserve spinifex textures, or occur as foliated fuchsite cherts and chert breccias. One sample has previously been interpreted as stromatolite. Tourmaline composition is dravitic, and many crystals show patchy zoning, especially in Cr-content (0.0 - 0.5 Cr p.f.u.).

In-situ boron isotope analyses revealed an extreme range of $\delta^{11}\text{B}$ values, from -22 to +7 ‰ (1 s.d. uncertainty is 1‰). Three samples yielded narrow ranges of $\delta^{11}\text{B}$: two of them between -6 to -8 ‰, and a third between +4 to +7 ‰. The frequency distribution of $\delta^{11}\text{B}$ in the more heterogeneous samples shows a peak between -6 to -8 ‰, and a large number of light $\delta^{11}\text{B}$ values from -10 to -22 ‰. Our preliminary interpretation of this variation of B-isotopes is based on different fluid sources. We interpret the positive $\delta^{11}\text{B}$ values to represent boron derived from serpentinites. The most common $\delta^{11}\text{B}$ values of -6 to -8 ‰ are present in nearly all samples and may represent a metamorphic fluid whose B-source lies in the greenstone magmas or in the surrounding granitoids. Negative $\delta^{11}\text{B}$ values have been attributed to non-marine evaporates in earlier studies; however, another source of highly negative $\delta^{11}\text{B}$ values might be mature continental crust, such as S-type granite clasts preserved in the basal conglomerate of the Moodies Group (Sanchez-Garrido et al., 2011). Additionally, our results also point to a crystal-chemical and structural control on the $\delta^{11}\text{B}$ values. Some samples show a positive correlation between the $\delta^{11}\text{B}$ and Cr-content and the largest isotopic diversity is found in the deformed and brecciated samples. However, a full explanation for the large range of $\delta^{11}\text{B}$ remains open.

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T08

Triple oxygen isotope analysis of cherts - implications for the temperature and $\delta^{18}\text{O}$ of ancient oceans

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The change of $\delta^{18}\text{O}$ and/or temperature of seawater throughout the past 4 Gyrs is a debated issue in Earth science. Oxygen isotope studies of ancient marine chemical sediments suggest that the ancient oceans were either very hot (up to 80°C; [1]) or had a low $\delta^{18}\text{O}$ (e.g. -12‰; [2]). They are also suspected to be a result of diagenesis [3]. We address this classical problem using high-precision triple Oxygen isotope ratios of cherts. Recently, [4] resolved mass-dependent variations in $\Delta^{17}\text{O}$ in terrestrial rocks that are related to high- and low-T fractionation processes and reservoir mixing.

We have analysed cherts, ages spanning from Archean to modern, by fluorinating them with BrF_5 in conventional Ni bombs. The Archean cherts are found to have $\delta^{18}\text{O}$ of ~ 16‰ and a $\Delta^{17}\text{O}$ of ~ -150 ppm (± 10 -15 ppm) (see [3] for definition of $\Delta^{17}\text{O}$). Phanerozoic cherts have $\delta^{18}\text{O}$ of about +30‰ and $\Delta^{17}\text{O}$ around -250 ppm. The composition of the Proterozoic cherts falls in between these two in the triple isotope space. We will discuss the results with respect to the temperature and $\delta^{18}\text{O}$ of Precambrian and Archean seawater.

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T09

U-Pb Dating of Opaline Silica (Siebengebirge, Rhenish Massif)

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Low-temperature, hydrous weathering eventually leads to characteristic products such as silica indurations. Elevated U concentrations and the ability of opaline silica to maintain a closed system permits silica to be dated by the U-Pb method, which, in turn, will potentially allow constraining the timing of near-surface processes. To test the feasibility of silica U-Pb geochronology, we sampled opal from the Siebengebirge area. The investigated samples include silicified gravels from the Mittelbachtal locality, renowned for the embedded wood opal. Structural characterization of the silica phases (Raman spectroscopy) was combined with *in situ* isotopic analyses, using ion microprobe and LA-ICPMS techniques.

In the Siebengebirge area fluvial sediments of Oligocene age were covered by an extended trachyte tuff at around 25 Ma. Silica is known to indurate some domains within the tuff and, in particular, certain horizons within the subjacent fluvial sediments ("Tertiärquarzite"). Cementation of the gravels occurred during at least three successive growth stages: early paracrystalline silica (opal-CT), fibrous chalcedony, and late microcrystalline quartz. It has traditionally been assumed that this silica induration reflects intense weathering, more or less synchronous with the deposition of the volcanic ashes.

Results from U-Pb geochronology returned a range of discrete ^{206}Pb - ^{238}U ages, recording a protracted silicification history. For instance, we obtained 22 ± 1 Ma for opal-CT cement from a silicified tuff, 16.6 ± 0.5 Ma for silicified wood and opal-CT cement in the fluvial gravels, as well as 11 ± 1 Ma for texturally late chalcedony. While silicification of the sampled tuff might be contemporaneous with late-stage basalts, opaline silicification of the subjacent sediments and their wood in the Mittelbachtal clearly postdates active Siebengebirge volcanism, and the clastic sedimentation by about 8 Myr.

To account for the age discrepancies, opal-CT formation might be a local and episodic phenomenon. Alternatively, the dominant silicification event of the Mittelbachtal silcretes could be of regional significance (climatic optimum). Our relatively fast approach by LA-ICPMS dating will be used to further expand the database.

Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-T10

Isotope (C, O, S, Pb) geochemistry of the Ozbak-Kuh carbonate-hosted Pb-Zn deposit, East Central Iran

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The Ozbak-Kuh Pb-Zn deposit is located 150 km north of Tabas city in East Central Iran. The Pb-Zn mineralization occurs in dolostones of the Middle Devonian Sibzar Formation. The ore minerals include galena and sphalerite which are associated with calcite and subordinate dolomite and bitumen as gangue minerals. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of hydrothermal calcite samples fall in the ranges of -0.3–0.8‰ and -14.5–-11.9‰, respectively. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values overlap with the carbon and oxygen isotopic compositions of Paleozoic seawater (Fig. 1; Veizer et al., 1999), indicating that the Paleozoic seawater had possibly important participation in the ore-forming fluid. The $\delta^{34}\text{S}$ values of galena and sphalerite samples occupy the ranges of 12.2–16.0‰ and 12.1–16.8‰, respectively. These values suggest that the most probable source of sulfur is seawater sulfate (Ohmoto and Rye, 1979; Hoefs, 2009). The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the galena samples yield average values of 18.08, 15.66, and 38.50, respectively. These ratios show that galena Pb likely originated from an orogenic source in which supracrustal rocks with high $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios were dominant (Fig. 2; Zartman and Doe, 1981). The average lead isotope model age (Stacey and Kramers, 1975) represents Cambrian age. It is probable that the pre-Middle Devonian model age indicates the derivation of Pb from older sources either from host rocks of Cambrian age or from deposits previously formed in these rock units. According to the proposed genetic model, mineralization formed in fractured and brecciated host rocks along shear zones and faults from metal-bearing connate waters that were discharged due to deformational dewatering of sediments.

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Stable and radiogenic isotopes – clocks and tracers of rocks

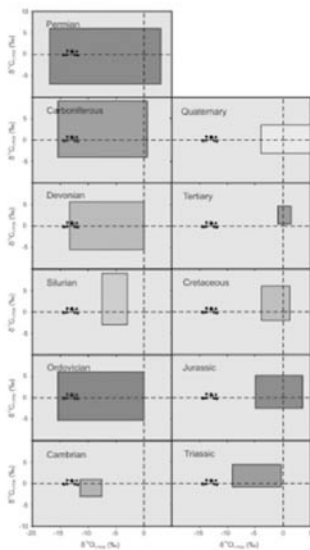


Fig. 1: Carbon and oxygen isotope data from the Oribak-Kuh deposit (solid circles) compared with the isotopic composition of the Phanerozoic seawater (shaded boxes; Veizer et al. 1999).

