

HALLESCHES JAHRBUCH FÜR GEOWISSENSCHAFTEN

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der Martin-Luther-Universität Halle-Wittenberg

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Band 31

**87. Tagung der
Deutschen Mineralogischen Gesellschaft
vom 13. – 16. September 2009
an der Martin-Luther-Universität Halle-Wittenberg**

Programm, Kurzfassungen, Exkursionen /
Programme, Abstracts, Excursions



Halle (Saale) 2009
Institut für Geowissenschaften
der Martin-Luther-Universität Halle-Wittenberg

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(Tagungsleitung)

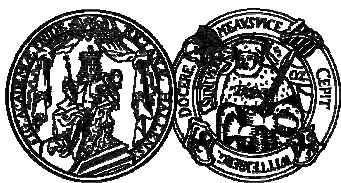
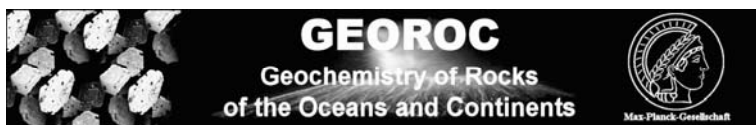
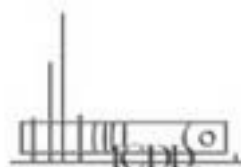
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13.-16. September 2009 in Halle (Saale)

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Sponsoren der DMG-Tagung 2009 in Halle (Saale):



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Vorwort

Mit dem vorliegenden Band 31 des Halleschen Jahrbuchs für Geowissenschaften sollen die, anlässlich der Jahrestagung der Dt. Mineralogischen Gesellschaft vom 13. bis 16. September in Halle, eingereichten Vorträge und Poster als Abstracts zusammengefasst werden. Die verschiedenen Symposien, die von den Tagungsorganisatoren Gregor Borg, Kurt Friese und Herbert Pöhlmann zusammen mit den Convenern der einzelnen Symposien erarbeitet wurden, sind nachstehend zusammengefasst.

1 SYMPOSIUM GEOCHEMIE/PETROLOGIE

1.1 Metamorphe Prozesse

Convener: Walter Maresch, Universität Bochum [walter.maresch\(at\)rub.de](mailto:walter.maresch(at)rub.de)

Keynote speaker: Armin Zeh, Universität Würzburg : *Detailed P-T-t Paths – new methods – new challenges*

1.2 Geochronologie, etablierte Verfahren – neue Ansätze

Convener: Rolf Romer, GFZ Potsdam [romer\(at\)gfz-potsdam.de](mailto:romer(at)gfz-potsdam.de) &

Axel Gerdes, Universität Frankfurt [gerdes\(at\)em.uni-frankfurt.de](mailto:gerdes(at)em.uni-frankfurt.de)

1.3 Magmatische Prozesse:

Conveners: Kevin Klimm, Goethe-Universität Frankfurt am Main [klimm\(at\)mineralogie.uni-hannover.de](mailto:klimm(at)mineralogie.uni-hannover.de),

Ralf Halama, CAU Kiel [rh\(at\)min.uni-kiel.de](mailto:rh(at)min.uni-kiel.de) & Francois Holtz, Universität Hannover
[f.holtz\(at\)mineralogie.uni-hannover.de](mailto:f.holtz(at)mineralogie.uni-hannover.de)

Keynote speaker: Andreas Stracke, ETH Zürich : *Linking basalt to mantle source signatures*

2 SYMPOSIUM MINERALPHYSIK / MINERALCHEMIE / KRISTALLOGRAPHIE

2.1 Analytische Methoden

Convener: Peter Stemmermann, FZ Karlsruhe GmbH [Peter.Stemmermann\(at\)itc-tab.fzk.de](mailto:Peter.Stemmermann(at)itc-tab.fzk.de) & Falko Langenhorst, Universität Bayreuth [Falko.Langenhorst\(at\)uni-bayreuth.de](mailto:Falko.Langenhorst(at)uni-bayreuth.de)

Keynote speaker: Max Wilke : *X-ray spectroscopic techniques using synchrotron radiation for studying geomaterials*

2.2 Allgemeine und Angewandte Kristallographie

Convener: Volker Kahlenberg, Universität Innsbruck [Volker.Kahlenberg\(at\)uibk.ac.at](mailto:Volker.Kahlenberg(at)uibk.ac.at)

Keynote speaker: Clivia Hejny, Universität Innsbruck : *Minerale mit inkommensurabel modulierten Kristallstrukturen*

3 SYMPOSIUM LAGERSTÄTTENKUNDE

3.1 Methodik in der Lagerstättenforschung

Convener: Jens Gutzmer, TU Bergakademie Freiberg [jens.gutzmer\(at\)mineral.tu-freiberg.de](mailto:jens.gutzmer(at)mineral.tu-freiberg.de)

Keynote speaker: Frank Melcher, BGR Hannover : *Discriminating "coltan" from African rare element pegmatites on the basis of mineralogy and geochemistry*

3.2 Supergene und hypogene Metallogenese

Convener: Gregor Borg, Universität Halle [gregor.borg\(at\)geo.uni-halle.de](mailto:gregor.borg(at)geo.uni-halle.de)

Keynote speaker: Gregor Markl, Universität Tübingen : *Fluid-mineral interaction during weathering of hydrothermal ore deposits deciphered from supergene mineral assemblages in the Schwarzwald area, SW Germany*

3.3 Exploration/Bergbau in Deutschland

Convener: Wolfgang Werner, LGRB Freiburg i. Br. [wolfgang.werner\(at\)rpf.bwl.de](mailto:wolfgang.werner(at)rpf.bwl.de) &

Jens Gutzmer, TU Bergakademie Freiberg [jens.gutzmer\(at\)mineral.tu-freiberg.de](mailto:jens.gutzmer(at)mineral.tu-freiberg.de)

Keynote speaker: Diethard Mager, Bundesministerium für Wirtschaft und Technik, Berlin : *Nationale und Europäische Aspekte der mineralischen Rohstoffsicherung*

4 SYMPOSIUM UMWELTMINERALOGIE / UMWELTGEOCHEMIE

4.1 Tonmineralphasen in Böden

Convener: Reinhold Jahn, Universität Halle [reinhold.jahn\(at\)landw.uni-halle.de](mailto:reinhold.jahn(at)landw.uni-halle.de)

Keynote speaker: Enver Murad, Marktrechwitz : *Tonminerale in Lagerstätten und Böden: die Rolle von Eisen und Titan*

4.2 CO₂-Sequestration

Convener: Christof Lempp, Universität Halle [christof.lempp\(at\)geo.uni-halle.de](mailto:christof.lempp(at)geo.uni-halle.de)

4.3 Mineral Interface Processes / Mineraloberflächenprozesse Mehr

Convener: Andrew Putnis, Universität Münster [Putnis\(at\)nwz.uni-muenster.de](mailto:Putnis(at)nwz.uni-muenster.de) &

Timm John, PGP Oslo / Münster [tim.john\(at\)fys.uio.no](mailto:tim.john(at)fys.uio.no)

Keynote speaker: Thorsten Geisler, Universität Münster / Universität Hamburg : *The interaction of minerals with aqueous solutions*

4.4 Mineralogische und geochemische Prozesse in Bergbauseen

Convener: Kurt Friese, UFZ Magdeburg [kurt.friese\(at\)ufz.de](mailto:kurt.friese(at)ufz.de)

Keynote speaker: Javier Sanchez, IGME, Madrid, Spanien : *Geochemical and mineralogical processes in the pit lakes of the Iberian pyrite belt (SW Spain)*

4.5 Umweltmineralogie

Convener: Dieter Rammlmair, BGR Hannover [Dieter.Rammlmair\(at\)bgr.de](mailto:Dieter.Rammlmair(at)bgr.de) &

Robert Heimann, Oceangate Consulting [Robert.heimann\(at\)ocean-gate.de](mailto:Robert.heimann(at)ocean-gate.de)

Keynote speaker: Petr Sulovsky, University of Olmouc, Tschechische Republik : *Mineralogy and human well-being: changing insights into nature*

5 SYMPOSIUM TECHNISCHE MINERALOGIE

5.1 Nichtkristalline Feststoffe

Convener: Gert Klöss, Universität Leipzig [kloess\(at\)rz.uni-leipzig.de](mailto:kloess(at)rz.uni-leipzig.de) &

Hans Roggendorf, Universität Halle [hans.roggendorf\(at\)physik.uni-halle.de](mailto:hans.roggendorf(at)physik.uni-halle.de)

Keynote speaker: Walter Lehmann, Fa. Heraeus Holding GmbH, Bitterfeld

5.2 Mineralogische Prozesstechnologien

Convener: Herbert Pöllmann, Universität Halle [herbert.poellmann\(at\)geo.uni-halle.de](mailto:herbert.poellmann(at)geo.uni-halle.de)

Keynote speaker: Johan de Villiers, Pretoria, Südafrika : *Process mineralogy: An ongoing challenge and opportunity for mineralogy and crystallography in the 21st century*

5.3 Hydrothermalforschung in Technik und Natur

Convener: Thomas Fehr, Universität München [fehr\(at\)min.uni-muenchen.de](mailto:fehr(at)min.uni-muenchen.de)

Keynote speaker: K. Byrappa: *Hydrothermal research: a soft-technology*

5.4 Baustoffe, Rohstoffe und Bauchemie

Convener: Stefan Stöber, Universität Halle [stefan.stoeber\(at\)geo.uni-halle.de](mailto:stefan.stoeber(at)geo.uni-halle.de)

Keynote speaker: Thomas Matschei, Fa. Holcim, Schweiz : *The way towards engineering cement hydrate phase assemblage*

5.5 Archäometrie und Denkmalpflege

Convener: Klaus Bente, Universität Leipzig [Bente\(at\)uni-leipzig.de](mailto:Bente(at)uni-leipzig.de)

Keynote speaker: Marcondes da Costa, Univ. Belem, Brasilien : *Archaeometric studies of ceramic materials from Amazon Dark Earth (ADE)*

6 ALLGEMEINE THEMEN

6.1 Museen und Sammlungen

Convener: Rupert Hochleitner, Universität München [Rupert.hochleitner\(at\)lrz.uni-muenchen.de](mailto:Rupert.hochleitner(at)lrz.uni-muenchen.de)

Keynote speaker: Hubert Roeser, Ouro Preto, Brasilien : *Die Mineralogischen Sammlungen der Bergbauschule (Escola de Minas) der Bundesuniv. Ouro Preto, in Minas Gerais, Brasilien*

6.2 Freie Themen

Convener: Thomas Witzke, Universität Halle [thomas.witzke\(at\)geo.uni-halle.de](mailto:thomas.witzke(at)geo.uni-halle.de)

Neben dem Vortragsprogramm findet auch ein umfangreiches Workshop- und Exkursionsprogramm statt :

Workshop GEMMOLOGIE : Reinhard Wegner, Bundesuniversität Campina Grande Paraiba Brasilien

Praktische Edelsteinkunde (Farbsteine) : Geplant ist ein Streifzug durch die Edelsteinkunde, in dessen Verlauf alle wichtigen Aspekte dieses Themenbereiches angesprochen werden. Besonderes Gewicht wird auf die praktische Edelsteinbestimmung gelegt und jeder Teilnehmer wird nicht nur die dazu notwendigen (einfachen) Geräte kennen lernen, sondern in deren praktischer Anwendung vorgelegte Steine selbst bestimmen. Die Grundlagen der Diamantgraduierung sind – aufgrund der Komplexität des Themas – aus diesem Kurs absichtlich ausgeklammert.

Workshop UMWELTISOTOPE UND IHRE ANWENDUNG : Stephan Weise & Gerhard Strauch, UFZ Halle/Leipzig

Der Kurzlehrgang (1,5 Tage) gibt eine Einführung und Übersicht über die Anwendung der stabilen Isotope von H, O, C, N und S u.a. in Fragen des Wasserkreislaufes, der Karbonatbildung, der Paläoklimaindikation und von Redoxprozessen. Am Nachmittag des 1. Tages findet eine Führung durch das Isotopenlabor des UFZ-Departments Isotopenhydrologie mit Demonstrationen statt. Der Kurs wendet sich an Interessenten ohne Vorkenntnisse.

Workshop ACID MINE DRAINAGE : Kurt Friese, UFZ Magdeburg, Dagamar Kock (BGR Hannover) & Ralph Schöpke (BTU Cottbus)

Der Kurzlehrgang gibt eine Einführung und einen Überblick über geochemische, mineralogische und mikrobiologische Aspekte der im Zuge von Bergbauaktivitäten auftretenden sauren Minenwässer. Am Ende des Kurses werden verschiedene Sanierungs- und Neutralisierungsverfahren vorgestellt. Der Kurs wendet sich an Studierende und Wissenschaftler ohne Vorkenntnisse.

Workshop FEUERFESTMATERIALIEN : Johannes Södje, Fa. Refaktechnik Cement GmbH

Im Kurs werden die wesentlichen Grundlagen feuerfester Roh- und Werkstoff behandelt. Anwendungsbeispiele aus der Praxis mit besonderer Betonung von Korrosionserscheinungen aus der Zement- und Stahlindustrie werden an Anschliffen während des Kurses besprochen.

Das umfangreiche Exkursionsprogramm stellt die nähere Umgebung von Halle mit seinen weit über die Landesgrenzen hinaus bekannten Lagerstätten, aber auch Industriestandorte Bergbaufolgelandschaften und kulturelle und historische Aspekte in den Vordergrund. Die folgenden Exkursionsangebote vor und nach der Tagung stehen auf dem Plan.

Exkursion 1 :**HALDE TEUSCHENTHAL, MINERALNEUBILDUNGEN, INVENTAR UND SPEKTRALE ERFASSUNG**

Organisatorin: Cornelia Gläßer [cornelia.glaesser\(at\)geo.uni-halle.de](mailto:cornelia.glaesser(at)geo.uni-halle.de)

Am Beispiel der Kali- und Steinsalzhalde Teuschenthal sollen die sehr kurzfristig ablaufende Ablaugung und Rekristallisation demonstriert werden. Die Ablaugungsprozesse unterliegen einem strengen jahreszeitlichen und meteorologischen Regime. In Abhängigkeit von Temperatur, Niederschlag und Luftfeuchtigkeit finden an der Oberfläche der Halde und im Bereich des Interflows des Haldenkörpers kurzzeitige Wechsel von Mineralphasen statt. Dadurch verändert sich die Ablaugungsgeschwindigkeit permanent. Durch hypodermischen Abfluss und dem Abfluss in oberflächennahen Grundwasserleitern tritt die Ablaue in Quellen in der Weitschkeniederung aus. Die Sickerwässer passieren ein ehemaliges Braunkohlentiefbaugelände und werden dabei hydrochemisch modifiziert. Die Verdunstung des Quellwassers führt ebenfalls zu jahreszeitlich unterschiedlichen sekundären Mineralsausscheidungen.

Exkursion 2**MINERALBILDUNGEN IN BÖDEN TECHNOGENER SUBSTRATE**

Organisatoren: Reinhold Jahn [reinhold.jahn\(at\)landw.uni-halle.de](mailto:reinhold.jahn(at)landw.uni-halle.de) & Thomas Kühn [thomas.kuehn\(at\)landw.uni-halle.de](mailto:thomas.kuehn(at)landw.uni-halle.de)

Auf Grund der Industrie- und Bergbaugeschichte ist Halle (S.) und die Umgebung reich an jungen Böden aus technogenen Substraten. Demonstriert werden Böden aus Kipp-Ruppeltonen (Versauerung und Glimmertransformation), aus Aschen der Braunkohlverbrennung (Ca- und Si-Dynamik, auftretende amorphe Phasen) und aus Ca-reichen Abfällen der Soda-Produktion (Bildung und Transformation von LDHs) mit Diskussion der aktuell ablaufenden bodenbildenden Prozesse, den auftretenden Mineraltransformationen und Neubildungen sowie den daraus resultierenden ökologischen Eigenschaften.

Falls zugänglich, findet auch eine Besichtigung der jüngst entdeckten chirotheriden und prosauropoden Fährten im Muschelkalk (ca. 243 Mio. Jahre) bei Bernburg.

Exkursion 3**KUPFERSCHIEFER ZWISCHEN HALLE UND HARZ – MINERALOGIE, GEOLOGIE, GESCHICHTE**

Organisatoren: Gerhard Bachmann [gerhard.bachmann\(at\)geo.uni-halle.de](mailto:gerhard.bachmann(at)geo.uni-halle.de) & Thomas Witzke [thomas.witzke\(at\)geo.uni-halle.de](mailto:thomas.witzke(at)geo.uni-halle.de)

Im Mansfelder Land zwischen Halle und Harz liegen neben einigen der wenigen instruktiven Aufschlüsse der Kupferschiefervererzung auch die historischen Haldenlandschaften. Die Exkursion

besucht zudem kulturgeschichtliche Stätten in der Heimat Martin Luthers die dessen familiäre Bindung an den mittelalterlichen Mansfelder Bergbau erläutern. Dieser Hintergrund macht seine Persönlichkeit und sein Werk noch klarer verständlich.

Exkursion 4

BRAUNKOHLEBERGBAU UND TAGEBAUSEEN

Organisatoren: Kurt Friese [kurt.friese\(at\)ufz.de](mailto:kurt.friese(at)ufz.de) & Martin Schultze [martin.schultze\(at\)ufz.de](mailto:martin.schultze(at)ufz.de)

Die Exkursion soll einen Überblick über den Braunkohlenbergbau in Mitteldeutschland von der Gewinnung über die Aufbereitung bis zur Renaturierung geben. Die Route wird den aktiven Bergbau am Beispiel des Tagebaus »Vereinigtes Schleenhain« (MIBRAG; mit Behandlung saurer Sumpfungswässer und Rekultivierungsmaßnahmen), die in Flutung befindlichen Altbergbaue »Witznitz« und »Zwenkau« (LMBV) sowie den ehemaligen, aus der Bergaufsicht entlassen Tagebau Cospuden (heute Badensee mit Sportbootaktivitäten) umfassen.

Exkursion 5

BERNBURG SALZ

Organisator: Thomas Degen [thomas.degen\(at\)geo.uni-halle.de](mailto:thomas.degen(at)geo.uni-halle.de)

Die Exkursion nach Bernburg wird uns in die esco european salt company, ein Unternehmen der K + S Gruppe führen und uns einen Einblick in einen über 700 m tief gelegenen Bergbau ermöglichen. Vorrangig findet der Salzabbau in Kavernen von 300 m Länge und 30 m Höhe statt. In einer Grubenbefahrung werden eine Borazit-Fundstelle und eine ausgespülte Kaverne zu sehen sein.

Exkursion 6

EXKURSION ZUR KULTURGESCHICHTE: AUF LUTHERS SPUREN

Organisator: Gerhard Bachmann [gerhard.bachmann\(at\)geo.uni-halle.de](mailto:gerhard.bachmann(at)geo.uni-halle.de)

Die Exkursion führt in die Lutherstadt Wittenberg mit ihren berühmten Stätten der Reformation, in die Dübener Heide und, nahe Leipzig, zu zwei großen Schlachtfeldern des Dreißigjährigen Krieges bei Breitenfeld (1631) und Lützen (1632) und verbindet dieses mit dem geologischen Hintergrund.

Abgeschlossen wird dieser Abstractband durch einige Exkursionsbeschreibungen. Selbstverständlich sind diese Abstractbeiträge für die Tagungsteilnehmer auch auf einer CD noch einmal zusammengefasst. Allen Beteiligten und Helfern, insbesondere auch unseren Sponsoren, die am Zustandekommen der Tagung mit beigetragen haben, soll auch an dieser Stelle noch einmal ganz gedankt werden.

Herbert Pöllmann, Halle (Saale)



Willkommen zur 87. Tagung der
Deutschen Mineralogischen Gesellschaft
an der Martin-Luther-Universität Halle-Wittenberg
13.-16. September 2009



Vorläufiges Tagungsprogramm

www.dmg2009halle.de

Sonntag, 13. September 2009

Vorexkursionen

Treffpunkt für alle Exkursionen: Institut für Geologische Wissenschaften, Von-Seckendorff-Platz 3, 06120 Halle / Saale. Die genauen Uhrzeiten werden noch bekannt gegeben.

HALDE TEUTSCHENTHAL, MINERALNEUBILDUNGEN, INVENTAR UND SPEKTRALE ERFASSUNG

Organisatorin: *Cornelia Gläßer*

Preis: bis zum 1. Juni 2009 30 EUR, danach 40 EUR

MINERALBILDUNGEN IN BÖDEN TECHNOGENER SUBSTRATE

Organisatoren: *Reinhold Jahn & Thomas Kühn*

Preis: bis zum 1. Juni 2009 30 EUR, danach 40 EUR

KUPFERSCHIEFER ZWISCHEN HALLE UND HARZ – MINERALOGIE, GEOLOGIE, GESCHICHTE

Organisatoren: *Gerhard Bachmann & Thomas Witzke*

Preis: bis zum 1. Juni 2009 30 EUR, danach 40 EUR

Workshop

GEMMOLOGIE, 13.9.09

Reinhard Wegner, Bundesuniversität Campina Grande Paraíba Brasilien

MLU, am Institut für Geowissenschaften

Preis: bis zum 1. Juni 2009 50 EUR, danach 60 EUR

18:00 Icebreaker-Party im Foyer des Audimax, Universitätsplatz

16:00–19:00 Uhr Teilnehmerregistrierung Melanchthonianum, Universitätsplatz, Medienraum im Erdgeschoss

Montag, 14. September 2009

08:00 Öffnung des Tagungsbüros im Melanchthonium, Medienraum im Erdgeschoss											
09:00 Eröffnung im Audimax, Saal XXII:											
Grußworte, Musik											
10:30-11:00 Kaffeepause											
Preisverleihungen: AG Werner Medaille: Prof. Putnis Georg-Agricola-Medaille: Prof. Filatov Kuzel-Preis: Promotion – Dr. Th. Matschei, Dipl.-Arbeit – Dipl.-Chem. Yang Han Öffentlicher Vortrag: Dr. Susanne Faulhaber, DFG: Fördermöglichkeiten der DFG											
12:20-13:30 Mittagspause											
Melanchthonianum, Saal 1			Audimax, Saal XXII			Melanchthonianum, Saal 3			Melanchthonianum, Saal 4		
5. Technische Mineralogie 5.2 Mineralogische Prozesstechnologie (Pöhlmann, MLU)			1. Geochemie / Petrologie 1.1 Metamorphe Prozesse (Maresch, Uni Bochum)			2. Mineralphysik / Mineralchemie / Kristallographie 2.1 Analytische Methoden (Stemmermann, FZK; Langenhorst, Uni Bayreuth)			4. Umweltmineralogie / Umweltgeochemie 4.1 Tonmineralphasen in Böden (Jahn, MLU)		
13:30	KEYNOTE 5.2 Johan de Villiers	Process mineralogy: An ongoing challenge and opportunity for mineralogy and crystallography in the 21 st century	13:30	KEYNOTE 1.1 Amin Zeh	Detailed P-T-t Paths – new methods – new challenges	13:30	KEYNOTE 2.1 Max Wilke	X-ray spectroscopic techniques using synchrotron radiation for studying geomaterials	13:30	KEYNOTE 4.1 Enver Murad	Tonminerale in Lagerstätten und Böden: die Rolle von Eisen und Titan
14:00	Johannes Södjé	Einfluss der aktuellen Prozessbedingungen beim Zementbrand auf das Feuerfestmaterial	14:00	Hans-Peter Schertl, Rolf D. Neuser	Cathodoluminescence (CL) microscopy of HP- and UHP-metamorphic rocks: New avenues for petrological applications	14:00	Maria Mrosko, Monika Koch-Müller, Ulrich Schade	A Synchrotron Microscope for pressure-dependent Far-Infrared Measurements in Diamond Anvil Cells under vacuum at BESSY	14:00	Reiner Dohrmann, Stephan Kaufhold	Wie genau sind CEC-Methoden?
14:20	Thomas Kühn, Herbert Pöhlmann	Synthese und Charakterisierung von zinkhaltigen Layered Double Hydroxides mit organischen Zwischenschichtanionen	14:20	Bernhard Schulz	EMP-monazite dating and thermobarometry of Variscan high-grade garnet gneiss (French Massif Central) – how can monazite provide time constraints on a P-T evolution?	14:20	Monika Koch-Müller, Dieter Rhede	IR absorption coefficients for H ₂ O in nominally anhydrous minerals	14:20	Thomas Witzke, Luis Omar Torres-Dorante	Untersuchungen zum Einsatz von LDH's der Hydrotalcit-Gruppe als Zwischenspeicher für Nitrat im Boden
14:40	Uwe Schweike, Krassimir Garbev, Günther Beuchle, Peter Stemmermann	Hydrothermale Herstellung von calciumarmen Zementen am Beispiel von Beitzement	14:40	Sven Sindern, Axel Gardes, Annika Dziggel, Yuri Ronkin, Ralf Hetzel	Metamorphic conditions and age of Proterozoic shearing at the eastern margin of the East European Craton	14:40	Peter Stemmermann, Krassimir Garbev, Biliana Gasharova	Anwendung von Synchrotronstrahlung in der Zementindustrie	14:40	Georg H. Grathoff	Allophane-Imogolite in young dunal soils replacing wood
15:00	Thorbjørn Schoenbeck, Roger Meier, Uwe Koenig	Application of Rietveld Analysis in the Aluminium Industry		15:00			Birgit Schampera, Stefan Dultz		Effect of bound H ₂ O layers on diffusive transport in compacted clays		
15:00-15:30 Kaffeepause											
			Cont.	Cont.			4.2 CO ₂ -Sequestration (Lempp, MLU)				
			15:30	Matthijs Smit, Erik Scherer, Michael Brocker, Herman van Roermund	Lu-Hf and Sm-Nd dating of zoned garnet in eclogites from the southernmost Scandinavian Caledonides	15:30	Krassimir Garbev, Günther Beuchle, Biliana Gasharova, Peter Stemmermann	Order-disorder in calcium silicate hydrate solid solutions as revealed by synchrotron based X-ray diffraction, thermogravimetry and Raman spectroscopy	15:30	Katja Beier, Wolf-Achim Kahl, Astrid Holzheld	CO ₂ -Sequestration on the laboratory scale – first results of chemical interaction processes between injected CO ₂ , saline fluids and potential reservoir materials
			15:50	Stefan Augustin, Kirsten Drüppel, Richard Wirth, Dieter Rhede	Mikroreaktionsgefüge und P-T-Entwicklung von Osumilitgneis, SW-Norwegen	15:50	Michael Ecker	Präzise Temperaturregelung für Probenträger	15:50	H. Marbler, K. Erickson, C. Lempp, M. Schmidt, H. Pöhlmann	The behaviour of CO ₂ and CO ₂ mixtures during the storage in deep geological formations
			16:10	Sönke Brandt, Volker Schenk, Michael M. Raith, Peter Appel, Axel Gardes	Sapphirine-bearing Mg-rich paragneisses from the Palni Hills (South India): Evidence for late Neoproterozoic UHT metamorphism in the Southern Granulite Terrane	16:10	Martina Menneken, Thorsten Geisler, Harald Strauß, Elen Kooijman	Applicability and limitations of Raman mass-spectroscopy on CO ₂ inclusions	16:10	K.M. Shams, H. Marbler, C. Lempp	Stress Conditions in Salinar Cap Rocks of the North German Basin as an Important Aspect of CCS Risk Assessment
16:30 Postersession und Ausstellung: Audimax Foyer und Melanchthonianum											
Audimax, Saal XXII											
18:30	DMG-Mitgliederversammlung										
20:00	Öffentlicher Abendvortrag: Prof. Dr. Ernst Pernicka, Universität Tübingen und CEZ Mannheim: Geochemische Spuren in Metallen – Herkunftsbestimmung archäologischer Metallfunde										

Dienstag, 15. September 2009

07:30 Öffnung des Tagungsbüros im Melanchthonianum, Medienraum im Erdgeschoss														
Melanchthonianum, Saal 1			Audimax, Saal XXII			Melanchthonianum, Saal 3			Melanchthonianum, Saal 4			Melanchthonianum, Saal 5		
5.5 Archäometrie & Denkmalpflege (Bente, Uni Leipzig)			1.1 Metamorphe Prozesse (Maresch, Uni Bochum)			2.2 Allgemeine und angewandte Kristallographie (Kahlenberg, Uni Innsbruck)			4.3 Mineraloberflächenprozesse (Putnis, Uni Münster; John, PGP Oslo)			6. Allgemeine Themen 6.1 Museen/Sammlungen (Hochleitner, LMU)		
08:30	KEYNOTE 5.5 Marcondes Lima da Costa	Archaeometric studies of ceramic materials from Amazon Dark Earth (ADE)	08:30	KEYNOTE 1.1 Walter Maresch, Michael Burchard, Nikos Doltsinis, Juliane Gross, Th. Fockenberg	Aqueous silicate solutions in metamorphic rocks at high pressures: What do we still need to know and how do we get the data?	08:30	KEYNOTE 2.2 Clivia Hejny, Hannes Krüger, Predrag Vulić	Minerale mit inkommensurabel modulierten Kristallstrukturen	08:30	KEYNOTE 4.3 Thorsten Geisler, Andrew Putnis	The interaction of minerals with aqueous solutions	08:30	KEYNOTE 6.1 Hubert Roeser, Ouro Preto	Die Mineralogischen Sammlungen der Bergbauschule (Escola de Minas) der Bundesuniv. Ouro Preto, in Minas Gerais, Brasilien
09:00	Matthias Krismer	Petrology of Pyrometallurgical Slags from the Prehistory: a indispensable tool for unravelling archaeometallurgical processes	09:00	Waheed Adeniyi Adeagbo, Nikos L. Doltsinis, Michael Burchard, Walter V. Maresch, Th. Fockenberg	Speciation of Ca ²⁺ in water as a function of T, P and PH. Ab-initio molecular dynamics simulation study	09:00	Andreas Richter, Matthias Göbbels	Stabilität und Kristallchemie von CaYAlAl ₂ O ₇ – einem Ca-Y-Al-Gehlenit	09:00	Samia Gurmani, Sandro Jahn, Heinrich Brasse, Frank R. Schilling	Atomic Scale View on Partially Molten Rocks via Molecular Dynamics Simulations of Mineral-Melt Interfaces	09:00	Massanek, Wolf Andreas	Bildungsangebote im Konzept der neuen mineralogischen Ausstellung terra mineralia im Freiburger Schloss Freudenstein
09:20	Manuela Frotzcher	Geochemische Charakterisierung mitteleuropäischer Kupfervorkommen zur Herkunftsbestimmung des Kupfers der Himmelscheibe von Nebra	09:20	Ralf Halama, Folkmar Hauff, Petra Herms, Volker Schenk, Timm John	Metasomatic processes in eclogites: Evidence from radiogenic (Sr, Nd) and stable (O) isotopes	09:20	Moritz-C. Schlegel, Reinhard X. Fischer	Comparison of crystal structure refinements of mordenite based on single-crystal and powder diffraction data	09:20	Encarnación Ruiz-Agudo, Christine V. Putnis, Andrew Putnis	Interactions between organophosphonates and calcite cleavage surfaces	09:20	Klaus Thalheim	Das „Silbernes Kreuz“, eine außergewöhnliche Silberstufe aus dem Nachlass von Kurfürstin Sophie von Sachsen (1568–1622)
09:40	Kirsten Drüppel, Andreas Kratzig, Helene Brätz, Lutz Martin, Nadja Cholidis, Gerhard Franz, Stefan Geismeyer	Aramaic basalt statues from Tell Halaf, Syria: localization of the ancient quarries	09:40	Friedrich Lucassen, Gerhard Franz, Peter Dulski, Rainer Abart, Dieter Rhode, Rolf L. Romer	Variations of HFSE (Nb, Zr) contents in rutile after partial replacement by titanite	09:40	Nouri-Saïd Rahmoun, Lars Peters, Wulf Depmeier	Sodalite-like layer structures in the series 4CaO* 3Al ₂ O ₃ * 3H ₂ O – 4CaO* 3Ga ₂ O ₃ * 3H ₂ O and their 3D sodalite-type dehydration products: The first gallate-sodalite established	09:40	C. Fischer, G. Darbha, A. Michler, Th. Schäfer, A. Lüttge	Colloidal particles and mineral surfaces: Surface reactivity as a function of surface roughness	09:40	J. Schlüter, D.C. Hezel, H. Kallweit	A new meteorite field in the united Arab emirates
10:00	Barbara Dammers, Klaus Bente, Robert Sobott, Hans-Joachim Höbner, Alexandra Franz	Archäometrische Untersuchungen an Keramikern der spät-neolithischen Vinča-Kultur (Rumänien)	10:00	Niels Jöns, Wolfgang Bach, Frieder Klein, Timothy Schroeder	Plagiogranitic melt impregnations in abyssal peridotites: their formation, alteration and influence on serpentinization	10:00	Susan Schorr, Boris Korzun, Christiane Stephan, Hannes Jahnke	Phase relations in the Cu ₂ S-FeS-FeS ₂ system	10:00	Arne Janßen, Maureen MacKenzie, Andrew Putnis	STEM/EELS investigations of the mechanism of experimental ilmenite alteration in dilute acids	10:00	Wolfgang Homann, Cornelia Bockrath	Goldrausch im Museum? Goldwäschversuche zur Standort-Bestimmung einer mittelalterlichen Pochmühle im Edergebiet
10:30-11:00 Kaffeepause														
11:00	Zoila Luz Eposi Ntah, Robert Sobott, Klaus Bente, Alexandra Franz	Archaeometrical analyses of pottery fragments from Cameroon	11:00	Ellen Kooijman, Klaus Mezger, Jasper Berndt	In situ LA-ICP-MS U-Pb dating of rutile from the Pikwitonei Granulite Domain, Canada: implications for Pb diffusion and the closure temperature	11:00	S.K. Filatov	Negative linear thermal expansion of crystals caused by rising symmetry	11:00	Christine V. Putnis, Bjørn Jamtveit, Anders Malthe-Sørensen, Thorsten Geisler	Reaction Induced Fracturing During Fluid-Rock Interaction	11:00	Gilla Simon	Die neue Internetseite des Arbeitskreises Mineralogische Museen und Sammlungen der DMG
11:20	Franz Ötner, Christoph Mitterlehner, Stefan Hartinger	Methoden zur Charakterisierung historischer Ziegel aus Wien	11:20	Axel K. Schmitt	In-situ U-Pb dating of Micro-Baddeleyite	11:20	Danylo Zhrebetskyy, Georg Amthauer, Michael Grodzicki	Electronic and magnetic structure of pyroxenes II. Orthoferrosilite	11:20	Andrea Koschinsky, James R. Hein	Sequestration of rare metals from seawater by ferromanganese oxides – implications from sorption experiments and XANES/EXAFS studies	11:20	Birgit Kreher-Hartmann	A very special collection for teaching
11:40	Joachim Lutz, Ernst Pernicka	Spurenelementchemische und bleisotopische Untersuchungen an frühbronzezeitlichen Metallfunden aus Mitteldeutschland				11:40	Ulrich Bismayer, Carsten Paulmann	Metamiktite Titanite	11:40	Andreas Mutter, Wulf Depmeier	Internal structure parameters of crystals and their morphological influence: A bond-valence approach	11:40	Melanie Kaliwoda, Rupert Hochleitner, Th. Ludwig, Rainer Altherr	New Investigations on the Meteorite Neuschwanstein
						12:00	Ramona Langner, Michael Fechtelkord	Solid state NMR spectroscopic investigations of Al-rich phlogopites synthesized at 873 K	12:00	Kilian Pollok, Dennis Harries, Julian Hopf, Katrin Hellige, Jana Sitte, Stefan Peiffer, Kirsten Küsel, Michael F. Hochella Jr., Falko Langenhorst	Biotic and abiotic alteration and formation of sulfides: differences and commonalities	12:00	Rupert Hochleitner, Karl Th. Fehr, Christian Rewitzer	Tiefhydrothermale Mo – V – Mineralisationen in der Betschen Kordillere, Südsanien
						12:20	S. Stöber, O. Prokhnenko, T. Döring, H. Pollmann	Eigenschaften von Perovskiten Ca(Fe,Mn,Ti)O _{3-d}				12:20	Hans-Joachim Höbner, Gert Klotz	200 Jahre Mineralogisch-petrographische Sammlung der Universität Leipzig

Dienstag, 15. September 2009, Cont.