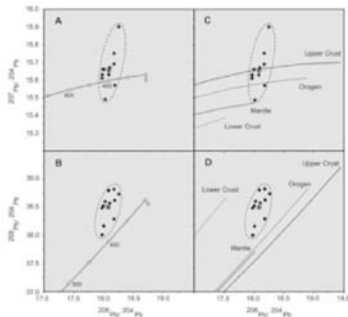


Fig. 2: Pb-isotopic ratio of galena from the Oribak-Kuh deposit plotted in diagrams showing the model curves for the Pb isotope evolution of the average crust (a and b) (Stacey and Kramer 1975), and in the plumbotectonic diagrams (c and d) (Zartman and Doe 1981). The red squares correspond to the average Pb-isotope composition of the analyzed samples.

Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-P01

Fe isotope fractionation in carbonatite melt systems

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The Earth's mantle is assumed to be the world's largest carbon reservoir. Yet it is hardly explored compared to the near-surface carbon cycle, which is thoroughly investigated for its influence on climate and ecosystems [1]. One means of learning more about mantle processes is the investigation of carbonatites. These are rare igneous rocks derived from the Earth's mantle and composed mostly of carbonates. Due to their physical and chemical properties, they are highly efficient agents for mass transport from mantle to crust [2].

A new tool applied to carbonatites are Fe stable isotopes. They are a potential oxybarometer of mantle melting, since Fe isotope fractionation is controlled by oxidation state and bonding environment of Fe. Significant Fe isotope fractionation in natural rocks was found between carbonate, oxide, and silicate minerals [3]. Because isotope fractionation factors between different phases in carbonatites are predominantly unknown, interpretation and application is still hampered. Nevertheless, even for high temperatures (> 1200°C) measureable fractionation is predicted from theoretical studies [4]. To be able to interpret the Fe isotope differences measured in carbonatite rocks, experimental studies under controlled conditions (P, T, redox) are needed.

The aim of this project is to experimentally determine the fractionation factors of Fe isotopes between carbonatite melt and magnetite as well as between silicate and carbonate immiscible melts. Enriched ⁵⁸Fe isotope tracers will be used to trace kinetic and equilibrium isotope exchange reactions. Samples are synthesized in an internally heated gas pressure vessel. Experimental challenges are 1) developing a container design preventing the reaction of Fe and Pt, and 2) the preparation of run products containing soft and highly hygroscopic Na-rich carbonate quench products next to magnetite. Fe isotopes are analysed with solution MC-ICP-MS and UV-fs-Laser Ablation MC-ICP-MS. The results are used to test the potential of Fe isotopes as a sensitive tracer of processes contributing to carbonatite genesis.

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Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-P02

The GFZ Potsdam 1280-HR SIMS Laboratory - Current State

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A CAMECA 1280-HR SIMS (secondary ion mass spectrometer) was installed at the Deutsches GeoForschungsZentrum Potsdam / Helmholtz Zentrum Potsdam in November 2013. The new ion microprobe laboratory functions as an open user facility, in accordance with the Helmholtz Society's support of the scientific community through providing access to top-end infrastructure. The 1280-HR instrument will be integrated into the Helmholtz SIMS network, whereby the activities in the Potsdam laboratory will be closely coordinated with new SIMS infrastructure currently being installed in both Dresden (accelerator SIMS using a CAMECA 7f auto as its source) and Leipzig (NanoSIMS 50L). The Potsdam 1280-HR is intended mainly for geoscientific studies, however, the facility will also support a limited number of well defined material science investigations as well as serving as a platform for instrumentation development work.

The state-of-the-art, ultra-high sensitivity and large geometry instrument consists of the basic 1280-HR design, including the five trolley multi-collection system along with a Resistive Anode Encoder, thus making the system optimized for both low-uncertainty isotope ratio determinations (e.g., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$) as well as quantification and distribution mapping of low concentration elements in minerals, glasses or biological materials. The possibility of very high mass resolution of $M/dM \geq 30,000$ will also allow the separation of isobaric masses, such as ^{40}Ca and ^{40}K . Envisioned key research topics include H, B, C, O, S and Pb isotopic studies, geochronology applications and the quantification of volatile elements in geological materials.

Although our SIMS team is still gaining initial experience with this new technology, we have already successfully carried out several isotope, solubility and diffusion studies. This contribution provides a brief overview on the current state of the Potsdam SIMS facility, its analytical progress and present operational capabilities. We invite the community to take advantage of this geochemical tool.

Stable and radiogenic isotopes – clocks and tracers of rocks

ISO-P03

Zircon M127 – a future reference material for U-Pb combined with Hf- and O-isotope analysis*

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** This paper is dedicated to Jan Košler (University of Bergen, Norway), who passed away earlier this year at the age of 49. Jan was involved in the initial characterisation of zircon M127.*

The determination of zircon U-Pb ages from micro-areas of polished sample surfaces, by means of SIMS analysis, depends on the availability of well-characterized, natural calibrant materials. Here we propose a gem-quality zircon (Univ. Mainz sample no. M127) as a future zircon reference for SHRIMP U-Pb combined with stable-isotope analysis. Zircon M127 is an orange brown, clear stone originating from a gem placer in the Ratnapura area, Sri Lanka; its weight (faceted) was 2.54 g (12.7 ct). The concordant U-Pb age is 524.3 ± 0.5 Ma (Fig. 1) and the U-(Th)/He age is 427 ± 20 Ma [1], which corresponds to the trend of non-heat treated Sri Lanka zircon [2]. The moderate unit-cell expansion [V 266.22(4) Å³] and Raman-band broadening {FWHM [$\nu_3(\text{SiO}_4)$] 14 cm⁻¹} indicate moderate radiation damage, which is in accordance with elevated actinide (U 924 ppm [3]; Th 439 ppm) and Pb concentrations. The latter will result in sufficiently high count rates. Structural, chemical, and isotopic homogeneity was confirmed by extended EPMA, LA-ICP-MS, Raman, and photoluminescence line-scanning. The material is to be used in SHRIMP U-Pb analyses, combined with LA-ICP-MS analyses of Hf and O, and potentially also Li [4] isotopes. Results of the detailed characterisation are presented.

Stable and radiogenic isotopes – clocks and tracers of rocks

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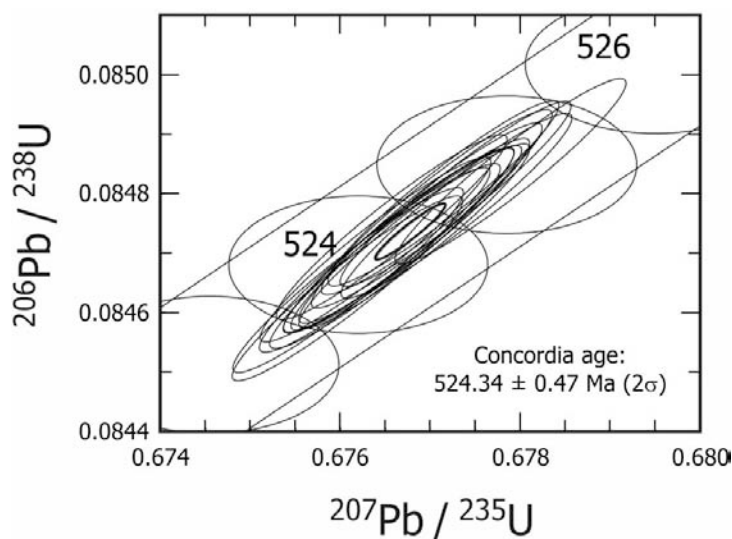


Fig. 1. Results of U-Pb analyses: Concordia plot of CA-TIMS data obtained at the University of California at Santa Barbara (17 plateau steps).

TEC-T01

Zirconia in medical application – advantages and drawbacks

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Yttria-stabilized Zirconia is widely used in medical and dental applications as it meets both clinical as well as aesthetical requirements due to its biocompatibility and favorable optical properties. It also belongs to the most tough ceramic materials due to transformation toughening. Cracks induced by high mechanical stresses facilitate structural transformation from the tetragonal to the monoclinic phase, which is accompanied by an increase in specific volume that retards the growth of cracks. However, moisture (water or water vapor) may also induce a widespread surficial phase transformation process, in this case leading to detrimental effects by degradation of the physical material properties. This phenomenon is known to occur at low temperatures, as low as human body temperatures, and is termed 'low temperature degradation' accordingly. The contrast of both favorable (transformation toughening) and detrimental (low temperature degradation) properties of the t-m transition has sparked extensive research efforts in order to broaden our understanding of both processes and their respective relevance and interrelations especially for clinical applications, for which lifetime predictions are of first importance.

In this presentation we outline current knowledge about both the favorable and detrimental aspects of this phase transformation and present an overview of possible chemical mechanisms causing the transformation process. We discuss how the presence of phase transformation may be determined and how transformation kinetics may be studied by coupling analytical methods such as X-ray diffraction, Raman spectroscopy, scanning electron microscopy and electron-backscattered diffraction. Based on these newly acquired data on transformation kinetics we discuss limitations in the applicability of Zirconia and present a boundary lifetime prediction model for the material in dental applications.

TEC-T02

Corrosion of silicate glasses at the nanometer scale – a TXM and XANES approach

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Just as minerals, glasses are subject to physical degradation and chemical conversion. Weathering of silicate glasses contributes to the elemental budget of ocean water and the release of nutrients in continental volcanic terranes. In many technical applications, such as radioactive waste storage, glass is an indispensable material.

Hence, understanding the corrosion of glasses is of crucial importance but still lacks a proper description ^[1]. However, alteration layers forming between the pristine glass and the weathering agent have often been recognized and seem to play a major role in the dynamics of this process ^[2].

Here, we present a new approach for characterizing these alteration layers by high resolution transmission X-Ray microscopy (TXM) and combined X-Ray absorption near-edge spectroscopy (XANES) ^[3].

For this purpose two different CaO-MgO-Na₂O-Al₂O₃-SiO₂ glasses were synthesized and altered at 85°C in a Teflon reactor filled with 25% HCl solution. The investigated periods of alteration were 60 min and 14 days. In addition, a technical glass was altered in a glass flask at 65°C for 8 days. Thin foils were cut perpendicular to the surface of the corroded glass monoliths with a focused ion beam mill. Subsequent TXM analysis allowed chemical and structural investigations without inducing beam damage to the glassy sample, which is a severe problem in electron microscopy. Results show that alteration layers do not necessarily form, but if they do, their evolution can be explained by interplay of both dissolution/re-precipitation and diffusion. Additionally, spatially resolved

XANES spectroscopy at the O K-edge provided insight to structural changes in the corrosion layer on the atomic scale. Comparison to spectra of silicate minerals and hydrous glass as well as ab-initio calculations of the O K-edge of model structures indicate that changes of the fine structure at the edge may be assigned to the formation of siloxane groups in the corrosion layer.

^[1] Geißler, T., Janssen, A., Schreiter, D., Stephan, T., Berndt, J., Putnis, A., 2010 Aqueous corrosion of borosilicate glass under acidic conditions: A new corrosion mechanism. *Journ. Non-Cryst. Sol.* 356:1458-1465.

^[2] Caillateau, C., Angeli, F., Devreux, F., Gin, S., Jestin, J., Jollivet, P., Spalla, O., 2008 Insights into silicate-glass corrosion mechanisms. *Nat. Mat.* 7: 978-983.

^[3] Guttman, P., Bittencourt, C., Rehbein, S., Umek, P., Ke, X., Van Tandeloo, G., Ewels, C.P., Schneider, G., 2012 Nanoscale spectroscopy with polarized X-Rays by NEXAFS-TXM. *Nat. Phot.* 6:25-29.

TEC-T03

Beitrag zur Festigkeitsentwicklung von Gipsstein und zum Festigkeitsabfall bei Durchfeuchtung

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Wie die Festigkeit von Gipsstein entsteht ist eine in der Literatur kontrovers diskutierte und bislang nicht abschließend geklärte Frage. So wurde eine Verfilzung einzelner Kristalle als festigkeitsbildend beschrieben, ebenso wurde ein Verwachsen einzelner Kristalle zur Begründung herangezogen. Ein Versagen wird unter Anderem durch ein Brechen einzelner Kristalle beschrieben. Der Festigkeitsverlust bei Durchfeuchtung ist dann entweder über ein Auflösen einzelner Kristalle aus dem Gefüge oder über ein Lösen der Verwachsungsstellen zu erklären. Fraglich bleibt aus Sicht der Autoren wie einzelne Dentalgipse, die nur aus kurzen, unverzweigten Kristallen bestehen, Festigkeit über Verfilzung bilden können. Verwachsungen einzelner Kristalle konnten nur äußerst selten beobachtet werden. Mit den vorliegenden Untersuchungen soll ein Beitrag zu dieser Diskussion geleistet werden.

Eigene Untersuchungen zeigen, dass die Festigkeit von Dentalgipsen nicht allein durch ein Verfilzen bzw. nur bedingt durch ein Verwachsen erklärt werden kann und legen eine neue Theorie nahe. Neben der Verfilzung kommt es demnach zu einer Festigkeitsbildung über Wechselwirkungen der Oberflächen untereinander unter Anderem durch Reibung. Bei Durchfeuchtung würde dann ein Abgleiten bedingt durch einen Wasserfilm entstehen. Der Reibungsmechanismus würde von Fest-Fest-Reibung auf Fest-Flüssig-Reibung wechseln, was ein Absinken des Reibwertes um eine Zehnerpotenz mit sich bringt. 20% Restfestigkeit bei Durchfeuchtung von Gips wie in der Literatur beschrieben ist zu erklären, weil eine gewisse Mischreibung erhalten bleibt. Um diese Theorie zu stützen wurden Gipssteinprüfkörper verschiedener Gipskristallmorphologien bei unterschiedlichen Luftfeuchten und in Wasser sowie Gipslösung gelagert und die Festigkeiten bestimmt, außerdem wurden die Festigkeiten von Probekörpern gemessen die auf 60°C, 400°C und 800°C erhitzt wurden. Mit der Temperaturlagerung sollte die Theorie überprüft werden, die besagt, dass Wasser benötigt wird um Festigkeit unter Anderem in Gipsstein zu erzeugen [1].

[1] Roland J.-M. Pelleng and Henri Van Damme; Why does concrete set?: The Nature of cohesion forces in hardend cement-based materials; MRS Bulletin; pp. 319-323

TEC-T04

Characterization of a Clay by TG-DSC-MS and Dilatometer-MS Measurements

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Clays are often used for ceramic applications. The “royal” clay mineral is Kaolin which is employed for the production of porcelain products. For stoneware, bricks and tiles the material from the mined deposits often contains a mixture of several other clay minerals (like Smectite, Illite, Chlorite etc.) and also other small grained minerals such as quartz, feldspar, iron and titanium compounds [1,2].

The investigated clay was obtained from a western German deposit rich in Illite, Smectite and Quartz. The sintering was studied using a TMA. By coupling the TMA to a Mass Spectrometer it was possible to investigate the evolving gases during sintering simultaneously. Additional TG-DSC-MS measurements in inert gas and oxidizing atmospheres gave further information about the mineral content as well as the burnout process of the organic impurities of this material.