Mittagspause 12:00-13:30			Mittagspause 11:40-13:30			Mittagspause 12:40-13:30			Mittagspause 12:20-13:30			Mittagspause 12:40-13:30		
Melanchthonianum, Saal 1			Audimax, Saal XXII			Melanchthonianum, Saal 3			Melanchthonianum, Saal 4			Melanchthonianum, Saal 5		
5.4 Bau- / Rohstoffe, Bauchemie (Stöber, MLU)			1.3 Magmatische Prozesse (Holtz, Uni Hannover, Kimm, Uni Frankfurt, Halama, CAU Kiel)			3.3 Methodik in der Lagerstättenforschung (Gutzmer, TU BA Freiberg)			Cont.			6.2 Freie Themen (Witzke, MLU)		
13:30	KEYNOTE 5.4 Thomas Matschei	The way towards engineering cement hydrate phase assemblages	13:30	Tatiana Shishkina, Roman Botcharnikov, Renat Almeev, Francois Holtz	The solubility of H ₂ O and CO ₂ in basaltic melt at pressures up to 500 Mpa	13:30	KEYNOTE 3.1 Frank Melcher, Torsten Graupner, Maria Stinikova, Thomas Oberthür, Friedhelm Henjes-Kunst, Hans-Eike Gähler, Axel Gardes, Helene Brätz, Gerd Rantitsch, Stijn Dewaele	Discriminating "coltan" from African rare element pegmatites on the basis of mineralogy and geochemistry	13:30	Gerhard Franz, Friedrich Lucassen, Dieter Rhede	Ti-Al zoning of experimentally grown titanite in the system CaO-Al ₂ O ₃ -TiO ₂ -SiO ₂ -NaCl-H ₂ O-(F) at 4 kb and 600°C	13:30	Robert Krickl, Jens Götze, Dieter Grambole, Reinhard Kaindl	Radiohaloes in feldspar group minerals
14:00	Christopher Stabler, Friedlinde Götz-Neunhoeffer, Jürgen Neubauer, Michael Bräu, Michael Kutschera	Einfluss von Weinsäure auf Phasenentwicklung und Rheologie während der Portlandzementhydratation	13:50	Quach Duc Tin, Hans Keppler	The origin of the lanthanide tetrad effect in granites	14:00	Thomas Oberthür, Frank Melcher, Maria Stinikova, N.S. Rudashevsky, V.N. Rudashevsky, Louis J. Cabri, Jerzy Lodziak, Detlef Kloss, Lothar Gast	Novel mineralogical methods applied to platinum mineralisation: Examples from pristine ores (Great Dyke, Bushveld) and placers	14:00	Bastian Joachim, Emmanuel Gardes, Rainer Abart, Wilhelm Heinrich	Diffusion-controlled growth of monomineralic Akermanite reaction rims in the ternary system CaO-MgO-SiO ₂	14:00	Martina Klinkenberg, Reiner Dohrmann, Stephan Kaufhold, Siegfried Siegesmund	Influence of clay microfabrics on the petrophysical properties of clays
14:20	Detlev Götz, Roger Meier, Bastian Raab, Herbert Pöllmann	Non-ambient Study of Polymorphic Phase Transformations of C ₂ S	14:10	Adrian Fiege, Clemens Kirchner, Alexander Bartels, Francois Holtz, Robert L. Linnen	Influence of fluorine on the solubility of mangano-tantalite (MnTa ₂ O ₆) and manganocolumbite (MnNb ₂ O ₆) in natural rhyolitic, synthetic haplogranitic and pegmatitic melts	14:20	Jens Gutzmer, B. Schulz	The contribution of geometalurgy to the sustainable use of mineral resources	14:20	Stephan Kaufhold	Wasserumverteilung im System Salz – Bentonit	14:20	Ulrich Bläß, Falko Langenhorst	Constraints on the Formation of Sulfertite in Martian Meteorites
14:40	Michael Schmidt, Herbert Pöllmann, Armin Egersdörfer	Untersuchungen zur Verwendung von Glasmehlen als Zusatz zu zementären Systemen	14:30	André Stechern, Max Wilke, Christian Schmidt, Karen Rickers, Sakura Pascarelli, Craig E. Manning	Zircon solubility and complexation of Zr in subduction zone fluids (bis 14:50 Uhr)	14:40	Reinhard Ramdohr	Suche nach Uranthorianit – Lagerstätten im SE Madagaskars – aus der Praxis der Exploration. Problematik der U-Th-Bestimmung	14:40	Nicholas Norberg, Gregor Neusser, Dieter Rhede, Daniel E. Harlov, Rainer Abart	Microstructure evolution during hydrothermal replacement of potassium-rich alkali feldspars by high albite/high sanidine in aqueous NaCl/KCl solutions	14:40	Serkan Kulaksiz, Michael Bau	Anthropogenic Gadolinium as Micropollutant in Drinking Water in Berlin
15:00-15:30 Kaffeepause														
Cont.			Cont.						Cont.			Cont.		
15:30	Bastian Raab, Herbert Pöllmann	Synthese und Hydratation von Mayenit 12CaO-7Al ₂ O ₃	15:30	KEYNOTE 1.3 Andreas Stracke	Linking basalt to mantle source signatures				15:30	Anselm Loges, Matthias Barth, Thomas Wagner, Gregor Markl	REE and U systematics in secondary fluorites, goethites and Mn oxides from a hydrothermal ore deposit	15:30	Milovan Berić, Miroslav Francuski	Possibility of enlarging capacity within the metamorphic reservoirs of the Mokrin-Jug (south) field
15:50	Karl Thomas Fehr, Saskia Bernstein	Determination of the Reaction Kinetics of Al-Tobermorite under Hydrothermal Conditions by in-situ Neutron Diffraction	16:00	Timm John, Reiner Klemm, Stephan Klemme, Jörg Pfänder, J. Elis Hoffmann	Separating the twins: Nb-Ta fractionation by partial melting at the titanite-rutile transition				15:50	Waheed Adeniyi Adeagbo, Nikos L. Doltsinis, Michael Burchard, Walter V. Maresch, Thomas Fockenberg	First-principles molecular dynamics investigation of chemical interactions and transport processes at Quartz-Water Interfaces	15:50	Soraya Hadj Zobir, Romain Bousquet	Mineralogical variability in Edough Massif micaschists (Annaba, Northeast Algeria)
16:10	Petr Sulovsky, Theodor Stanek	The berlinite substitution in clinkers; environmental aspects	16:20	Ibrahim Uysal, Necla Köprübaşı	Formation of highly-refractory mantle peridotites by melt-peridotite interaction, Orhaneli (Bursa), NW-Turkey				16:10	Thorsten Geisler, Andrew Putnis	The interaction of minerals with aqueous solutions	16:10	Claudia Weidenthaler	Complex aluminum hydrides as potential solid-state hydrogen storage materials
16:30	A.M Soltan, M. Hazem	Quicklime reactivity as a function of limestone microstructure and firing conditions	16:40	Stephen Foley, Gregory Yaxley, Anja Rosenthal, Stephan Buhre, Ekaterina S. Kiseeva, Dorrit E. Jacob	Experimental melting of peridotite with CO ₂ and H ₂ O in the lower cratonic lithosphere and applications to the origin of carbonate-rich igneous rocks				16:30	Chris Ballhaus, Tim Mansfeldt, Cornelia Bockrath, Carole Gee	Experimental silicification of wood			
17:00 Postersession und Ausstellung: Audimax Foyer und Melanchthonianum; Im Anschluss: Sitzung FKL														
20:00 Gesellschaftsabend														

Mittwoch, 16. September 2009

08:00 Öffnung des Tagungsbüros im Melanchthonianum, Medienraum im Erdgeschoss											
Melanchthonianum, Saal 1			Audimax, Saal XXII			Melanchthonianum, Saal 3			Melanchthonianum, Saal 4		
3.1 Exploration /Bergbau in Deutschland (Werner, LGRB; Gutzmer, TU BA Fb.)			1.3 Magmat. Proz. (Holtz, Uni Hannover, Klimm, Uni Frankf.)			5.1 Nichtkristall. Festst. (Kloess, Uni Leipzig; Roggendorf, MLU)			4.4 Mineralogische & chem. Prozesse in Bergbauseen (Friese, UFZ)		
08:30	KEYNOTE 3.3 Diethard Mager	Nationale und Europäische Aspekte der mineralischen Rohstoffsicherung				08:30	KEYNOTE 5.1 Walter Lehmann	NN	08:30	KEYNOTE 4.4 Javier Sánchez-España	Geochemical and mineralogical processes in the pit lakes of the Iberian pyrite belt (SW Spain)
09:00	Søren Lund Jensen, Jeroen van Gool, Henrik Sabra	Mineral Exploration in the Harz Mountains – Preliminary Results	09:00	Tatjana Rehfeldt, Dorrit E. Jacob, Stephen F. Foley, Geoff M. Nowell	Petrogenesis of dunite-wehrlite and websterite xenoliths from Kimberley, RSA: Constraints from Sr-Nd-Hf isotopes	09:00	Hans Roggendorf	Korrosion von Natriumdisilicatgläsern in wässrigen Lösungen als Funktion des pH-Wertes	09:00	Klaus-Dieter Grevel, Juraj Majzlan	Internally consistent thermodynamic data for MgSO4-hydrates: Enthalpies of formation and stability related to temperature and relative humidity
09:20	Udo Flüchter	Holcim Rheingold – Ein Mythos wird wahr	09:20	Bernd Lehmann, Ray Burgess, Dirk Frei, Boris Belyatsky, Datta Mainkar, N.V. Chalapathi Rao	Diamondiferous kimberlites in central India synchronous with Deccan flood basalts	09:20	T. Pfeiffer, D. Enke, H. Roggendorf	Herstellung von Wasserglas durch hydrothermale Aufschluss von Opal, Quarz oder Kieselglas in Natronlauge	09:20	Schultze, Martin	Die Tagebauseen Mitteldeutschlands – Entstehung, Limnologie, Management
09:40	Stephan Uhlig, Peter Szymczak, Ivona Woloszyn, Hartwig Lange	Aufwältigung der Fluss- und Schwespaflagerstätte Niederschlag	09:40	Henrike Franke, Kirsten Drüppel, Helene Brätz	Petrogenese von Fe-Ti-Oxidkörpern des anorthositischen Kunene-Intrusiv-Komplexes, NW-Namibia	09:40	Martin Ende Gert Kloess	Nanocrystals in natural glass as fingerprint of provenance?	09:40	Linda Sachse, Ulrike Haferkorn, Gerhard Strauch	Entwicklung des Austragsverhaltens von Kippenböden, am Beispiel der Lysimeter der Kippe Espenhain
10:00	Wolfgang Werner	Welchen Beitrag können die Staatlichen Geologischen Dienste zur Rohstofferkundung in Deutschland leisten?	10:00	Philipp Gleißner, Kirsten Drüppel, Rolf L. Römer, Heinrich Taubald	Mantle source and crustal contamination of anorthosites of the Proterozoic Kunene Intrusive Complex, NW Namibia	10:00	Dirk Enke, Jens Kullmann, Kathleen Hobritz, Andreas Hochmuth	Glas-Monolithe mit kontrolliert einstellbarer Mikroporosität – Herstellung und potentielle Anwendungen	10:00	Kock, Dagmar	Investigations for the quantification of microorganisms in sulfidic mine waste dumps
10:20-10:50 Kaffeepause											
3.2 Supergene und hypogene Metallogenese (Borg, MLU)			1.3 Cont.			5.3 Hydrothermalforschung in Technik und Natur (Fehr, LMU)			4.5 Umweltmineral. (Rammilmair, BGR; Heimann, Oceangate Consult.)		
10:50	KEYNOTE 3.2 Gregor Markl	Fluid-mineral interaction during weathering of hydrothermal ore deposits deciphered from supergene mineral assemblages in the Schwarzwald area, SW Germany	10:50	Julian Schilling, Michael Marks, Thomas Wenzel, Dorrit Jacob, Gregor Markl	From the early magmatic to the post-magmatic stage: Approaching the source characteristics and tracking the post-magmatic evolution of the alkaline Mont Saint-Hilaire complex, Canada, using stable and radiogenic isotopes	10:50	KEYNOTE 5.3 K. Byrappa	Hydrothermal research: a soft-technology	10:50	KEYNOTE 4.5 Petr Sulovsky	Mineralogy and human well-being: changing insights into nature
11:20	Katharina Pfaff, Ludwig H. Hildebrandt, Gregor Markl	The Nonsulfide Zn-Ag Mineralization in Wiesloch, SW Germany	11:10	Jan A. Schuessler, Ronny Schoenberg, Frank Melcher, Ingo Horn	Exploring inter-mineral Fe isotope variations in sulphide ore deposits using UV femtosecond laser ablation MC-ICP-MS	11:20	Andreas Laumann, Karl Thomas Fehr, Bo Brummerstedt Iversen, Michael Holzapfel	Bestimmung von Phasenbeziehungen und thermodynamische Berechnungen im System Li-Ti-O-H mittels in-situ XRD-Messungen	11:20	Juraj Majzlan, Martin Chovan, Bronislava Lalinska, Jörg Göttlicher, Ralph Steininger	Minerals as Sb and As reservoirs and vectors in the mining waste from the Pezínok Sb-Au deposit (Slovakia)
11:40	Gregor Borg, Ryan Mathur	Concomitant Cu isotope and base metal fractionation at the supergene Skorpion zinc deposit, Namibia	11:30	Ph. Kegler, A. Holzheid, H. Palme	Non-ideal behavior of Cu in core forming metal alloys. Implications for siderophile element contents of the Earth mantle	11:40	Saskia Bernstein, Karl Thomas Fehr	Formation of 1.13 nm Tobermorite: New insights by In-situ neutron diffraction	11:40	Mostafa Redwan, Dieter Rammilmair	Quantitative Environmental Mineralogy
12:00	Sebastian Staudé, Gregor Markl	Fluid mixing and Sr-source recorded by radiogenic Sr isotopes of barite from the Wittichen mining area, Schwarzwald, SW Germany				12:00	Melanie Kaliwoda	Light elements as tracer minerals for hydrothermal or magmatic overprint in natural rocks	12:00	Daniel Höllen, Stephan J. Köhler, Martin Dietzel	Bildung amorpher und polymerer Kieselsäure durch zyklisches Gefrieren verschiedener wässriger Lösungen
12:20	Annika Dziggel, Katharina Wulff, Jochen Kolb, Torsten Vennemann, Michael Böttcher, F. Michael Meyer	Stable isotope systematics of the Navachab gold deposit, Namibia: implications for the source of fluids in sediment-hosted orogenic gold deposit				12:20	Rupert Hochleitner, Karl Thomas Fehr, Christian Rewitzer	Low temperature hydrothermal crystallisation of minerals in the system Cu-Zn-Cl-O-H-N	12:20	Mostafa Redwan, Dieter Rammilmair	Simultaneous monitoring of changes of both electrical conductivity and water saturation in column experiments
12:40	Jens Gutzmer, Thomas Ditttrich, K. Osburn, C.R. McClung, B. Schulz	Lithological architecture, age and metamorphism of the polymetallic Salt River VMS deposit, Northern Cape Province, South Africa				12:40	Karl Thomas Fehr, Saskia Bernstein	Determination of the Reaction Kinetics of Al-Tobermorite under Hydrothermal Conditions by in-situ Neutron Diffraction			
						13:00	Nataliya Vlasova, Michael Kersten	Arsenite Adsorption on Goethite at Elevated Temperatures			
Ca. 13:10 Uhr: Tagungsende; im Anschluss Grillen auf dem Gelände des Instituts für Geologie an der MLU, Von-Seckendorff-Platz 3 (Interessenten melden sich bitte während der Tagung vor Ort im Tagungsbüro)											

Donnerstag, 17. September & Freitag, 18. September 2009

Nachexkursionen

Treffpunkt für alle Exkursionen: Institut für Geologische Wissenschaften, Von-Seckendorff-Platz 3, 06120 Halle / Saale. Die genauen Uhrzeiten werden noch bekannt gegeben.

BRAUNKOHLEBERGBAU UND TAGEBAUSEEN, 17.9.09

Organisatoren: Kurt Friese & Martin Schultze

Preis: bis zum 1. Juni 2009 40 EUR, danach 50 EUR (Mittagsversorgung inklusive)

BERNBURG SALZ, 17.9.09

Organisator: Thomas Degen

Preis: bis zum 1. Juni 2009 30 EUR, danach 40 EUR

EXKURSION ZUR KULTURGESCHICHTE: AUF LUTHERS SPUREN, 17.9.09

Organisator: Gerhard Bachmann

Preis: bis zum 1. Juni 2009 30 EUR, danach 40 EUR

Workshops

FEUERFESTMATERIALIEN, 17.09.2009

Johannes Södje, Fa. Refaktechnik Cement GmbH

MLU, am Institut für Geowissenschaften

Preis: bis zum 1. Juni 2009 50 EUR, danach 60 EUR

UMWELTISOTOPE UND IHRE ANWENDUNG, 17.-18.09.2009

Stephan Weise & Gerhard Strauch, UFZ Halle/Leipzig

MLU, am Institut für Geowissenschaften

Preis: bis zum 1. Juni 2009 60 EUR, danach 70 EUR

ACID MINE DRAINAGE, 18.09.2009

Kurt Friese, UFZ Magdeburg, Dagmar Kock (BGR Hannover) & Ralph Schöpke (BTU Cottbus)

MLU, am Institut für Geowissenschaften

Preis: bis zum 1. Juni 2009 50 EUR, danach 60 EUR

Kurzfassungen / Abstracts

Speciation of Ca^{2+} in water as a function of temperature, pressure and pH: Ab-initio molecular dynamics simulation study

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In order to understand and model both the macroscopic thermodynamic properties as well as the atomistic structure of high-pressure aqueous solutions in systems such as $\text{CaO-SiO}_2\text{-H}_2\text{O}$, new data on the speciation of dissolved Ca are required (e.g., Adeagbo and Doltsinis, 2007; Adeagbo *et al.*, submitted; Doltsinis *et al.*, 2007a, 2007b). In this work, we have used first principles molecular dynamics simulations to study the Ca^{2+} ion in water at various temperatures and pressures, starting with either Ca^{2+} or CaO in a reactive volume of 63 H_2O molecules. In the case of aqueous Ca^{2+} , the ion is surrounded by six H_2O molecules in the first hydration shell at 300 K / 0.3 GPa, with rare exchange between first and second hydrations shells. At 900 K / 0.9 GPa the coordination number in the first hydration shell fluctuates between six and eight, the average being 7.0. CaO immediately reacts with the surrounding H_2O molecules to form $\text{Ca}^{2+} + 2\text{OH}^-$. The hydroxyl ions form transient $\text{Ca}(\text{OH})^+$ and $\text{Ca}(\text{OH})_2$ complexes and have a mean residence time in the first coordination shell of Ca^{2+} of 6 ± 4 ps at 500 K and 3 ± 3 ps at 900 K, respectively. At 500 K / 0.5 GPa the time-averaged relative concentrations of the transient Ca^{2+} , $\text{Ca}(\text{OH})^+$, and $\text{Ca}(\text{OH})_2$ species are 14, 55, and 29 percent, while at 900 K / 0.9 GPa they are 2, 33, and 65 percent, respectively.

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First-principles molecular dynamics investigation of chemical interactions and transport processes at Quartz-Water Interfaces

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High temperature and pressure Car-Parrinello molecular dynamics (CP-MD) simulations were performed in order to gain insight into the mechanisms, chemical interactions and transport activities at the alpha-quartz-water interface [1]. The model system initially consists of a periodically repeated quartz slab with O-terminated and Si-terminated (1000) surfaces sandwiching a film of liquid water. At a temperature of 1000 K and a pressure of 0.3 GPa, dissociation of H₂O molecules into H⁺ and OH⁻ is observed at the Si-terminated surface. The OH⁻ fragments immediately bind chemically to the Si-terminated surface while Grotthus-type proton diffusion through the water film leads to protonation of the O-terminated surface. Eventually, both surfaces are fully hydroxylated and no further chemical reactions are observed. Due to the confinement between the two hydroxylated quartz surfaces, water diffusion is reduced by about one third in comparison to bulk water. Diffusion properties of dissolved SiO₂ present as Si(OH)₄ in the water film are also studied. We do not observe strong interactions between the hydroxylated quartz surfaces and the Si(OH)₄ molecule as would have been indicated by a substantial lowering of the Si(OH)₄ diffusion coefficient along the surface. No spontaneous dissolution of quartz is observed. To study the mechanism of dissolution, constrained CP-MD simulations are done. The associated free energy profile is calculated by thermodynamic integration along the reaction coordinate [2]. Dissolution is a stepwise process in which two SiO bonds are successively broken. Each bond breaking between a silicon atom at the surface and an oxygen atom belonging to the quartz lattice is accompanied by the formation of a new SiO bond between the silicon atom and a water molecule. The latter loses a proton in the process which eventually leads to protonation of the oxygen atom in the cleaved quartz SiO bond. The final solute species is Si(OH)₄.

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Atomistic modeling of grain boundaries in forsterite

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Real materials are generally polycrystalline and the material properties can be significantly modified by the presence of grain boundaries. When considering mantle rocks these boundaries become important since they provide a means for creep and ion migration, likely causes of mantle rheology. Forsterite is a major component of the Earth's upper mantle and is thus of considerable importance in controlling its properties, rheological and thermal structure.

The atomistic simulation offers an opportunity to understand the grain boundary (GB) structures, which can now be compared with the direct observation of the atomic positions using high-resolution transmission electron microscopy (Heinemann et al. 2005). In the present study, we use molecular dynamics simulations to model GB structures in forsterite. The interactions between the atoms are described by the aspherical ion model (AIM) that accounts for polarization and deformation of the ions (Jahn and Madden, 2007). We construct geometrically a [100] symmetrical GB with tilt angle α by aligning a chosen crystallography plane (0kl) parallel to the tilt axis [100] and misoriented with $\alpha/2$ to (010) plan. One-half crystal (grain) is rotated by a 180° rotation relative to the other about the normal [0kl]. Since we need to use periodic conditions, our simulations have large cells containing a few thousands of atoms. Here, we report preliminary results on the atomic structure and the respective energies of symmetric tilt grain boundaries in forsterite with different tilt angles.

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Mineralogisch-erzpetrographische Untersuchung an nickelhaltige lateritische Eisenerze des Vorkommens von Nome (Albanien)

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In Albanien treten einige nickelhaltige lateritische Eisenerze auf, die von großer wirtschaftlicher Bedeutung sind. Zu den wichtigsten Vorkommen des Landes zählen die von Bilishti-Bitincka und Pogradec im Südosten sowie die von Kukës und Nome im Nordosten. In den vergangenen Jahren wurde ein Teil der albanischen Eisennickelerze von der griechischen Firma LARCO A.G. zur Erzeugung von Fe-Ni-Legierungen im metallurgischen Werk von Larymna, gefördert.

Das Gebiet von Has-Kukës-Nome befindet sich im nordöstlichen Albanien und gehört zu der geotektonischen Zone von Mirdita (Albanides). Die Eisennickelerze werden dem Ophiolithkomplex der Mirdita-Zone zugeordnet. Das Vorkommen von Nome liegt 25 km südwestlich von Kukës. Die Eisennickelerze entwickeln sich über ultrabasische Gesteine (Harzburgite) in Form von Lagern über eine Länge von mehr als 2 km bei einer durchschnittlichen Mächtigkeit von 7 m und werden von Kalksteinen der Unterkreide überlagert. Die geologische Struktur der Lagerstätte ist ähnlich der des Has-Kukës-Gebietes.

Die mineralogischen Bestandteile sowie die Gefüge der Fe-Ni-Erze wurden erzmikroskopisch und röntgenographisch ermittelt. Die chemische Zusammensetzung der einzelnen Proben wurde mittels AAS bestimmt.

Die Fe-Ni-Erze setzen sich meist aus Hämatit, Goethit, Quarz, Chlorit, Chromit und in untergeordneten Mengen aus Ni-Chlorit, Kaolinit sowie Calcit zusammen. Das unter dem Fe-Ni-Vorkommen liegende Basisgestein ist ein serpentinierter Harzburgit. In direktem Kontakt zum verwitterten Basisgestein folgt eine stark silifizierende Saprolith-Zone, die eine Mächtigkeit von 2 m aufweist und kontinuierlich in einer 1 m dicken Tonschicht übergeht. Die Tonschicht setzt sich meist aus Kaolinit, Ni-Chlorit, Hämatit, Goethit und Calcit zusammen. Hier treten einige Ooide, Peloiden und komplexe Sphäroide auf, die aus Hämatit bestehen und z.T. einen goethitischen Saum aufweisen. Das über dieser Tonschicht liegende Lager besteht aus pisolithischem Erz, das eine Mächtigkeit über 8 m aufweist. Dieser Horizont zeichnet sich durch das Auftreten von Ooiden, Pisoiden, Peloiden und komplexen Sphäroiden aus. Sie bestehen überwiegend aus Hämatit-Goethit und untergeordnet Kaolinit. In den komplexen Sphäroiden, die eine Größe bis zu 3 mm aufweisen, sind zahlreiche Ooide bzw. Peloiden z.T. als Bruchstücke eingeschlossen. In der Grundmasse der Fe-Ni-Erze, die unterschiedlich intensiv von epigenetischem Goethit verdrängt wird, überwiegt neben dem Kaolinit, Chlorit (Klinochlor, selten Ni-Chlorit). Hämatit entsteht auch hier meist durch Dehydrierung von Goethit. Als detritische Minerale kommen in der Grundmasse Chromit, Spinelle sowie Quarz vor, die oft auch als Einschlüsse in den komplexen Sphäroiden zu finden sind. Die Struktur der Fe-Ni-Erze wird meist als allotriomorph und ungleichmäßig körnig bezeichnet, während die Textur als oolithisch-pisolithisch. Die Gehalte der Erze an Nickel und Kobalt variieren zwischen 0,41-0,88% und 400-630 ppm entsprechend.

Das Auftreten von Ooid-, Pisoidfragmenten sowie von Klasten und komplexen Sphäroiden in den Fe-Ni-Erzen ist ein Hinweis dafür, dass ein präexistierendes, ooidführendes Sediment vorhanden war, das abgetragen, umgelagert und resedimentiert wurde. Nur die unteren Horizonte des Vorkommens (Saprolith-Zone und Tonschicht) sind weitgehend von der Abtragung verschont geblieben. Desweiteren ist allgemein zu erkennen, dass die Ooide, Pisoiden und Peloiden stärker als deren Grundmatrix vererzt sind. Damit muß davon ausgegangen werden, dass die umgelagerten Ooide, Pisoiden und Peloiden bereits im vererzten Zustand vorlagen. Anhand der erzmikroskopischen Untersuchung geht hervor, dass das Vorkommen von Nome als ein sekundäres pseudoautochthones Vorkommen charakterisiert wird.

The influence of portlandite crystallite size during the carbonation of Natural Lime and Natural Hydraulic Lime

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The calcination of limestone or marble produces lime that transformed by air or wet slaking to portlandite [$\text{Ca}(\text{OH})_2$] and could be characterized as Natural Lime (NL). During firing of marly limestones, larnite (Ca_2SiO_4) and minor amounts of $\text{Ca}(\text{Al,Fe})_2\text{O}_4$ are formed, as well as lime that change after slaking into the form of portlandite. Products containing mainly portlandite and larnite are known as Natural Hydraulic Limes (NHL).

Current research deals with the carbonation process of portlandite affected by factors such as relative humidity (RH), temperature (T), concentration of CO_2 and grain size [El-Turki (2009), Castellote (2008)]. This paper exhibits the importance of the portlandite crystallite size during carbonation process. The raw materials used for NHL and NL were marly limestones and a pure fine crystalline calcitic marble, fired at 900°C for 12 hours. A pure synthetic larnite was also produced by mixing CaO and SiO_2 , in 2:1 mol ratio. The produced NHL and NL were slaked in open air with RH 55-60% (slow hydration) and rapidly with water. The slow hydration of CaO , of NHL or NL in air slaking, forms a poor crystallized portlandite with crystallite size $< 250 \text{ \AA}$, while the rapid hydration produces a well crystallized portlandite with crystallite size $> 1800 \text{ \AA}$. To study the carbonation process of the above portlandites, a quantity of 3 gr of NL and NHL of small and large crystallite size, was exposed in continuous humidified airflow of 90% RH. Samples of NHL and pure larnite were additionally exposed as pastes by addition of water. The samples were placed in PVC cylinders of 2 cm in diameter and 2 cm height to ensure identical geometry and uni-directional carbonation on the exposed surface. From each of the above mentioned specimens, four separate samples were exposed. The analysis was performed after 0 (reference sample), 10, 20 and 30 days. The mineralogical analysis was carried out by X-ray powder diffraction, while quantitative analysis was performed by the Rietveld method using the TOPAS software program. Additionally Infrared (I.R) and thermogravimetric analysis were performed. The carbonation of portlandite in well crystallized samples (large crystallite size) forms calcite (figure 1), while the poor crystallized portlandite forms vaterite, aragonite and calcite (figure 2). Furthermore, the total amount of the carbonate mineral phases is higher compared to the well crystallized portlandite. The same trend and behavior of portlandite was observed in NHL samples.

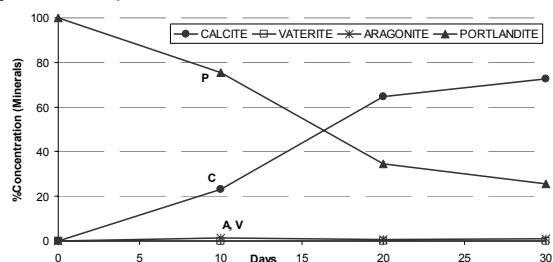


Figure 1: Carbonation process of portlandite with large crystallite size (1800 Å)

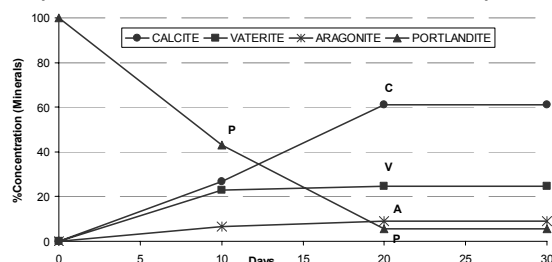
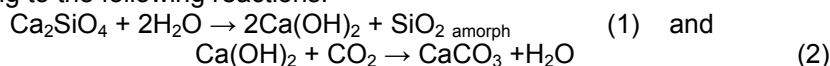


Figure 2: Carbonation process of portlandite with small crystallite size (250 Å)

In the pure larnite sample, portlandite and calcite were observed after curing of 30 days. The absence of portlandite in the reference pure larnite sample indicates that the decomposition of larnite took place according to the following reactions:



The same reactions are observed in NHL, followed by reduction of the larnite amount, which is connected with the increase of the total amount of portlandite and the carbonate mineral phases during the carbonation process. It is assumed that the amorphous SiO_2 content in NHL, reacts with the primary or secondary portlandite improving the pozzolanic properties of this material. The hydration of $\text{Ca}(\text{Al,Fe})_2\text{O}_4$ was also observed by the formation of $\text{Ca}_3(\text{Al,Fe})_2[(\text{OH})_4]_3$ in the NHL samples.

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Mineralogy of soils derived from quaternary limestone in the Philippines

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The origin of soils derived from Quaternary limestone particularly in humid tropical islands is until now poorly understood. This is because relatively less research has been done on these soils compared to those from other parent rocks particularly volcanic rocks (Asio et al. 2006). Based on mineralogical and geochemical evidence from the Caribbean region, volcanic ash and atmospheric dusts deposition has recently been suggested to play a major role in the formation of soils from Quaternary limestones (Muhs, 2001; Muhs and Budahn, 2009). For instance the clayey texture and clay mineralogical characteristics of some young soils from limestone cannot be explained satisfactorily by the geochemical composition of the parent rocks. The purpose of this paper is to present the mineralogical characteristics (and thus help explain the origin) of soils from 14 Quaternary limestone sites on the four neighboring islands of Leyte, Samar, Camotes, and Bohol in central Philippines. Leyte which is located in the middle of the four islands, is largely volcanic and serves as the major source of the volcanic materials that have influenced the formation and characteristics of limestone soils in the three other islands (all three are built up by sedimentary rocks such as sandstones and coralline limestones). More than 50 soil and rock samples were collected and subjected to mineralogical examination by X-ray Diffractometry

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Mikroreaktionsgefüge und P-T-Entwicklung von Osumilithgneis, SW-Norwegen

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Migmatische osumilithführende Paragneise wurden in einer Entfernung von 3 bis 4 Kilometern um den anorthositisch-noritischen Rogalandkomplex in SW-Norwegen beprobt. Nach Jansen et al. (1985) und Westphal et al. (2003) durchliefen diese Gesteine im Zuge der svekonorwegischen Orogneise um ca. 1000 Ma (Möller et al., 2002) eine amphibolitfazielle Regionalmetamorphose (M1; c. 6-8 kbar, 700-800°C) gefolgt von einer granulitfaziellen, kontaktmetamorphen Überprägung (M2; c. 4-5 kbar, 900-1000°C) während der Platznahme des Rogalandkomplex von 930 bis 920 Ma (Schärer et al., 1996).

Um die Mineral-Reaktionsgeschichte und den detaillierten P-T-Pfad der Osumilithgneise zu rekonstruieren, wurde konventionelle Geothermobarometrie mit berechneten PTX-Phasendiagrammen im Na₂O-CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O (NCKFMASH)-System kombiniert. Früher Biotit und Sillimanit, die als Einschlüsse in Granat aus osumilithfreien Proben erhalten sind, wurden im Zuge von Schmelzreaktionen im Verlauf prograder Erwärmung auf 950-970°C bei 5-6 kbar durch Granat (X_{Mg} : 0,37-0,35)-Orthopyroxen (X_{Mg} : 0,56-0,59)-Feldspat-Quarz ($\pm$ Spinell)-Paragenesen ersetzt. Die kalkulierten Temperaturen sind konsistent mit den hohen Al₂O₃-Gehalten von bis zu 11,2 Gew.-% in Orthopyroxen. In den Osumilithgneisen sind peakmetamorpher Orthopyroxen, Granat und herzynitischer Spinell durch breite Osumilithsäume getrennt, die noch während der Ultra-Hochtemperaturmetamorphose oberhalb von 950°C gebildet wurden. Die Bildung von Crd-Kfs-Qtz($\pm$ Opx)-Symplektiten auf Kosten von Osumilith und Neuwachstum von idioblastischem Granat (X_{Mg} : 0,33-0,35) in Osumilith, als Saum um Spinell, Magnetit und peakmetamorphem Granat dokumentieren Abkühlung auf $T < 900^\circ\text{C}$ bei $P > 5,5$ kbar. Eine späte Biotitbildung zeigt Abkühlung auf $T < 800^\circ\text{C}$ bei 5,5kbar an. Hochauflösende Mikrosondenanalysen und TEM-Untersuchungen machen deutlich, dass die Crd-Kfs-Qtz($\pm$ Opx)-Symplektite hauptsächlich aus feinkörnigen Crd-Qtz-Verwachsungen bestehen, in denen kristallographisch orientierter, Mikrometer größer, wurmartiger Quarz von einer Cordieritmatrix umgeben ist.

Die für die Osumilithgneise bestimmten annähernd isobaren P-T-Pfade dokumentieren Erwärmung auf granulitfazielle Peak-Bedingungen von 950-970°C und 5-6 kbar, gefolgt von annähernd isobarer Abkühlung auf $T < 800^\circ\text{C}/5,5$ kbar. Diese P-T-Entwicklung ist in guter Übereinstimmung mit der postulierten kontaktmetamorphen Überprägung der Gesteine während der Intrusion des Rogalandkomplexes vor 930 – 920 Ma.

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Experimental silicification of wood

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Fossilization of organic tissue necessitates its removal from an environment that causes decomposition and its replacement by inorganic material. An interesting and important process for palaeobotany is fossilization by silicification. Here, organic structures of plant tissue are replaced by silica, occasionally to such fine detail that physiological processes can still be recognized (cf. Kerp et al. 2003). But what are the factors driving SiO_2 to enter plant tissue and be precipitated as opal, and how long does it take to mineralize huge trees that measure meters in diameter by silica? Three studies from the late 60ies and 70ies (Drum 1968a,b, Leo and Barghoorn 1976) exposed wood to sodium orthosilicate and ethyl silicate solutions and thereby achieved appreciable silicification, but the reagents used then are not known to occur in nature. A long-term field experiment was reported by Akahane et al. (2004) who suspended wood trunks in a silica-saturated hot spring. When the trunks were retrieved after seven years, bulk analysis for SiO_2 showed that some parts were silicified to up to 30 wt.% SiO_2 . However, owing to the empirical nature of that study the forces driving silicification were not identified with certainty.

We report here on experiments to silicify wood under natural conditions using volcanic glass as a source for amorphous silica. We show that the early stages of silicification are driven by a gradient in pH which is established between the wood and its lithic substrate in which the wood is buried. Volcanic ash, once acidic aerosols scavenged by the ash fall are leached away, imposes a pH on its pore water of around 10 to 10.5 (90°C). Wood, in contrast, imposes a low pH regime when it is immersed in water, of around 4 (90°C). Hence, when a tree log is buried by volcanic ash, a pH gradient may develop between the wood and its lithic environment that encompasses around six orders of magnitude in H_3O^+ concentration. This pH gradient may impose a concentration gradient in SiO_2 , driving SiO_2 from the lithic matrix into the wood structure where it may be precipitated as opal.

To test this scenario, several cubes of Pinus wood 4 to 6 cm³ in size were placed above ground volcanic ash in brass autoclaves, topped up with de-ionized water, and equilibrated at 90°C. Every ten days the autoclaves were opened, pH was measured, and one wood cube was retrieved and cut in 1 mm thick slices parallel to its tracheids. The slices were coated with gold, then examined with SEM for any silica precipitate. After only ten days in solution, some tracheids of the wood structure were found to be completely filled with opal. The most common structure the opal precipitates take is in the form of microspheres with an underlying nanospheric substructure, nearly identical to the morphology of natural recent opal precipitates

The silica concentrations of the experimental solutions allow a rough estimate as to how long pervasive silicification of wood may take in nature. Silica (aq) increases with increasing alkalinity from ~30 mg/l (acidic to neutral pH) to > 1200 mg/l at a pH of 11.5. Assuming the porosity of the unconsolidated volcanic ash is around 25 percent and silica in the pore water is moved solely by diffusion, diffusivity and mass flux of silica can be approximated from Fick's law and the Stokes-Einstein relation. Based on the experiments presented, one may speculate that wood logs as massive as those found in the petrified forests of Arizona or Lesvos may have become silicified within hundreds of years.