Comparisons of the dilatometer, mass loss, differential scanning calorimetry and mass spectrometer curves are shown and discussed.

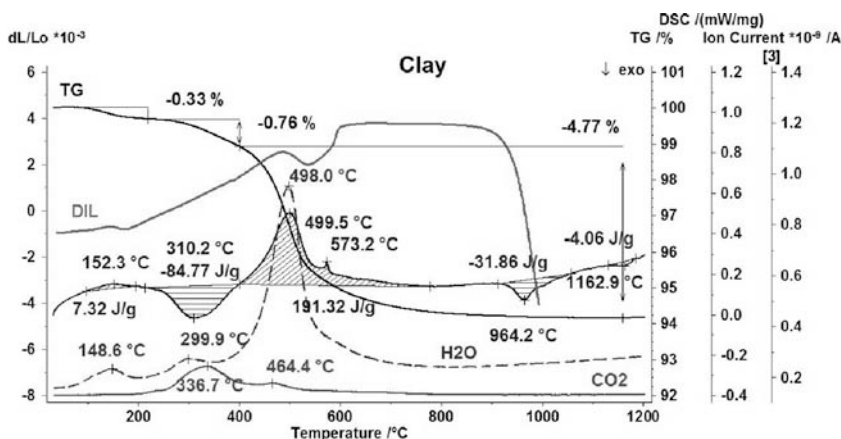


Figure 1. TG, DSC, dilatometer and mass spectrometer curves of water and carbon dioxide

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TEC-T05

Synthesis and Characterization of the different modification of doped Dicalcium Silicates (C_2S)

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C_2S (Ca_2SiO_4 ; $C=CaO$ $S=SiO_2$) was synthesized and doped with foreign ions (Al^{3+} , K^+ , Mg^{2+} , Sr^{2+} , Ba^{2+}) with molar compensation $(Ca^{2+}+M)/(Si^{4+}+M)=2$, $M=metal$. The C_2S phases were synthesised in the laboratory, using the Pechini method [1]. The dicalcium silicate exists in several polymorphic forms with different hydraulic reactivities: α - C_2S , α'_H - C_2S , α'_L - C_2S , β - C_2S and γ - C_2S [2]. In order to enhance the hydraulic reactivity, the dicalcium silicate is synthesized with foreign ions, which can be incorporated in the structure and lead to the stabilization of high temperature modifications. Undoped C_2S provides a mixture of β - C_2S with small quantities of α'_H - C_2S . Doping concentrations of 1wt.%, 3wt.%, 5wt.%, 7wt.% and 10wt.% of foreign oxides were investigated. The X-ray diagrams of the synthesis products (Fig. 1) show, that the incorporation induce higher contents of the high temperature modification (α'_H - C_2S) and lower content of the β -modification. The charge balance was not taken into account, so that it has to be assumed that the electro neutral conditions are produced by defects in the crystal-phases.

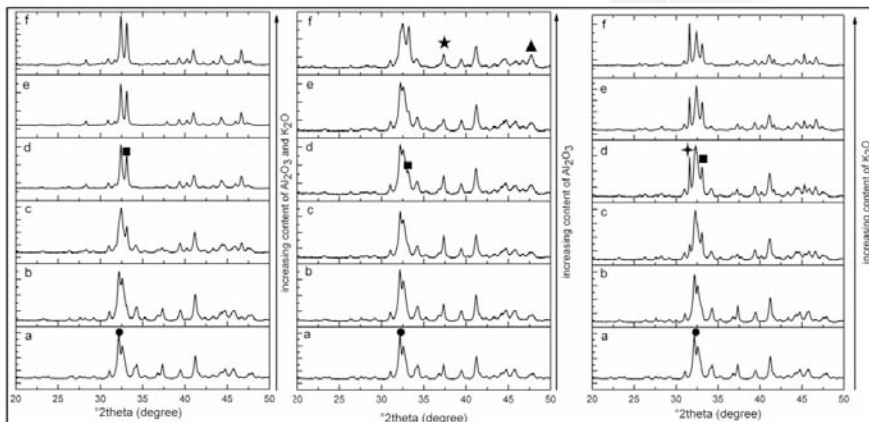


Figure 1: XRD studies of the undoped and doped Ca_2SiO_2 synthesized at 800°C 2h; a-b-c-d-e-f correspond with C_2S and C_2S doped with 1, 3, 5, 7 and 10 wt.% foreign; left: coupled substitution of Al_2O_3 and K_2O , middle: substitution with Al_2O_3 and right: substitution with K_2O ; circles ()= $\beta\text{-C}_2\text{S}$; squares ()= $\alpha'\text{-H-C}_2\text{S}$; cross ()= $\text{K}_2\text{Ca}_2\text{Si}_2\text{O}_7$; triangle ()= C_3A ; star ()= CaO

References

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TEC-T07

Phenomenology of the alpha-beta transition of ultra-high purity cristobalite

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The characterisation of cristobalite has recently renewed the attention of the volcanological and applied mineralogical communities. High levels of *cristobalite* in respirable volcanic ash raise concerns about *health* effects, whereas the room temperature stabilized beta-*cristobalite ceramic* powder has great potential for use in production of engineering ceramic materials due to its high resist.

For this study we prepared cristobalite by using milled ultra-high purity glassy precursor material and heated the glass for 12 hours in platinum crucibles at fixed temperatures of 1400°C, 1500°C and 1600°C in air. The fused silica ranged from the “type 1” to the “type 4” category. The synthesis products were studied with a differential scanning calorimeter from Netzsch (404 C/3/F Pegasus). The effect of different heating and cooling rates and heating cycles have been evaluated by the determination of the alpha-beta transformation of cristobalite through: a) the extrapolated onset temperature of inversion -TI- b) the width of the inversion temperature interval c) the shape of the inversion peak, and d) the hysteresis between TI during heating and cooling.

For lower heating and cooling rates the true inversion dynamics is revealed in a “inversion temperature range” indicated by individual peaks relating to differently ordered domains; generally the individual peak positions and areas are reproduceable during heat cycling. However, sometimes some peaks are growing on the expense of the others. A so far undescribed feature is that during slow cooling the individual peaks resolved by heating collapse to a single broad peak; indicating a difference in the transformation process during the inversion from the tetragonal low-temperature (alpha) form to the cubic high temperature (beta) form. All cristobalites synthesized from high purity glasses are characterized by different inversion temperatures, but independent of the applied temperature. All new cristobalites show equal or higher degree of “order” than synthesized crystals by conventional routes (such as transforming amorphous silica gel or quartz).

The new high purity cristobalites will enable a concise understanding of structure-property relationships of tectosilicates with an alpha-beta transition behavior.

TEC-T08

Determination of the bulk heat conductivity of chondritic material by numerical modelling of the composition

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Measurements of the bulk heat conductivity of chondritic material from different meteorites varies by a factor of ~4. This is most likely due to differences in the composition and structure of the material. As shown in [1], thermal models depend significantly on the bulk heat conductivity. We have developed a model for the thermal evolution of asteroids where we treat the bulk heat conductivity as a free parameter and used a parameterised dependence on porosity.

To improve this model we theoretically determine the value of the heat conductivity of chondritic material via numerical modelling. We model the rate of heat flow in a heterogeneous medium consisting of several materials and including pore space. We solve the heat conduction equation for a cube with a certain mineral composition that is held at a temperature T_1 on one surface and at a temperature T_2 on the opposite surface while the other surfaces are assumed to have periodic boundaries. The heat conduction equation is solved using a finite differences method until a stationary state is achieved. An effective heat conductivity is derived from the heat flow in the final stationary state. We present the current progress of our modelling for cubes of different composition and porosity to explore the dependence of heat conductivity on the composition at different temperatures. The results will be compared to existing measurements of chondritic material in the literature.

[1] Henke et al. 2012a, A&A 537:A45-1-19

TEC-P01

Phase transitions of $\text{Ca}(\text{Ti,Fe,Mn})\text{O}_{3-d}$ perovskites

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Phases with perovskite and perovskite-type structures have a strong technical potential for example in the field of fuel cells, as catalysts, clinker phases in different types of cements. Because temperature is an important factor in all of those fields of technical interests, those phases were investigated for possible phase transitions, stability fields and disintegration temperatures.

Perovskite solid solutions with the chemical composition $\text{CaFe}_x\text{Ti}_{(1-x)/2}\text{Mn}_{(1-x)/2}\text{O}_{3-d}$ with $0 \leq x \leq 0.33$ were synthesised by the Pechini process, applying Ca-, Fe-, Mn- nitrates and $\text{C}_{12}\text{H}_{28}\text{O}_4$ Ti together with citric acid and ethylene glycol.

After sintering the precursors pure perovskites with space groups Pnma, I4/mcm and Pm-3m were obtained. The structures of those ternary perovskites are composed of octahedra, which belong to specific tilting systems described by Glazer (1972), Howard et al. (1998), Woodward (1997).

X-ray data were collected on a Panalytical X'pert and Empyrean system equipped with a HTK 1200 applying molybdenum radiation. Lattice and structural parameters were refined by rietveld method using the software package Topas academic 4.1.

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TEC-P02

Hydrothermal Solution of Heavy Metals from MSWI Residues

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The solid residues produced during municipal solid waste incineration (MSWI) may be grouped into bottom ashes and fly ashes. Pure metals like Fe, Al or Cu can be separated from the bottom ashes by physical methods but there are no attempts to extract NE metals like Zn and Pb which are incorporated in oxide, chloride or silicate mineral phases. In MSWI bottom ashes the Zn- and Pb-contents vary from 2000 ppm up to 7000 ppm and 1000 ppm up to 3500 ppm, respectively. The fly ashes were usually collect by filters like electrostatic precipitator (ESP). In ESP residues the Zn- and the Pb-contents are much higher covering a range from 5000 ppm up to 100000 ppm for Zn and from 2500 ppm up to 25000 ppm for Pb, respectively. Due to the high concentration of heavy metals as well as trace amounts of organic pollutants (dioxins, furans) the ESP residues are classified as hazardous material. In the last years a paradigm change took place. Now hazardous material becomes a resource for the heavy metals if the organic pollutants can be destroyed. A promising technique is the hydrothermal solution, transport and precipitation leading to separation and enrichment of heavy metal compounds. In addition dioxins and furans were destroyed in the presence of an oxy-hydrous vapor phase at a temperature of 180°C. The yellowish material exists of spherical glass droplets of ca. 100 µm diameter, condensed alkali-chlorides and black carbon particles. Some of the glass droplets are devitrified forming gehlenite, clinopyroxene and spinel. The Zn- and Pb-content of the investigated ESP residues are 36000 ppm for Zn and 19000 ppm for Pb. The Zn- and Pb-bearing mineral phases were characterized by X-Ray Powder Diffraction (XRPD) and Electron Microprobe Analysis (EMPA). In ESP residues Zn and Pb forms mainly chlorides. Zn is also condensed on the surface of the spherical glass droplets. The solution process is mainly controlled by ionic strength of the solvent next to surface and temperature. The leaching experiments were performed under hydrothermal conditions in the temperature range from 50°C up to 200°C, at pH pH <2 by using a solid-liquid ratio of 1:10 or 1:16.5. The Zn- and Pb-concentrations of the eluates were analyzed by AAS. The extraction of Zn and Pb of the ESP residues strongly depends on the pH-value. The kinetic studies reveal a high solution rate. At these conditions up to 100% of total Zn and up to 90% of total Pb of ESP ashes can be recovered.

[1] S. Heuss-Assbichler, G. Magel and K.T. Fehr, *Waste Management*, 30,1871, (2010). [2] A.B. Bayuseno and W.W. Schmahl, *Waste Management*, 30, 1509-1520 (2010)

TEC-P03

Usage of secondary raw materials (residual bauxite, laterite and residual kaolin) for the synthesis of CSA-based cements

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In the synthesis of CSA-based (CSA= calcium sulfoaluminate) cements the application of the experiment planning program STAVEX will be tested for the optimization of this cement system. CSA-Cements are of importance due to their lower energy production compared to Portland cements. The sintering temperature is up to 200 °C lower [1]. In addition, the CO₂- emissions are lower for a CSA-Cement production. With the use of secondary raw materials also some reduction in CO₂ and protection of the environment can be obtained.

The weight proportions of the components are set to 30-70 wt.-% limestone, 10-20 wt.-% anhydrite, 0-40 wt.-% laterite or bauxite and 20-50 wt.-% kaolin (Fig. 1). The milled blends are sintered for one hour in a furnace at 1100-1200 °C. With X-ray powder diffractometry the different phases in the cement system can be analysed and quantified. STAVEX enables the statistical analysis of the test results, gives an idea on optimization and generates if necessary succession plans

experiment no.	limestone (wt.-%)	laterite/bauxite (wt.-%)	anhydrite (wt.-%)	kaolin (wt.-%)	temperature (°C)
1	70	0	10	20	1100
2	30	40	10	20	1100
3	60	0	20	20	1100
4	30	30	20	20	1100
5	30	0	20	50	1100
6	40	0	10	50	1100
7	70	0	10	20	1200
8	30	40	10	20	1200
9	60	0	20	20	1200
10	30	30	20	20	1200
11	30	0	20	50	1200
12	30	10	10	50	1200
13	41	11	14	32	1200
14	50	20	10	20	1100
15	30	35	15	20	1100
16	30	25	10	35	1100
17	55	0	10	35	1200

Fig. 1: Experimental plan generated with STAVEX.

[1] Álvarez-Pinazo, G. et al. (2012): Rietveld quantitative phase analysis of Yeelimite-containing cements. Cement and Concrete Research, 42, 960-971.

TEC-P04

Investigations of lamellar tetrastrontium aluminate hydrates

$[\text{Sr}_3\text{A} \cdot \text{SrX} \cdot n\text{H}_2\text{O} (\text{X} \in \{(\text{OH})_2, \text{Cl}_2, (\text{NO}_3)_2, \text{CO}_3, \text{SO}_4\})]$.

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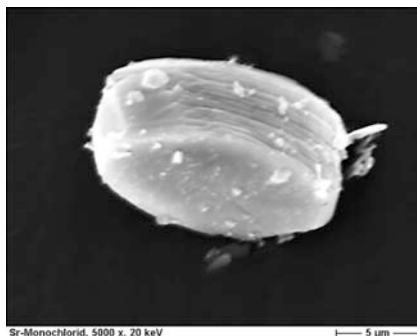
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Calcium aluminates are the main phases in calcium aluminate cements and can form calcium aluminum hydrate phases during the hydration. These phases are significant for the setting process of cements as well as for the formation of mineral reservoirs. Strontium aluminates were used for many different applications like high refractory cements and photoluminescent materials. Results from previous studies [1, 2] revealed that strontium aluminates have similar hydration properties like calcium aluminates. Mono- and tristrontium aluminate hydrates form the same crystal habit like the calcium equivalent and generally show temperature and time dependent conversions during the hydration process. For this reason, the reactive behavior between strontium aluminates (SrA / Sr_3A), the strontium salts $\text{Sr}(\text{OH})_2$, SrCl_2 , $\text{Sr}(\text{NO}_3)_2$, SrSO_4 and SrCO_3 were studied to compare the formation of TCAH- and TSrAH-phases. The reactions were tested at different temperatures (8 °C, 25 °C & 45 °C) and water/solid-ratios (1, 2 & 5) in 60 ml PET bottles under a nitrogen atmosphere.