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Sulfur solubility in hydrous Etna basalt: an experimental study at temperatures between 1150 and 1250°C and 200 MPa

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Volcanic degassing is controlled by exsolution of multicomponent magmatic volatiles, which are mainly composed of H₂O, CO₂, SO₂, H₂S, HCl, etc. The S/Cl ratio of gasses measured in the volcanic plums is closely linked to the dynamics of volcanic eruptions. For instance, this correlation was observed at Mt. Etna [1, 2], which is one of the world's most active and intensively surveyed volcanoes, discharging alkali basalt-trachybasaltic magmas and a large amount of volatiles during both, effusive and explosive eruptions.

The degassing behaviour of multicomponent volcanic fluids is quite complex and even the physicochemical properties of binary component volcanic fluids (e.g. H₂O-Cl and H₂O-S) at magmatic relevant pressure and temperature are not well studied. Furthermore, S speciation in magmatic phases is very redox sensitive (S^{+VI} at oxidizing and S^{-II} at reducing magmatic conditions) and thus degassing of S-rich volatiles can be largely affected by oxygen fugacity (*f*O₂). However, only a few data concerning the S solubility in hydrous basalts at high temperature (above 1050 °C) exist [4], because sulfur is very reactive component limiting the application of experimental approaches that use noble metal capsules (e.g. Pt and AuPd). The development of degassing models for basaltic magmas requires experimental datasets at given pressure, temperature and *f*O₂.

In this study we performed S solubility experiments in internally heated pressure vessels (IHPV) of natural hydrous Etna basalt at 200 MPa and temperatures from 1150 to 1250 °C at different *f*O₂ (~ QFM and ~ QFM+2, where QFM corresponds to the *f*O₂ of the quartz-fayalite-magnetite buffer at given P and T). Run durations were 1 to 3 days. To minimize the experimental problems with S, we applied an olivine-AuPd double capsule technique. Single-crystal olivine capsules closed with an olivine piston (San Carlos olivine) were used as sample containers, which were inserted into outer Au₈₀Pd₂₀ capsules. Starting material was a fused and water presaturated trachybasalt from Mt. Etna (2001 eruption), containing 5 wt.% H₂O. S sources were FeS and CaSO₄ and the initial bulk amounts of S were between 1.5 and 2 wt.% S (with respect to the mass of starting material).

All glasses, obtained from these experiments, were enriched in MgO (due to equilibration with MgO-rich olivine at high T) and CaO or FeO (dependent of added sulfur source). The amount of dissolved water was about 2 - 2.5 wt.% H₂O ("by difference" and IR) and S concentrations were 0.3 to 0.4 wt.% S (FeS added) and up to 1.0 wt.% S (CaSO₄ added). These values are in agreement with data of Jugo et al. [2, 3] and Liu et al. [4]. However, no temperature dependence between 1150 and 1250 °C and no effect of variations in melt composition on S solubility was observed.

Although the intrinsic *f*O₂ of the IHPV vessel is ~ QFM+4, the *f*O₂ (calculated as a S peak shift in WDS spectra, recorded by electron microprobe analysis) in the olivine capsules were about QFM (FeS added) and QFM+2 (CaSO₄ added), indicating that the sulfur source material is the predominant oxygen buffer. Using both, FeS and CaSO₄ in various amounts as S source, should allow us to perform hydrous S solubility experiments at various redox conditions. In natural primitive magmas of Mt. Etna, containing about ~ 3.5 wt.% H₂O and 0.3 wt.% S [5], no S bearing mineral phase was observed. Thus, with respect to oxidation state of Etna magmas close to ~ QFM+1 [6], our experimental setup will allow us to clarify, if they are close to S saturation, which is of importance to get more detailed insight of degassing mechanisms of Mt. Etna and basaltic volcanoes in general.

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CO₂-Sequestration on the laboratory scale – first results of chemical interaction processes between injected CO₂, saline fluids and potential reservoir materials

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Experimental studies about chemical interaction processes between injected CO₂, saline fluids and potential reservoir materials as well as influences of these chemical interactions on the micro-structure of the used materials are realised in one subproject of the joint research project CO₂-MoPa (Modelling and Parameterisation of CO₂ storage in deep saline formations for dimension and risk analyses). One primary aim is to determine kinetic constants based on geochemical data. These kinetic constants are used as input parameters for geological and geochemical models, which other subprojects deal with. A literature survey showed that strong simplified experiments were accomplished to determine dissolution rates of different minerals in the past. Pokrovsky et al. (2005) for example use a 0.001 to 1 M NaCl solution to define dissolution rates of calcite, dolomite and magnesite. Other authors like Dove et al. (1990) made experiments with pure water and clear quartz crystals to determine the dissolution rates. Most models for dimension and risk analyses are based on these simplified kinetic data. It is therefore obvious that the following question arises: To which extent can results of simplified experiments be extrapolated to complex natural systems?

To answer this question, we perform a systematic study on chemical interaction processes in complex systems under more realistic reservoir conditions (T: 60-150°C / p: 100 bar). First experiments were realized by using well characterized sandstone samples: (a) a fine to medium grained sandstone located in a stone pit near Bad Bentheim (BBh, Germany) and (b) a fine grained sandstone located near Obernkirchen (OK, Germany). Both samples vary in their effective porosity (BBh: 21.5% / OK: 12.7%; Pusch et al., 2001) and thus their permeability (BBh: 1-2 D / OK: 10 mD; Pusch et al., 2001). Based on natural formation water of various stratigraphic horizons simplified brines were assembled to use as saline, fluid phase. Aliquots of sandstone and fluid phases were exposed to 150°C and 100 bar and post-run fluid compositions were measured by ICP-OES (inorganic geochemistry lab, IfG, Kiel)

First results of silicium (Si) dissolution rate calculations for BBh-Sandstone show r_{Si} values varying between $1.03 \cdot 10^{-6}$ and $5.55 \cdot 10^{-7}$ mole/m²*s. This variation might be caused by small solid particles in the fluid. In the future the fluid phase will be therefore centrifugalized before ICP-OES measurements. Compared with literature data our dissolution rates are up to four orders of magnitude higher. Blake et al. (1999) declare dissolution rates for Si with $r_{Si} \sim 1.1 \cdot 10^{-10}$ mole/m²*s. The experiments were accomplished on quartz in various NaCl solutions. Other authors like Dove et al. (1990) calculate dissolution rates on pure quartz in distilled water ($r_{Si} \sim 1.18 \cdot 10^{-8}$ mole/m²*s). These differences might be attributed to different experimental conditions (T, p, run duration etc.). However, our experiments were performed using poly-mineral material (sandstone), while mono-mineral material (e.g. quartz) was used by the other studies. It is possible that the Si dissolution is not only influenced by quartz but also influenced by other silicates (e.g. feldspar, mica) resulting in higher dissolution rates. Further interactions between several mineral phases can in addition influence the dissolution rate in a poly-mineral material.

Based on the results of our poly-mineral experiments it becomes apparent, how important experiments with mono-mineral materials are. The choice of the material regards to the composition of the potential reservoir and cap rocks. Thus among others quartz and feldspar varieties as well as carbonates utilize as proxy for potential reservoir material. Well defined clay minerals reflect cap rock substances. According to the poly-mineral experiments brines with simplified formation water compositions of different stratigraphic horizons are used. This second set of experiments is under progress and dissolution rates based on "mono-mineral" experiments will be presented at the DMG meeting.

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Formation of 1.13nm Tobermorite: New Insights by In-situ Neutron Diffraction

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The mineral phase 1.13nm tobermorite (tobermorite), belonging to the group of Calcium-Silicate-Hydrate (CSH)-phases, is synthesised by the hydrothermal treatment of ground quartz sand, quicklime and water to produce steam cured building materials. Tobermorite is the predominant CSH-phase in Aerated Autoclaved Concrete (AAC) and significantly controls physicochemical properties of the building material. At common conditions (190°C/P_{sat}) Tobermorite is metastable, hence, kinetic data is essential to control the reaction.

Neutron diffraction is an excellent method to collect data of the reaction process in-situ. A hydrothermal autoclave for neutron diffraction (HAND) was recently designed to record the dynamic process during the hydrothermal reaction with the D20 powder diffractometer of Institute Laue-Langevin (ILL) in Grenoble. The technical specification of this instrument enabled us to collect data within the range of 8 and 153.6°2 θ with a time resolution of 1 diffractogram per minute. The chosen wavelength of 2.4Å allows the analysis of d-spacing up to 11.3Å, where the basal reflection of the evolving Tobermorite is expected. The position of this reflection provides information of the intercrystalline ordering state of tobermorite.

To see the influence of different independent parameters, experiments were carried out in the temperature range of 170 up to 210°C in the systems CaO-SiO₂-D₂O and CaO-SiO₂-Al₂O₃-D₂O using two different grain sizes of quartz. Lime-silica based green bodies instead of suspensions were prepared for the measurements, to stay as close as possible to the industrial production process of AAC.

The first mineral phases formed are poorly crystallized with a varying Ca/Si ratio between 1.1 and 1.3. Subsequently tobermorite is formed by the reaction of this precursor phases with quartz. The mechanism of the reaction can be described by the conversion of quartz and displays a non-isokinetic behaviour. It changes from a solution controlled initial step of the reaction to a diffusion controlled one. A second change, again leading to a solution controlled mechanism, occurs at durations as low as 3h depending on temperature, quartz grain size and Al-content.

High-temperature XRD and thermal analysis of TPP-montmorillonite and changes induced by NaBr

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Tetraphenylphosphonium-montmorillonite (TPP-MMT) has been investigated as a fire retarding agent in composite materials (1, 2). It is produced by cation exchange of Na-MMT with TPP-Br. In this study, the thermal behavior of TPP-MMT and of mixtures of TPP-MMT with NaBr was investigated in situ by high-temperature X-ray diffraction (HT-XRD) and thermogravimetric analysis (TGA).

In the TGA, pure TPP-MMT shows a single weight-loss event at 584 °C during heating. As is revealed from HT-XRD, during this event the d-spacing of the basal reflection (0 0 1) of TPP-MMT contracts continuously from about 19 Å to about 10 Å – which corresponds fairly well to that of dehydrated montmorillonite. Since no sodium is present in the sample the negative charge of the T-O-T sheets must be balanced by some positively charged remnant of the volatile TPP ions or its decomposition products, respectively. In fact, during the long-term HT-XRD measurement, the decrease in d-spacing is a slowly evolving process, starting at about 500°C and finishing somewhat above 600°C. This indicates that TPP does not escape as an integrated whole from TPP-MMT but decomposes into smaller pieces, driving the continuous decrease in d-spacing.

For a mixture of TPP-MMT with a few weight percent of NaBr a completely different behavior is observed. In the TGA, a new decomposition step at a markedly lower temperature appears. E.g., for 98 wt.% TPP-MMT + 2 wt.% NaBr, the respective lower decomposition temperature is 442°C, the upper one remains at 580°C. For higher concentrations of NaBr, the upper step approaches the lower one, while at its high temperature tail a third event appears as a broad shoulder reaching to about 630°C. HT-XRD reveals that the NaBr peaks disappear within a temperature range of 350 to 450°C. In the same range the intensity of the (0 0 1) peak of TPP-MMT decreases to zero – while it is not shifted in position! This indicates a completely different decomposition process: TPP is not decomposed within the interlayers of MMT as in pure TPP-MMT but it obviously escapes from the MMT interlayers as an integrated whole. From the XRD data we infer that a retro-reaction takes place: TPP-MMT + NaBr → TPP-Br + Na-MMT. Thus Na⁺ ions would guarantee charge balancing for the MMT. At these elevated temperatures, the recombining TPP-Br will decompose (3). In fact, in the respective temperature range, preliminary TGA measurements coupled with mass spectrometry reveal evolving bromobenzene, one of the typical decomposition products of TPP-Br at high temperatures.

For the second event, we assume that some products of the first event will eventually evaporate, while the third event in samples with high NaBr contents most probably corresponds to the well-known dehydroxylation of montmorillonite – the loss of water from the T-O-T sheets (4, 5) – that we also observed for pure Na-MMT samples. It does not involve prominent changes in the XRD pattern of montmorillonite, except for a small shift of the hk0 band and an increase in its intensity. Thus, this event probably takes place in all our samples but is simply concealed in TGA of samples low in NaBr.

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Metamikte Titanite

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Die Details der strukturellen Merkmale von Titanit (CaTiSiO_5), darin vorkommende ketten- und ecken-verknüpfte TiO_6 -Oktaeder, SiO_4 -Tetraeder sowie 7-fach koordinierte Ca Positionen sind seit den 80iger Jahren gut bekannt (Higgins and Ribbe 1976). Später gelang es, die Details der Kristallstruktur synthetischer und natürlicher Titanite sowie das damit korrelierte thermische, antiferrodistortive Transformationsverhalten $A2/a - P2_1/a$ aufzuklären (Kek et al. 1997)

Von den Autoren wurden Studien an metamikten Titaniten mittels integrierender und lokaler Methoden ausgeführt, um ein besseres Verständnis für die Details der strukturellen Störungen und deren sequenzielle thermische Ausheilung zu gewinnen. Mittels eines erweiterten Lifshitz-Dzialoshinskii-Modells gelang es, wesentliche Merkmale des inhomogenen metamikten Zustands über ein internes Stress-Feld-Potential und das Wachstum naheordneter kristalliner Cluster in einer ungeordneten Matrix phänomenologisch zu behandeln (Tolédano, Bismayer 2005). Die Mehrzahl der bisherigen spektroskopischen Untersuchungen geht auf FTIR Studien zurück, die einerseits quantitative Rückschlüsse auf das thermische Verhalten der OH-Spezies sowie Näherungen zum Verhalten der Si-O Bindungen ermöglichen jedoch im niedrigeren Wellenzahlbereich durch extrem breite Banden geprägt sind, deren Verschiebungen und integrierte Absorbanzen nur qualitative Ergebnisse liefern. Ramanstreuexperimente an synthetischem, kristallinen und an metamiktem Titanit zeigen, dass der Ordnungszustand und lokale Phänomene sehr gut mittels Ramanspektroskopie quantifiziert werden können (Abb. 1). Durch aktuelle Studien mittels Mikro-Ramanspektrometer mit Dreifachmonochromator und variabler Anregungsfrequenz von UV-VIS lassen sich die lokalen strukturellen Baumuster und Bindungsmodifikationen detailliert erfassen. Anregungsfrequenzen im UV erlauben zudem die Maskierung von Fluoreszenzeffekten in natürlichem, teilweise verunreinigtem Material.

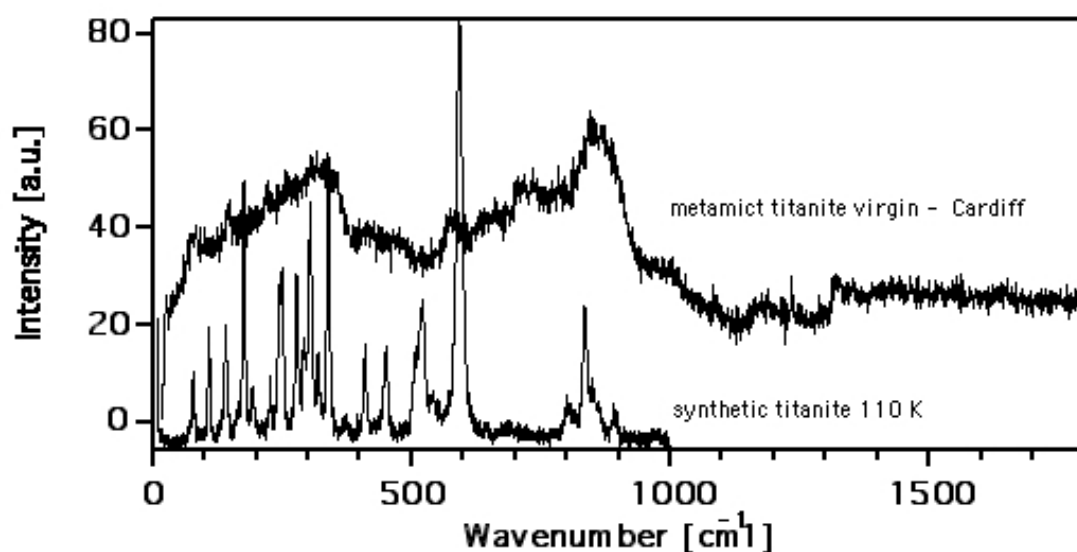


Abb. 1 Unpolarisierte Ramanspektren (514 nm) von synthetischem, kristallinem (110 K) und metamiktem Titanit (305 K).

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Constraints on the Formation of Seifertite in Martian Meteorites

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SiO₂ polymorphs are frequent constituents in Shergottites. These meteorites represent the basaltic subgroup of SNC-meteorites, which are supposed to originate from Mars as indicated by their distinct petrology and noble gas signatures. Their characterisation yields therefore essential information on the origin and magmatic evolution of the Red Planet, as well as a detailed understanding of their shock history and cratering processes on Mars. Usually high pressure phase transformations occur at certain transition pressures and are used as crucial markers for estimating maximum shock pressures and temperatures arising during severe meteoritic impacts on planetary bodies. Such shock-induced transformations of silicates comprise either amorphisation processes, like the formation of maskelynite, or the crystallisation of high-pressure polymorphs from shock melt veins or pockets (Langenhorst & Poirier, 2000). However, high-pressure polymorphs of SiO₂ may represent an exception, since the recent discovery of several tens of microns large crystals in Shergotty that transformed to Seifertite (α -PbO₂ structured SiO₂) point to an unknown fast solid state transformation process or appreciably higher shock conditions (e.g. Sharp et al., 1999, El Goresy et al., 2008). In order to constrain the formation conditions of Seifertite during shock metamorphism, we investigated its occurrence in the meteorites Shergotty and Zagami, for which maximum shock pressures of 29 and 31 GPa are estimated by Stöffler et al. (1986). We compare these observations with results of Dhofar 378, which suffered extremely high pressures of 55 to 75 GPa (Ikeda et al., 2006).

Thin sections of all three Shergottites were examined by optical microscopy and electron microprobe. Selected areas containing SiO₂ polymorphs were subsequently prepared for transmission electron microscopic investigations by careful ion thinning. Low electron doses have been applied to avoid a rapid amorphisation of irradiation sensitive SiO₂ polymorphs.

The results from Shergotty and Zagami have shown that silica polymorphs occur frequently in the mesostasis together with maskelynite and traces of either tranquillityite or iron sulfides. Silica phases are typically a few microns large and show characteristic sets of amorphous lamellae as first described by Sharp et al. (1999). All observed electron diffraction patterns of crystalline SiO₂ fragments are consistent with Seifertite. Whereas accessories exhibit high densities of shock related defects, crystalline fragments of silica phases show no further defects besides the amorphous lamellae. However, the defect microstructure of accessory phases in Shergotty and Zagami indicate that Seifertite-bearing areas are not remolten during the impact event and therefore Seifertite must have been formed by a solid state process. Significantly higher shock pressures would cause by far more severe melting like in Dhofar 378, where former plagioclase crystals are completely remolten, apparent by the formation of bubbles and recrystallised needles occurring in the rim of such areas. The absence of such features in Shergotty and Zagami does not suggest that both meteorites have experienced significantly higher shock pressures than estimated earlier by Stöffler et al. (1986). Seifertite must have been therefore formed metastably at pressures well below the equilibrium pressure of around 80 GPa. In contrast no post-stishovite phases have been identified in Dhofar 378 despite such extremely high shock pressures and may indicate that the recovery of potentially formed post-stishovite phases has been prohibited by high post-shock temperatures.

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RFA mobil - Möglichkeiten und Grenzen

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Die RFA (Röntgenfluoreszenz-Analyse) ist eine etablierte Methode zur Elementanalyse in der Metallurgie, Zementindustrie, chemischen Industrie, aber auch in der Geologie und Mineralogie. Ihr Vorteil ist die schnelle und vor allem zerstörungsfreie Analyse in Bezug auf die vorliegende Probe. Denn obgleich die Probe ggf. präpariert werden muss, steht sie nach der RFA noch für weitere Untersuchungen zur Verfügung. Untrennbar verbunden mit der RFA sind Fragen der Kalibration und der der Matrixkorrektur, welche für die in der Geologie/ Mineralogie meist eingesetzten stationären RFA-Geräte hinlänglich bekannt sind. Bei diesen werden meist Röntgenröhren mit einer Anregungsspannung von 50-60 KV und einer elektrischer Leistung von 3-4 KW eingesetzt.

Noch bis vor wenigen Jahren, waren mobile und tragbare RFA-Geräte ausschließlich mit Radionuklid-Quellen geringer Aktivität ausgestattet. Diese bleiben zunehmend nur noch speziellen Anwendungen vorbehalten, wie der Analyse Seltener Erden auf den K-Linien mit Hilfe hochenergetischer Radionuklid-Quellen (wie Cd-109 mit 88 keV im Niton XLp 522K Rare Earths Analyzer).

Heute haben mobile und tragbare RFA-Geräte Röntgenröhren mit Anregungsspannungen bis 50 KV und Leistungen von wenigen Watt (Beispiel Niton XL3t-Serie : 50 KV/ 2 W). Im Gegensatz zu stationären RFA-Geräten waren diese von Anfang an für die mobile Anwendung und damit auf robuste Analysen auch an schwierigen Proben konzipiert. In der Praxis erfordert das gewisse Kompromisse an den uneingeschränkt universellen Einsatz, weil jeweils bestimmte Programme (für Metalle, Böden, Mineralstoffe, usw.) in Bezug auf die entsprechende Probe anzuwenden sind. Wie für jede neue Technik gab und gibt es in der Fachwelt viel Pro und Contra, teils technischer Art aber auch mit diversen subjektiven Ängsten verbunden. Der vorliegende Beitrag wird deshalb auf technische Aspekte eingehen, wie:

- Physikalische Detektor-Artefakte (Escape-Peaks, Pile-up, Tailings und Shelf)
- Kalibration (empirische vs. FP-Kalibration)
- Untergrund-Korrektur
- Matrix-Korrektur (Absorptions- und Sekundär-Fluoreszenz)
- Compton-Normalisierung
- Proben-Geometrie (Abstand, Oberfläche, Größe, Dicke)

Weiterhin geht der Beitrag auf eine Reihe subjektiver Vorbehalte ein wie:

- Aspekte zum Strahlenschutz (Rechtliche Situation, praktische Handhabung)
- Screening mit tragbarer RFA (wird das Labor nun überflüssig oder sinnvoll ergänzt?)

Anwendungen unter Nutzung der neuesten Detektor-Technologie (SDD – Silicon Drift Detector, am Beispiel Niton GOLDD-Technologie) werden vorgestellt.

Analyse der Schadstoffmobilität in Auenböden zum Test von Phytoremediationsmaßnahmen mit biotechnologisch optimierten *Salix*- und *Populus*-Klonen – Konzept und erste Ergebnisse

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Großflächige Schadstoffbelastungen in deutschen und russischen Auengebieten erfordern die Entwicklung einer kostengünstigen Methode der Bodensanierung für wechselfeuchte Standorte. Nach aktuellem wissenschaftlichem Stand kann die Phytoremediation als ein aussichtsreiches Verfahren hierfür angesehen werden.

Für eine erfolgreiche Entwicklung von *in situ*- Sanierungsstrategien ist ein detailliertes Verständnis der die Schadstoffdynamik bestimmenden bodenchemischen Prozesse erforderlich. Ziel dieser Studie ist es daher, die Prozesse der Mobilisierung und Immobilisierung von Schadstoffen (Schwermetalle wie As, Cd, Hg und Zn sowie organische Kontaminanten) in den wechselfeuchten Böden der Elbe- und Okaauen zu untersuchen. Die Ergebnisse sollen im weiteren Projektverlauf für Phytoremediationsfeldversuche mit biotechnologisch optimierten *Salix*- und *Populus*-Klonen verwendet werden.

Im Rahmen der Studie werden verschiedene Untersuchungen auf drei verschiedenen Skalenebenen durchgeführt. Zum einen wird in Mikrokosmen unter einstellbaren bodenchemischen Bedingungen der Frage nach der Mobilisierung der Schadstoffe nachgegangen. Des Weiteren wird in *in-situ* entnommenen und monolithisch gefüllten Kleinlysometern (Instrumentierung mit Saugkerzen, FD-, Temperatur- und Redox-Sonden) der Einfluss von verschiedenen Grundwasserständen auf die Schadstoffmobilität simuliert. Als dritter Versuchsbaustein werden die Laborergebnisse an Feldversuchen mit Hilfe von entsprechend ausgerüsteten bodenhydrologischen Messplätzen (Ausrüstung wie Lysimeter) validiert.

Auf der Grundlage des aktuellen Wissenstands können als die hauptsächlich zu untersuchenden Einflussfaktoren Redoxpotential, Temperatur, pH-Wert (wird vorerst nur in Mikrokosmen erfasst) und Bodenfeuchte (nur Freiland und Lysimeter) angesehen werden.

Als Ergebnis wird vor allem eine Abhängigkeit der Schadstoffmobilität vom Bodenwassergehalt, dem oberflächennahen Grundwasserstand und den daraus resultierenden bodenchemischen Faktoren Redoxpotential und pH-Wert erwartet.

Im weiteren Projektverlauf sind die Anwendung von Phytoremediationsmaßnahmen auf russischen und deutschen Standorten sowie die energetische Verwertung der gewonnenen Biomasse vorgesehen.

Die Studie wird im Rahmen des Forschungsprojekts „Phytoremediation von kontaminierten Auenböden im Wolga-Einzugsgebiet“ vom Bundesministerium für Bildung und Forschung finanziell unterstützt (Förderkennzeichen 02WT0869).

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Partitioning of Sr between aqueous fluids and silicate melts – implications for Sr complexation

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Interaction between fluids and melts is widespread in many geological processes and results in element fractionation. The element fractionation depends on the PT conditions of equilibration and compositional (x_i) and structural parameter of the system. Partitioning between silicate melts and aqueous fluids has been the subject of several studies (e.g., Bai et al. 1999; Webster et al. 1989). Still, the knowledge about it is fragmentary, particularly on the relationship between complexation and element fractionation.

In a recent study, we investigated the effect of the alumina saturation index (ASI = $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ in moles) on the partitioning of Rb and Sr between haplogranitic melts and aqueous fluids at 750 to 950°C and 200 to 500 MPa. The experiments were done in externally and internally heated pressure vessels. The starting materials included a series of synthetic haplogranitic glasses (ASI: 0.6 – 1.4, corresponding to typical natural granites) doped with ~2500 ppm Rb and Sr each, and two aqueous fluids, H_2O and $\text{H}_2\text{O} - 1\text{ m NaCl} - 1\text{ m KCl} - 0.02\text{ m HCl}$. The salt solution was used because the Cl content has a particularly strong effect on fluid-melt partitioning (e.g., Bai et al. 1999; Webster et al. 1989). The partitioning data ($D^{f/m}=c^f/c^m$) of Rb and Sr display different trends with composition (Fig. 1). The $D^{f/m}_{\text{Rb}}$ values increase linearly with Cl concentration in the fluid and are not affected by the melt composition (Fig. 1A). However, Sr partition coefficients are a function of both melt and fluid composition (Fig. 1B). Temperature and pressure did not have a significant effect on the partitioning of both elements at pressures ≤ 500 MPa, i.e. at conditions at which the mutual solubility of aqueous fluids and silicate melts is small.

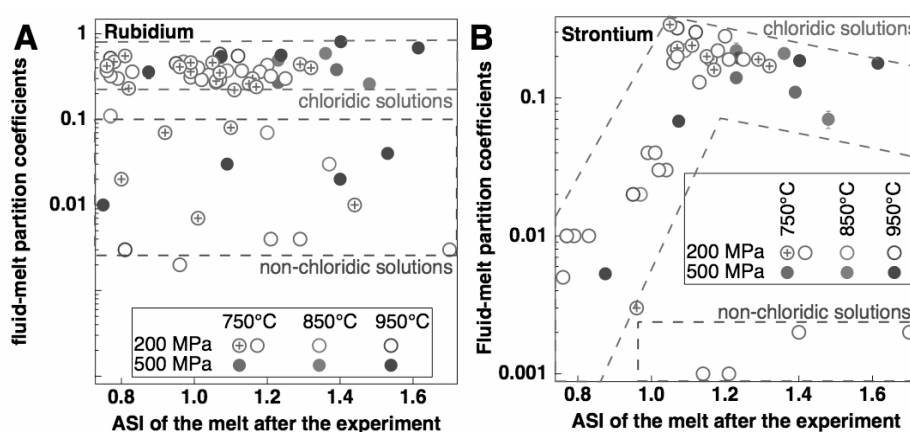


Figure 1. Rubidium (A) and Strontium (B) partition coefficients vs. ASI and as function of fluid composition.

The partitioning behavior of a given element is related to its complexation in the fluid and its incorporation in the melt. The latter is due to ASI dependent differences in the melt structure. While these structural parameter appear to be constant for Rb over the studied compositional range, our partitioning data for Sr imply a change in the complexation in at least one of the two phases. For silicate melts, Kohn et al. (1990) found only small changes in the first coordination shell of Sr in a suite of melts with various degree of polymerization. Thus, they argued that incorporation of Sr in the melt should not play a major role in controlling the Sr partitioning. If we accept the finding for the melt, our results suggest changes in the complexation of Sr in the aqueous fluid, perhaps the formation of Sr-silicate complexes. Therefore, we are on the course to study the complexation of Sr in aqueous fluids equilibrated with haplogranitic melts with varying ASI in-situ at elevated P-T using hydrothermal diamond-anvil cells (HDAC) and extended X-ray absorption fine structure (EXAFS).

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Concomitant Cu isotope and base metal fractionation at the supergene Skorpion zinc deposit, Namibia

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Skorpion Mine in southern Namibia is a zinc non-sulphide deposit with an unusual supergene ore paragenesis consisting predominantly of sauconite, subordinately of hemimorphite and hydrozincite, and minor to rare occurrences of scholzite, tarbuttite, and skorpionite (Borg et al. 2003). Distinct zones of subeconomic economic Cu and Pb grades occur in an overlapping fashion between the zinc ore body in the SE and a gossanous Fe-Mn zone in the NW. The latter has been shown to be the oxidized remains of a pre-existing Zn-(Cu-Pb) massive sulphide body (pyrite, sphalerite with minor chalcopyrite and galena), remnants of which are still preserved down-dip at more than 500 m depth. The supergene ore body is hosted in a highly faulted and micro-fractured package of Late Proterozoic, metamorphosed, rhyolitic hyaloclastic, volcanoclastic and siliciclastic rocks, adjacent to a major marble unit. The position of the supergene ore is unusual in that it occurs within silicate host rocks rather than within carbonates, which is the more common situation for supergene zinc deposits world-wide. The current metallogenic model involves acidic supergene ore fluids from oxidation of sulphide protore that have dissolved/replaced feldspar and mica by Zn-hydrosilicates, which had a buffering effect on the fluid. The supergene fluid was thus metal-stripped and pH-neutral when reaching the marble unit, which acted as a hydraulic barrier and caused ponding.

Samples of sulphide protore and secondary sulphide ore (containing microscopic brunnkite), as well as supergene ore from the Fe-Mn-, Pb-, Cu-, and Zn-zone of the deposit have been analysed for their metal contents and Cu isotope composition. Approximately 0.05g of powdered sample material was dissolved in aqua regia over night at 200°C and dried on a hot plate at 40°C. Cu was separated from the matrix through ion exchange chromatography (IEC) as outlined in Mathur et al. (2005) without the use of hydrogen peroxide. To ensure all of the Cu was recovered, gravimetric yields were checked for IEC samples and only samples with >90% yield are reported. The samples purified with IEC were diluted to approx. 100 ppb Cu. Samples were injected into a MC-ICPMS (Micromass Isoprobe at the University of Arizona and Neptune at Washington State University) in low resolution mode using a microconcentric nebulizer to increase sensitivity for the samples with lower concentrations of Cu. Cu isotope ratios are reported in delta notation where the standard (std) was the NIST 976 Cu standard. Two blocks of 25 ratios are reported as an average for each run.

The results show near-zero negative $\delta^{65}\text{Cu}$ values for the primary sulphide ore and distinctly positive values (+0.2‰ to +1.7‰) for mobilized, i.e. supergene non-sulphide ores. A clear and systematic zonation exists between the various supergene metal zones and Cu-isotope signatures. Protore-proximal zones are Fe- and Mn-rich with lower positive $\delta^{65}\text{Cu}$ values and grade (via a distinct Cu- and Pb-zone) into the Zn-ore body where $\delta^{65}\text{Cu}$ values are significantly more positive. The $\delta^{65}\text{Cu}$ fractionation factor at Skorpion ranges between 0.6 and 1.8 ‰ between in-situ hypogene and distal mobilized supergene ore. This is in agreement with fractionation factors determined experimentally for chalcopyrite ores and differs from those of chalcocite ores, where the factor is in the range of 3‰ - 4‰ (Mathur et al. 2005). From their (still limited) number of experiments, the same authors determined a $\delta^{65}\text{Cu}$ fractionation factor range of approx. 0.6‰ for biotic and 1.5‰ for abiotic Cu isotope fractionation.

The supergene Skorpion ore body with its systematically zoned ore body might thus have formed in a meteoric, near-surface environment with both abiotic and possibly biotic ore-forming processes involved.

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Sapphirine-bearing Mg-rich paragneisses from the Palni Hills (South India): Evidence for late Neoproterozoic UHT metamorphism in the Southern Granulite Terrane

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The Southern Granulite Terrane (South India) is a key area for studying the formation of the supercontinent Gondwana in the Neoproterozoic to Cambrian, as it is situated in a central position of postulated paleogeographic reconstructions of Eastern Gondwana (e.g. Meert, 2003). However, due to the lack of sufficient geochronological and petrological data an unequivocal correlation of the Southern Granulite Terrane with other formerly adjoining Gondwana fragments (e.g. Madagascar, Sri Lanka, East Antarctica, Dharwar Craton) failed so far. Such linking requires the knowledge of protolith formation ages as well as of the nature and timing of metamorphic events. In the present contribution we focus on the reconstruction of the metamorphic evolution of sapphirine-bearing granulites from the Palni Hills, which are situated in the central part of the Madurai Block, the largest crustal block of the Southern Granulite Terrane. Late Neoproterozoic UHT metamorphism has been constrained for the migmatitic sapphirine-bearing granulites, by combining zircon and monazite age determinations with *P-T* pseudosection modelling and geothermobarometric calculations. The sapphirine-bearing granulites occur in a sequence of Mg-rich migmatitic paragneisses, which is surrounded by charnockitic orthogneisses. The sapphirine-bearing granulites are subdivided into three types: MgAl-rich Qtz-bearing or Qtz-free Opx-Sil granulite (bulk rock X_{Mg} : 0.86), less magnesian Qtz-free Grt-Opx-Sil granulite (bulk rock X_{Mg} : 0.67) and less aluminous Qtz-bearing or Qtz-free Grt-Opx granulite (bulk rock X_{Mg} : 0.68-0.62). Clockwise *P-T* paths with a steep decompression segment at UHT conditions are reconstructed for the sapphirine-bearing granulites through the application of pseudosection modelling in the NCKFMASHT system: The coarse-grained diagnostic peak-assemblages Opx-Sil±Qtz±Spr, Grt-Opx-Sil and Grt-Opx±Qtz formed through progress of biotite-dehydration-melting reactions during heating up to UHT conditions of c. 1020°C/12 kbar. Subsequent near-isothermal decompression to c. 9.5 kbar/1030°C is recorded by Opx-Pl coronas resorbing Grt-Qtz assemblages in the Grt-Opx granulite. Continued UHT-decompression led to the growth of Crd-Spr symplectites in Qtz-free Opx-Sil granulite, whereas Opx-Spl-Pl and Opx-Spr-Pl symplectites formed at the expense of garnet in the Grt-Opx granulite at c. 950°C/8 kbar. The Grt-Sil assemblage of the Grt-Opx-Sil granulite was resorbed by Spl-Pl-Crn symplectites, which in turn were replaced by Spr-Pl symplectites. UHT-decompression is consistent with rimward increasing Al content of orthopyroxene inclusions (up to 9.6 wt. % Al_2O_3) in garnet and of porphyroblastic orthopyroxene (up to 9.8 wt. % Al_2O_3) and with the high Al content of unzoned coronitic (up to 10.1 wt. % Al_2O_3) as well as symplectitic (up to 10.4. wt % Al_2O_3) orthopyroxene. Back-reactions with crystallizing melt led to re-growth of biotite during post-decompressional cooling.

In-situ electron microprobe U-Th-total Pb dating of monazite provides evidence for two metamorphic stages: core ages of 551 ± 28 Ma are interpreted as the timing of the UHT metamorphic event, while broad rims with an age of 506 ± 20 Ma are attributed to monazite re-growth during back-reactions with the crystallizing melt. The monazite age of the UHT event is also supported by a concordant U-Pb age of 554 ± 5 Ma from zircon of a leucosome of the Opx-Sil granulite. Zircons of the surrounding charnockitic orthogneiss preserve late Archaean magmatic cores (upper-intercept age: 2534 ± 28 Ma), which are overgrown by late Neoproterozoic (lower intercept age: 558 ± 7 Ma), UHT metamorphic rims. This indicates that the igneous precursors of the orthogneisses did not act as the heat source for UHT metamorphism. The clockwise *P-T* path and the age data indicate that UHT metamorphism in the central part of the Southern Granulite Terrane is related to collisional tectonics during the final assembly of the Gondwana supercontinent in the late Neoproterozoic to Cambrian. Fast uplift of the rocks, as recorded by steep UHT decompression with well-preserved reaction textures and chemical zonation pattern, may reflect extension of the overthickened crust.

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Untersuchungen zur Verbesserung der chemischen Stabilität eines Bodenadditivs auf LDH-Basis durch Coating

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LDHs („layered double hydroxides“) der Hydrotalcit-Gruppe bestehen aus alternierenden Metall²⁺-Metall³⁺-Hydroxid- und Anionen-Wasser-Schichten, deren Struktur durch Brucit-ähnliche, trioktaedrische Hydroxidschichten bestimmt wird. In Folge des Einbaus dreiwertiger Kationen entsteht ein positiver Ladungsüberschuss, der über Wasserstoffbrücken durch die Anionen in der Zwischenschicht kompensiert wird. Ihre mechanische, aber vor allem die chemische Stabilität des LDHs beziehungsweise des LDH-Granulats im Boden sind wichtige Faktoren für die Eignung als Bodenadditiv – Langzeit-Nitrataustauscher. Um die chemische Stabilität zu erhöhen, wurde Granulat mit zwei verschiedenen Hüllenmaterialien gekapselt [Tetra-Calcium-Aluminat-Hydrat; Karbonat-beziehungsweise Nitrat-TCAH] und die Stabilität in verschiedenen sauren Lösungen untersucht.

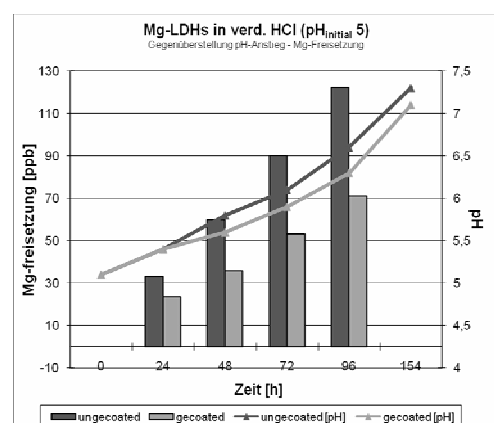
Niedrige Boden-pH-Werte können zu einer Auflösung bis zu etwa 25 % des eingebrachten LDHs innerhalb von zwei Jahren führen. Bei steigendem pH-Wert verringert sich die Löslichkeit sehr deutlich. Dementsprechend müsste der im Boden vorliegende pH-Wert durch die teilweise Auflösung der Hülle soweit gepuffert werden, dass dieser Bereich der geringen Löslichkeit erreicht wird. Versuche mit TCAH haben zur signifikanten Verminderung der Auflösungsgeschwindigkeit des MgAl-LDHs geführt.

Für die Versuche wurde Nitrat- bzw. Karbonat-TCAH verwendet, welches nach dem Kopartizipationsprinzip hergestellt wurde. Drei verschiedene Methoden zur Kapselung wurden erprobt: 1) Das Wälzen in einer TCAH-Suspension, 2) Das Aufwachsen von TCAH auf Granulat, 3) topotaktisches Aufwachsen von TCAH auf LDH-Kristalle („Kristall-Coating“).

1) Das Wälzen des Granulats in der Suspension hat zu guten Ergebnissen geführt. Es entstand eine gleichmäßige Hülle, welche jedoch in Folge der Trocknung Risse aufweist. 2) Die TCAH-Kristalle wachsen eindeutig auf der Oberfläche des Granulats, weisen jedoch deutlich unterschiedliche Größenverhältnisse auf und bilden ein sehr ungleichmäßiges Gefüge, welches die Bildung von Wegsamkeiten begünstigt. 3) Bei diesem Ansatz konnte kein eindeutiges Ergebnis erzielt werden. Die TCAH-Kristallite scheinen trotz der sehr ähnlichen Struktur nicht auf den MgAl-LDHs aufzuwachsen, sondern verwachsen mit anderen TCAH-Kristalliten.

Das Kapseln des Granulats mit einer TCAH-Suspension, hier durch wälzen in einer Suspension realisiert, hat großes Potential. Durch kurze Alterungsdauer des TCAH lassen sich relativ kleine Kristallite erzeugen, wodurch es möglich ist die Kristallite durch leichtes anpressen auszurichten. Die tafelförmigen Kristallite orientieren sich parallel zur Oberfläche des Granulats und bilden ein dichtes Gefüge. Die Verringerung von Wegsamkeiten und dementsprechend die verringerte Diffusion erhöhen die Wirksamkeit der Hülle und führen effektiv zur Verminderung der Auflösungsgeschwindigkeit des MgAl-LDHs.

Der pH-Wert der Lösung steigt bei gekapselten sowie bei nicht gekapseltem Material nahezu identisch an. Jedoch ist die Magnesiumfreisetzung bei dem beschichteten Material signifikant reduziert. Dementsprechend muss das Hüllenmaterial für den Anstieg verantwortlich sein. Die Auflösung des LDHs wurde somit eindeutig vermindert.



Ergebnisse der Auflösungsversuche von mit Carbonat-TCAH gekapselten Nitrat-LDH [durch wälzen in Suspension gekapselt]
Linie: Änderung des pH-Wert über die Zeit;
Balken: Magnesiumfreisetzung über die Zeit

Der Einfluss von Boroxid auf die Devitrifikation eines Kalk-Natron-silicatglases

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Untersucht wurde das Kristallisationsverhalten eines Kalk-Natronsilicatglases der Zusammensetzung von Devitrit [$\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$], dem sukzessiv, in Schritten a 5 % Stoffmengengehalt, B_2O_3 zugesetzt wurde.

Devitrit ist das Devitritationsprodukt üblicher Kalk-Natronsilicatgläser, die als Fenster- oder Flaschenglas eingesetzt werden. Die Phasendiagramme, die in den Standardwerken der wissenschaftlichen Literatur veröffentlicht wurden, gehen auf Morey (1925, 1932) zurück. In ihnen wird der Devitrit als inkongruent schmelzend dargestellt, dessen Kristallisationsneigung durch Zugabe von Borsäure vermindert werden kann. Ursache sei die Verminderung der Liquidustemperatur durch das Flussmittel B_2O_3 . In den beschriebenen Arbeiten sollte untersucht werden, ob genügend große B_2O_3 – Zusätze kongruentes Schmelzen des Devitrits provozieren können.

Für die Gläser wurden, entsprechend des stöchiometrischen Verhältnisses von Devitrit, CaCO_3 , Na_2CO_3 und SiO_2 eingewogen, homogenisiert und im Platintiegel bei 1500°C aufgeschmolzen. Anschließend wurde die Schmelze im Wasserbad abgeschreckt, gemörsert mit den entsprechenden Mengen B_2O_3 versetzt und homogenisiert. Das somit erzeugte Pulver wird anschließend bei 1500°C geschmolzen, für 1 h bei dieser Temperatur gehalten, abgeschreckt, gemörsert und ein weiteres Mal bei der gleichen Temperatur erschmolzen. Nach dem zweiten Durchgang wird die Schmelze kurz, bis zum Ende der Rotglut, abgekühlt und anschließend in einem Muffelofen mittels eines definierten Temperaturprogrammes herunter gekühlt. Die so erzeugten Grundgläser wurden für die weiteren Versuche in Scheiben gesägt und die Reste zu Pulver gemahlen.

Mit Hilfe von Differenzthermoanalysen konnte gezeigt werden, dass die Transformationstemperatur der Gläser mit steigendem B_2O_3 – Gehalt nur wenig ändert. Bei der Zugabe von 5 % B_2O_3 (Stoffmengengehalt) sinkt der Schmelzpunkt von Devitrit deutlich [von 1080° auf 930°C] und die Kristallisationstemperatur [von 804° auf 794°C] leicht ab, wobei neben Devitrit mindestens eine weitere Phase [Quarz; womöglich auch Wollastonit] auskristallisiert (Nachweis durch Thermoanalyse und Röntgenbeugung). Bei höheren B_2O_3 -Gehalten sinkt der Anteil von Devitrit deutlich und ist ab einem Gehalt von 20% B_2O_3 nicht mehr eindeutig nachweisbar.

Ein Vergleich der Röntgendiffraktogramme des borfreien Glases mit dem Glas, das 5 % B_2O_3 (Stoffmengengehalt) enthielt, zeigte eine leichte Verschiebung der Devitrit-Reflexe in Richtung größerer Werte. Das könnte bedeuten, dass sich die chemische Zusammensetzung leicht verändert hat. Eine Bewertung des Schmelzverhaltens ist noch nicht eindeutig möglich. Der im borfreien Glas kristallisierte Devitrit zeigt das eindeutigste Schmelzsignal in der Thermoanalyse. Auch die Röntgenbeugungsanalyse legt nahe, dass die Borsäure nicht als reines Flussmittel dient, sondern die Struktur der Schmelze und des Kristallisats verändert. Ersteres würde sich zwanglos durch die Borsäureanomalie erklären lassen.

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Milde Hydrothermalsynthese von Cancrinit Nanopartikeln $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_3)_2(\text{H}_2\text{O})_4$ bei 60°C und Untersuchungen zur thermischen Stabilität

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Cancrinite (CAN) sind Gerüstsilikate, die wegen Ihrer Struktur zur Gruppe der Zeolithe gezählt werden. Sie sind auf Grund Ihres spezifischen Aufbaus mit α -Käfigen und Strukturkanälen für zukünftige Nutzungen als mikroporöse Wirtsmatrix von besonderem wissenschaftlichen Interesse [1]. Untersuchungen an Cancriniten besitzen außerdem grundlegenden Modellcharakter für die technisch so wichtigen Zeolithe.

Im Mittelpunkt der Arbeit stehen Untersuchungen zur milden Hydrothermalsynthese bei einer Synthesetemperatur von nur 60°C, die Charakterisierung der Produkte sowie Versuche zu deren thermischer Stabilität. In drei kinetischen Versuchsreihen wurden jeweils Synthesen ohne vorherige Gelfällung, mit Gelfällung (aus Na-Silikat- sowie Na-Aluminatlösung) sowie Synthesen mit vorheriger Gelfällung und Zugabe des Additivs Triethanolamin (TEA) durchgeführt. Die Synthesenzeiten betragen pro Reihe jeweils 1h, 3h, 6h, 12h, 24h, 48h sowie 96h.

Zur Analyse und Charakterisierung der Syntheseprodukte dienten die FTIR-Spektroskopie, Röntgenpulverdiffraktometrie (XRD) und Rasterelektronenmikroskopie (REM). Untersuchungen zur thermischen Stabilität wurden mittels Heiz-IR-Spektroskopie sowie im Muffelofen durch Temperaturerhöhung auf 600°C und mit Hilfe der Thermogravimetrie und Differential-Thermoanalyse (TGA und DTA) durch Aufheizen bis zu 1400°C durchgeführt. Die Syntheseexperimente zeigten, dass eine vorherige Gelfällung der Komponenten im Vergleich die besten Ergebnisse bei der Strukturbildung des Cancrinites lieferte. In allen Fällen wurde mehr oder weniger stark fehlgeordneter CAN mit Stapelsequenzen ABA'B' sowie ABCA'B'C', bzw. intermediäre Phasen zwischen CAN und Sodalith (SOD) gebildet. Eine milde Hydrothermalsynthese bei nur 60°C und kurzer Reaktionszeit führt somit zu Produkten, die sich sehr deutlich von Nitrat-Cancrinit der üblichen 200°C-Synthese unterscheiden. Diese Unterschiede liegen nicht nur in weitaus niedrigerer Kristallinität und Perfektion sowie hohen amorphen Anteilen der Kristallisate begründet, sondern vor allem auch in der starken Fehlordnung der Struktur und deutlich verminderter thermischer Stabilität [2].

Der Einsatz von TEA bei der Nitrat-CAN-Synthese wurde bei dieser Arbeit erstmalig untersucht. TEA sollte eine Bildung größerer Kristalle begünstigen, da durch die Al-Komplexbildung mit Hilfe von Additiven bei Zeolithen bereits Kristallitgrößen um 50 Mikrometer und mehr erreicht wurden [3]. Die Zugabe von TEA brachte im Zusammenhang mit Na-Cancrinit hingegen keine Strukturverbesserung der Syntheseprodukte. Es wurden im Gegenteil sogar weit kleinere Kriställchen von wenigen Nanometern Größe synthetisiert. Durch den Einsatz von TEA im Nitrat-CAN-System bei nur 60°C konnte somit eine Methode für die Herstellung fehlgeordneter NO_3 -Cancrinite im Nanomaßstab erarbeitet werden. Da in diese Kristallisate deutliche Mengen an Nitrat eingelagert und Kristallitgrößen auf der Nanoskala analysiert wurden, stellen diese Verbindungen sehr interessante neue Materialien dar [2].

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Archäometrische Untersuchungen an Keramiken der spätneolithischen Vinča-Kultur (Rumänien)

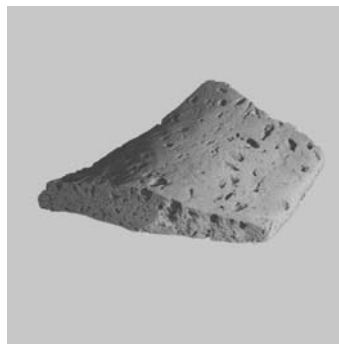
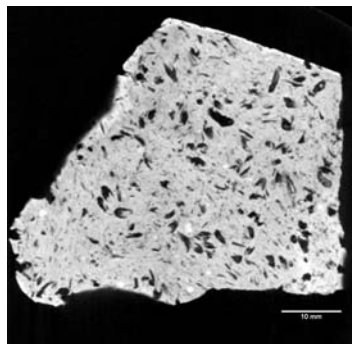
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Die im Laufe mehrerer Kampagnen aus einem Siedlungshügel bei Uivar im rumänischen Banat geborgenen Keramiken sind dem Mittel- und Spätneolithikum der Vinča-Kultur in Serbien, Ost-Kroatien und im westlichen Rumänien zuzuordnen. Neben Keramik der Vinča-Kultur kommt dort auch Keramik benachbarter Kulturen vor. Aufgrund unterschiedlicher Verzierungsstechniken wurde die Vinča-Keramik fünf archäologisch definierten Gruppen zugeordnet. Durch archäometrische Untersuchungen sollten diese Zuordnungen untermauert und ein Katalog von naturwissenschaftlich definierten Gruppenmerkmalen erstellt werden.

Die Keramiken weisen die üblichen grauen, roten und schwarzen Farben auf, die während des Brandes oder in der Abkühlungsphase durch Redox-Reaktionen erzeugt werden. Die Oberflächen zeigen Bearbeitungsspuren durch Glätten und Polieren sowie Verzierungen durch Ritzmuster und farbige Überzüge.



Der Phasenbestand der Scherben wurde mittels Röntgenbeugung (Raumtemperatur, in-situ-Hochtemperatur) Polarisationsmikroskopie und chemischer Analytik (EPMA) bestimmt. Die Ergebnisse erlauben Rückschlüsse auf die Brenntemperatur und Ofenatmosphäre. Die Anwesenheit flüchtiger Bestandteile wurde durch Thermogravimetrie untersucht.

Abb1: 3D-Visualisierung und 2D-Schnittbild (rechts) einer tomographischen Aufnahme der Scherbe XI/3757/15792 a

Die Anwendung der genannten Methoden führte für eine polierte, dunkelgrau-schwarze Scherbe zu interessanten Ergebnissen. Entgegen der von Archäologen geäußerten Vermutung wird die glänzende Schwarzfärbung der Oberfläche nicht durch Graphit hervorgerufen. Mit der C-Elementaranalyse konnte weder anorganischer noch organischer Kohlenstoff nachgewiesen werden. Auch Fe-Spinelle, die bei attischer Keramik als schwarzes Pigment diskutiert werden, konnten nicht identifiziert werden. Durch Mikrosondenanalyse am Anschliff wurde Ilmenit (FeTiO_3) als ein farbgebendes Pigment nachgewiesen. Im Röntgendiffraktogramm wurden Quarz und Feldspäte detektiert.

Das Gefüge der Tonscherben wurde mit 3D-Röntgencomputertomographie untersucht. Schrumpfrisse und Poren, die zum Beispiel durch Verbrennung von Pflanzenhäcksel, das als Magerungsmittel verwendet wurde, entstanden sind, treten als schwarze Flecken in einer Grauwert-Matrix deutlich in Erscheinung (siehe Abbildung).

Die Klassifikation aufgrund unterschiedlicher Verzierungsstechniken wird nur teilweise durch archäometrische Befunde zur Herstellungstechnologie bestätigt.

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Structural and magnetic studies of $\text{Bi}_2(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_9$

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The Bi_2M_4O_9 structure ($M = \text{Fe}, \text{Ga}$ and Al) contains nonmagnetic planes of bismuth oxide that sandwich a M^{3+} metal oxide region providing two types of metal sites with tetrahedral and octahedral coordination. In the present work, we study the local structure and magnetic properties of the solid solution $\text{Bi}_2(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_9$ ($0 \leq x \leq 0.9$) using X-ray diffraction, SQUID and in situ ^{57}Fe Mössbauer spectroscopy in the broad temperature range (4-1100 K).

The orthorhombic structure of $\text{Bi}_2(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_9$ with the space group $Pbam$ (No. 55) was refined using Rietveld method. Magnetic susceptibility measurements revealed that $\text{Bi}_2(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_9$ is paramagnetic for $x > 0.5$ in the whole temperature range, whereas it displays antiferromagnetic behaviour for $x \leq 0.5$. The Néel temperature (T_N) of the solid solution was found to be zero for $x > 0.5$. T_N decreases with aluminum doping from $T_N = 249$ K for $x = 0$ to $T_N = 4$ K for $x = 0.5$. Moreover, spin-glass behaviour is observed for the material with $x > 0.2$.

It is evidenced that independent of the Al content, the Mössbauer spectra of $\text{Bi}_2(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_9$ measured in the temperature range of 293-1100 K exhibit two doublets corresponding to Fe^{3+} cations in tetrahedral and octahedral coordination. At 4 K, Mössbauer spectra show magnetically split lines for $x \geq 0.4$ in accordance with the results of the magnetic susceptibility measurements. Quantitative information on the iron site occupation in the crystal structure of the material is obtained. It was found that independent of the Al content, Fe cations occupy both available sites in the orthorhombic structure with the same probability. Hyperfine parameters as a function of the Al concentration are derived from the spectra of $\text{Bi}_2(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_9$.

Process mineralogy: An ongoing challenge and opportunity for mineralogy and crystallography in the 21st century

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Process mineralogy has been the subject of numerous studies involving metallurgical processes worldwide and this has seen a resurgence in the past decade. The recent economic downturn led to a discussion regarding the relevance of mineralogical research in general and process-related research in particular.

The minerals that provide the commodities required by society are usually quite common and they have been studied in some detail in the past. In many cases however, it turns out that there is an underlying complexity that needs to be investigated with modern methods available to the materials science and mineralogical communities. This complexity is also reflected in the behaviour of the minerals in the various processes. A number of examples will be given:

Pyrrhotite is a common mineral occurring in numerous mineral deposits, notable in nickel and platinum-group element (PGE) deposits. The characteristics of this mineral are very complex with at least three new superstructures recently characterised. These minerals are also differing in their flotation characteristics and their tendency to oxidise. The characteristics of the mineral are in need of further detailed investigation. This is probably true for many other economically important (especially sulphide) minerals such as bornite, chalcopyrite and the sulfides containing rare, valuable elements such as Ga, Ge, Ag, Au, and PGE.

The sintering of iron ores is a common metallurgical practice to utilise fine-grained material. Sinters and pellets are preferred feedstock for blast furnaces because of their consistent composition and their high grade. The so-called SFCA bonding phases that form is important in that they enhance strength and reducibility in the materials. These phases have not been fully characterised in spite of important Australian research. Clearly there is scope for further work on a material that is produced in millions of tons.

Many fine-grained mineral equivalents are precursor phases for the production of catalysts. These range from fine-grained hydrous iron, cobalt, and manganese oxides that are further treated to produce catalysts, to the materials used for substrates of these catalysts. The study of these materials can be an important contribution by the mineralogical community.

The treatment and immobilization of hazardous waste materials will become increasingly important in the future as the impact of humanity increases. The study of low-temperature reactions to produce stable phases that can immobilise harmful elements and compounds will therefore assume an increased importance.

These examples emphasize the possibilities for mineralogical research in the near future. There is a perception that all common minerals have been studied and that mineralogical research has reached a point of diminishing return. This is far from the case and the importance of mineralogical research in metallurgical and chemical process research is assuming a new relevance.

Solubility of fission-derived platinum group elements in radioactive wastes under repository conditions

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Significant amounts of various stable and radioactive isotopes of the platinum group elements (PGE) ruthenium, rhodium, and palladium are formed by nuclear fission processes in nuclear reactors. In spent nuclear fuel (SF), these fission products are mainly included in micron- to nanometer-sized hexagonal closed packed (hcp) intermetallic alloy particles (epsilon-phase) that contain also molybdenum and technetium-99, and are situated often on grain boundaries in the original uranium-oxide fuel matrix (e.g. Buck et al. 2004). The chemical composition of the epsilon-phase and the relative proportions of the respective PGE depend on the original oxygen-to-metal ratio and the burn-up of the fuel, with higher yields of palladium and decreasing molybdenum contents with increasing burn-up (e.g. Kleykamp 1985, 1990; Buck et al. 2004). In vitrified high-level radioactive wastes (HLW) from fuel reprocessing, the PGE occur as finely dispersed micrometer-sized metallic and oxide particles in the glass matrix (cf. Galois et al. 1998; Grambow 2006). In addition, intermediate-level waste streams (ILW) may also contain significant inventories of radioactive PGE-isotopes such as palladium-107 and ruthenium-106 with miscellaneous solid speciation, depending on waste sources and treatment (e.g. NDA 2008).

The safe disposal of radioactive waste requires that the waste is isolated from the geo-/biosphere until radioactive decay has reduced its radio-toxicity to innocuous levels for humans and the environment. Long-term containment of waste and subsequent slow release of radionuclides into the geosphere will rely on a combined system of natural and engineered barriers including a robust waste containment design. For accomplishing the isolation of SF/HLW and ILW from the environment for an adequate space of time, the disposal in deep geological formations is usually favoured. Kinetic and chemical thermodynamic modelling studies are required in support of safety cases and performance assessments associated with concepts for radioactive waste repositories to assess the long-term release of radionuclides from the wastes and their potential to migrate via the groundwater pathway into the biosphere.

In this context, thermodynamic modelling studies were performed to evaluate the solubility and speciation of various PGE in the near-field and far-field of a repository for radioactive wastes, starting with a compilation and critical review of relevant thermodynamic data for conditions pertinent to geological disposal. The scenarios considered comprise the disposal of SF/HLW in granite or clay-rich rocks as well as the cementitious environment of an ILW disposal facility. The speciation calculations and estimated solubility limits take into account the variability in the geochemical conditions (e.g. pH, redox conditions, ionic strength, solution chemistry) associated with the respective disposal options. Solubility limiting PGE phases comprise mainly the metals as well as simple sulphides, and possibly – in case of more oxidising conditions – oxides and/or (oxy)hydroxides (e.g. RuO₂), depending on the geochemical environment in the near- and far-field of the geological disposal facility. In contrast to palladium and ruthenium, thermodynamic data for aqueous complexes and solid phases of rhodium are rather sparse and of uncertain reliability for the conditions relevant to nuclear waste disposal. Thus the aqueous speciation and solubility of rhodium in the repository environment can only be poorly constrained at present.

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Preliminary Study on the Mineral Chemistry and Fluid Inclusion Properties of Pb-Zn-Cu Ore Deposits from the Kabadüz Area (Ordu, NE-Turkey)

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A number of hydrothermal type Pb-Zn-Cu ore veins with a thickness reaching up to 2 meters are located in The Kabadüz area (Ordu-NE Turkey) along the fault zones formed in NW-SE directions. The primary mineral paragenesis of the ore veins are composed of pyrite, chalcopyrite, sphalerite, galena, tennantite with quartz and less amount of calcite and barite as a gangue mineral. Optical studies indicate that the investigated ore veins have been intensively deformed after the first stage mineralization. Concentrically zoned replacement of pyrites, and sphalerite exsolutions in chalcopyrites as well as cataclastic textures are the most common textures observed in the investigated ore veins.

Pyrite, chalcopyrite and galena have stoichiometric composition and pyrite contains up to 0.04 wt% Ni, 0.95 wt% Zn, and 0.60 wt% As, and chalcopyrite contains up to 0.86 wt% Zn, 0.14 wt% Au, and 0.07 wt% Ag. Galena is found to contain up to 0.18 wt% Ag. Sphalerite is poor in Fe and contains up to 0.35 wt% Mn, 2.18 wt% Cu, 0.07 wt% Ag, 0.89 wt% Cd, and 0.10 wt% Hg. Tennantite is also poor in Fe and it contains up to 1.40 wt% Bi. Different phases from the each different veins are found to be similar in composition.

All inclusions classified as liquid-rich two phases according to the fluid inclusion studies performed on sphalerite and quartz minerals. Measured eutectic temperatures indicate that CaCl_2 , MgCl_2 and FeCl_2 were dominant during the first stage mineralisation, whereas NaCl and KCl dominant at the second stage. The salinity of the fluid inclusions are in the range of 15.1 to 1.7 % (avg=10.5) NaCl equivalent. The range of the temperature of the fluid was found to be between 433-193 °C (avg=294) during the crystallization of the sphalerite minerals, whereas it is in the range of 436-228 °C (avg=313 °C) determined during the crystallization of the quartz.

Measured homogenisation temperature suggests hypothermal-mesothermal stage for the ore veins investigated. Calculated salinity contents of the inclusions are determined to be typical for hydrothermal ore deposits. Also, Zn/Cd ratio of the sphalerites, ranging between 100 and 235, characteristically consistent with hydrothermal type ore deposit (Gottesmann and Kampe, 2007). Homogenization temperatures, salinity of the fluid inclusions, mineral paragenesis and succession as well as textural properties of the investigated ore veins show similarity. According to textural properties, mineral composition and fluid inclusion data, it is suggested that the ore veins in the investigated area may have formed from the same/or similar ore forming processes.

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Wie genau sind CEC-Methoden?

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Seit mehr als 150 Jahren wird die Kationenaustauschkapazität (CEC) zur Charakterisierung von Böden und Tonen verwendet. Die CEC wird außerdem in der Qualitätskontrolle technischer Prozesse oder von Produkten eingesetzt. Zur Bewertung von Mineralreaktionen dienen Parameter wie die CEC als signifikante Indikatoren, zum Beispiel in Versuchen mit geotechnischen Barrieren in der Endlagertonforschung.

In der Praxis ist die Wahl der geeigneten Methode ein Problem, ihre zuverlässige Durchführung und auch die Bewertung der Ergebnisse. Langjährige Untersuchungen haben gezeigt, dass alle Faktoren für sich ein hohes Fehlerrisiko aufweisen.

i) Wahl der geeigneten Methode. Die unproblematischsten Tone im Zusammenhang mit CEC-Experimenten sind solche, die nur Tonminerale und weitere typische sedimentäre Minerale wie Quarz und Feldspäte enthalten. Bei derartigen Proben können nahezu alle gängigen Methoden eingesetzt werden. Schwierig wird es, wenn lösliche Minerale wie der häufig auftretende Calcit bzw. auch Gips vorliegen. Diese Minerale werden typischerweise partiell aufgelöst und verfälschen so (je nach Methode) erheblich die CEC sowie die ebenfalls relevanten Parameter der austauschbaren Ca^{2+} -Kationen. In solchen Fällen müssen angepasste Methoden verwendet werden, die zum Beispiel mit einer vorherigen Sättigung der betreffenden Minerale arbeiten.

ii) Zuverlässige Durchführung. CEC-Experimente erfordern eine gewisse Routine, deswegen ist es notwendig einen gewissen Durchsatz zu haben.

iii) Bewertung der Ergebnisse. Zur Bewertung reichen gute Übereinstimmungen von Doppelbestimmungen keinesfalls aus. Es müssen regelmäßig Standardproben (mit jeder Serie) analysiert werden (z.B. Regelkarten). Die gemessenen Ergebnisse müssen außerdem auf Plausibilität überprüft werden, dazu gehören 1) die Übereinstimmung zwischen CEC und der Summe der austauschbaren Kationen (muss nicht zwingend gut sein, ist es aber häufig) und 2) die Kontrolle der Höhe der CEC mit dem Mineralbestand (z.B. über Smektitgehalt). Übereinstimmungen der CEC-Werte identischer Proben hängen davon ab in welchem zeitlichen Abstand, von welchem „Operator“ und mit welcher Methode gearbeitet wurde.

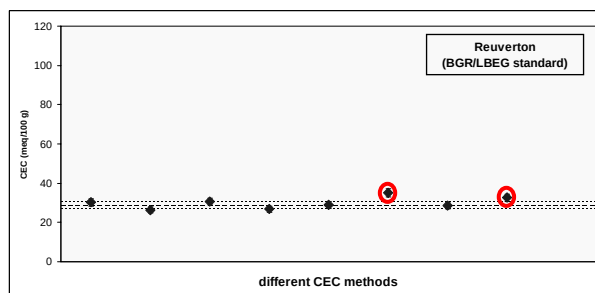


Abb. 1: CEC-Ergebnisse eines Reuvertons mit verschiedenen CEC-Methoden

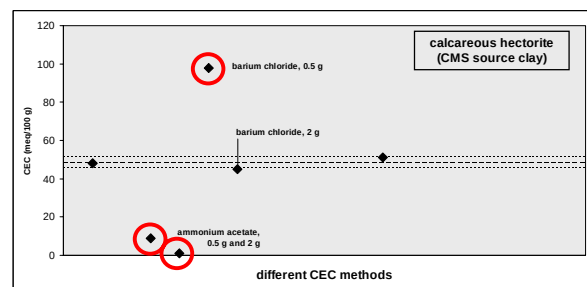


Abb. 2: CEC-Ergebnisse eines Hektorits (ca. 50 % Calcit) mit verschiedenen CEC-Methoden

Abbildung 1 zeigt CEC-Werte mit acht verschiedenen Methoden an einem Reuverton (frei von löslichen Ca-Mineralen). Der Fehlerbereich kennzeichnet die Präzision die möglich ist, wenn es neben dem Kationenaustausch nicht zu weiteren unerwünschten Reaktionen wie Mineralauflösung kommt. Zwei der verwendeten Methoden liefern erkennbar systematisch zu hohe Werte, diese sind als verfälscht zu bewerten, alle anderen sind korrekt; präziser kann man die CEC also nicht messen wenn das Ergebnis als Verfahrens-unabhängig gelten soll.

Abbildung 2 zeigt Beispiele für stark systematisch verfälschte CEC-Werte einer Hektoritprobe. Hier kam es neben dem Kationenaustausch zu starken Reaktionen, die je nach Verfahren und Masseinsatz die CEC-Werte um ca. 100 % erniedrigt bzw. erhöht haben. Drei Methoden liefern richtige CEC-Werte. Es ist also in jedem Fall zu prüfen ob die CEC-Ergebnisse Sinn ergeben.

Aramaic basalt statues from Tell Halaf, Syria: localization of the ancient quarries

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The Aramaic city of Guzāna (modern name Tell Halaf), northeastern Syria, was built approximately 1000 B.C. after the decline of the Hittite empire. It was excavated by Max von Oppenheim in the years 1911-1929 (Langenegger et al., 1950; Moortgat, 1955). Selected basalt and limestone artwork was brought to Berlin in 1928 and presented in the Tell Halaf museum Charlottenburg, which was completely destroyed by bombing during an air raid in WW II. Fragments of the basaltic statues were recovered and stored in the basement of the Pergamon museum. Recently, restoration of the art work within the frame of the Tell Halaf-Project already achieved considerable success (Cholidis & Martin, 2002; www.tell-halaf-projekt.de).

The statues of Tell Halaf were made from monolithic blocks of basaltic flows, with considerable heterogeneity, comprising massive as well as amygdaloidal types. Despite the long-time geological investigation of the surroundings of Tell Halaf the exact place of the original quarries, where the Aramaic people extracted the raw material, was yet unknown. References given in von Oppenheim (1931) combined with observations of geological maps, suggested that these quarries were located along the flanks of the El Kbise volcano of South Turkey, approximately 6 km north of Tell Halaf. Other basalt volcanoes suited as potential raw material are the southern Karacalidag, Turkey (c. 15 km north of Tell Halaf) and the Ard Esh-Sheik plateau, Syria (c. 60 km south of Tell Halaf). Following this, the main archaeometric question was to identify the original quarries. Of special interest were the chosen transport routes from the quarry to the Tell Halaf and the history of mining activity. In order to answer these questions reconnaissance mapping and sampling concentrated on the main basaltic centres of Turkey/Syria, in the vicinity of Tell Halaf. In addition, basalt artefacts from the two nearby archaeological sites of Tell Beydar (c. 2700-2300 B.C.) and Djebel el Beida (c. 2500-2300 B.C.) were investigated for comparison. All basalt samples were analysed for both their bulk rock major and trace element composition (x-ray fluorescence and ICP-MS analysis) and the mineral chemistry of individual minerals (combined electron microprobe analysis and laser-ablation ICPMS).

The data reveal, that the raw material for the basalt artefacts from Tell Halaf was extracted from the southern Ard-esh Sheik plateau, Syria, situated c. 60 km south of Tell Halaf and disprove the suggestion of von Oppenheim (1931) that the ancient quarries were located along the mountain side of the nearby El Kbise volcano, Turkey. Another, rather unexpected outcome of this study is the excellent accordance of data constrained for the three archaeological sites, i.e. Tell Halaf, Djebel el Beida, and Tell Beydar, with almost identical compositions of both bulk artefacts and main minerals. Following this, the artefacts from all three sites must have been derived from the same quarrying area, i.e. the Ard-esh Sheik plateau. Accordingly, the same basalt quarry was actively exploited over a considerable time span of c. 1700 a, from 2700 B.C. to 1000 B.C. Last but not least, the study demonstrates that petrographical investigations of basalt combined with electron microprobe and laser ablation ICP-MS analysis of minerals are a powerful tool to discriminate between possible sources of raw material, especially if isotopic or geochemical data yield unsatisfying results.

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Fluid assisted replacement of feldspar – structure of the reaction interface and the role of amorphous material formation

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Two different types of fluid assisted replacement processes were investigated, i.e. (1) the replacement of labradorite plagioclase (An_{66}) by albite and (2) the conversion of albite (An_{0-1}) to sodalite, both occurring as subsequent reactions in metasomatized anorthosites from Namibia (Drüppel et al., 2005). A total of 46 experiments were performed in the system $NaAlSi_3O_8-SiO_2-NaCl-H_2O$ (P: 3-5 kbar, T: 200-800°C, 5-21 days) to provide a better understanding of the processes involved. Experiments were performed in cold seal hydrothermal vessels. A perforated inner gold capsule was filled with cleavage fragments of natural plagioclase, whereas the shut outer capsule was filled with silicon monoxide (albitization) or $\gamma-Al_2O_3$ (sodalitization) and an aqueous brine of varying salinity. Reaction products were investigated using high-resolution SEM, high-resolution TEM, and cathodoluminescence petrography. Changes in major element chemistry were determined using EMP analysis.

Sodalitization: At high salinities sodalite was found to be the stable phase over the whole temperature range whereas albite occurred at low bulk salinities of the fluid. The replacement textures displayed by the natural rock samples and the run products of the experiments are remarkably similar. In both cases the transformation starts along the grain margins of plagioclase and, if present, along cracks or albite twin lamellae. Along the reaction front synthetic sodalite crystallises as porous, euhedral grains forming polycrystalline aggregates, whereas larger grains of massive sodalite dominate in the outermost domains of the reaction zones, suggesting recrystallization of early sodalite. Sodalite in natural rock samples displays only minor porosity but fluid and secondary mineral inclusions, pointing to coarsening of a previously present microporosity. Sodalitization of plagioclase displaying polysynthetic twinning occurs along distinct sets of albite twin lamellae, with the reaction zones propagating from twin planes towards the centre of individual lamellae. The sharp reaction interface between sodalite and albite, as investigated by HR-TEM, is marked by open channels. In most synthetic samples, a Si-rich amorphous zone developed in between the ancestor albite and newly formed sodalite. This amorphous material is only present during the early stages of the experiments (< 6 days) as several nanometer to up to 350 μm wide amorphous rims around albite, and may in extreme cases form a complete pseudomorph after albite. These amorphous domains then react to form the crystalline product phases. **Albitization:** The run products of short high-T experiments > 500°C (6 days) revealed replacement of labradorite plagioclase by almost pure albite (An_{0-3}), with development of a sharp reaction interface. Reaction starts along the plagioclase margins, twin lamellae, and cracks and progressively enters the central parts of the grains. The textural characteristics resemble those described by Putnis et al. (2008) and of natural albitised plagioclase observed in our Namibian rock samples and elsewhere (e.g. Engvik et al., 2008). Like in the albite-sodalite transformation experiments narrow Si-rich amorphous zones developed along the reaction fronts within labradorite plagioclase, which have not been observed in the corresponding natural rock samples, so far.