Finally, the strontium-AFm-phases Sr-monochloride and Sr-mononitrate were observed. X-ray diffraction studies have revealed structural similarities to the calcium equivalents. The basal spacings, measured at room temperature, were at 8.06 Å (Sr-monochloride) and 8.61 Å (Sr-mononitrate). The phases were analyzed with SEM for optical characterization. The obtained crystals were well formed with a hexagonal (pseudo-hexagonal) and layered habitus (Fig. 1). The experiments, while using $\text{Sr}(\text{OH})_2$, SrSO_4 and SrCO_3 , did not formed LDH-structures, because the solubility and reactivity were probably too low.

Figure 1: SEM image of Sr-monochloride (conditions of hydration: $t = 7\text{d}$, $w/s = 5$, $T = 25^\circ\text{C}$).

- [1] Pöllmann, H. & Kaden, R. (2014): Mono(strontium/ calcium) aluminate based cements. - Proceedings Conference on Calcium Aluminates (Avignon), 99-108.
- [2] Kettmann-Pommnitz, M. R. (2014): Synthesis and Characterization of strontium and barium aluminate hydrates. - Master thesis (german), Martin-Luther-University Halle-Wittenberg, Halle.



TEC-P05

In-situ studies on Li-mobility in compacted powdered solids

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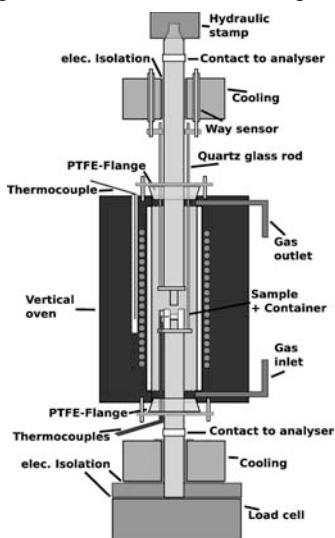
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While developing new lithium conducting materials with specific properties, it is beneficial to understand processes and parameters controlling Li-diffusion in solids. In particular in the field of materials for rechargeable batteries, an important issue is how boundaries in the interior of solids affect charge mobility. The present study is focussed on lithium-conducting glasses. New insights on volume- and grain-boundary diffusion in such materials are obtained by in situ impedance spectroscopy using a new type of axial compression apparatus. Powders with defined grain size fractions are compacted between two Inconel pistons within a vertical furnace. The apparatus allows varying temperature up to 600°C and pressure up to 10 kbar. Electrical conductivity and volume of the powdered sample (grain size from nanometer to several hundred of micrometer) as well as the force on the sample are continuously monitored. Powders can be pre-conditioned at temperature by flushing with gases before closing the sample chamber. Thus, effects of oxygen and water fugacity on powder properties can be studied.

First measurements were performed on silicate and aluminosilicate glasses. While heating below the glass transition temperature the powder is only mechanically compacted. At higher temperature, glasses start to flow resulting in welding the powder to a complex structure of grains and pores. With increasing pressure, sample volume and pore space decrease. Thus, it is possible to study the effect of pore space and grain connectivity on Li-transport.

Dielectric studies on glasses show two distinct contributions to overall conductivity featuring two separate time-constants. The findings can be explained by fast Li-motion in the grain interior and slower motion along grain boundaries. With increasing grain-grain contact during compaction, overall conductivity increased up to values of the corresponding glass, while the contribution in the lower frequency region gradually disappeared. This makes tuning of the ratio of both processes in the compressed sample possible.



TEC-P06

Modeling of Blast Furnace Slag induced Corrosion of fully Y_2O_3 -Stabilized Zirconia

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The corrosion of cubic Zirconia with 12mol% Yttria (FSZ) ceramic by model silicate slags was investigated at 1600°C as part of a work to evaluate the mechanisms and kinetics of degradation processes in Zirconia based blast furnace refractories by this kind of slags. The observed degradation phenomena of the ceramic were analyzed by Raman spectroscopy and electron microprobe.

In experiments a model slag with an anorthitic composition (25 mol% CaO, 25 mol% Al_2O_3 , 50 mol% SiO_2) was used to provide a simple but typical slag composition with a good knowledge of slag parameters like basicity, wetting behavior and viscosity. The experiments were performed as crucible tests at 1600°C for 12 h using a FSZ-crucible containing the melt.

We found a strong infiltration and interaction of the slag with the ceramic of the crucible. Both ZrO_2 dissolution and leaching of the stabilizing Y_2O_3 into melt occur. As a consequence we observe a disintegration of individual grains and phase transformations from the fully stabilized cubic zirconia into tetragonal and monoclinic modifications.

In contrast to other corrosion related Zirconia phase transformations, where a grain-by-grain process is observed (e.g. during hydrothermal low-temperature degradation processes), the leaching of the stabilizer in our melt corrosion experiments starts at the grain boundaries and seems to proceed continuously towards the grain interior. The interplay of grain disintegration into smaller grains and stabilizer leaching creates core-shell structures, either c- ZrO_2 with rims of t- ZrO_2 or t- ZrO_2 grains with shells of monoclinic ZrO_2 . The allover picture is thus one of a quasi-layer like build up starting from regions of c- ZrO_2 to those of t- ZrO_2 and finally m- ZrO_2 . However, the process differs from simple diffusion controlled layer forming corrosion, because the disintegration by cracking due to expansion stresses from the t- ZrO_2 to m- ZrO_2 transformation is capable to modify the boundary conditions while the process is active. We present evidence for this model by Raman-single-grain-tomographic-mappings performed on several grains at different stages of transformation process. These qualitative Raman analyses comply with the quantitative WDS analyses of these grains. We will discuss the resulting quantitative kinetic descriptions in our contribution.

The mineral record of impact events

IMP-T01

The Lake Bosumtwi impact structure: Ivory Coast tektites and microtektites, fall back glass and glass shards in suevites: geochemical distinctions and similarities

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The excellently preserved, 1.07 Ma Bosumtwi impact structure, Ghana (D ~10.5 km), is a very rare example of a terrestrial crater: It is not only source of a tektite (Ivory Coast tektites - IVC) and a widespread microtektite (IVC-MT) strewn field but also has preserved glass particles (FBG) in the fall back layer that seals the breccia sequences. In addition, suevites around the crater contain impact glass shards (BOT 12), and target rocks are well exposed and have been recovered in ICDP drill cores. These extraordinary circumstances allow constraining precursor lithologies, and differences in geochemical processes during formation and ejection of these four groups of impact glasses. Analytical techniques used include EMP (major elements), in situ LA-ICP-MS (42 trace elements), and TIMS (Sr, Nd isotope compositions). Major element differences between the four groups of glasses are largest with regard to MgO, CaO, and Na₂O with notable CaO depletion in IVC and IVC-MT compared to the upper continental crust (UCC). Meta-graywacke, the most prominent target rock, is obviously the only precursor material in all glass. Some meta-graywacke samples have very high contents of Ni, Co, and Cr due to contributions of meta-volcanics in the Bosumtwi target region. Trace element distributions show little variations within the groups of glass, but differences between the groups exist. IVC, IVC-MT, and BOT 12, yet not FBG have similar high abundances of “meteoritic” tracer elements, obviously inherited from the meta-graywacke precursor, masking any possible contribution of projectile matter to the impact glasses. REE distribution patterns of all four groups are homogeneous within each group, and very similar to UCC patterns; only IVC show a minor Ce anomaly, pointing to some alteration in the precursor material. Compared to UCC, distribution patterns of the other trace elements in the glass all display major, yet different depletion of moderately volatile elements. Most drastic is this effect in IVC-MT, followed by IVC and FBG, while glass in BOT 12 is less affected. This result indicates that the four groups of glass were subjected to strongly different maximum temperatures. Sr in samples from (recent) soil is by far more radiogenic than Sr in IVC, and hence, can be excluded as significant precursor material.