In general, the observed reaction textures in both model systems indicate interface-coupled dissolution-reprecipitation mechanisms, with the shape of the respective parent feldspars being preserved. Hereby, grain and interphase boundaries act as preferred pathways for the aqueous solutions. High-resolution electron microscopic investigations (HR-SEM and HR-TEM) combined with electron backscatter diffraction (EBSD) and small angle X-ray scattering (SAXS) of the interfaces are in progress to gain more detailed information about the structural properties and composition of the transitional zones. Of special interest is the characterization of a possible internal microstructure of the amorphous material, that formed early during the reaction process in the experimental runs, and the determination of its role in the fluid-assisted replacement processes.

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The origin of the lanthanide tetrad effect in granites

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In some highly evolved granites, the abundance of rare earth elements does not follow a smooth pattern. Rather, the pattern is often divided into four segments, the tetrades, with distinct maxima and minima in rare earth abundance. The origin of this “lanthanide tetrad effect” is uncertain and sometimes the effect has even been discounted and attributed to analytical uncertainties. Sometimes it was suggested that the lanthanide tetrad effect indicates that the granites underwent significant hydrothermal interaction. In this study, we systematically investigated the solubility of rare earth phosphates in granitic melts, since these phases are usually the main carriers of lanthanides in felsic systems and the lanthanide abundance in the melt is controlled by the equilibrium with these phases.

Crystals of pure rare earth phosphates were synthesized for each rare earth element (except Pm) by the reaction of rare earth oxides with aqueous solutions of phosphoric acids at 800 °C and 2 kbar. The light rare earths from La to Gd formed crystals of monazite, while the heavy rare earths from Gd to Lu formed xenotime. The GdPO₄ samples were a mixture of the monazite and xenotime polymorph. The solubility of the rare earth phosphates in hydrous (6 wt. % H₂O) haplogranitic melts with aluminum saturation index ranging from 0.7 to 1.2 was investigated at 2 kbar and 800 °C with run durations between one and two months. The influence of phosphorus and fluorine rare earth phosphate solubility was also studied under the same conditions. One additional series of experiments was carried out at 1100 °C. Run products were investigated by electron microprobe. Equilibrium rare earth concentrations were estimated both from average microprobe analyses and from the extrapolation of measured diffusion profiles around dissolving crystals to the crystal-melt interface. To demonstrate equilibrium, runs with variable duration and reversed experiments were carried out as well.

The solubility of rare earth phosphates was found to be not a simple continuous function of atomic number or ionic radius. Rather, the solubility shows a typical “tetrad” pattern with several local maxima of solubility at individual rare earth elements. The solubilities of neighboring rare earth elements sometimes differ by more than a factor of two; these effects are far outside any analytical error. The tetrad pattern is particularly clearly seen in some of the peralkaline melts and in the fluorine-rich metaluminous melts. Some features, however, such as a solubility maximum at Ytterbium, are seen in virtually all melts.

The lanthanide tetrad effect in some highly evolved granites is therefore likely to be a result of monazite and xenotime fractionation. The ultimate cause of the tetrad effect is probably electronic repulsion between the partially filled f-orbitals of the rare earth and the surrounding oxygen atoms. If the coordination geometry is different in the melt and the solid phase, the rare earth partition coefficients or solubilities will depend on the precise electronic configuration in the 4f shell, not just on the effective ionic radius. The solubility of monazite and xenotime in silicate melt probably shows this tetrad effect, because of the very unusual coordination of the rare earth elements in these phosphate minerals.

The lanthanide tetrad effect in some highly evolved granites is real. However, it cannot be used as an indicator of fluid/rock or fluid/melt interaction experienced by these granites, since the effect can be experimentally reproduced in the laboratory in the absence of any fluids.

Stable isotope systematics of the Navachab gold deposit, Namibia: implications for the source of fluids in sediment-hosted orogenic gold deposit

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The Navachab gold deposit in the Damara belt of Central Namibia is situated in an amphibolite facies sequence of shelf-type metasediments, including marble, calcsilicate rock, and biotite schist. Gold is hosted by quartz-sulfide veins and semi-massive sulfide lenses that are developed along the steep northwestern limb of the Karibib dome, a northwest-verging, noncylindrical anticline. Although the deposit shares many characteristics with orogenic gold deposits, including the strong structural control and epigenetic nature of the mineralization, some of the geological and geochemical characteristics are genetically distinct from typical orogenic gold deposits elsewhere. For example, the mineralized zones are characterized by a polymetallic ore assemblage of pyrrhotite, chalcopyrite, spalerite, arsenopyrite, bismuth, gold, bismuthinite, and bismuth tellurides. This unusual metal association is typically interpreted to be related to intrusion-related gold deposits. An igneous origin is also implied by the presence of abundant syn-tectonic lamprophyre, aplite, and pegmatite dykes in the Navachab open pit, indicating magmatic activity coeval with the mineralization (e.g. Dziggel et al., 2009a). In order to provide constraints on the origin of the mineralizing fluid, the stable isotope (O, H, C, S) systematics were investigated.

The majority of quartz from the veins has an oxygen isotope composition between $\delta^{18}\text{O} = 14$ and 15 ‰ (V-SMOW). The total variations in $\delta^{18}\text{O}$ values in the biotite schist and calcsilicate rock are relatively small (12 to 14 ‰), whereas the marble records steep gradients in O-isotope ratios (17 to 21 ‰), the lowest values being recorded at the vein margins. Calculations using a Rayleigh type decarbonation model show that there is no correlation between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and the carbonate content of the rocks, indicating that fluid-rock interaction alone cannot explain the observed isotopic changes. In addition, the (isotopically) altered samples of the marble record increasing $\delta^{13}\text{C}$ values. The high $\delta^{13}\text{C}$ values most likely resulted from the formation of methane due to the interaction of hydrogen from the fluid with CO_2 from the marble. Gold is interpreted to have precipitated in equilibrium with metamorphic fluid ($\delta^{18}\text{O} = 12$ to 14 ‰; $\delta\text{D} = -40$ to -60 ‰) at peak metamorphic conditions of ca. 550°C and 2 kbar (Dziggel et al., 2009b), consistent with isotope fractionations between co-existing Cal, Grt and Cpx in the alteration halos. Even though the oxygen isotope composition of a fluid in equilibrium with the aplite and pegmatite dykes is indistinguishable from that of vein quartz, the δD values of the igneous samples are considerably lower. Taken in conjunction, the data suggest that the most likely source of the mineralizing fluid are mid-crustal equivalents of the Damara metapelites that underwent prograde metamorphism at amphibolite- to granulite facies grades. Although there is no isotopic evidence for the contribution of magmatic fluids, they must have been important in contributing to the hydraulic regime and high apparent geothermal gradients (ca. 80°C/km⁻¹) in the mine area.

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Partitioning of Barium and Lead between aqueous fluids and haplogranitic melts at 750°C and 200 MPa

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The distribution of elements between melts and aqueous fluids represents an important process in many geological environments, e.g. during the crystallization of magma intrusions or at formation of hydrothermal ore deposits. Therefore, partitioning of metals between silicate melt and coexisting aqueous phase have been extensively studied e.g., Holland (1972), Urabe (1985), and Keppler et al. (1991). However, very few experimental data exist for Ba and Pb (e.g., Bureau et al., 2003; Khitarov et al., 1982). The Pb fluid-melt partitioning data ($D_{Pb}^{f/m} = c_{Pb}^{fluid}/c_{Pb}^{melt}$) presented in these experimental studies suggest a preference for the melt ($D^{f/m} < 1$) in the case of experiments with salt-bearing fluids, but show distinctly higher values in the case of pure H₂O as starting solution. These experimental results not only contradict data from natural cogenetic fluid and melt inclusions (Audétat and Pettke, 2003), but also the idea that Cl is an efficient complexing agent for many metals (e.g., Helgeson, 1964). In the case of Ba, the experimental data suggest a preference for the melt, but no partition coefficients were calculated due to insufficient precision of the experimental technique (Bureau et al. 2003).

In this study, partitioning of Ba and Pb between aqueous fluids and synthetic haplogranite melts is investigated at 750°C and 200 MPa using various melt compositions and aqueous solutions. The melt composition is varied as function of the alumina saturation index (ASI = Al₂O₃/(Na₂O+K₂O) in moles) between 0.8 and 1.5. To study the influence of Cl two aqueous fluids, H₂O and a 1 m NaCl + 1 m KCl solution are used. The starting glasses are doped with 2000 ppm Ba. Lead is added as PbO directly to the high pressure run in concentrations of ~ 1 wt% Pb. During the run, part of the Pb is lost to the capsule material leading to final concentrations in the glass of ca. 320 - 4340 ppm. All experiments are performed in rapid-quench cold-seal autoclaves using gold or platinum (for Pb runs) capsules and with a run duration of 7 days to ensure equilibrium conditions. The compositions of the quenched phases are determined by electron microprobe analyses of the glasses, and ICP-OES and Ion-Chromatography of the fluids.

In experiments with H₂O as starting solution Ba and Pb partition coefficients indicate a preference for the melt. Partitioning data of Ba in the H₂O-melt system vary between 0.003 and 0.005, independently of the ASI of the melt. In the case of the chloridic solution a dependence on the melt composition is observed. The $D_{Ba}^{f/m}$ increase from 0.002 ± 0.001 (ASI: 0.83) to 0.201 ± 0.012 (ASI: 1.21) and then decrease to 0.084 ± 0.004 (ASI: 1.29). This behaviour of Ba is similar to observations made for Sr (Borchert et al. 2008). For Pb, analysis of the first run products yield $D_{Pb}^{f/m} = 0.04 \pm 0.025$ for pure water as starting material and increase to $D_{Pb}^{f/m} = 9 \pm 2$ for the NaCl/KCl solution at an ASI of 1.15. These observations correspond well with data of Audétat and Pettke (2003). They obtained a $D_{Pb}^{f/m}$ of 5 at a fluid salinity of 4.9 wt.% using cogenetic fluid and melt inclusions.

In current experiments we are determining the influence of $f(O_2)$ on the partitioning of Pb.

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Präzise Temperaturregelung für Probenträger

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Sehr viele Minerale treten bereits bei Temperaturen, die innerhalb der Bandbreite natürlicher Klimaten auftreten, in unterschiedlichen polymorphen Modifikationen auf. In unmittelbarer Nähe zur Raumtemperatur ändern insbesondere Hydratphasen häufig sogar ihre Zusammensetzung – sie besitzen in einem schmalen Temperaturintervall verschieden hohe Wassergehalte. Diese Vorgänge der Hydratation, Dehydratation und Rehydratation sind zudem technisch wichtig oder spielen z.B. in den Geowissenschaften eine große Rolle.

In den meisten Fällen wird die Phasenzusammensetzung mineralischer Proben durch Röntgendiffraktometrie bestimmt. Während der Messung herrschen an der Probe ohne zusätzliche Maßnahmen Temperaturen von ca. 18 – 30 °C. Bereits in diesem Temperaturbereich existieren bei einigen Mineralen verschiedene Hydratationsstufen.

Aus diesem Grund ist zur röntgenographischen Phasenanalyse dieser Phasen eine exakt definierte, konstante Temperatur der Probe erforderlich.

Klimatisierte Röntgenräume engen die Schwankungsbreite der Temperatur im Röntgendiffraktometer deutlich ein. Durch die Wärmeentwicklung im Diffraktometer ist eine exakte Temperatur an der Probe allein durch diese Maßnahme aber nicht gewährleistet. Exakte Bedingungen werden erst durch aufwändige und teure Heiz- bzw. Klimakammern geschaffen.

Um ohne kosten- und energieintensive Technik an der Probe eine Temperatur zwischen 0 und 90 °C zu garantieren, wurde ein kompakter, exakt temperierbarer Probenträger entwickelt. Er arbeitet mit einem Peltier-Element, das am Probenträger direkt unterhalb der Probe angebracht ist. Durch Umpolen des Peltier-Elements kann sowohl geheizt als auch gekühlt werden. Die Wärme an der Gegenseite des Peltier-Elements wird über einen Wasserwärmetauscher von einem CPU Kühler abgeführt.

Die Temperaturmessung erfolgt über einen Pt 100 Fühler im Probenträger. Die Regelung der Temperatur geschieht über Steuerelektronik und Software. Der Temperatursensor besitzt eine Genauigkeit von $\pm 0,1$ °C. Die Messelektronik hat 16 Bit Auflösung. Die Regelung arbeitet auf $\pm 0,02$ °C genau. Die Regelsoftware erkennt selbständig, ob geheizt oder gekühlt werden muss, wodurch Messungen bei schwankender Raumtemperatur, zum Beispiel trotz Tag-Nacht-Schwankungen, ermöglicht werden.

Durch die Ansteuerung über Software lassen sich sehr viele weitere Funktionen, wie zum Beispiel das Abfahren von Temperaturprofilen, verwirklichen.

Der Probenträger ist sehr kompakt und kann in die meisten Probenhalterungen ohne großen Aufwand eingebaut werden. Die Elektronik befindet sich in einem 19 Zoll Einschub, der im Untergestell des Diffraktometers Platz findet.

Copper and gold deposits of south-west England: Geochemical composition and comparison with Bronze Age artefacts

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SW England represents an important metallogenic province within the British Isles. Whereas tin exploitation can be traced, more or less continuously, from at least 2000 B.C. (Muhly, 1985), the beginning of gold exploitation is rather uncertain and is generally linked to the Cornish tin stream works as a major by-product (O'Brien, 1999). As evidence of early mining in Britain is dominantly distributed along the western seaboard, the numerous records of autonomous metal production in source regions of Mid and Northern Wales (O'Brien, 1999) contrast strongly with the dearth of evidence for early copper mining in SW England. However, provenance studies by Budd et al. (2000) identify SW England to be the source of Copper Age artefacts, which warrant further investigations on linking Bronze Age artefacts with ore deposits of this province.

Embedded in copper and gold provenance studies of the hoard find of Nebra (including the Sky Disc), the goals of this study are to supplement the existing project database on copper and gold deposits in Western, Central and Eastern Europe and to better understand the prehistoric significance of copper and gold deposits from SW England during the European Bronze Age. Striking distribution patterns can be found in the data of Hartmann (1982) where the geochemistry of European artefact gold forms clusters spatially coinciding with auriferous geological (Variscian) domains (Figure 1). This might be due to geologically similar sources.

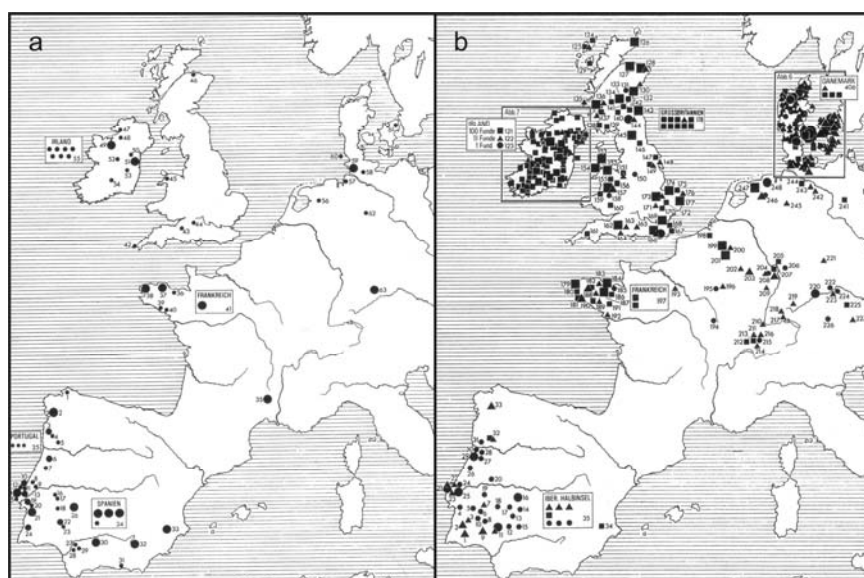


Figure 1: Distribution patterns of Bronze Age gold artefacts of compositional type S (a) and type N/NC/MC (b) in Western and Central Europe (modified from Hartmann, 1982).

Against this background, copper and gold deposits from different mining districts in Cornwall were sampled in public and private collections as well as in the field. By determining possible differences between the trace element (Cu, Au) and lead isotope (Cu) compositions of the sampled deposits and/or districts, further comparisons with Bronze Age artefact copper and gold from SW England as well as potential prehistoric trading partners (see Figure 1) can be carried out to distinguish or exclude source areas of artefacts with unknown provenance. Reference data from literature and the existing project database will be incorporated to verify the results.

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Volumeninhomogenitäten eines Sesterzes des Tiberius

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Während der Römischen Kaiserzeit gehörten Münzen aus Gold (Aureus), Silber (Denar) und Messing (Sesterz und Dupondius) zum Währungssystem. Gegenstand der archäometrischen Untersuchungen sind Messingmünzen der julisch-claudischen Dynastie; hier am Beispiel eines Sesterzes des Tiberius. Der Sesterz des Tiberius aus der Münzsammlung des Herzog Anton Ulrich-Museums in Braunschweig wird auf das Jahr 22-23 n.Chr. datiert und der Münzprägestätte in Rom zugeordnet (RIC 51 [1]).

Mittels XRD wurden in der Verwitterungskruste Kupfer, Cuprit, Smithsonit, Tenorit, Malachit und Quarz nachgewiesen. Die Untersuchung mittels EPMA zeigt eine inhomogene Zusammensetzung der Oberfläche. Zu beobachten sind Spuren von Gold. Von Interesse sind neben zerstörungsfreier Oberflächenanalyse nicht-invasive Methoden zur Volumenuntersuchung. Deshalb wurden röntgencomputertomographische Messungen durchgeführt. Diese ergänzen vorliegende chemische Analysen von Riederer [2] (Rathgen-Forschungslabor Berlin) mittels AAS, welche durch Probenentnahme eine repräsentative Volumenuntersuchung sicherstellen sollte.

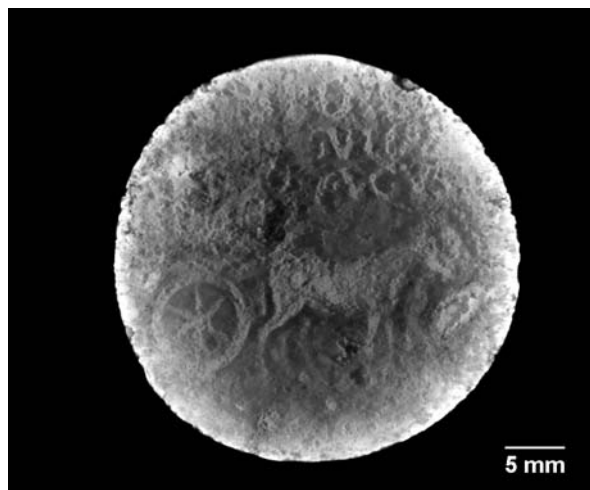


Abb. 1: 2D-Schnittbild einer röntgencomputertomographische Aufnahme der oberflächennahen Schichten des Sesterzes

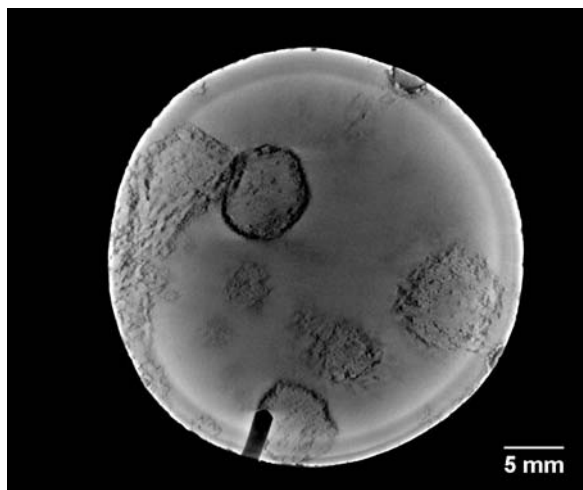


Abb. 2: 2D-Schnittbild einer röntgencomputertomographische Aufnahme der inneren Schichten des Sesterzes

Im Unterschied zu anderen Münzen weist der Sesterz des Tiberius großvolumige Inhomogenitäten auf, die auf zinkverarmte Gebiete hinweisen. Abbildung 2 zeigt zum einen die Inhomogenitäten im Inneren des Sesterzes und zum anderen das Bohrloch der früheren invasiven Analyse. Weitere Untersuchungen sollen die Entstehung der Volumendefekte aufklären.

Wir danken Professor Dr. Wolfgang Leschhorn (Herzog Anton Ulrich-Museum Braunschweig) für die Bereitstellung der Münzen und ihm sowie Professor Dr. Charlotte Schubert (Universität Leipzig, Historisches Seminar) für hilfreiche Diskussionen.

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Nanocrystals in natural glass as fingerprint of provenance?

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Provenance analysis of natural glass is generally determined using geochemical data and/or physical properties. The present study focuses on quantifying the amount of crystalline phases and their size distribution in natural glass samples by means of X-ray powder diffraction (XPD). The main problem is the low crystal content in glass, e.g. in obsidian typically around 1...2 volume %.

Recent development of area detectors (Taguchi 2006) and line detectors (Taguchi et al. 2008) result in shorter measurements and in significantly better signal to background ratios. Thus a much lower detection limit is reached. We were able to quantify amounts of hematite and quartz in obsidian to be less than 0.1 weight %. For this purpose powder diffraction experiments were performed at ESRF high energy beamline (ID15B) as well as using standard equipment.

Mineral typical size distribution can be obtained using the Haas and Birringer method. In figure 1 the variance of nanosized hematites in two different obsidians of the Ikizdere region (Turkey) is displayed. Both samples differ in median and half-width.

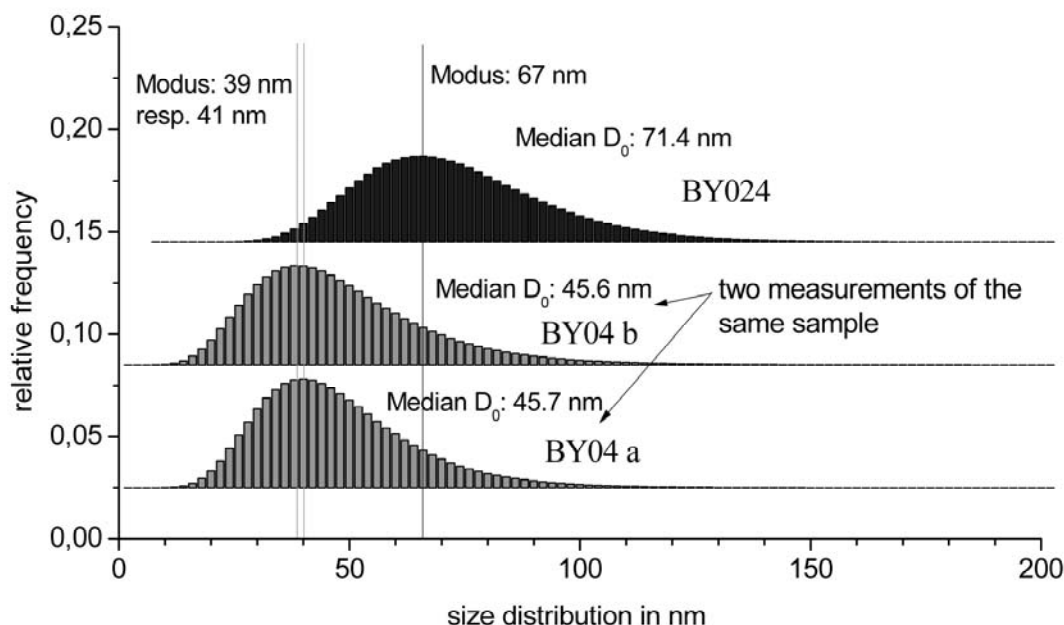


Fig.1: Distribution of the coherent scattering domain size of two different obsidians from East Pontides, Turkey.

The study of several obsidians reveals that the combined quantification of mineral content and size is a possible classifier for provenance discrimination. Further attention is given to other types of natural glass like opals, impactites, fulgurites and so on.

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Glas-Monolithe mit kontrolliert einstellbarer Mikroporosität – Herstellung und potentielle Anwendungen

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Poröse Gläser als Extraktionsprodukte phasengetrennter Alkaliborosilikatgläser zeichnen sich durch eine Reihe vorteilhafter Eigenschaften aus. Es ist möglich, Hohlraumsysteme mit Porengrößen im Nanometerbereich zwischen 4 und 1000 nm bei weitgehend uniformer Porengrößenverteilung herzustellen. Die Gläser weisen in Abhängigkeit von der Porengröße hohe innere Oberflächen von bis zu 500 m²/g und Porenvolumina zwischen 0.1 und 1.1 cm³/g auf [1]. Die an der inneren Oberfläche vorhandenen Silanol-Gruppen ermöglichen vielfältige Oberflächenfunktionalisierungen. Bedingt durch den Herstellungsprozess sind die porösen Gläser durch hohe mechanische, thermische und chemische Stabilitäten gekennzeichnet. Weiterhin können sie als Monolithe mit sehr flexibler geometrischer Form und hoher Qualität (Reproduzierbarkeit der Eigenschaften, Rissfreiheit) hergestellt werden. Neben Kugeln und Stäben sind dünne und flache Membranen von besonderem kommerziellem Interesse. Diese Eigenschaftskombination wird derzeit von keinem anderen porösen Material erreicht.

Auf Grund ihrer speziellen Eigenschaften erleben die porösen Gläser derzeit eine Renaissance. Poröse Gläser in Form von Granulat, Kugeln und Membranen werden derzeit in vielen innovativen Applikationen eingesetzt oder getestet. Beispiele sind die Bereiche Katalyse, Wirt-Gast-Chemie, Chemo- und Biosensorik sowie Informationsspeicherung [2].

Trotz intensiver Forschungen auf dem Gebiet der porösen Gläser bestehen noch einige offene Fragestellungen. So konnte beispielsweise die reproduzierbare Herstellung monolithischer Glaskörper mit gezielt einstellbarer Mikroporosität (< 2 nm) bisher nicht realisiert werden. Diese Materialien besitzen großes Potential als Modellsystem bzw. für Gastrennungen.

In diesem Beitrag wird die Herstellung poröser Glasformkörper mit kontrollierter Porengröße im Bereich unterhalb von 4 nm vorgestellt. Die Genese dieser Materialien erfordert die Modifizierung bzw. Optimierung praktisch aller Herstellungsparameter (Ausgangsglaszusammensetzung, Abkühlung aus der Schmelze, Thermobehandlung zur Phasentrennung, Formgebung, Extraktionsbedingungen und Nachbehandlung). Die Charakterisierung der Mikrostruktur (Porengröße, Porenverteilung) sowie erste Anwendungen werden ebenfalls präsentiert.

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„Fluor-Schörl“ vom Erzgebirge, dem Gebiet der Typlokalität für Schörl

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„Fluor-Schörl“, das Fluor-Analogon von Schörl, wurde unter anderem bereits von Ertl et al. (2006) von Grasstein, Südtirol, detailliert beschrieben. Turmalin von dieser Fundstelle zeigt mit $X(\text{Na}_{0.8}\square_{0.2}) Y(\text{Fe}^{2+}_2\text{Al}) Z\text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 V(\text{OH})_3 W[\text{F}_{0.8}(\text{OH})_{0.2}]$ ($a = 16.00$, $c = 7.18$ Å) eine dem Endglied sehr nahe Zusammensetzung. Von verschiedenen ehemaligen Zinnlagerstätten des Erzgebirges (unter anderem auch aus Zschorlau, Sachsen), die nach Ertl (2006) als Typlokalitäten von Schörl angesehen werden können, wurden 20 schwarz gefärbte Turmaline röntgenographisch untersucht. Strukturverfeinerungen anhand von Einkristallintensitätsdaten ergaben für die Gitterkonstanten $a = 15.98\text{--}16.01$ Å und $c = 7.15\text{--}7.21$ Å. Interessanterweise zeigt sich trotz der verschiedenen Lokalitäten und der größeren Anzahl von untersuchten Einkristallen nur eine geringe Variation der Gitterkonstanten. Die kristallchemische Formel, basierend auf den Strukturverfeinerungen, variiert von $X(\text{Na}_{0.6}\square_{0.4}) Y(\text{Fe}^{2+}_{1.7}\text{Al}_{1.3}) Z\text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 V(\text{OH})_3 W[(\text{OH})_{0.7}\text{F}_{0.3}]$ bis $X(\text{Na}_{0.8}\square_{0.2}) Y(\text{Fe}^{2+}_2\text{Al}) Z\text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 V(\text{OH})_3 W[\text{F}_{0.8}(\text{OH})_{0.2}]$. Es zeigt sich somit, dass sowohl Na mit F, als auch Fe^{2+} mit F positiv korreliert. Die meisten dieser Turmaline weisen eine deutlich F-dominante W-Position auf. Somit ist überraschenderweise eine große Anzahl der untersuchten Turmaline aus dem Gebiet der Typlokalität für Schörl dem „Fluor-Schörl“ zuzuordnen. Allerdings ist die Anwesenheit eines signifikanten Fluor-Anteils in den Proben nicht ganz so überraschend, wenn man das Auftreten von Fluorit und von Pyknit (stengelig ausgebildeter Topas) in vielen Zinnlagerstätten Sachsens berücksichtigt, wobei der Pyknit bekanntlich durch Reaktion von Kalifeldspat mit pneumatolytischen Fluiden (hauptsächlich HF) gebildet wurde. Eine Untersuchung der Wasser- und Fluor-Gehalte in Schmelzeinschlüssen hochdifferenzierter Granite des Erzgebirges ergab teilweise sehr hohe Fluor-Werte (bis ~11 Gew.%; Müller et al., 2006).

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Phase relations in the Al_2O_3 – TiO_2 system at pressures up to 20 GPa

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Aluminium is one of the trace elements in rutile that may provide information on the P-T conditions of the rutile bearing metamorphic rocks. In fact, exsolved corundum lamellae have been reported in diamondiferous eclogites from South Africa [Sobolev 2000]. It has also been suggested that the accommodation of trivalent cations can enhance the hydrogen solubility in rutile and thus influence the water transport into the mantle [Bromiley 2004]. On the other hand, TiO_2 is widely used, due to its photoconductive and catalyst characteristics, in both research and industrial applications, i.e. hydrogen production and UV-induced oxidation of organic compounds in wastewater. TiO_2 is also used as a white pigment. The photocatalyst properties of TiO_2 can be modified by introducing small amounts of impurities in its structure. For example, the introduction of Al in rutile reduces its photoactivity and prevents the degradation of paints and other coatings by forming oxygen vacancies that can trap charge carriers [Gesenhues 2001]. The effect of the pressure on the solubility of Al in TiO_2 remains unexplored up to now. Thus, the knowledge of the effect of the pressure on the structure of Al - doped TiO_2 is of great value not only Geochemistry, but also in Material Science.

The effect of pressure on phase stabilities and Al solubility in TiO_2 for a 50% TiO_2 – 50% Al_2O_3 composition (mol %) has been studied. Samples have been synthesised from commercial Al_2TiO_5 at the Bayerisches Geoinstitut from 0.5 to 3 GPa and 1300°C for 24 hours in a piston cylinder and from 5 to 20 GPa and 1300°C for 3 hours in a 1200 tonne MA8 Kawai-type multi-anvil press. They have been characterised by XRD, ²⁷Al MAS-NMR, SEM and TEM.

Our results show that at 1300°C Al_2TiO_5 decomposes into Al-doped rutile and almost pure corundum from at least 0.5 GPa. The Al-doped TiO_2 transforms into the high pressure polymorph with the α – PbO_2 structure at 8.6 GPa. The further transformation of TiO_2 into the baddeleyite type TiO_2 , expected at about 17 GPa and 1300°C, has not been observed. The presence of Al in TiO_2 seems to stabilize the α – PbO_2 structure and inhibit the transformation into the baddeleyite type polymorph. Aluminium solubility in rutile increases with pressure. Moreover, the incorporation of Al^{3+} into the rutile structure produces a slight decrease of the rutile symmetry, which transforms from tetragonal into orthorhombic at 2.5 GPa.

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How do microstructure and secondary phases affect sulfide dissolution?

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Mining activities on sulfured ores transfer large amounts of rocks to heap dumps and thus into an oxidizing environment. Weathering of these deposited sulfides often result in acid mine drainage with the production of sulfuric acid and the release of high concentrations of metals into ground and surface waters. Accordingly, a large number of experimental dissolution studies on various sulfide minerals have been conducted in the past decades including both chemical and microbial leaching under a wide range of oxidizing conditions. Applying measured rates to another system requires knowledge about the mechanisms of dissolution and the reactive surface area. However, reactivity is considerably influenced by the microstructure (exsolution, twin planes, stacking sequences) and the defects (vacancies, dislocations, grain boundaries) present. Surprisingly, the influence of the microstructure on the dissolution is rarely addressed. Furthermore, hazardous element release is not only controlled by the reactivity of the primary sulfides but also by the formation of a secondary mineral assemblage. Many of the newly formed phases (oxides, hydroxides, elemental sulfur, sulfates) exhibit small grain sizes, which affects their stability as well as their adsorption capacity. The secondary phases can directly (as coating) or indirectly (adsorption, solubility) influence the dissolution kinetic of the primary sulfide.

Natural sphalerites are well known for their wealth of microstructure including stacking faults, twin boundaries and oscillatory zoning, usually combined with elevated trace element concentrations, which can affecting the dissolution of sphalerite. In contrast, the dissolution of galena is closely related to the formation of secondary phases with low solubility (anglesite, lead oxides) which can passivate the reactive surface. For this study, sulfides of several localities have been characterized using TEM for the microstructure, EMPA for major and trace element compositions as well as SEM and AFM to document surface evolution. Batch dissolution experiments are performed using single crystals as well as powders under conditions that facilitate the precipitation of secondary phases. The influence of microstructure and secondary phases on the dissolution of sphalerite and galena as well as the solution chemistry will be demonstrated and discussed.

Probing the aluminium coordination in Al-rich phlogopite by ^{27}Al and ^{17}O MAS and MQMAS experiments

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Many NMR studies of F- containing minerals are focused on spin one-half nuclei like ^{19}F , ^1H , and ^{29}Si (Circone et al. 1991). It is much more difficult to obtain structural information from quadrupolar nuclei like ^{27}Al and ^{17}O due to their strong quadrupolar interactions and in the case of ^{17}O to its low magnetogyric ratio and low natural abundance. By using multi quantum excitation in combination with MAS (MQMAS) enhanced resolution and additional structural information can be obtained.

The MQMAS technique has had a major impact on the study of quadrupolar nuclei by solid state NMR spectroscopy (Frydman and Harwood 1995; Medek et al. 1995). This technique enhances resolution in the spectra of quadrupolar nuclei with non-integral spins; because the two-dimensional MQMAS experiment separates the MAS spectrum along an isotropic F1 dimension with shifts that are a weighted sum of the isotropic chemical and isotropic quadrupolar shifts.

The influence of fluorine substitution on the local structure of Al in the tetrahedral and octahedral sheets of synthetic Al-rich phlogopite samples with nominal gel compositions of $\text{K}(\text{Mg}_{3-x}\text{Al}_x)[\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_{10}](\text{OH})_y(\text{F})_{2-y}$ between $0.0 \leq x \leq 0.8$ and $0.5 \leq y \leq 1.8$, was studied by ^{27}Al and ^{17}O MAS and MQMAS solid state NMR experiments. Signals from the different phases can be separated in the ^{27}Al MQMAS NMR spectra by generation of an isotropic dimension in F1. The ^{27}Al quadrupolar parameters of the four phases were estimated from ^{27}Al MAS NMR spectra obtained at 104.26 MHz. The quadrupolar coupling constant and isotropic chemical shift increases with increasing Al content for the $^{\text{IV}}\text{Al}$ site in phlogopite. The $^{\text{VI}}\text{Al}$ site shows a clear increase of the asymmetry parameter and C_Q with increasing F content. The estimated ^{27}Al signal areas show the lowest amount of impurity phases at high OH contents and a stabilization of $^{\text{VI}}\text{Al}$ sites by hydroxyl groups. ^{17}O MAS and MQMAS experiments should be able to distinguish between OH, SiOAl , SiOSi , SiOMg , AlOAl and AlOMg environments. Thus especially oxygen is able to give information of atom linking between octahedral and tetrahedral sheets.

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Determination of the reaction kinetics of Al-Tobermorite under hydrothermal conditions by in-situ Neutron Diffraction

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In aerated autoclaved concrete 1.13 nm tobermorite is the predominant CSH-phase with semi-crystalline CSH I and CSH II as minor components. Tobermorite can substitute Al for Si up to 13 atom% at 175°C/ P_{sat} and 7.5 at 190°C/ P_{sat} . The amount and crystallinity of 1.13 nm tobermorite mainly control the physical and mechanical properties of the product in means of the raw material quality. The kinetics of tobermorite formation under hydrothermal conditions within the pure system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ have been studied by in-situ methods in order to determine reaction mechanism and kinetics of the formation of Al-bearing 1.13 nm tobermorite.

Neutron diffraction has the capacity to collect data of the reaction progress under hydrothermal conditions in-situ. An autoclave cell has been designed for performing time-resolved neutron diffraction analyses (1 minute) of the dynamic processes during the hydrothermal reactions (Zürn et al., 2002; Fehr et al., 2009). Experiments were conducted at 190 to 210°C under saturation pressure and within a time-range of 8 hours. As initial materials for the mixtures $\text{CaO}, \text{C}_3\text{A}$ and natural quartz were used. The Al content referred to the tobermorite structure (Si^{4+} replaced by Al^{3+} at the tetrahedral sites) was in the range of 10 atomic percent. In the experiments the amount of quartz decreases with time. The fraction of poorly crystallized CSH-phases rises to a maximum and decreases with the time by continuous crystallisation of 1.13 nm tobermorite in accordance to the Al-free system. In addition a hydrogrossular-grossular solid solution with 15% grossular-component occurs. This primary hydrogarnet disappears with increasing reaction time and is replaced by a pure hydrogrossular within 3 hours. Al-Tobermorite is not formed initially but by the reaction of poorly crystallized CSH-phases with quartz and the primary Si-rich hydrogrossular solid solution after 165 min. The precursor CSH-phases are more Ca-rich and vary in their Ca/Si in the range of 1.1 to 1.3, characteristic for poorly crystalline phase C-S-H (I) displaying no constant Ca/Si due to its disordered structure.

The primarily crystallized Al-tobermorite display (hk0)-reflections only, implying the existence of ab-planes. With increasing time after 260 min. the ab-planes of Al-bearing 1.13 nm tobermorite are forming stacks along the c-axis, indicated by the existence of a (002)-reflection. The mechanism of the reaction can be described by the reaction conversion of quartz and display a non-isokinetic behaviour. In the early stage of the hydrothermal hardening process the reaction is determined by the solution of quartz and of Si-rich hydrogrossular solid solution up to 0.6 hours and subsequently followed by a diffusion controlled mechanism. After 2 hours the mechanism changed once more to a solution controlled process. The reaction kinetics can be described according to an Avrami equation and the crystallization of Al-tobermorite takes place as spontaneous nucleation and can be described in terms of nucleation and growth of transformed regions, where the rate of reaction may be limited by either nucleation, interface reaction, or long-range diffusion.

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Charakterisierung von Schleifscheiben zur Herstellung von Hochleistungs-Zerspanungswerkzeugen mittels Rasterelektronenmikroskopie (REM/EDX) und Röntgendiffraktometrie (XRD)

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Ziel der Untersuchungen war es einen Überblick über den Aufbau verschiedener Schleifscheibentypen zu verschaffen, ihre Veränderungen durch den Schleifvorgang zu dokumentieren und die Schliffbilder zu vergleichen.

Allgemeine Bemerkungen zum Schleifen

Schleifen ist wie Drehen oder Fräsen ein Zerspanprozess. Im Gegensatz zu allen anderen spanenden Fertigungsverfahren erfolgt der Materialabtrag nicht mit einer definierten Schneide, sondern durch eine Vielzahl unregelmäßig geformter Schneiden. Die Schneiden sind die Spitzen und Kanten der einzelnen Schleifkörner aus natürlichen oder synthetischen Schleifmitteln, die fest in einer Matrix eingebunden sind. Jede Schneide erzeugt einen eigenen Span oder hinterlässt eine Furche auf der Werkstückoberfläche, was schließlich zum Materialabtrag führt. Der Materialabtrag resultiert aus verschiedenen Einzelmechanismen: Zerspanen, Pflügen, Furchen und Reiben. Diese vier Einzelprozesse treten bei verschiedenen Körnern gleichzeitig bzw. bei der Spanbildung nacheinander auf, wobei der Anteil an Zerspanung möglichst hoch, an Reiben und Furchen möglichst niedrig sein sollte.

Ergebnisse bezüglich des Aufbaus der untersuchten Schleifscheiben

Um die Schleifwerkzeuge zu charakterisieren, wurden die einzelnen Bestandteile der Schleifscheiben mittels EDX untersucht und die daraus resultierenden Ergebnisse durch röntgendiffraktometrische Untersuchungen verifiziert und erweitert. So wurde durch die EDX-Analyse der Chemismus der Schleifscheiben ermittelt und anschließend durch die Röntgenbeugung die jeweilige kristalline Verbindung, die die Schleifkörner bildet, exakt bestimmt.

Anhand der Ergebnisse lassen sich die untersuchten Schleifscheiben in zwei Hauptgruppen einteilen: CBN-Schleifscheiben und Korundschleifscheiben. Die Korundscheiben können noch weiter unterteilt werden in kunstharzgebundene und keramisch gebundene Scheiben. Bei den CBN-Scheiben kommt immer ein weiteres Schleifkorn (Korund/Siliziumcarbid) zum Einsatz. Durch den Zusatz eines günstigeren Schleifmittels soll der Preis der Schleifscheibe niedriger gehalten werden, um so einen wirtschaftlicheren Einsatz zu ermöglichen. Mit steigendem Gehalt an Bornitrid wird das Abrichten der Schleifscheibe deutlich erschwert und führt durch seine große Härte zu einem verstärkten Verschleiß des Diamantwerkzeuges.

Bei den Korundscheiben sind deutliche Strukturunterschiede zwischen den keramisch und den kunstharzgebundenen Schleifscheiben zu erkennen. Die Schleifkörper der Keramikscheiben bilden Sonderformen wie Plättchen oder Stäbchen aus. Sie haben ein extrem großes Porenvolumen, welches Raum für die Aufnahme von Spänen bietet, Kühlmittel aufnimmt, an die Kontaktzone transportiert und somit für einen kühlen Schliff sorgt. Neben den reinen Abrasivstoffen für den Materialabtrag kommen bei den Korundscheiben noch weitere Zusätze wie Pyrit, Kryolith, Fluorit und Cassiterit zum Einsatz. Sie erfüllen die Aufgabe der Schleifaktiven Füllstoffe die die Standzeit der Scheibe erhöhen und die Wärmebelastung reduzieren.

Deutliches Indiz hierfür sind die geringen Härtewerte (Mohs) von Pyrit (6), Fluorit (4) und Kryolith (3) die einen größeren Anteil an der Zerspanung unmöglich machen.

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Influence of fluorine on the solubility of manganotantalite (MnTa_2O_6) and manganocolumbite (MnNb_2O_6) in natural rhyolitic, synthetic haplogranitic and pegmatitic melts

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Solubility experiments of manganotantalite (MnTa_2O_6) and manganocolumbite (MnNb_2O_6) were conducted under nearly water-saturated conditions in natural rhyolitic (RHY), synthetic haplogranitic (HPG) and pegmatitic (PEG) melts containing different amounts of fluorine (F) at 800°C to 1035°C and 2000 bar. The experiments were carried out in cold seal pressure vessels (experiments at 800°C) with water as pressure medium and internally heated pressure vessels (1035°C and 1000°C) with Ar as pressure medium. The F contents vary from 0.26 to 3.14 wt% in RHY, from 0.72 to 9.01 wt% in HPG, and from 2.99 to 5.46 wt% in PEG melts. The PEG melts are also enriched in B_2O_3 (1.78 to 2.75 wt%), Li_2O (1.16 to 1.68 wt%) and P_2O_5 (1.55 to 2.75 wt%) and the RHY melt contains minor amounts of P_2O_5 (~0.30 wt%).

The attainment of equilibrium is demonstrated by concentration profiles of MnO, Ta_2O_5 and accordingly Nb_2O_5 from the mineral interface into the melt. Additionally, the molar Mn/Ta-ratios have been calculated in order to verify stoichiometric dissolution of the crystals.

Overall, the solubility products of both, MnTa_2O_6 ($K_{\text{sp}}^{\text{Ta}}$) and MnNb_2O_6 ($K_{\text{sp}}^{\text{Nb}}$) are not significantly affected by the F content for a given melt composition (data are identical within error). The experimental glasses RHY are nearly subaluminous (aluminium saturation index (ASI): 0.94 to 1.11) and the $\log(K_{\text{sp}}^{\text{Ta}})$ and $\log(K_{\text{sp}}^{\text{Nb}})$ vary from -3.04 ± 0.11 to $-2.78 \pm 0.11 \text{ mol}^2/\text{kg}^2$ and from -3.62 ± 0.19 to $-3.44 \pm 0.11 \text{ mol}^2/\text{kg}^2$ at 800°C respectively. In the subaluminous HPG melts (ASI: 0.91 to 0.97) the solubility product values yield $\log(K_{\text{sp}}^{\text{Ta}})$ ranging from -3.16 ± 0.10 to $-2.92 \pm 0.19 \text{ mol}^2/\text{kg}^2$ at 800°C and do not differ significantly. Thus, no systematic effect of F on MnTa_2O_6 and MnNb_2O_6 solubility was observed in synthetic and natural rhyolitic compositions. This effect is also confirmed at higher temperatures.

This observation is in contrast to previous data on granitic systems (e. g. Keppler, 1993), indicating that increasing F concentrations may increase MnTa_2O_6 and MnNb_2O_6 solubility. It has to be noted that the data of Keppler (1993) is in good agreement with our data when the molar Mn/Ta ratio in the melt of Keppler (1993) is 0.5. In such experiments, MnTa_2O_6 and MnNb_2O_6 dissolve stoichiometrically, indicating that equilibrium was achieved. Thus, the positive correlation between solubility product and F observed by Keppler (1993) may be an artefact resulting from the combination of equilibrium and non-equilibrium data.

In the peralkaline PEG melts (ASI: 0.92 to 0.91) $\log(K_{\text{sp}}^{\text{Ta}})$ varies from -2.89 ± 0.14 to $-2.67 \pm 0.11 \text{ mol}^2/\text{kg}^2$ at 800°C and from -2.09 ± 0.09 to $-1.85 \pm 0.06 \text{ mol}^2/\text{kg}^2$ at 1000°C. The $\log(K_{\text{sp}}^{\text{Nb}})$ ranges from -3.12 ± 0.05 to $-2.95 \pm 0.10 \text{ mol}^2/\text{kg}^2$ at 800°C and from -2.04 ± 0.06 to $-1.79 \pm 0.08 \text{ mol}^2/\text{kg}^2$ at 1000°C (Bartels et al., 2009). It is not clear if the elevated solubility products in PEG melts when compared to RHY and HPG melts are related to higher B, Li and P content or to the lower ASI value. Preliminary data indicate that the presence of Li most likely leads to a higher solubility of manganotantalite and manganocolumbite as previously observed by Linnen (1998) in HPG melts. However, changing Li concentration also affects the ASI value. Thus, more systematic experiments need to be conducted to evaluate the influence of Li on MnTa_2O_6 and MnNb_2O_6 solubility.

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Negative linear thermal expansion of crystals caused by rising symmetry

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Temperature rising leads to disordering of matter and rising its symmetry. For characterization of crystal symmetry E.S. Fedorov's s -index is usually used – a number of symmetry operations of the holohedric point group of a system.

A tendency of thermally rising symmetry of polymorphic modifications is well known. For example, SiO_2 demonstrates α ($s = 12$) – β (24) quartz transformation at 573 °C and then to tridimite (24) at 870 °C and to cristobalite (48) at 1470 °C, finally it melts at 1728 °C ($s = \infty$). V.V. Dolivo-Dobrovolsky [1], using data on mineral composition of the Earth's spheres by K.E. Bullen, T. Barth, and A.E. Ringwood, has shown also that the mean symmetry of the spheres increases due to rising of temperature from 6 and 9 (A_1 and A_2 zones of the earth-crust, correspondingly) to 13 for the upper mantle B, 25 for C_1 , 32 for C_2 spheres of the mantle, and 47 for the D-sphere of the lower mantle.

Hence, the temperature dependence of symmetry is used traditionally for an interpretation of phase transitions (for discrete points on the temperature axis) although this dependence is practically not taken into account for understanding of thermal expansion (current thermal process) and for further advance in a thermal expansion theory.

The following general concept of increasing symmetry with increasing temperature [2, 3] is discussed in the talk: *An increase in crystal temperature is equivalent to an increase in the intensity of thermal motion (vibrations, rotations and jumps) of atoms and molecules and gives rise to the following transformations whose tendency is towards increasing the crystal symmetry: increasing vibrational symmetry of atoms and molecules $\rightarrow$ deformation–structural rearrangement in the direction of increasing symmetry $\rightarrow$ transformation into more symmetrical high-temperature phase.* According to our position the value of thermal expansion is dictated by the strength of chemical bonds, and its anisotropy – mainly by the tendency of crystal symmetry to increase upon heating. This allows us to achieve a better understanding of real thermal expansion, explain expansion anisotropy, and predict many cases of linear contraction on heating, which is important for technique and science [3, etc.].

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Colloidal particles and mineral surfaces: Surface reactivity as a function of surface roughness

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Adhesion of colloidal particles onto mineral and rock surfaces is an important process in the environment that is crucial to manage effects such as contaminant transport, drinking-water quality, and nuclear waste management. Trapping of trace elements or element complexes may be governed by micrometer- to submicrometer topography variations of mineral and rock interfaces. Therefore roughness variations of mineral surfaces have an environmental importance. A systematic approach to surface roughness variations on mineral and rock interfaces will be a key prerequisite to determine reactivity ranges for colloidal reactions at mineral surfaces.

Surfaces of natural secondary mineral were studied in order to quantify lateral and vertical surface topography deviations (FISCHER et al., 2008). We applied *converged* surface roughness parameters to provide a statistically-based quantification of surface topography differences (FISCHER and LÜTTGE, 2007). Surface roughness variations of secondary minerals which show half-pore diameters in the hundreds of nanometer range were quantified and compared to geochemical patterns. The identified roughness ranges were applied to constrain experimental conditions for particle adsorption at mineral surfaces.

First experiments were carried out to investigate reactivity ranges of colloidal reactions, based on surface data over a large field of view of several mm². Here we present first results about the interaction of colloids with calcite surfaces. Freshly cleaved calcite surfaces were reacted. A well-defined topography with etch pits and steps in the height range of several tens to hundreds of nanometers was formed. Lateral pit dimensions are about several microns. This well-defined surface was exposed to a colloidal suspension. As an analog to natural particles we used a bimodal particle size distribution of polystyrene latex (average diameter 499 and 903 nm).

Vertical Scanning interferometry (Lüttge et al., 1999) was applied to investigate the particle distribution on the surface and to quantify the retention of latex colloids. For both particle types, first experiments showed that an increased adsorption was found for two surface characteristics: Firstly, at surface sections with etch pits of approx. 200 nm in depth, and, secondly, at surface steps of similar height. On the other hand, the adsorbed number of particles per area is smaller for surface sections dominated by surface steps compared to pitted surface sections. The overall height distribution of the surface has, however, a more important influence on adsorption than the number of etch pits. For a surface topography height range below 100 nm, it was found that the smaller particles were predominantly adsorbed. It is expected to improve the understanding of colloidal retention in the environment as a function of macroporous surface topography of minerals and rocks. Because colloids are ubiquitous in natural fluids, a broad field of engineering applications exists for the results of this study.

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Holcim Rheingold – Ein Mythos wird wahr

Udo Flüchter

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Der Mythos vom Rheingold geht auf das 5. Jahrhundert nach Christus zurück. Schriftliche und mündliche Sagenfassungen vom Nibelungenlied kursierten im ober- und niederdeutschen Sprachraum und erzählten von einem Schatz bestehend aus 144 Pferdewagen voll mit Gold und Edelsteinen. Diesen ließ der Erzschorke Hagen von Tronje angeblich nach der Ermordung von Siegfried um 430 südlich von Worms »zu Loche im Rhein« versenken. Obwohl sich Abenteurer und teilweise auch ernstzunehmende Wissenschaftler alle erdenklichen Mühen gaben den Schatz zu finden, ist er genau wie die Nibelungen selbst, bis heute eine Legende geblieben.

Trotzdem hat die Nibelungen-Saga mit Helden wie Siegfried und Kriemhild und dem Brüdertrio Gunther, Gernot, Giselher als Bösewichten die Menschen über anderthalb Jahrtausende in seinen Bann gezogen. Nicht nur Wagners Oper trägt diesen Namen, auch einfache Hotel- und Restaurantbesitzer oder Schiffseigner haben es von jeher verstanden, das Charisma und die Mystik des Wortes Rheingold zu nutzen, um möglichst werbewirksam auf ihre Leistungen und Produkte aufmerksam zu machen. Die Nibelungen-Legende und ihre Umsetzung in Kunst, Musik oder Literatur haben gemeinsam dafür gesorgt, dass der Mythos Rheingold entstehen konnte und die Menschen – nicht nur in Deutschland – bis heute fasziniert.

Schon die Kelten wuschen vor 2000 Jahren an den Ufern des Rheins Gold. Das gleiche taten die Römer. Im Mittelalter und später bis ins 19. Jahrhundert gab es vor allem in Baden und in der Pfalz zahlreiche arme Bauern, Fischer und Handwerker, die dieser Beschäftigung nachgingen, um ihren Lebensunterhalt aufzubessern. In der ersten Hälfte des 19. Jahrhunderts erlangte die Goldwäscherei einen Höhepunkt. Bis 1854 wurden in der badischen Münze in Karlsruhe Golddukatens aus Rheingold geschlagen. Nach der Regulierung des Rheins Mitte des 19. Jahrhunderts kam die Goldgewinnung zum Erliegen, da wegen der Staustufen kein frisches Gold mehr an den mittleren Oberrhein gelangte. Der letzte Goldwäscher in Rheinland-Pfalz hängte Ende des 19. Jahrhunderts in Speyer seinen Beruf an den Nagel. Allein zwischen 1748 und 1874 wurden mindestens 363 Kilogramm Gold gewaschen.

Die Holcim Kies und Beton GmbH in Süddeutschland fördert in ihrem Kieswerk in Rheinzabern Gold, bereitet dieses auf und vertreibt es weltweit. In Deutschland handelt es sich um die einzige industrielle Goldgewinnung. Die Aufbereitungsanlage wurde für einen Durchsatz von ca. 140 Tonnen (Sand 0/2 mm) pro Stunde ausgelegt. Täglich können so beachtliche Mengen Schwermineralkonzentrate erzeugt werden, die in mehreren Aufbereitungsschritten weiter bis zum fertigen, für den Goldschmied geeigneten Gold verarbeitet werden. Sämtliche Schritte, auch das Einschmelzen der Konzentrate, erfolgen in eigener Regie vor Ort. Die Gewinnung des Goldes aus den Konzentraten wird rein gravimetrisch durchgeführt. Es werden keine chemischen Hilfsstoffe eingesetzt, folglich handelt es sich um »Biogold«.

Experimental melting of peridotite with CO₂ and H₂O in the lower cratonic lithosphere and applications to the origin of carbonate-rich igneous rocks

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The oxidation state of the upper mantle is debated, but probably varies between reduced conditions in which H₂O and CH₄ would be stable and carbonates cannot form to more oxidized conditions in which CO₂ and H₂O dominate and carbon is much more mobile as carbonate-bearing melts. The latter conditions appear to be particularly applicable to continental rift environments in or close to cratons.

Partial melting experiments at 40, 50 and 60 kbar pressure on three peridotite compositions with 0.5-0.63 wt% H₂O and 2.0-3.2 wt% CO₂ added indicate melting temperatures only marginally above continental geotherms. Results show that the melting point of peridotite with H₂O and CO₂ at all pressures above 20 kbar is lower than with either H₂O or CO₂ alone, and so this study maps the most likely melting conditions wherever the mantle is oxidized.

Most experiments were performed on a composition with 1.5 wt% K₂O added, which causes a further decrease of about 40°C in melting temperature. Melts progress gradually from carbonate-rich to carbonated silicate in composition: near-solidus melts have Ca/(Ca+Mg) of 0.46-0.53, which fall to <0.40 more than 50°C above the solidus. With increasing temperature for the K-enriched peridotite at 50 kbar, melts are characterised by strong increases in SiO₂ (<3 to >30 wt%) and Al₂O₃ (<1 to >9 wt%) and concomitant decrease in CaO (>20 to <3 wt%), with little change in MgO. K₂O and TiO₂ exhibit maxima at intermediate temperatures, reflecting the stability of phlogopite and ilmenite above the solidus, indicating the presence of up to 13 wt% K₂O and 2.6 wt% TiO₂ in carbonate-rich melts with only 13 wt% SiO₂. Of 30 trace elements, only Cr, Mn, Ni, and Zn are compatible in the residue, whereas U, Rb, Ba and the LREE are most enriched in the melts. Low melt fractions exhibit troughs in trace element patterns for Hf, Nb, Ta and Cs that are diminished or eliminated at higher degrees of melting. Apart from these features and larger LREE/HREE ratios, trace element compositions are similar to silicate melts of peridotite in CO₂-free conditions.

Partial melts of peridotite with CO₂ and H₂O are too low in MgO to resemble kimberlites, but are more similar to aillikites. They will act as effective metasomatic agents enriching the lithosphere in K and carbonates, of relevance for the origin of ultramafic lamprophyres and kamafugites. Higher-degree melts (15-35%) have >20 wt% SiO₂, are only mildly enriched in trace elements, and will not cause large time-integrated isotopic in-growth except over long geological time intervals. The temperature interval over which melts are carbonatitic with SiO₂ contents <10 wt% narrows with increasing pressure from 30- 60 kbar, meaning that the metasomatic effects of carbonatitic melts may be greatest at 20-30 kbar.

The strong association of carbonate-rich magmatism with continental rifts may be explained by a concentration of carbon as diamond or graphite in reduced conditions which is later remobilized by oxidation to carbonate. The progressive oxidation of the mantle lithosphere may thus be characteristic for the development of continental rifts.

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Possibility of enlarging capacity within the metamorphic reservoirs of the Mokrin Jug (South) field

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Mokrin-jug (South) structure is located at the SE part of Pannonian basin, at the Northern part of Banat depression. Mokrin-jug oil-gas field is characterized by very complex geological structure and structural-tectonic relationships. The structure is one rise at the bottom of Neogene sediments, made of metamorphic rocks.

The oldest drilled rocks at the structure "Mokrin-jug" are presented by crystalline shales from the group of amphibolite, epidote-amphibolite, biotite–albite shales, muscovite-biotite shales, muscovite-biotite gneiss, as well as chlorite-sericite schists. Rocks of the basic rocks are fractured and deformed as a result of tectonic activities, containing a lot of macro- and micro-fractures, making them to be convenient reservoirs. They are of Paleozoic age. Biotite gneiss is fine-grained rock, dark-grey, with schistose structure. It is made of sericite feldspar, fine-grained quartz and chlorite biotite, with garnet as accessory constituent.

Amphibolite-epidote shale is made of amphibole and hornblende as main constituents. Quartz is present in less extent. Epidote is spread through the rock in form of individual grains or aggregates. Among other minerals, ilmenite is existent, transforming into leucoxene along the edges.

Amphibole shales are grey-green, fine-grained, with parallel schistosity. They are made of amphibole, quartz and calcite. Biotite-amphibole shale is made of quartz, sericite feldspar and biotite.

At the southern part of the structure, palaeorelief is made of biotite gneiss and biotite-muscovite shales with garnet. Main constituents are: quartz, muscovite, biotite and sericite feldspars.

Chlorite-sericite shales are grey-green, with high content of sericite and muscovite over the cover surfaces. Main constituents are: quartz and thin sheets of parallelly oriented chlorite. Feldspar is present in the form of rare grains of plagioclase. Among accessory constituents, garnet and tourmaline as large crystals, are predominant.

After long-term oil exploitation at the oil-gas field Mokrin-jug, something should be performed. By complex synthesis of production data, as well as mineralogical and petrological analyses, AKOR method was proposed. The method has been proven as the most efficient one in EOR at numerous oil fields throughout the world.

Petrogenese von Fe-Ti-Oxidkörpern des anorthositischen Kunene-Intrusiv-Komplexes, NW-Namibia

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Massige Fe-Ti-Erze treten als scharf begrenzte, ovale Körper von bis zu 80m Durchmesser innerhalb des mesoproterozoischen Anorthosit-Massivs des Kunene-Intrusiv-Komplexes, NW-Namibia auf (Drüppel et al., 2007). Die Erzkörper sind stets mit frühen Pyroxen-führenden Anorthositen assoziiert. Sie bestehen hauptsächlich aus grobkörnigem Magnetit (60-80 Vol.%; reintegrierte Zusammensetzung $\text{Fe}_{2.3}\text{Al}_{0.4}\text{Ti}_{0.3}\text{O}_4\text{-Fe}_{2.1}\text{Al}_{0.4}\text{Ti}_{0.5}\text{O}_4$) mit feinen Ilmenit-, Spinell- und Korund-Entmischungen sowie Ilmenit mit Hämatit-Entmischungen (20-30 Vol.%; reintegrierte Zusammensetzung $\text{Fe}_{2.1}\text{Ti}_{1.7}\text{Mn}_{0.1}\text{Mg}_{0.1}\text{O}_3\text{-Fe}_{1.9}\text{Ti}_{1.9}\text{Mn}_{0.1}\text{Mg}_{0.1}\text{O}_3$). Untergeordnet tritt Spinell auf (bis zu 5 Vol.%; $\text{Mg}_{0.5}\text{Al}_{1.9}\text{Fe}_{0.6}\text{O}_4$). Akzessorisch sind in den Erzkörpern Orthopyroxen (X_{Mg} : 0.92-0.97; bis zu 2.6 Gew.% Al_2O_3) und/oder Ti-reiche Hornblende (TiO_2 : 4.4-4.9 Gew.%; X_{Mg} : 0.71-0.74) enthalten, welche sich aufgrund ihrer Mg-reichen Zusammensetzung deutlich von den Silikaten der umgebenden Anorthosite unterscheiden und meist durch feinkörnige Gemenge aus Chlorit, Biotit (X_{Mg} : 0.81-0.82), Magnetit und Epidot ersetzt werden. Selten kann idiomorpher Apatit, assoziiert mit feinkörnigem Chlorit in den Zwickeln zwischen den Erzphasen beobachtet werden.

Die Fe-Ti Erzkörper sind durch hohe Gehalte an Fe_2O_3 (34-49 Gew.%), FeO (21-34 Gew.%), TiO_2 (15-25 Gew.%), Al_2O_3 (4-8 Gew.%) und MgO (1.5-4 Gew.%) charakterisiert mit nur geringen Konzentrationen von SiO_2 (bis zu 2.7 Gew.%). Im Vergleich zu den angrenzenden Anorthositen zeigen die Erze höhere Spurenelementgehalte an V, Zn, Cr, ($\pm$ Zr, Sn, Co, and Nb), wohingegen die Anorthosite reicher an Ba, Y, U, Th, Ta und den LREE sind. Die Spurenelementgehalte von Magnetit und Ilmenit, welche mit Hilfe von La-ICPMS analysiert wurden, sind stark variabel mit stets hohen Konzentrationen von V (0.1-0.9 Gew.%), Cr (bis zu 0.2 Gew.%), Zn (bis zu 0.2 Gew.%), Mn (bis zu 0.1 Gew.%), Ni (bis zu 0.1 Gew.%) und Ga (20-100 ppm) in Magnetit und von Mn (0.5-0.8 Gew.%) und V (bis zu 0.1 Gew.%) in Ilmenit.

Die kalkulierten Temperaturen für koexistierenden Ilmenit und Magnetit liegen zwischen 950°C und 850°C mit Sauerstoffugazitäten am QFM-Puffer. Deutlich geringer sind die über Sauerstoff-Isotopenfraktionierung an separierten Ilmenit- und Magnetit-Körnern berechneten Temperaturen von 650-400°C, die auf eine späte Re-equilibrierung der Sauerstoff-Isotopenwerte hinweisen.

Die Petrogenese von mit Anorthositen assoziierten Fe-Ti-Erzen wird kontrovers diskutiert. So werden unterschiedliche Mechanismen wie liquidmagmatische Entmischung, Magmenmischung und fraktionierte Kristallisation für die Bildung der Erzkörper vorgeschlagen (Charlier et al., 2006). Hinsichtlich der geologischen Beziehungen zwischen den Fe-Ti-Erzen und den angrenzenden Anorthositen in Namibia sowie der hohen kalkulierten Kristallisationstemperaturen von Ilmenit und Magnetit von bis zu 950°C ist eine Genese der Erzanreicherungen über liquidmagmatische Entmischung naheliegend. Die Gefüge der Erze und die Zusammensetzung der Fe-Ti-Oxide und Silikate deuten dagegen eher auf eine frühe Akkumulation von Titanomagnetit, Ilmenite und Pyroxen ($\pm$ Spinell) aus einer gering differenzierten basaltischen Schmelze hin, aus der sich später auch die Anorthosite gebildet haben könnten. Da die Erzkörper ausschließlich in den frühen, Pyroxen-führenden Anorthositen nicht aber in den jüngeren, Olivin-führenden Anorthositen auftreten scheint die Zusammensetzung der Ausgangsschmelze eine elementare Rolle bei der Bildung der Fe-Ti-Erze zu spielen.

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Ti-Al zoning of experimentally grown titanite in the system CaO-Al₂O₃-TiO₂-SiO₂-NaCl-H₂O-(F) at 4 kb and 600°C

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Chemical zoning is a common phenomenon in minerals and can be used to reconstruct the growth conditions. Titanite frequently is zoned according to the substitution $\text{Al}+(\text{OH},\text{F}) = \text{Ti}+\text{O}$. We synthesized titanite from natural rutile in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2-\text{NaCl}-\text{H}_2\text{O}(-\text{CaF}_2)$ at 600°C and 0.4 GPa and run duration between 1 and 107 days. The rutile crystals were placed in a perforated Pt-tube within an outer Au-capsule containing wollastonite, $\gamma\text{-Al}_2\text{O}_3$, optional powdered CaF_2 , and a NaCl brine, to simulate conditions, where rutile is transformed into titanite by a Ca-Si-Al fluid, driven by a chemical potential gradient between inner and outer capsule. Such a situation mimics the observation from natural rocks, where rutile from high-pressure rocks is transformed into titanite in a dissolution-precipitation process at retrograde conditions.

The growth of titanite is restricted to the inner capsule at the rutile surface. Its growth proceeds after 1 day from sparse titanite as isolated crystals (up to 100 μm) on the rutile surface to assemblages of several 100 μm large crystals in a reaction rim in the long-time runs, but considerable parts of the rutile surface always remain in contact with the fluid. In short-time runs ≤ 7 days perovskite was observed as a run product, which however disappeared at ≥ 14 days. In the outer capsule grossular and plagioclase are formed. Titanite is strongly zoned in Al-Ti (Fig. 1) and shows the compositional range known from natural titanite up to the maximum replacement of ~ 0.5 Ti per formula unit. The extent of the Ti-Al exchange in the titanite is controlled by the availability of F, is already large in short

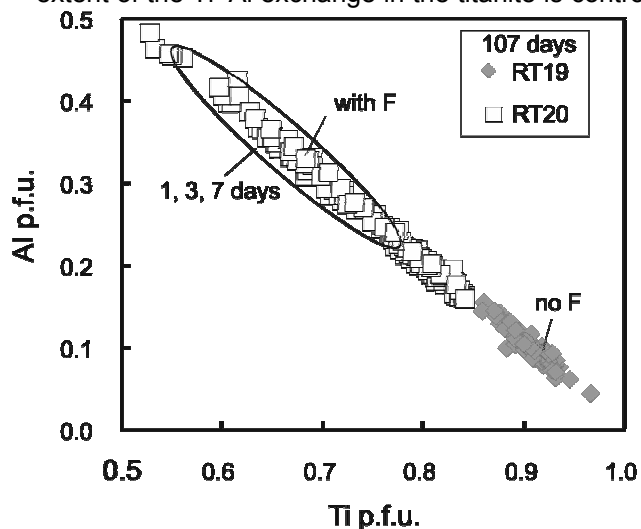


Fig 1 Al-Ti composition of titanite from 107 days runs and compositions with and without F. The field of 1, 3, and 7 days runs are for F bearing compositions. p.f.u. = per formula unit

after the formation of the dominant grossular – anorthite in the outer capsule. Neither garnet nor plagioclase is zoned.

Mineral growth zoning represents disequilibrium, in the case of fluid-mediated growth at super-saturated conditions in the fluid. Nucleation of titanite is spontaneous at the rutile surface, but restricted to a small number of crystals. The concentration of Ti in the fluid is likely the limiting factor for titanite growth considering the low (and slow) solubility compared to that of the other cations. Ti is not transported into the outer capsule, indicating a relatively low mobility, in contrast to Al, Ca and Si, which are transported into the inner capsule. Assuming buffered Al concentration from dissolution of the Al-source, we speculate that the Ti/Al of the fluid at the precipitation site was determined by the local Ti concentration, which must vary over the distance from the rutile surface to the growing titanite crystal. This could explain variable Ti/Al ratios in titanite.

run-times and does not disappear in the long-time runs. Without F, it is limited to ≈ 0.15 Al pfu. The Al-Ti distribution (with and without CaF_2) is patchy and irregular. Borders between compositional domains (up to several tens of μm) are sharp, less common transitional. The zoning does not relate to the growth of the crystals that proceeds at the faces in contact with the fluid, i.e. no relation of the zoning with time (core – rim) or preferred crystallographic (growth) directions is observed. The transitional stage in the evolution of the fluid's composition with the formation of perovskite appears to have no influence on the compositional variability (1, 3, 7 days experiments; Fig. 1). The zoning remains enigmatic with respect to time-growth relations, surface effects related to crystallographic directions, and evolution of the fluid composition. The formation and destruction of the perovskite is likely due to shift from a Ca-rich fluid in the early stages of the reaction of CaSiO_3 and Al_2O_3 to grossular and feldspar to a more SiO_2 -rich fluid

Struvit- und Newberyit-Wechselagen in Enterolithen

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Im Dickdarm des Pferdes kann es unter nicht genau bekannten Bedingungen zur Kristallisation von Darmsteinen (Enterolithe) kommen. Dabei treten bis zu 8 kg schwere Darmsteine auf, deren Morphologie von tetraeder-, oktaeder- und würfelförmig bis zu ellipsoidal oder kugelförmig reicht [1].

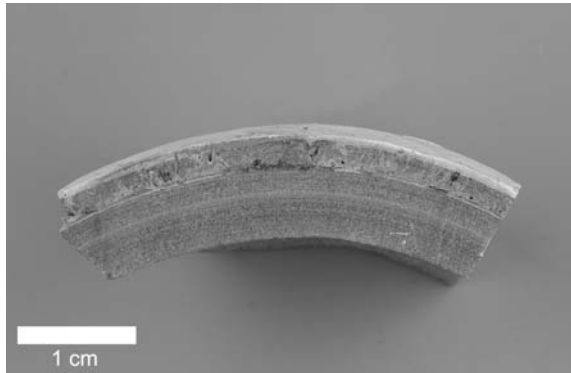


Abb.1: Mikrofoto der "Wachstumsringe" eines Pferdedarmsteins



Abb.2: 3D-Darstellung einer röntgencomputertomographischen Aufnahme mit einem Hufnagel als „Wachstumskeim“ eines Pferdedarmsteins

Beim Menschen bilden sich hingegen sehr selten Darmsteine (Phytobezoare) nach einer längeren Stase von pflanzlichen Verdauungsbestandteilen in Dünndarm-Divertikeln [2].

Hauptbestandteil der untersuchten Enterolithe ist Struvit ($\text{NH}_4\text{MgPO}_4 \times 6 \text{H}_2\text{O}$) [3]. Mittels XRPD- und EPMA-Untersuchungen wurden als Nebenphasen Newberyit $\text{MgHPO}_4 \times 3\text{H}_2\text{O}$, Brucit $\text{Mg}(\text{OH})_2$ und Kaliumhydrogenphosphat $\text{K}_3\text{H}_5(\text{P}_2\text{O}_7)_2$ gefunden.

Typisch für Darmsteine ist die Bänderung sehr dünner schalenartiger Schichten, die durch abwechselnde Kristallisation mehrerer Phasen durch Konzentrationsfluktuationen entsteht. In der äußersten Schicht liegt reiner Newberyit vor. Der dünne braun gefärbte äußere Bereich weist Korngrößen unter der Auflösungsgrenze des Lichtmikroskops auf. In den inneren Schichten ist Struvit und als Nebenbestandteil Newberyit nachweisbar. In radialer Richtung nach außen erhöht sich deren Porosität. In inneren dichten Bereichen zeigen Körner von einigen 10 μm bis 100 μm Durchmesser hohe Interferenzfarben bei gekreuzten Polarisatoren. Die Körner weisen ein Längswachstum senkrecht zu den Bändern auf. Die Dicke der Bänder variiert um einige Zehn Mikrometer.

In den Darmsteinen, deren Inneres aus einem Agglomerat von Pflanzenfasern besteht, ist Quarz nachweisbar.

Die computertomographischen Aufnahmen zeigen, dass bis zu einer bestimmten Größe (variierend, wenige Zentimeter) die äußere Form der Enterolithe vom Keim geprägt wird. Bei größeren Exemplaren ist kein Rückschluss von der Morphologie des Steins auf den Keim möglich (s. Abb. 2). Die Dicke der Wachstumsringe variiert mit dem Futter. Dünne Struvit-Schichten, die mit Quarzkörnern durchsetzt sind, sind der Frischfutterperiode zuzuordnen.