IMP-T02

Influence of porosity on shock metamorphism and classification

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During an impact event target rocks are affected by a shock wave. High pressures and temperatures generated by the passage of the shock wave cause a progressive sequence of shock effects (deformation, transformation, decomposition, melting) in the minerals (e.g., Langenhorst 2002). The shock classification is based on these progressive stages of shock metamorphism (Stöffler and Grieve 2007). Shock recovery experiments are employed for the calibration of shock effects. In the past mainly single crystals were used for such calibration. Nevertheless, the influence of multi-phase assemblages and especially porosity can not be neglected. Two examples are introduced: (1) Within the experimentally shocked H6 chondrite Kernouvé (porosity ~9 %) the onset of mosaicism in olivine is observed already at 10 GPa in contrast to 15 GPa in experiments with olivine single crystals. The phase transformation of oligoclase to maskelynite (diaplectic feldspar glass) occurs between 25 and 30 GPa in contrast to 30 to 34 GPa in single crystal experiments. (2) In experimentally shocked Seeberger sandstone (porosity ~27 %) melting of quartz starts already at shock pressures as low as 5 GPa, and increases continuously at higher pressures. At 17.5 GPa about 80 % of the quartz is transformed to diaplectic quartz glass, normal glass, and SiO₂ melt. This is significantly different to the results of experiments with quartz single crystals, where the transformation of quartz to diaplectic glass occurs at ~35 GPa. These observations can be explained by pore collapse that leads to significant shock pressure and temperature amplification not only restricted to the pores but also to larger areas in their environs (Kowitz et al. 2013).

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The mineral record of impact events

IMP-T03

New high-pressure phases in the Tissint Martian meteorite indicate small size of Mars impacting body

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The olivine-phyric shergottite Tissint is a Martian meteorite that was observed falling to Earth in July 2011 in Morocco [1]. Here we report on its shock metamorphic effects and, in particular, the occurrence of high-pressure mineral phases in melt pockets that provide insights into the time scales of mineralogical processes during shock loading and unloading.

Five thin sections prepared from two fragments of Tissint were studied using optical microscopy, electron microprobe analysis and Raman spectroscopy at the Museum für Naturkunde Berlin.

The complete transformation of plagioclase to maskelynite and the occurrence of planar fractures and strong mosaicism in olivine constrain the peak shock pressure in Tissint to 30-42 GPa. The high-pressure phases ringwoodite, ferropericlase, vitrified MgSiO₃-perovskite, xieite and jadeite, as well as the newly found (Na,Ca)-hexaluminosilicate and Mg- and Fe-rich Ca-Eskola-containing pyroxene formed in shock melt during pressure release at pressures between >23 and 1.5 GPa.

Three shock melt pockets have nearly completely crystallised to highly aluminous, non-stoichiometric pyroxene with an average formula of (Ca_{0.39}Na_{0.10}□_{0.06})(Mg_{0.67}Fe_{0.43}Al_{0.31})(Si_{1.89}Al_{0.11})O₆ (□: cation vacancy) and endmember components CaTs₁₁ CaEs₁₂ Jd₈ Aug₁₁ Opx₅₀ Ti-Px₁. This pyroxene is different from the new mineral *tissintite* (Ca,Na,□)AlSi₂O₆ [2], in that it contains significant Mg and Fe. There is only one other reported occurrence of this phase in meteorites [3].

Shock melt pockets of ca. 100 µm in size cooled in 10⁻²-10⁻³ s and, as the preservation of high-pressure phases requires temperature and pressure to decrease at similar rates, the shock duration is ca. 10⁻²-10⁻³ s. From this we deduce that the pre-impact location of the Tissint source lithology was 5-250 m beneath the surface of Mars and the size of the impacting projectile was 50-2500 m. These results are consistent with previous estimates for Tissint and other shergottites but strongly contrast those of Baziotis et al. [4], who claimed that high-pressure phases in Tissint are indicative of a very large impactor size (10 km).

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IMP-T04

Two stages of liquid immiscibility preserved in young impact glasses

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Hypervelocity impacts cause melting of the projectile (meteoritic material) and the target (e.g., rocks of the upper crust). Heterogeneities of impact melts may result from mingling of melts produced by partial melting of various lithologies and the admixture of projectile material, both followed by incomplete homogenization. We present case studies that document these heterogeneities of impact melts involving liquid immiscibility of silicate melts. The impact melt rock of the Wabar craters (Saudi Arabia) has mainly formed from melting of quartz-rich dune sand and shows a very low [M.E.1] degree of crystallization. The Wabar glass has preserved the dynamics of projectile-target interaction with Fe-Ni-droplets (molten iron meteorite) that have entered the molten target, thereby supplying various amounts of iron to the silicate melt [1]. Cooling of the Fe-rich high-temperature silicate melt resulted in liquid immiscibility and the formation of an emulsion of Fe-rich ultramafic melt (L_{Fe}) and Si-rich melt (L_{Si}). Crystallization of fayalite may occur in L_{Fe} . Impact melt rock from the Barringer Crater (Arizona, USA) shows a much higher degree of crystallization, although some glassy parts of the melt rock also have preserved small droplets of the projectile (Canyon Diablo[CH2] iron meteorite). Textures and chemical compositions of [CH3] pyroxene and olivine indicate fast disequilibrium crystallization. Residual melt in the mesostases shows emulsions of Fe- and Ca-rich ultramafic and Si-rich melts formed by low-temperature liquid immiscibility induced by fast crystallization, shifting the remaining melt composition into a well-known two-liquid field [2]. Melt compositions and textures strongly resemble immiscible liquids in the mesostases of tholeiitic basalts [2]. Almost identical processes of projectile-target interaction including high-temperature liquid immiscibility have been reproduced under controlled conditions by hypervelocity impact experiments of the MEMIN research group at <6km/s projectile speed [3].

[1] Hamann C. et al. (2013) *GCA* 121, 291-310. [2] Philpotts A.R. (1982) *CMP* 80, 201-218. [3] Ebert M. et al. (2014) *GCA* 133, 257-279.

The mineral record of impact events

IMP-T05

Element partitioning processes between iron-rich projectiles and silica-rich targets in hypervelocity impact experiments

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Introduction: The investigation of projectile traces in impactites is of great value for reconstructing the type of extraterrestrial material that penetrated the Earth [1]. We present experimental results about how impact energy, water-saturation of the target, and target porosity affect partitioning of projectile elements during mixing of projectile and target melts.

Method: In the context of the MEMIN program [2], impact experiments were performed at the acceleration facilities of the Fraunhofer Ernst-Mach-Institute (Freiburg, Germany) using steel and Fe-meteorite projectiles, and targets of quartzite and sandstone; some of the latter have been saturated with water. Projectile masses of 0.07 and 7.33 g and an impact velocity of $\sim 5 \text{ km s}^{-1}$ result in impact energies of $\sim 0.76 \text{ kJ}$ and 81 kJ , respectively.