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Hochaufgelöste Elementanalytik (XRF core scanner) an feinelaminierten Sedimenten aus Bergbauseen der Lausitz (RL-111)

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Sedimente aus Bergbauseen der Braunkohlenfolgelandschaft der Lausitz zeigen häufig eine feine Laminierung der obersten 10 bis 20 cm. Die anzutreffenden laminierten Sedimentmächtigkeiten stehen nach bisherigen Untersuchungen in Übereinstimmung mit dem Alter der Seen. Demnach handelt es sich bei diesen Ablagerungen um die See-interne Sedimentation. Untersuchungen von Wendt-Potthoff et al. (in prep.) am Bergbausee RL-111 (Niederlausitz, Revier Lauchhammer) deuten auf eine Jahresschichtung der Laminierung, ähnlich der Warvenbildung in meromiktischen Seen. Es liegt daher der Verdacht nahe, dass es sich bei der durch unterschiedliche Farbgebung erkennbaren Laminierung auch um Ausfällungen unterschiedlicher Eisenminerale, wie Jarosit, Schwertmannit oder Goethit handeln könnte. Neben mineralogischen Analysen, die sich noch in der Bearbeitung finden, sollte mit Hilfe der neuen „core scanner-“ Röntgenfluoreszenztechnik für den sub-mm Bereich eine Analyse der Elementverteilung mit der Tiefe an Sedimentkernen aus dem RL-111 erfolgen. Ziel dieser Untersuchungen ist es, einen möglichen parallelen Verlauf der Elementverteilung und der Laminierung zu erkennen, falls diese ursächlich in Zusammenhang stehen.

Die Messungen wurden im Labor der Arbeitsgruppe POLAR des Geographischen Institutes der Universität Bremen an einem ca. 30 cm und einem ca. 20 cm langen Sedimentkern aus dem Bergbausee RL-111 durchgeführt. Die Kerne mit einem Durchmesser von 9 cm wurden auf einem Schneidblock in Längsrichtung halbiert und eine Halbschale für die XRF core scanner Messungen verwendet. Es wurde das ITRAX der Firma COX (Schweden) verwendet; die Schrittweite der Messpunkte war 0,2 mm. Zusätzlich wurde an den beiden Kernen noch eine Suszeptibilitätsmessung durchgeführt.

Der Beitrag diskutiert die Ergebnisse der XRF core scanner Messungen im Zusammenhang mit der Laminierung und herkömmlichen RFA-Messungen an vertikal geringer aufgelösten Sedimentkernen (1 bis 2,5 cm) des gleichen Bergbausees.

Geochemische Charakterisierung mitteleuropäischer Kupfervorkommen zur Herkunftsbestimmung des Kupfers der Himmelscheibe von Nebra

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Die Himmelscheibe von Nebra ist Teil eines frühbronzezeitlichen Hortes und als älteste konkrete Himmelsdarstellung ein Fund von herausragender Bedeutung. Daher wird in einem DFG-finanzierten interdisziplinären Forschungsprojekt verschiedenen archäologischen, archäometallurgischen, lagerstättenkundlichen und astronomischen Fragestellungen zur Himmelscheibe und zur Frühbronzezeit in Mitteleuropa nachgegangen. Eine dieser Fragen ist die nach der Herkunft der Rohstoffe Kupfer, Zinn und Gold. So wurden im Rahmen einer Promotionsarbeit in einem der Projektmodule über 140 Kupfererzproben von 58 Kupfervorkommen in Mitteleuropa geochemisch untersucht. Dazu gehören unter anderem die stratiforme Vererzung im Buntsandstein von Helgoland, Gangvererzungen im Harz, oder im östlichen Rheinischen Schiefergebirge und die Kupferschiefervererzung einschließlich der so genannten „Mansfelder Rücken“. Die Analysen umfassten Messungen der Pb-Isotopenzusammensetzung mittels Multikollektor-ICP-MS und TIMS, sowie Messungen der Spurenelementzusammensetzung mittels RFA und teils auch INAA. Damit steht erstmals eine umfangreiche Datenbank mit den Spurenelement- und Pb-Isotopendaten von Kupfererzen in Mitteleuropa für geoarchäologische Provenienzuntersuchungen zur Verfügung. In der bereits begonnenen zweiten Projekthälfte wird diese Datenbank noch auf Kupfererze in West-, Südwesteuropa, sowie Südosteuropa ausgeweitet. Der Vergleich der Erze mit der Himmelscheibe von Nebra und ihren Beifunden ergab, dass sich die bearbeiteten Kupfervorkommen sehr klar anhand ihrer Pb-Isotopenzusammensetzung und teils auch anhand der Spurenelementzusammensetzung als Rohstoffquelle für den Hortfund von Nebra ausschließen lassen. Dies umfasst auch einige dem Fundort der Himmelscheibe geographisch nahe gelegenen Lagerstättendistrikte, wie den Harz oder den mitteldeutschen Kupferschiefer. Zusätzlich wurden in der Literatur publizierte geochemische Daten zu Kupfervorkommen im Arbeitsgebiet (z.B. Leveque & Haack 1993 und Durali-Müller 2005) mit den Daten der Nebraer Artefakte verglichen und auch hier wurde keine Übereinstimmung gefunden. Zu diesen Kupfervorkommen gehören unter anderem der Rammelsberg und Gangvorkommen im Taunus, bei Erbdorf und Wölsendorf. Ein Vergleich der Kupfererze mit weiteren frühbronzezeitlichen Artefakten aus Sachsen-Anhalt erbrachte dagegen einige wahrscheinlich positive Zuordnungen von Lagerstätten zu Artefakten: So zeigen Gangvererzungen im Kupferschiefer bei Mansfeld und Kamsdorf eine deutliche Pb-isotopische Überschneidung und auch Ähnlichkeiten in der Spurenelementzusammensetzung mit den Artefakten der Horte von Naumburg und Schkopau, in geringem Maße auch mit den Horten Bennewitz, Kanena III und eventuell Dieskau III, so dass zumindest für die erstgenannten Horte die Herkunft des Kupfers aus diesen Gangvererzungen als wahrscheinlich angenommen werden kann. Die betreffenden Gangvorkommen wurden bzw. werden nachgeprobt. Ein Vergleich der genannten Artefakte mit Pb-Isotopendaten aus der Literatur (Leveque & Haack 1993, Tischendorf et al. 1993 und andere) ergab außerdem signifikante Ähnlichkeiten zwischen Gängen im Oberharz und bei St. Andreasberg und allen oben genannten Horten, sowie zwischen Rammelsberger Erzen und einem der Artefakte von Schkopau. Die Ähnlichkeiten der Spurenelementdaten der betreffenden Oberharzer Erze ist allerdings weniger ausgeprägt als im Falle der Gangerze von Mansfeld und Kamsdorf.

Diesen Indizien weiter nachzugehen dürfte lohnend sein. Auch stellen die bisher vorgenommenen Vergleiche von Erzen und Artefakten nur einen ersten Schritt dar, dem noch umfangreichere Vergleiche folgen sollen.

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Bushveld Complex Main Zone at Phosiri: Geochemical evidence for convection-triggered lithological variation in a replenished but marginally fractionated magmatic system

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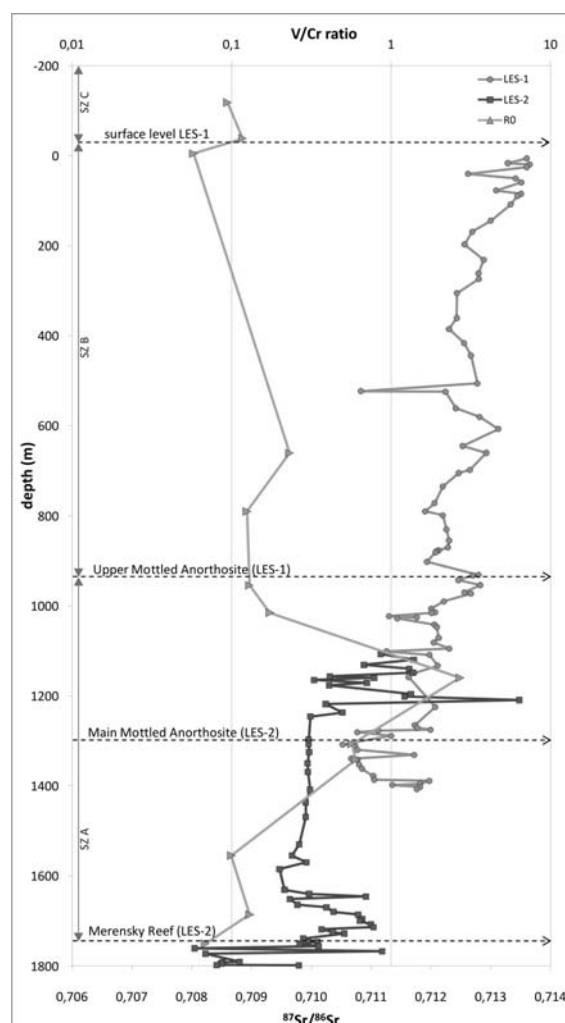


Figure 1 Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (plag.) as magma lineage indicators and $\text{V}/\text{Cr}_{\text{M/D}}$ ratios as fractionation indicators

mafic cumulate rocks of the Main and Upper Zone in the north-western part of the Eastern Bushveld Complex are exposed on the eastern side of the Stoffpoort fault adjacent to the Phosiri Dome. Recent exploration drilling has intersected Upper Critical Zone lithologies including the PGE-rich Merensky Reef and UG2 chromitite units on the southern (Scoon, 2002) and eastern of the Phosiri Dome. The aim of this study was to investigate mineralogical and geochemical variations of cumulate rocks of Phosiri's Main Zone (MZ). The results of this study exhibit large correspondence with the findings of former works such as those of Von Gruenewaldt (1973) or of Kruger (2005). However, the MZ at Phosiri presents a lot of unique characteristics. The following sequence of events is suggested for its formation: The MZ magma became more evolved from bottom to top, indicating a certain amount of fractional crystallization, and possibly the injection of new magma pulses. The presence of significant marker horizons allows a (litho-) stratigraphical subdivision in subzones by means of macroscopical characteristics, supporting the existence of cryptic variation in the upper part the differentiated chamber. The significant change in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of plagioclase separates (R_0) and of whole rock V/Cr ratios (Fig. 1) shows that a relatively abrupt change from an integration to a differentiation stage took place. The process of double-diffusive convection is postulated for the origin of the four distinct pyroxenitic horizons at the elevation of the Pyroxenite Marker Zone; these layers could have their origin in relatively viscous and under-cooled magma, which possibly prohibited thorough magma mixing in the upper part of the MZ chamber. The high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (avg. $R_0 = 0.7094$) give evidence that the Main Zone melt represents new magma pulse; samples from the upper Subzone A additionally indicate elevated crustal contamination (R_0 between 0.7107 and 0.7124). Petrographical and (mineral-) chemical data show that a few samples in Subzone A and B are contaminated by granitic material. Fractionation indicators such as V/Cr ratios or $\text{Mg}\#$ give the evidence that the fractionated crystallisation is the dominant process to explain the strong magmatic differentiation from the top of Subzone C to the bottom of Subzone A. The presence of exsolved pyroxenes (i.e. inverted pigeonite) in Subzone B indicates a very high cooling rate during fractional crystallisation and no further magma injection in this stage. The co-existence of compositional variable clino- and orthopyroxene supports the assumption of a fast crystallisation of the magma (element diffusion did not take place) particularly in Subzone B. The high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at Phosiri confirm that the MZ magma in this location has the same lineage as elsewhere.

Mafic cumulate rocks of the Main and Upper Zone in the north-western part of the Eastern Bushveld Complex are exposed on the eastern side of the Stoffpoort fault adjacent to the Phosiri Dome. Recent exploration drilling has intersected Upper Critical Zone lithologies including the PGE-rich Merensky Reef and UG2 chromitite units on the southern (Scoon, 2002) and eastern of the Phosiri Dome. The aim of this study was to investigate mineralogical and geochemical variations of cumulate rocks of Phosiri's Main Zone (MZ). The results of this study exhibit large correspondence with the findings of former works such as those of Von Gruenewaldt (1973) or of Kruger (2005). However, the MZ at Phosiri presents a lot of unique characteristics. The following sequence of events is suggested for its formation: The MZ magma became more evolved from bottom to top, indicating a certain amount of fractional crystallization, and possibly the injection of new magma pulses. The presence of significant marker horizons allows a (litho-) stratigraphical subdivision in subzones by means of macroscopical characteristics, supporting the existence of cryptic variation in the upper part the differentiated chamber. The significant change in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of plagioclase separates (R_0) and of whole rock V/Cr ratios (Fig. 1) shows that a relatively abrupt change from an integration to a differentiation stage took place. The process of double-diffusive convection is postulated for the origin of the four distinct pyroxenitic horizons at the elevation of the Pyroxenite Marker Zone; these layers could have their origin in relatively viscous and under-cooled

Order-disorder in calcium silicate hydrate solid solutions as revealed by synchrotron based X-ray diffraction, thermogravimetry and Raman spectroscopy

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Synchrotron based X-ray diffraction has been used to analyze a series of mechanochemically prepared calcium silicate hydrate (C-S-H) phases with aimed Ca/Si ratios from 1/5 to 3/2. Fumed silica and CaO were used as starting materials. All samples contain three-dimensionally ordered C-S-H phases. Pure C-S-H-phases are present in samples with Ca/Si ratios from 2/3 to 6/5. The samples with C/S ratios 1/5 and 1/2 contain silica, whilst those with C/S ratios 4/3 and 3/2 contain portlandite as minor component. A new approach has been used to track structural changes with C/S ratio involving assignment of an orthorhombic space group (*I2mm*) to the C-S-H phase followed by refinement of the unit cell parameters by the whole powder pattern decomposition (WPPD) method. The results reveal a discontinuity in the *c* parameter at C/S = 5/6 – 1/1, indicating that at least two different structural types separated by a miscibility gap are needed to describe C-S-H, there being two ordered end members with C/S ratios of 2/3 and 5/4, respectively. Nevertheless, both structural types of C-S-H may be well described by the defect-tobermorite model. At C/S = 2/3 the C-S-H consists of 14Å tobermorite slabs linked via H-bonds without interlayer Ca, resulting in the formula $\text{Ca}_4[\text{H}_2\text{Si}_3\text{O}_9]_2 \cdot x\text{H}_2\text{O}$, where $x = 4$. At this C/S ratio, the layer thickness is 13.2 Å. Increasing the C/S ratio leads to little change in the layer thickness, but to increased disorder due to competitive omission of bridging tetrahedra and incorporation of Ca in the interlayer in samples with $2/3 < \text{C/S} < 5/6$.

For C-S-H with C/S ratios above 1/1, structural ordering is increased and accompanied by a reduction in layer thickness, which reaches a theoretical minimum at C/S = 5/4. This end member has structural features of a tobermorite based dimer: $\{\text{Ca}_4\text{H}_2[\text{Si}_2\text{O}_7]_2\} \cdot \text{Ca} \cdot x\text{H}_2\text{O}$, where $x = 4$, with a layer thickness of 11.7 Å. Its powder pattern fits the *B11b* space group. Indexing according to *I2mm* sub cell and *B11b* true cell are also presented. X-ray diffraction and thermogravimetry have been used to analyse the limits of Ca incorporation in the series of C-S-H upon investigation. Results based on bulk weight loss and Rietveld refinements show higher C/S ratios than those corrected additionally for X-ray silent CaCO_3 and $\text{Ca}(\text{OH})_2$. After heating up to 1000°C, even samples with a low Ca content ($\text{Ca/Si} < 2/3$), show solely the calcium silicate wollastonite. This supports the idea of a slightly defected, unbranched single chain silicate anion. The observed change in the *d*-value of the basal reflection upon X-ray irradiation further supports the proposed model, relating the observed shrinkage to the loss of Ca coordinating H_2O molecules from the interlayer. The main feature of the Raman spectra is the silicate bending vibration at about 670 cm^{-1} . Comparison to bending frequencies of some known crystalline phases build up of single silicate chains allowed to estimate the mean Si-O-Si angles in the C-S-H(I) phases to be approx. 140°. Finite silicate chains (Q^2) dominate the structures of the samples at C/S ratios 0.2-1.0, the spectra showing characteristic bands from 1010 cm^{-1} to 1020 cm^{-1} . When the samples are measured in air, the spectra show carbonate bands arising from surface carbonation. The $\nu_1[\text{CO}_3]$ bands obscure the characteristic Raman scattering of silicate units at about 1080 cm^{-1} , which is clearly seen in the fresh samples analyzed in closed capillaries. At C/S > 1.0, dimers (Q^1) are the main building unit of the silicate anionic structure (bands at 889 cm^{-1}).

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Analysis of secondary shell preservation as a key to reconstruct diverse faunal assemblages within an Anisian low diversity assemblage

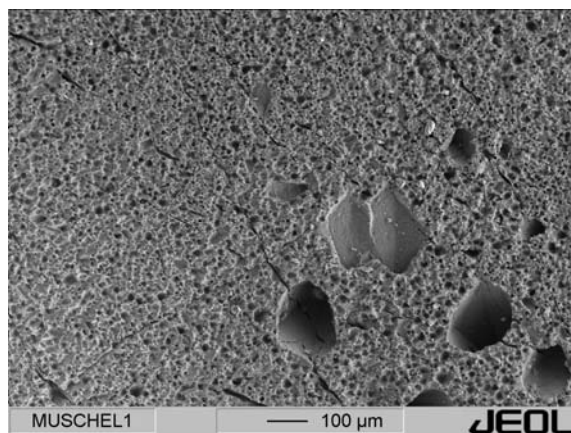
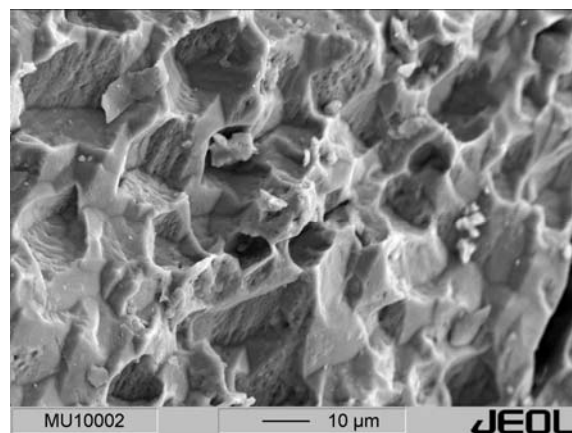
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Anisian carbonates of the Peri-Tethys Basin are considered as poor in fossil remains and fossil assemblages are described as low diverse. The key to understand such low diversity assemblages is preservation. Therefore, the present study focuses on the mineralogical composition of secondary preserved shells of a Middle Triassic epi-benthic faunal assemblage (Lower Muschelkalk, Anisian, Germany). Generally, the samples of the investigated Lower Muschelkalk type section Jena-Steudnitz yield very poorly preserved fossils, mostly steinkerns. Thus, a detailed taxonomical description remains difficult. However, during the sample preparation for micropalaeontological processing it was possible to extract a relatively high amount of white and glossy fossil material, representing an up to now unknown invertebrate assemblage. XRD analysis shows that the secondary preserved shells are composed of nearly 100% coelestine (SrSO_4). Early diagenetic processes within an oxic depositional environment favoured the dissolution of primary aragonite and calcite and its substitution for coelestine. SEM images document very fine-crystallised shell material with an average coelestine crystal size of 5 μm . Most details of the primary shell structure are still preserved and enable to determine the distinct fossil and thus lead to reconstruct the complete faunal assemblage. Furthermore, a comparison with other Anisian fossil assemblages yielding coelestine shells, e.g. from the Northern Calcareous Alps (*Natica* Beds, E Lechtal Alps), is presented for the first time.



SEM images of an gastropod coelestine shell

The interaction of minerals with aqueous solutions

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Solid reactions are driven by the tendency to equilibrate under changing P-T-X conditions, which may be achieved by solid-state mechanisms or by mechanisms involving the intervention of a fluid phase. Reactions induced by aqueous fluids are responsible for the chemical and mineralogical re-equilibration of large parts of the Earth's crust. Whereas solid state phase transitions have been studied in great detail over the last hundred years and are well described by theoretical models, fluid-mediated phase transformations or replacement reactions are not yet well understood. In contrast to isochemical solid-state phase transformations, the re-equilibration reaction in the presence of a fluid phase moves from the solid-fluid interface into the solid (discontinuous reaction) and involves a change in composition. Natural minerals often show alteration or replacement zones that are characterised by a chemically and structurally sharp (often on the nano-scale) interface towards the relict pristine parent phase. These zones have often been interpreted to be the result of a diffusion-controlled "leaching" (diffusion-reaction) process that operates in the solid state and may involve ion exchange, hydrolysis, hydration, electron transfer, and/or re-condensation reactions (e.g., Casey *et al.* 1993). To produce a sharp chemical or structural reaction interface between the parent and the product phase, the diffusion of chemical species into the parent solid has to be coupled with a reaction that is induced by the diffusing species. The competition between diffusion and reaction can also lead to the emergence of intricate spatial and/or temporal structures (e.g., Geisler *et al.* 2004).

Putnis (2002) has proposed that many replacement reactions can be better explained by an interface-controlled dissolution-precipitation process, where the congruent dissolution of the parent phase is temporally and spatially coupled with the precipitation of a thermodynamically stable (or metastable) phase or phase assemblage at an inward moving reaction interface. The strength of such a model is that it is able to explain the often observed formation of porosity inside the product phase, even in those cases where the molar volume of the product phase is higher than that of the parent phase. In such cases the porosity results from the difference in the solubility of the parent and the product phase(s) in the respective fluid, which also provides the driving force for the reaction. As the reaction front moves into the solid, the kinetics becomes increasingly controlled by the morphology and spatial arrangement of pores (or extended defects) in the product phase as they provide (diffusion) pathways for the exchange of chemical species between the reaction interface and the surrounding fluid reservoir. With increasing thickness of the product phase, the communication between the fluid at the reaction interface and the external fluid reservoir may cease, which results in an increasing deviation from equilibrium between the external and the interfacial fluid, sometimes reflected by the formation of distinct layers of different (metastable) phases within the alteration zones.

In physical terms, the distinction of both processes may seem to be semantic as a coupled dissolution-precipitation process is *sensu stricto* also a diffusion-reaction process; however, the distinction between these mechanisms is extremely important in geological processes, both due to the different temperature regimes in which they are dominant as well as the many orders of magnitude difference in the kinetics. Whereas the kinetics of a solid state diffusion-reaction process depends on the diffusion properties of the chemical species inside the parent phase, i.e., is diffusion-controlled, the overall kinetics of a coupled dissolution-precipitation process depends on the kinetics of the dissolution and precipitation processes at the reaction interface, i.e., is interface-controlled.

In this contribution we try to classify solid-fluid reactions with respect to the (i) actual mechanism of a replacement reaction, (ii) the structure of the parent phase, (iii) the role of the fluid phase in the replacement reaction, and (iv) the chemical and structural relationship between parent and product phase(s) on the basis of various replacement reactions that have been studied in our laboratory. This classification should serve as a guideline to a more detailed understanding of solid-fluid reaction processes and provides a basis for their mathematical description.

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Geology, Mineralogy and Geochemistry of Gold-bearing Polymetallic-Sulfide Quartz Veins in the French Gulch Mine, French Gulch–Deadwood District, Klamath Mountains, California, USA

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The French Gulch-Deadwood district was the most productive gold mining district in the Klamath Mountains, Northern California (Au production: 800,000 to 1,500,000 oz; Hotz, 1971; Clark, 1970). It is located in the southeast of the Eastern Klamath terrane, to which a succession of terranes has been accreted by eastward directed subduction during Late Paleozoic to Early Jurassic time.

Middle Devonian meta-basalts and Lower Carboniferous shales (Albers, 1964) are the host rocks of the mainly northeast to east-northeast and minor north trending, moderately to steeply dipping veins. These host rocks are intruded by Upper Jurassic dacite, early Lower Cretaceous rhyolite and younger bright aphanitic dikes and sills ("aplites"). The pinching and swelling veins are the youngest geological units in the mine. They developed in an active tectonic environment and are characterized by at least five mineralization stages with (I) quartz ± carbonate ± albite, (II) coarse pyrite, (III) fine pyrite + arsenopyrite + sphalerite ± chalcopyrite ± pyrrhotite, (IV) galena ± gold ± tellurides (hessite, petzite, altaite), and (V) carbonate ± quartz ± plagioclase. Stringer zones in the wall rocks, contact-parallel mineralized shear planes and angular wall rock fragments are typical features of the quartz veins. Lithological contacts are the favored positions of the veins, especially near or in contact to the dacite dikes, which acted as structural controls for the vein-forming fluids.

The ore contains up to more than 30 ppm Au (mean 20 ppm, n = 32), 156 ppm Ag (mean 16 ppm), 600 ppm Cu (mean 60 ppm), more than 5,000 ppm Pb (mean 1,95 ppm), 2.3 wt.-% Zn (mean 0.23 wt.-%), and 3.3 wt.-% As (mean 0.5 wt.-%). Wall rocks in contact to the veins show slightly elevated Au contents (means, dacite: 2,540 ppb, n = 11; rhyolite: 130 ppb, n = 2; meta-basalt: 2,260 ppb, n = 2). Sphalerite contains 4.1 to 9 wt.-% Fe (n = 30), and 0.9 to 2.1 wt.-% Cd. The Ag concentrations in gold range between 11.2 to 35.2 wt.-% (n = 50). Up to 2,200 ppm (mean 200 ppm, n = 70) submicroscopical gold is bound to pyrite. Meta-basalt-hosted veins show higher Ag contents in native gold (16 to 26 wt.-%) and lower Zn/Cd ratios in sphalerites (< 40 to 50), in comparison to veins hosted by shale and associated dacite intrusions (12-18 wt.-% Ag in gold; Zn/Cd > 40 to 50).

Sericitization and carbonatization are the most common alteration types in the wall rocks, accompanied by albitization, (arseno-) pyritization, silicification, and chloritization. Chondrite-normalized trace element and REE diagrams show an enrichment of LILE and LREE for all dike types, and strong negative Nb-Ta-Ti anomalies for the dacite and aplite dikes/sills, which is typical for subduction-related intrusions in a volcanic arc setting. A slight negative Nb-Ta anomaly of the rhyolite dikes/sills might indicate a changed geotectonic environment in the early Lower Cretaceous. The aplite dikes/sills show elevated concentrations of Cr (mean 725 ppm, n = 2), Ni (mean 175 ppm), Co (mean 35 ppm) and MgO (mean 8.2 wt.-%), which indicates a mantle-derived magma. The spatial and probably temporal association of igneous dikes/sills (aplites, possibly dacite) and Au-polymetallic veins suggests a genetic relationship.

The regional geology, the mineralogy, the gold geochemistry and possibly the time of mineralization of Au-veins in the French Gulch-Deadwood district are similar to the orogenic gold deposits of the Mother Lode belt, Sierra Nevada foothills. Furthermore, similarities were found with the Quartz Hill orogenic gold deposit, central Klamath Mountains.

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Tracing the provenance of beach sands from Gran Canaria

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Recent beach sands from the south and southwest of Gran Canaria have been sampled for a zircon provenance study: a light, feldspar-quartz-bearing (GC2; Maspalomas) and a dark, olivine-pyroxen-rich sand (GC1; Playa de Veneguera). As quartz is very rare or absent in the Miocene to Pliocene volcanic rocks of the island the light beach of Maspalomas appear to have a rather exotic origin. This is in line with Saharan dust plumes blown off the west coast of Africa and over the Canary Islands usually during early summer each year. If these plumes, however, can transport particles larger than 100 µm, including heavy minerals such as zircon, for more than 50-100 km is so far not well documented.

In both samples (each ca. 2.5 kg) the heavy mineral fraction contained more than 100 zircon grains. Their size ranges from 40-150 µm in length. Cathodoluminescence imaging reveals two distinct zircon populations: 1. idiomorphic grains, often broken, with weakly developed oscillatory or sector zoning and abundant inclusions of ilmenite, and 2. well-rounded grains often with sharply defined and fine-scaled oscillatory zoning and a secondary overgrowth domain.

Laser ablation SF-ICP-MS dating (30 to 40 µm spot size) reveals a bimodal age distribution with predominantly Miocene (~11-14 Ma) and subordinately Pliocene (~3-4 Ma) ²⁰⁶Pb/²³⁸U ages for the idiomorphic, weakly zoned grains of both samples. These age peaks are in agreement with the appearance of the main magmatic activity on the island, the Miocene pyroclastic flows and lavas of the Mogan and Fataga formations and the Pliocene Roque Nublo formation. Therefore, the zircon U-Pb ages are interpreted as dating the crystallisation of the mantle-derived volcanic rocks from Gran Canaria.

Uranium contents of 100-1000 ppm and crystallisation ages of 3-14 Ma result in ²⁰⁶Pb contents of only 0.05-2 ppm, which are close to the limit of detection of the ²⁰⁶Pb/²³⁸U age. This is reflected in the relative scatter of the ages with typical precision and reproducibility of +/- 1-3 Myr.

In addition, to the Miocene-Pliocene ages about 30% of the zircon grains from sample GC2 yielded Precambrian U-Pb ages, consistent with crystallization during Neoproterozoic to Neoarchean (0.6 to 2.5 Ga) magmatic/metamorphic events. As no older basement is documented from the Canary island these exotic ages pointing to the Aeolian transport of detrital material from the west coast of Africa. The data suggests that even heavy minerals, such as zircon with grains sizes of 50-100µm, can be transported under certain circumstances by dust plumes over far distance. This highlights the need to be cautious in interpreting detrital zircon population for provenance studies.

Bi₂M₄O₉: A thermal expansion investigation

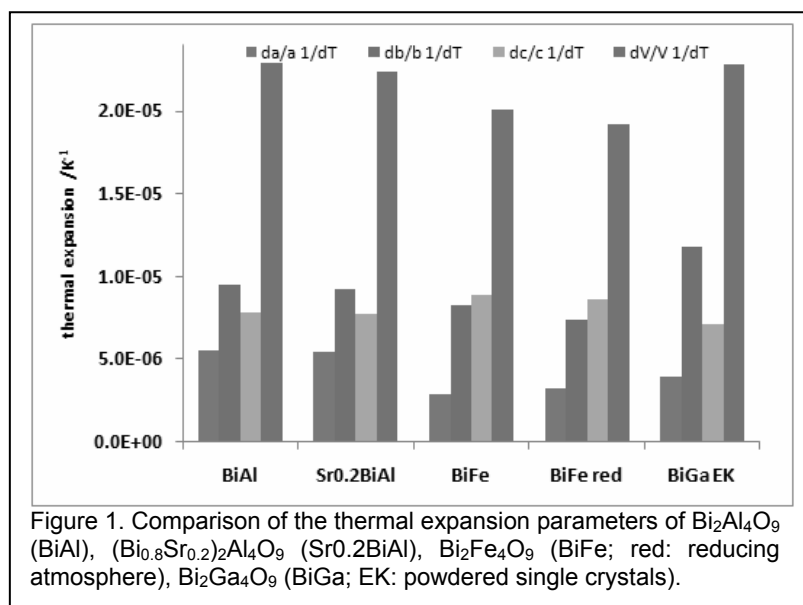
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Bi₂M₄O₉ (M = Al, Ga, Fe) and especially the corresponding phases with partial strontium replacement of the bismuth atoms, are known to have potential as electrolytes in solid oxide fuel cells (SOFC)^[1,2]. Samples synthesized using the glycerin method^[3] were investigated using X-ray powder diffraction methods. Additionally, a powdered single crystal of Bi₂Ga₄O₉^[4] was investigated. Heating experiments were carried out in a Paar HTK1200N heating chamber in air between 298 K and maximum 1273 K in steps of 50 K in heating and cooling cycles. In case of the single crystal powder a second heating and cooling cycle was performed.

All compounds investigated here crystallize in the space group *Pbam* and were classified as mullite-like materials^[5]. No phase transitions were observed during the temperature dependent runs. For Bi₂Al₄O₉ thermal expansion parameters of $5.529 \cdot 10^{-6} \text{ K}^{-1}$, $9.446 \cdot 10^{-6} \text{ K}^{-1}$, $7.795 \cdot 10^{-6} \text{ K}^{-1}$, $2.294 \cdot 10^{-5} \text{ K}^{-1}$ for *a*, *b* and *c* lattice parameters and the cell volume *V*, respectively, are observed (Fig. 1). The corresponding values for a strontium doped sample ((Bi_{0.8}Sr_{0.2})₂Al₄O₉) are: $5.391 \cdot 10^{-6} \text{ K}^{-1}$ (*a*), $9.179 \cdot 10^{-6} \text{ K}^{-1}$ (*b*), $7.707 \cdot 10^{-6} \text{ K}^{-1}$ (*c*), $2.241 \cdot 10^{-5} \text{ K}^{-1}$ (*V*). For this sample, decomposition between 1123 K and 1173 K was observed to undoped Bi₂Al₄O₉ and SrAl₁₂O₁₉, accompanied by a partial amorphization. The thermal expansion parameters for Bi₂Fe₄O₉ were measured under oxidizing and reducing conditions (ox/red): $2.817/3.145 \cdot 10^{-6} \text{ K}^{-1}$ (*a*), $8.257/7.376 \cdot 10^{-6} \text{ K}^{-1}$ (*b*), $8.889/8.583 \cdot 10^{-6} \text{ K}^{-1}$ (*c*), $2.007/1.918 \cdot 10^{-5} \text{ K}^{-1}$ (*V*). While the sample was stable in air up to the maximum temperature of 1173 K, decomposition was observed above 983 K under reducing conditions forming at first hematite (Fe₂O₃), then magnetite (Fe₃O₄) and finally wüstite (FeO). A significant difference in the temperature dependent lattice parameters of Bi₂Ga₄O₉ after the first heating/cooling cycle (*a*_{cooling} – *a*_{heating}, ...) was observed for the powdered single crystal. This effect was minimized after the second cycle. From these measurements,



a different expansion behavior (Fig. 1) is observed for the different metal atoms, especially for *a* and *b* lattice parameters, representing the directions which are influenced by the M₂O₇ double-tetrahedra units, whereas the *c* lattice parameter behavior is comparable for all metal atom types, showing the stiffness of the chains of MO₆ octahedra parallel to this axis.

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Framework modifications in sodium cancrinites

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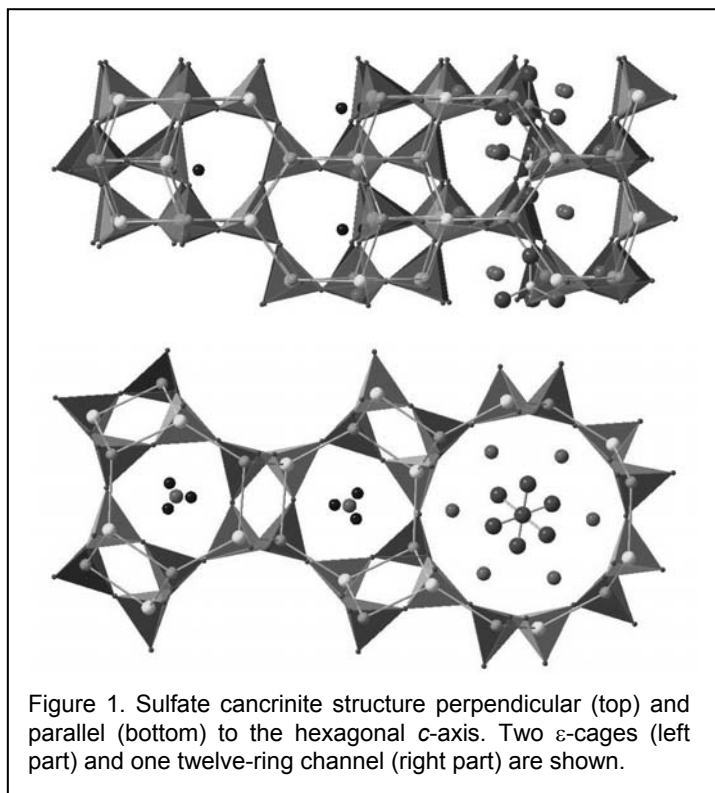
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The natural aluminosilicate cancrinite has a three dimensional rigid framework formed by hexagonal stacking of AlO_4^- and SiO_4^- tetrahedra six-rings. Therefore the crystal structure, first described by Jarchow [1], is mainly built up by 11-hedral cancrinite cages (ϵ -cages) which are linked in a way that six of these cages form a hexagonal channel parallel to the c -axis. One sodium atom lies in each of the two cages per unit cell on the threefold axis together with one water molecule which is found slightly away from this symmetry element and therefore threefold disordered (Fig. 1). Six sodium atoms reside within the twelve-ring channel along the 6_3 -axis together with the anions and/or water molecules. Cancrinites are mainly formed with anions such as NO_3^- [2], HCO_3^- [3], CO_3^{2-} [4], $\text{S}_2\text{O}_3^{2-}$ [5] having a three-fold symmetry, or OH^- [6] or N_3^- [7]. There are reports on T-site substitution of sodalite frameworks, however, similar substitution on cancrinite frameworks are only a few [8, 9]. Here we report a number of cancrinites where the T-sites have been partially or fully substituted by larger atoms for potential framework modification. By direct hydrothermal synthesis we were able to produce nitrate, carbonate and sulfate containing cancrinite phases:

$\text{Na}_8[\text{GaSiO}_4]_6(\text{NO}_3)_2(\text{H}_2\text{O})_2$ { $P6_3$: $a = 1279.47(5)$ pm, $c = 519.35(1)$ pm, $R_{\text{WP}} = 0.044$, $R_{\text{B}} = 0.010$ },
 $\text{Na}_8[\text{GaSiO}_4]_6(\text{CO}_3)(\text{H}_2\text{O})_2$ { $P6_3$: $a = 1277.44(9)$ pm, $c = 518.84(3)$ pm, $R_{\text{WP}} = 0.048$, $R_{\text{B}} = 0.021$ },
 $\text{Na}_8[\text{Al}_{1-x}\text{Ga}_x\text{SiO}_4]_6(\text{SO}_4)(\text{H}_2\text{O})_2$ { $x = 0.15(2)$; $P6_3$: $a = 1270.00(2)$ pm, $c = 517.46(1)$ pm, $R_{\text{WP}} = 0.039$, $R_{\text{B}} = 0.015$ }, and $\text{Na}_8[\text{Al}_{1-x}\text{Ga}_x\text{Si}_{1-y}\text{Ge}_y\text{O}_4]_6(\text{NO}_3)_2(\text{H}_2\text{O})_2$ { $x = 0.19(1)$, $y = 0.14(2)$; $P6_3$: $a = 1270.31(2)$ pm, $c = 518.64(1)$ pm, $R_{\text{WP}} = 0.035$, $R_{\text{B}} = 0.012$ }.