Results: During the highly dynamic impact process projectile droplets were injected into target melts. Element fractionation occurs during mixing of these melts. The target melts are enriched in the projectile tracer elements Cr, V, and Fe but have just minor enrichments of Co, Ni, W, and Mo. The degree of enrichment is controlled by the lithophile or siderophile character of the tracer elements. The fractionation results from differences in the reactivity of these elements with oxygen during interaction of metal melt with silicate melt. Different geochemical behavior of the tracer elements leads to element ratios in the target melts, which differ strongly from the respective element ratios of the projectile. The degree of water-saturation in the target and different impact energies obviously do not affect the described processes, at least at the scale of our experiments. Partitioning of the projectile elements into the target melts is intensified in experiments with non-porous quartzite compared the porous sandstone target. This is mainly the result of higher shock pressure and the related higher post-shock temperatures.

Conclusions: From our perspective, small scale geochemical processes, like (i) partitioning of projectile elements into target melts and (ii) associated phase separation into Fe-rich and Si-rich melts seem to be common feature during projectile/target melt-mixing.

[1] Palme H. et al. (1981) *GCA* 45, 2417-2424 [2] Ebert M. et al. (2013) *MAPS* 48, 134-149 [3] Hamann C. et al. (2013) *GCA* 121, 291-310

IMP-T06

Nanostructure of Popigai impact diamonds by HRTEM, SEM, and AFM studies

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Impact diamonds are widely studied around the world. In spite of numerous publications a description of micro- and nanostructures in the impact diamond polycrystalline aggregates is far from being complete. Therefore, high resolution investigations coupled with atomic scale studies are of paramount importance. Here we present the high resolution studies of impact diamonds from Popigai astrobleme (Siberia, Russian Federation) by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) supplemented by a complex of EELS, Raman spectroscopy, X-ray diffractometry and X-ray synchrotron measurements.

Different carbon states forming tight joint phase (cubic and hexagonal diamond polymorphs, graphite, amorphous carbon, fullerene-like/onion-like carbon) aggregates were found in Popigai impact diamonds (Shumilova et al., 2014). The formation of onion-like carbon is supposed to be connected with transformation of diamond nanocrystallites back to sp^2 carbon at remnant temperature or by high pressure graphite transformation.

The nanostructural studies of Popigai impact diamonds (at atomic resolution level as well) demonstrate that some varieties or parts of impact diamond grains contain large volume of elongated single nanocrystallites (Figure) and amorphous carbon (Shumilova et al., 2014).

The studied Popigai impact diamonds reveals some similar nanostructure features to the recently described “amorphous diamond” (Lin et al., 2011) and quasi-crystalline carbon (Wang et al., 2012) that could explain the high hardness of the impact diamonds.

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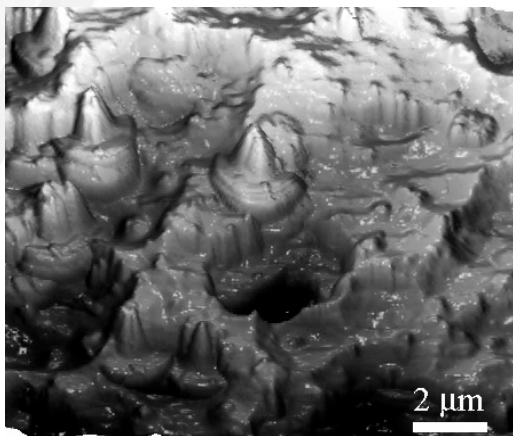


Fig. An AFM surface image of the nontextured Popigai impact diamond with planar and elongated nanocrystallites.

IMP-P01

A martensitic mechanism for the zircon-to-scheelite transformation

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Zircon transforms at high-pressure to the scheelite-structured polymorph reidite. This high-pressure polymorph has so far only been discovered in various impact craters. Reidite forms apparently in solid-state. Therefore a rapid two-stage transformation mechanism has been proposed to operate within the short time scale of an impact event [1]. In this study we readdress the details of this transformation process in the light of the defect microstructure of shocked zircon. Shock experiments have revealed abundant planar defects parallel to {100} planes of zircon and an epitaxial relationship between zircon (Zr) and reidite (Rei) with {100}Zr // {112}Rei and [001]Zr // <110>Rei [2]. Close inspection of the zircon structure shows that the cation positions of Zr and Si in zircon can be displaced into the positions expected in reidite by a glide system operating on the {100} planes with a displacement vector of $\frac{1}{4}$ <010>. After this martensitic shear mechanism displacive rotations of oxygens around the cations fully convert the zircon structure into the scheelite structure. This two-stage transformation mechanism is similar to that described by [1], but additionally introduces a glide system that enables martensitic shearing. Altogether the transformation model provides a consistent explanation for the conversion of chains of edge-sharing SiO₄ tetrahedra and ZrO₈ dodecahedra in zircon to chains of only corner-sharing polyhedra in reidite.

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[2] Leroux, H., et al., Experimental shock deformation in zircon: a transmission electron microscopic study. *Earth and Planetary Science Letters*, 1999. **169**(3-4): p. 291-301.

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IMP-P02

Laser shock experiments on olivine

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Among the various techniques (e.g. high-explosive experiments, gas guns) to experimentally reproduce the effects of natural impact events in minerals, the irradiation with laser light is one option to create high shock pressures, however, with the drawback of very short pressure pulses ($\sim$ ns). Here, we report on experiments with olivine thick-sections that were irradiated by ultrashort laser pulses (pulse duration ca. 100 fs) with different pulse energies (0.1 - 4.5 mJ) and different numbers of pulses at the same site. Damaged sample areas were characterized by polarized light microscopy and scanning electron microscopy (SEM).

The observations reveal the formation of planar fractures (PFs) within shallow, circular craters. The crater diameter varies from 40 μ m (at 0.1 mJ) to 200 μ m (at 4.5 mJ). PFs occur in dense arrays and are aligned in multiple orientations that appear to coincide with crystallographic planes. Optical measurements of the angles between two different sets of PFs in one crystal are compatible with the commonly known PF orientations in olivine. SEM inspection shows the detailed surface structure of the laser-affected material, which occurs as thin continuous sheets. Beyond the rim of these blankets there can be rays and droplets of deposited material. The overall appearance of the blankets suggests that they represent quenched melts.

The results of our study substantiate that, despite the short pressure pulse, intense laser irradiation is a suitable technique to generate microstructural impact effects known to occur in naturally shocked minerals.

IMP-P03

TEM-studies on the Tissint meteorite – chemical and structural characterisation of dendritic olivine in melt pockets

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Fragments of the martian shergottite fall were found in the Moroccan desert near the town Tissint in 2012 [1]. Preliminary petrographic investigations (including light microscopy, SEM and Raman spectroscopy) showed that the basaltic poikilitic texture yields a complex network of glassy shock veins and melt pockets, the latter containing dendritic olivine. Mechanical sizing of these crystals made them suitable for TEM-measurement. Diffraction patterns verified general olivine crystal structure. Most interesting were verifiable amounts of potassium in the crystals of >5 wt-%. Further analyses might explain the origin of this remarkable composition.

[1] Garvie et al, 2012. MetBull 100, Meteoritics & Planetary Science.

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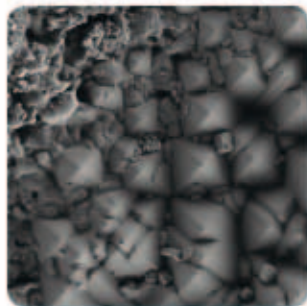
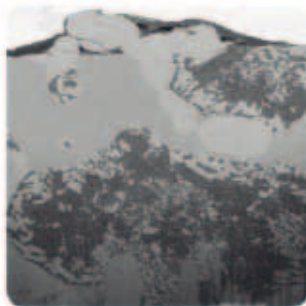
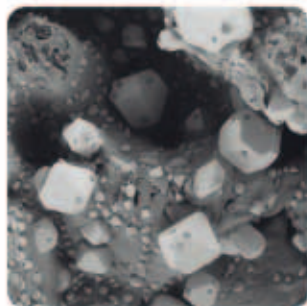


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