During the Rietveld refinements from powder X-ray data the population of both sodium and oxygen (water) atoms converged to a full occupancy; the values were fixed for each final run. For the nitrate molecules two different positions were located for nitrogen on $0,0,z$ slightly above the plane of the three surrounding oxygen atoms. In case of carbonate and sulfate cancrinites only a single anion per formula unit was refined. The carbonate anion was found with a planar configuration, while the sulfate anion showed a tetrahedral arrangement. In sulfate the sulfur and one oxygen atoms are located on the 6_3 -axis; the other three oxygen atoms are represented by one position off this axis. In both configurations, the oxygen atoms on the 6_3 -axis above and below the plane of the three outstanding oxygen atoms, were found statistically distributed. Identification of different anions and modification of the cancrinite frameworks were confirmed by FTIR investigations.

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Trace Element Distribution in Perovskite & Pyrochlore of Kaiserstuhl Sövite Carbonatites

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Pyrochlore and perovskite are considered as REE-rich accessory phases in many carbonatite complexes, which with their presence can effect the distribution of Trace elements especially REEs. By this study, pyrochlores of Orberg's sövite and perovskite of Badberg's sövite from Kaiserstuhl carbonatitic complex have been analysed for REE, U-Th-Pb as well as other trace elements (Ba, Sr, Nb, Hf,...) with the help of "LA-ICP MS Element 2" at the University of Frankfurt. For doing this, after measuring the samples (concentrates in resin) with laser, the main phase of each mineral was analysed via EPMA (Superprobe JXA-8900) in order to find the most suitable element for normalizing the data. Although perovskite and pyrochlore have a different concentration of trace elements, they have shown a parallel distribution of REEs i.e.: an increasing enrichment in REEs from Lu to La, with the exception of higher concentration of Ce than La. A very high concentration of Nb and Sr and low concentration of Hf were also one of their in common properties. The next step for collecting more data on the REEs distribution trend in pyrochlore and perovskite, is by analysing suitable crystals in thick section of their host rock (Sövite). In order to approach this, BSE and SEI photos were taken and main elements concentrations were analysed. An other further aim of this study is the in-situ measurements of the Hf-Nd ratio isotopes with the help of LA-ICP MS which can result in precise measurements. In-situ analysis allows the isotopic data to be interpreted within a microstructural context and the acquisition of multiple datasets (e.g. trace REE-Pb, PGE-Os, Pb-Hf, Pb-Os) on single grains or parts of grains (N.J. Pearson, W.L. Griffin, S.Y. O'Reilly, 2008).

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Crystallization experiments on iron-rich peralkaline melts

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Peralkaline melt compositions are represented by highly differentiated, SiO₂-undersaturated igneous rocks with (Na+K) / Al ratios >1, which are usually - but not exclusively - associated with continental rift settings. So far, the magmatic differentiation of such compositions has not been investigated experimentally in detail. Freise et al. (2003) found crystallization behaviour of phonolitic melt compositions (X_{Mg} up to ~0.25; FeO_{tot} < 7 wt%) to be very much dependent on oxygen fugacity. However, the composition we use has higher FeO_{tot} (~13 wt%) and lower X_{Mg} (~0.05) and resembles a peralkaline dyke rock associated with the plutonic Ilímaussaq complex (South Greenland), which is believed to represent a potential parental melt composition for the complex. This dyke rock crystallized during unusually reduced conditions at logfO₂ ~ ΔFMQ -1.5 to -3 and CH₄-bearing fluid inclusions were found to be typical for such rock types (e.g. Marks & Markl, 2003; Markl et al., 2001).

The starting material was mixed by using synthetic oxide powders, heated to 1600°C in a platinum crucible and quenched rapidly to obtain crystal-free glass. High *P* and *T* crystallization experiments were performed at 750°C and 1000 bar using Rapid Quench Vessels (RQV) with an intrinsic oxygen fugacity of nickel-nickeloxide (logfO₂ ~ ΔFMQ +1), gold capsules, and water as pressure medium. To reach near equilibrium conditions and to avoid kinetic problems, the starting glass was pre-saturated with water. With this precondition, run duration of 4 hours was found to be sufficient to obtain crystalline phases on a 10 μm scale. Preliminary results show ~30% crystalline phases (cpx, magnetite – ulvöspinel solid solutions) and an alkali-enriched residual melt.

We present data of oxidizing and reducing experiments and comparison of the results with naturally occurring dyke rocks in terms of mineral assemblages and compositions. In order to reduce oxygen fugacity, experiments with additional graphite capsules are in progress. The reaction of H₂O with graphite at the applied conditions is expected to form a CH₄-bearing C-O-H fluid (e.g. Huizenga, 2001), which was calculated to lower the oxidation state to logfO₂ ~ ΔFMQ -1.5 in case of equilibrium with graphite. Reproducing the crystallization conditions of the dyke rock, especially in terms of the proposed oxidation state, is expected to show significant differences to the oxidized experiments and reasonable similarities to the naturally occurring rocks. These results will elucidate the differentiation processes during the unusually high temperature interval of crystallization suggested for such magmas.

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Mantle source and crustal contamination of anorthosites of the Proterozoic Kunene Intrusive Complex, NW Namibia

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Massif-type anorthosite complexes that commonly form huge intrusions with minor volumes of mafic and felsic rocks are characteristic features of the Proterozoic crust. Their origin is generally discussed in terms of mantle derived parental melts (e.g. Ashwal, 1993; Morse, 2006) or partial melting of mafic lower crust (e.g. Duchesne et al., 1999; Schiellerup et al., 2000). Their apparent temporal restriction to the Proterozoic suggests unique tectono-thermal conditions during this period, although the specific crust-forming processes are still subject to debate.

The 1.38 Ga Kunene Intrusive Complex, NW Namibia, was emplaced within the high-grade metamorphic Epupa Complex at the southern margin of the Congo craton. The complex extends over 18,000 km² and mainly comprises two anorthosite bodies, i.e., a pyroxene-bearing anorthosite suite that is intruded by a suite of olivine-bearing anorthosites and leucotroctolites. The rocks experienced no metamorphic overprint after their intrusion and hence preserved primary magmatic phases and cumulate textures. The sporadic occurrence of andradite-rich garnet xenocrysts in the interstices between cumulus plagioclase (Drüppel et al., 2007) suggest the assimilation of crustal rocks during the formation of the early pyroxene-bearing anorthosites. Oxygen and radiogenic isotope data combined with LA-ICP-MS analyses of the anorthositic mineral assemblages provide new insights into the magma source and the magmatic processes like fractional crystallization and crustal contamination.

The isotope values of whole rock samples and plagioclase separates range between 6.0-7.5 ‰ $\delta^{18}\text{O}$, 0.70340-0.70430 $^{87}\text{Sr}/^{86}\text{Sr}(\text{T})$ and -3.1-1.7 $\epsilon\text{Nd}(\text{T})$ for the pyroxene-bearing anorthosite suite and 5.6-6.0 ‰ $\delta^{18}\text{O}$, 0.70282-0.70364 $^{87}\text{Sr}/^{86}\text{Sr}(\text{T})$, 0.8-6.4 $\epsilon\text{Nd}(\text{T})$ for the younger olivine-bearing anorthosite suite that fits well to a mantle-origin of the parental melts. Chondrite normalized REE patterns of plagioclase generally display variable enrichment of light REE ($\text{La}_\text{N}/\text{Nd}_\text{N}$: 2.1-5.3) and positive europium anomalies (Eu/Eu^* : 5-26). Trace element profiles across plagioclase display decreasing concentration of compatible Sr from the core towards the rim, controlled by extensive plagioclase fractionation. A negative correlation between incompatible V and LREE suggests simultaneous fractionation of Fe-Ti oxides. Increasing concentration of incompatible Zr from the core towards the rim of plagioclase in one pyroxene-bearing anorthosite in part reflects the assimilation of crustal material during plagioclase crystallisation.

The mantle-like isotopic composition of the most primitive anorthosites, the intrusion size of the Kunene Intrusive Complex, and its emplacement unrelated to major orogenic events (Drüppel et al., 2007) point to a mantle derived parental melt of the anorthosites. Relics of crustal minerals and trace element zoning profiles across cumulus plagioclase in combination with their isotopic composition reveal extensive crustal contamination prior and during formation of the early pyroxene-bearing anorthosites.

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Crustal contamination of anorthosites of the Kunene Intrusive Complex, Namibia: insights from LA-ICP-MS trace element analysis of plagioclase and intercumulus phases

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The Mesoproterozoic Kunene Intrusive Complex (KIC) extends over 18,000 km² from SW Angola into NW Namibia. In Namibia the Complex mainly comprises two anorthosite suites, i.e., a pale pyroxene-bearing anorthosite suite, the so called 'white anorthosite' that is intruded by a suite of olivine-bearing anorthosites and leucotroctolites, the 'dark anorthosite'. The rocks experienced no metamorphic overprint after their intrusion and hence preserved primary magmatic phases and cumulate textures. We present in-situ LA-ICP-MS data on the trace element composition of cumulus and intercumulus phases from both anorthosite varieties. These phases, which crystallised during subsequent stages of crystallisation and cumulate formation, provide important information on the parental magma composition and its magmatic evolution, involving assimilation and fractional crystallisation processes.

Rocks of the white anorthosite suite display the assemblage of cumulus plagioclase (X_{An} : 0.35-0.64) $\pm$ cumulus orthopyroxene (X_{Mg} : 0.57-0.73) + interstitial ortho- and clinopyroxene (X_{Mg} : 0.58-0.78) + ilmenite $\pm$ magnetite $\pm$ biotite $\pm$ pargasite $\pm$ apatite $\pm$ zircon $\pm$ sulphides. In contrast, the dark anorthosite suite is dominated by cumulus plagioclase (X_{An} : 0.50-0.75) + olivine (X_{Mg} : 0.54-0.74) and minor interstitial ortho- and clinopyroxene (X_{Mg} : 0.67-0.79) + ilmenite $\pm$ magnetite $\pm$ biotite. Plagioclase of the white anorthosite suite is characterised by high concentrations of incompatible trace elements like Ba, Sr, Be, and the REE. The concentrations of trace elements increase from huge cumulus plagioclases towards later and smaller crystals. Zoning profiles across plagioclase of leucogabbro display increasing trace element concentrations towards the rims. The chondrite normalized REE patterns display enrichment of LREE when compared to the M+HREE (La_N/Sm_N : 5-22) and strong positive Eu anomalies (Eu/Eu^* : 13-27) in all plagioclases. Intercumulus phases display variable trace element concentrations and chondrite normalized REE patterns. Negative europium anomalies in the intercumulus phases of part of the samples demonstrate their crystallization after contamination and extensive plagioclase fractionation whereas the absence of such anomalies in others suggests a contamination of the magma during and/or after the plagioclase formation. Plagioclases of the dark anorthosite suite display lower concentrations of incompatible trace elements than those of the white anorthosite. Chondrite normalized REE patterns reflect the lower and less variable REE values (La_N/Sm_N : 3-10, Eu/Eu^* : 7-18). Intercumulus clinopyroxene is characterized by high concentrations of incompatible trace elements, enrichment of M+HREE relative to LREE (La_N/Yb_N : 0.14) and a negative europium anomaly (Eu/Eu^* : 0.3) in accordance with its late interstitial crystallisation after extensive fractionation of plagioclase.

By the use of appropriate plagioclase-melt partition coefficients we found significant differences in the composition of the melts from which the white and dark anorthosites crystallized. Melt in equilibrium with plagioclase of the white anorthosites displays higher overall abundance and higher enrichment in LREE when compared to the HREE. The primitive normalized patterns are characterized by negative Rb and Sr anomalies. The melt from which the dark anorthosites crystallized shows significantly lower trace element concentrations and a flat pattern without anomalies. These data suggest that crustal contamination was prominent during the early stages of the magma evolution, producing magma with significant crustal characteristics. Trace element zoning patterns of the main phases demonstrate that the older white anorthosite was derived from this magma by simultaneous fractional crystallization of plagioclase, orthopyroxene and Fe-Ti oxides. The subsequently emplaced dark anorthosite evolved by fractional crystallization of plagioclase, olivine and Fe-Ti oxides after replenishment with undifferentiated mantle melts, and experienced less crustal contamination.

Non-ambient Study of Polymorphic Phase Transformations of C₂S

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The X-ray powder diffraction analysis of polycrystalline powder samples has advanced from its roots in laboratory research under room temperature conditions to non-ambient conditions. This allows to fully observe complex phase transitions during, e.g. heating and cooling. The knowledge about the material's structural changes in connection with the different temperature profiles is vital for the understanding of industrial sintering processes, and therefore a key tool for designing and optimizing these types of processes.

Non-ambient static XRD (X-ray diffraction) based on RTMS high speed detector technology was used in combination with different data analysis methodologies to extract all information from the observed data.

The present study shows the structural changes of C₂S during heating and cooling between room temperature and 1200°C. The collected measurements were evaluated by using a statistical data analysis tool prior to the classical identification to improve the efficiency of the data analysis and to identify the different reaction stages during the experiment, see Figure 1.

The combination of classical and statistical data evaluation speeds up the data analysis times as well as it reduces the operator effects regarding to the interpretation of the observed data.

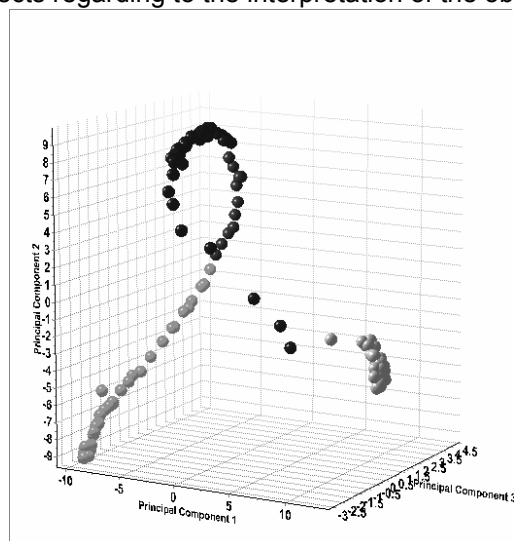


Figure 1: Cluster analysis of the successive phase transitions of C₂S during cooling from 1200 °C to RT differentiating 4 clusters.

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Elektronenoptische, physikalisch-chemische und phasenanalytische Untersuchungen an Neuburger Kieselerde mittels Rasterelektronenmikroskopie (REM / EDX), Röntgendiffraktometrie (XRD), Infrarotspektroskopie (IR) und Thermoanalyse (DTA / TG)

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SiO₂ bildet bei verschiedenen Temperaturen und Druckverhältnissen eine Reihe polymorpher Modifikationen, deren Wichtigste nach der mineralogisch kristallographischen Bezeichnung lauten: Tief-(alpha-)Quarz, Hoch-(beta-)Quarz, Tridymit, Cristobalit, Coesit und Stishovit. Weiterhin gibt es noch eine Reihe von seltenen (Lechatelierit, Melanophlogit, Keatit, ...) und synthetisch hergestellten SiO₂-Modifikationen. Bei Normaldruck existieren nach RÖSLER folgende Modifikationen: (Tief-) Quarz bis 573°C, Hochquarz von 573°C bis ~870°C, Tridymit von 573°C bis ~1470°C und Cristobalit. Die Umwandlung Tief- / Hochquarz ist enantiotrop (ineinander überführbar) bzw. leicht reversibel, verläuft in einem engen Temperaturbereich „blitzschnell“ und geht mit einer Volumenänderung von ca. 1% einher. Diese Transformation benötigt keine Lösung und Neubildung von Si-O Bindungen. Bis auf Hochquarz lassen sich alle kristallinen SiO₂-Phasen und die Schmelze (als sogenannte unterkühlte Schmelze) metastabil bei Normalbedingungen erhalten. Ein ursprünglich bei > 573°C ausgeschiedener Hochquarz liegt stets als Tiefquarz vor, wobei die Morphologie von ursprünglichem Hochquarz nach der spontanen Umwandlung in Tiefquarz erhalten bleiben kann. Während Tiefquarz natürlich in gut ausgebildeten Kristallen in verschiedenartigen Formen vorkommt, sind die Kristalle des ursprünglich, natürlich vorkommenden Hochquarzes meistens in einer hexagonalen Dipyramide ausgebildet. Bei den hexagonalen Dipyramiden können die Flächen des Prismas stark verkürzt sein oder völlig fehlen.

Allgemeine Vorbemerkungen: Neuburger Kieselerde:

Die klassische Neuburger Kieselerde (auch als Sillinit und Sillikolloid bezeichnet) ist ein natürliches Gemisch aus korpuskularer Kieselsäure und lamellarem Kaolinit. Beide Mineralphasen bilden ein unverwechselbares Haufwerk. Zusammen mit der natürlichen Feinheit der Kieselsäure und seiner runden Kornform und seiner natürlichgealterten Oberfläche entsteht eine einmalige Partikelstruktur.

Alleinstellungsmerkmal der Neuburger Kieselerde:

Die hier thermoanalytisch untersuchten Probenchargen weisen im Vergleich zu anderen untersuchten SiO₂-Proben keinen „Quarzsprung“ bei ca. 573 °C auf. Eine, ursprünglich bei > 573°C ausgeschiedene Hoch-(beta-) SiO₂-Modifikation liegt bei Raumtemperatur stets als Tief-(alpha) SiO₂-Modifikation vor, wobei die Morphologie von der ursprünglichen Hoch-(beta-) SiO₂-Modifikation nach der spontanen Umwandlung zur Tief-(alpha) SiO₂-Modifikation erhalten bleiben kann. Somit liegt in der Neuburger Kieselerde die Tief-(alpha) SiO₂-Modifikation signifikant als Pseudomorphose zur Hoch-(beta-) SiO₂-Modifikation vor. Der morphologische Nachweis der Hoch-(beta-) SiO₂-Modifikation gelang definitiv, es konnten gut ausgebildete, hexagonale Dipyramiden elektronenoptisch identifiziert werden. Die Kristalle der Pseudomorphose der Hoch-(beta-) SiO₂-Modifikation sind untereinander mit einer amorphen SiO₂-Matrix verkittet, verklebt, zum Teil opalartig überzogen bzw. zu einer „mineralischen Einheit“ verschmolzen und sind an der Oberfläche gealtert und zeigen amorphe, opalartige Struktur. Die Neuburger Kieselerde mit den hier untersuchten Probenchargen kann nicht annähernd, weder synthetisch noch natürlich aus den mineralischen Komponenten einer SiO₂-Modifikation mit Kaolinit, durch Mischen oder Abmischen hergestellt werden. Aus den gewonnen wissenschaftlichen Ergebnissen und aufgrund des sehr hohen Fehlordnungsgrades der SiO₂-Modifikation kann man daher von einer eigenen Neuburger – Kieselerde - SiO₂-Modifikation sprechen, bzw., die in der Neuburger Kieselerde enthaltene SiO₂-Modifikation kann als Neuburger Kieselsäure bezeichnet werden.

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Allophane-Imogolite in young dunal soils replacing wood

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Under circumneutral conditions Al has typically low solubility in soils. However in recent years new data indicate the Al can be move more readily in soils than previously thought. One example of such evidence is presented here. In 40ka old dunal soils (pH of 4.7 to 5.4) from the coast in Ona Beach, Oregon, USA, we find a allophane-imogolite phase replacing woody material. Allophane is replacing the organic fibers of the wood. It is not using the porosity of the wood to precipitate allophane in the porespace but it is replacing the wood fibers. This indicates dissolution-oxidation of the woody fibers and replacement by the allophane-imogolite (see Figure 1). The sands in which the woody material is incorporated contain significant amounts of feldspars (albite), the source of the Al. The albite in the surrounding dunal soils weathers to gibbsite, vermiculite, imogolite/allophane and halloysite as a function of depth and age. During weathering some of the Al stays in place however significant amount of Al is being translocated to the wood. From XRD, chemistry, and DTA the best mineral name for this phase is allophane. Under TEM long tubular stuctures (suggesting imogolite) as well as platy structures (allophane) can be identified.

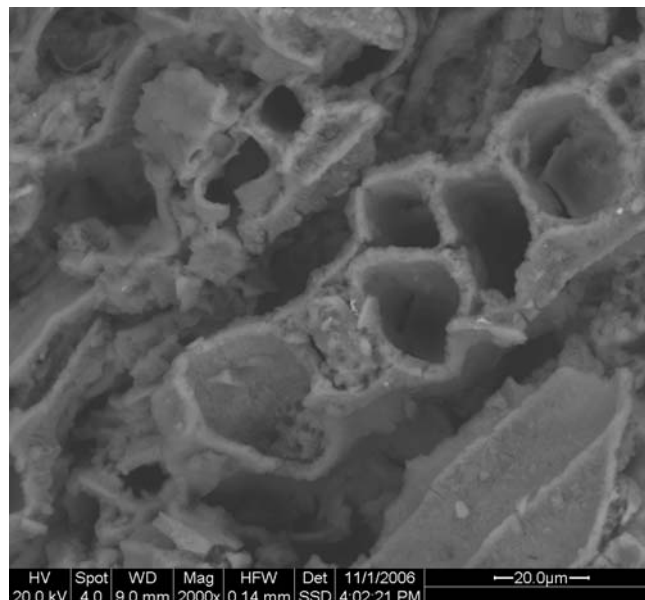


Figure 1: SEM photomicrograph of wood being replaced by allophane-imogolite, Ona Beach, Oregon, USA.

REE geochemistry of columbite- and pyrochlore-group minerals from granitic pegmatites of the LCT family: a LA-ICP-MS study

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The rare-earth element (REE) geochemistry of silicates and phosphates in rare-element pegmatites is well documented; however, REE data of columbite-group and pyrochlore-group minerals are rare in the literature. Here, we present new data on the REE concentrations and distribution patterns in columbite-group (CGM) and pyrochlore-group minerals (mostly microlite) from economically important Ta-ore districts worldwide. The REE geochemistry was studied using the Laser Ablation Inductively Coupled Plasma Mass Spectrometry technique (LA-ICP-MS).

The chondrite-normalized REE distribution patterns vary significantly between different Ta-bearing mineral phases. CGM are characterized by almost flat, trough-like or rising patterns from the light (La_N) to the heavy (Lu_N) REE. There is a trend of progressive REE-depletion (especially for the heavy REE) in CGM with increasing degree of fractionation (from columbite-(Fe) to tantalite-(Mn)) in a number of pegmatite bodies (Fig. 1A). Replacement of primary CGM by secondary CGM starting from the crystal surface or from micro-cracks is always characterized by significant modifications of the REE patterns (e.g. the middle REE/heavy REE ratios). Microlite generally shows strongly declining patterns from the light to the heavy REE and it appears to contain higher overall REE concentrations than CGM. Comparison of CGM from different ore provinces and pegmatite bodies yields significant differences in the REE distribution patterns. Some locations are characterized by very low REE concentrations (e.g. Kenticha, Ethiopia) others are highly enriched, especially in the middle REE and/or heavy REE (e.g. Bikita, Zimbabwe). Other important criteria for discrimination are the presence or absence and intensity of anomalies (cerium or europium anomalies) and the presence and intensity of tetrad effects (especially for the third segment of the REE pattern: $\text{Gd}_N\text{-Ho}_N$).

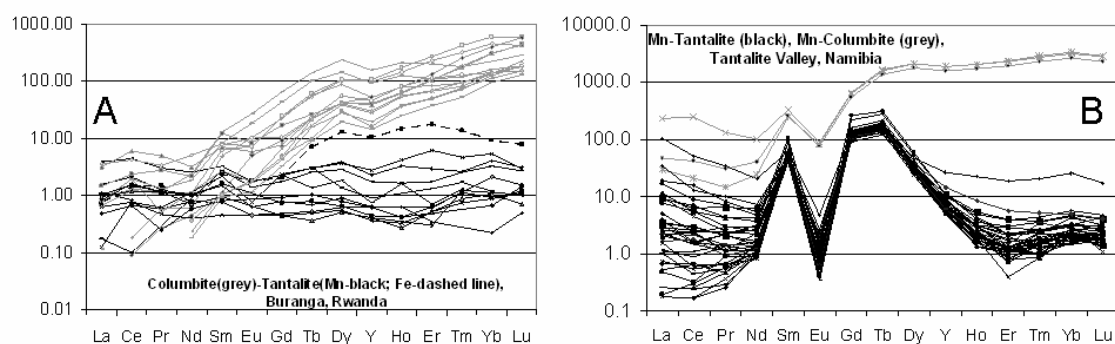


Figure 1. Chondrite-normalized REE distribution patterns for CGM from African deposits.

CGM show a significant variability concerning the existence of a Eu anomaly (positive to negative, or complete absence). Possible explanations range from small but significant differences in redox conditions during the evolution of the melt- H_2O systems in different geological settings to effects resulting from the differentiation of the melt by precipitation of minerals only (e.g. K-feldspar). CGM from the Kibaran Province in central Africa generally show a complete absence or a weak Eu anomaly only (Fig. 1A); however, this anomaly is (strongly) negative for many other locations worldwide (e.g. Tantalite Valley, Namibia; Alto Ligonha Province, Mozambique; Fig. 1B). CGM from each ore province have diagnostic features in their REE distribution patterns. Therefore, the REE are suitable, amongst other criteria, for fingerprinting the origin of ore samples or ore concentrates (Melcher et al. 2008).

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Internally consistent thermodynamic data for MgSO₄-hydrates: Enthalpies of formation and stability related to temperature and relative humidity

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Magnesium sulfate hydrates, especially epsomite (MgSO₄·7H₂O), hexahydrite (MgSO₄·6H₂O), and kieserite (MgSO₄·H₂O) are important constituents of marine evaporite deposits. Additionally, these minerals are often associated with acid mine drainage in surficial environments (Jambor et al., 2000). Results from the most recent Mars missions support the assumption that significant quantities of Mg-sulfate hydrates are also present on this planet (cf. Chipera and Vaniman, 2007). Experimental studies on the stability of several Mg-sulfate hydrates including epsomite, hexahydrite, starkeyite (MgSO₄·4H₂O), and kieserite as a function of temperature and relative humidity (Chou and Seal, 2003; Chou and Seal, 2007; Chipera and Vaniman, 2007) are in poor agreement with calculations based on thermodynamic properties of these substances taken from the literature (DeKock, 1986; Wagman et al., 1982). Therefore, we measured enthalpies of formation of four different hydrates by solution calorimetry at $T = 298.15$ K. The resulting enthalpies of formation from the elements are:

$$\Delta_f H_{298}^0 \text{ (epsomite)} = -3387.7 \pm 1.3 \text{ kJmol}^{-1}$$

$$\Delta_f H_{298}^0 \text{ (hexahydrite)} = -3088.1 \pm 1.1 \text{ kJmol}^{-1}$$

$$\Delta_f H_{298}^0 \text{ (sanderite, MgSO}_4\cdot 2\text{H}_2\text{O)} = -1894.9 \pm 1.3 \text{ kJmol}^{-1}$$

$$\Delta_f H_{298}^0 \text{ (kieserite)} = -1612.4 \pm 1.3 \text{ kJmol}^{-1}$$

Using mathematical programming (MAP) techniques (Grevel, 2004) standard values consistent both with our calorimetric data and humidity brackets could be derived:

$$\text{Epsomite: } \Delta_f H_{298}^0 = -3388.7 \text{ kJmol}^{-1}, S_{298}^0 = 371.3 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\text{Hexahydr.: } \Delta_f H_{298}^0 = -3087.3 \text{ kJmol}^{-1}, S_{298}^0 = 348.5 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\text{Starkeyite: } \Delta_f H_{298}^0 = -2496.1 \text{ kJmol}^{-1}, S_{298}^0 = 259.9 \text{ Jmol}^{-1}\text{K}^{-1}$$

$$\text{Kieserite: } \Delta_f H_{298}^0 = -1611.5 \text{ kJmol}^{-1}, S_{298}^0 = 126.0 \text{ Jmol}^{-1}\text{K}^{-1}$$

Calculations based on these data show that epsomite, hexahydrite, and kieserite have stability fields in the T -%RH space. As assumed before (Chou and Seal, 2007), the dehydration from hexahydrite to starkeyite seems to be metastable with respect to the dehydration directly to kieserite. Although no MAP data could have been derived for pentahydrite (MgSO₄·5H₂O) and sanderite, their transient existence suggest that both of them are metastable as well.

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Atomic Scale View on Partially Molten Rocks via Molecular Dynamics Simulations of Mineral-Melt Interfaces

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The presence of melt or fluid in rocks has significant influence on their physical and chemical properties. Partial melting is the first stage of magmatism and therefore has primary importance in the chemical differentiation of the Earth and in the transport of heat to the Earth's surface. The electrical conductivity of a partially molten rock is influenced by many factors, including melt conductivity, conductivity of the solid phases, and melt fraction, each of which is influenced by temperature. Grain and phase boundaries are known to play an important role in the diffusive, mechanical and electrical properties of partially-melted rocks. They are usually assumed to enhance conductivity since the transport of charge carriers (ions) along the grain and phase boundaries is faster than through the crystal lattice. Hence, these boundaries are important pathways for chemical transport in a rock.

Molecular dynamics simulation is a unique technique to study the atomic structure and respective transport properties at interfaces. This method can provide a picture of the underlying processes at the molecular scale and therefore complement experimental and field observations. To model partially molten rocks, we construct interfaces between melts and mineral surfaces with different crystal orientations and 'measure' various properties in the simulation. Here we discuss structural and transport properties of a model interface between MgSiO_3 melt and forsterite (Mg_2SiO_4) crystal at $T=2000$ K. The particle interactions are described by a polarizable ion model (Jahn and Madden, 2007). We examine how the chemical composition and the self-diffusion coefficients vary across the interface and estimate interfacial energies.

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Lithological architecture, age and metamorphism of the polymetallic Salt River VMS deposit, Northern Cape Province, South Africa

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The polymetallic Salt River deposit and related prospects occur in a narrow, E-W oriented trend in the SE portion of the Bushmanland Terrane of the Mesoproterozoic Namaqua-Natal Metamorphic Province in the Northern Cape Province, South Africa. As part of an ongoing exploration project, the lithological architecture, age and metamorphism of the ores and host rock succession to the Salt River deposit are investigated. The Salt River deposit comprises a tabular stratiform/stratabound massive sulfide lens intimately associated with a stratabound zone of disseminated and stringer-textured sulfide. The mineralogy of the sulfide ores is simple, with pyrite representing the most abundant sulfide, followed by sphalerite and chalcopyrite; galena and closely associated molybdenite occur as minor constituents. The sulfide ores are hosted by a suite of largely metavolcanic rocks that predominantly consist of grey biotite gneiss and minor amphibolites, calc-silicate rocks, and granitic gneiss. Recent SHRIMP U-Pb zircon dating (McClung, 2006) has constrained an age of ca. 1195 Ma for a stratigraphically younger felsic metavolcanic rocks in this portion of the Bushmanland Terrane. This age is regarded as a best estimate for the origin of sulfide mineralization. The succession then experienced several phases of high-grade metamorphism and deformation during the Namaquan Orogeny (Clifford et al., 2004). Peak metamorphic conditions were determined at 650 °C/6 kbar on poorly zoned amphiboles (kaersutite and ferro-hornblende), which crystallized along foliation planes. This is in good agreement with the northern and central portions of the Bushmanland Terrane. The timing of amphibolite-facies metamorphism was dated by Th-U-Pb electron microprobe monazite dating to ca. 1150 Ma (1170 - 1130 Ma). This age was obtained for the paragenetically oldest monazite generation identified in the samples; it associates high-grade metamorphism of the Salt River deposit with the intrusion of late-collisional granites during the Okiepian event of the Namaquan Orogeny (Clifford et al., 2004). Paragenetically younger generations of monazite in the same samples were found to have crystallization ages of 1050 - 1020 Ma and 990 - 970 Ma. The former age corresponds well to the early stage of the Klondikean event of the Namaquan Orogeny (Clifford et al., 2004), whereas the latter is regarded to date late-Klondikean exhumation associated with small-scale decompressional intracrustal melting and widespread fluid-induced retrograde metamorphism.

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The contribution of geometallurgy to the sustainable use of mineral resources

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Geometallurgy is an emerging interdisciplinary field of research that aims to close the gap between geoscientific ore body exploration and the technical exploitation of ore bodies through mineral processing and metallurgy. This gap is widely regarded as an interdisciplinary divide that holds significant potential not only to determine the economic value of mineral resources more objectively (Dunham and Vann, 2007), but also to utilize such resources more efficiently and sustainably (Hoal, 2008). In order to achieve this objective the spatial variability of material characteristics of the mineral resource with relevance to exploitation and utilization is comprehensively assessed for a representative set of samples. Relevant material characteristics include, of course, the concentration of value elements (i.e., grade), but also the concentration of deleterious components and physical (hardness, grindability) as well as mineralogical-petro-structural attributes (including mineralogy, grain-size distribution, grain boundary interlocking, phase relations, grain liberation). Several important hurdles still need to be overcome in the comprehensive application of geometallurgy. The first of these hurdles is the need for a geologically-informed sampling strategy. The comprehensive repertoire of analytical methods used during geometallurgical assessments render a closely spaced systematic sampling strategy as impractical. Instead, the smallest representative sample population needs to be identified that will permit the quantitative assessment of the spatial variability of selected material characteristics. Second hurdle is the identification of those material characteristics that have the greatest influence on mining, mineral processing and metallurgical behavior. Although common trends can be expected for ore deposit types, the actual combination of relevant characteristics must be expected to be unique for each individual ore body. Thirdly, analytical methods are needed to quantify the important material characteristics both efficiently and reliably. Whole rock geochemical proxies may be useful in this context and are state-of-the-art (Dunham and Vann, 2007). The Rietveld refinement of X-ray powder diffraction data is an important analytical tool for such rapid and largely automated acquisition of quantitative mineralogical data. However, Rietveld refinement and bulk rock chemical data are insufficient for a direct and quantitative characterization of mineralogical-petro-structural attributes in ores and products of mineral processing. For this purpose, SEM-based image analytical methods combined with automated element detection by energy-dispersive X-ray spectra in ores and grain mounts is the method of choice. All results obtained need to be integrated and interpreted to construct three-dimensional block models serving as basis of an optimized mining sequence, mineral processing strategies and also final waste storage concepts. Creating a spatial geometallurgical model of an ore body is, in principle, similar to creating a conventional grade-based resource model. However, the geometallurgical model considers a large number of additional variables, many of which require an estimation approach very different to that used for grade models (Dunham and Vann, 2007).

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Mineralogical Variability in Edough Massif Micaschists (ANNABA, Northeast Algeria)

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The Edough massif is the easternmost crystalline massif of the Maghrebides which represent the southeastern part of the west Mediterranean orogen. It occurs below the greenschist – facies Tellian units that represent the thrust Mesozoic to Eocene passive paleomargin of northern Africa deposited on thinned continental crust (Caby et al., 2001). The upper unit of the Edough massif is characterised by metasedimentary rocks affected by medium- to high-pressure and medium-temperature metamorphic conditions.

A detailed study of micaschists revealed two distinct kind of rocks. The first type is formed by weakly deformed garnet rich rocks while the second group, strongly foliated, is andalusite rich and garnet free. Thermo-barometric studies, using Gibbs' free energy minimization (de Capitani & Brown 1987) to compute stable mineral assemblages, indicate that garnet-rich as well andalusite-rich micaschists have undergone same P-T conditions ($P = 1.5\text{-}2\text{ kb}$, $T = 500\text{-}575^\circ\text{C}$). The estimated chemical index of alteration values ($\text{CIA} = 0.69\text{-}0.74$) reveals, that pre-metamorphic alteration is insignifiant. Therefore variations of metamorphic mineralogy is due to deformation -related chemical changes of the rocks. The formation and the break-down indicate element mobility. The mobility and mass changes are estimated by the chemical and mineralogical variations in the successive petrographic rock samples. Isocons-diagrams show that Si, Fe, Al and K were mobile during the transition from the first group to the second group of micaschist. This transition result in a loss in Fe and a gain in Al and K and Si. The mobility of the chemical elements is due to deformation-controlled fluid-flow that enables fluid circulation, solution and redistribution of these elements. We conclude that the transition from garnet micaschist to andalusite-bearing micaschis in the micaschist of Edough t is due to changes of metamorphic conditions or of weathering process but can be assigned to the fluids circulation freed during deformation.

Bestimmung des amorphen Phasengehalts in Industrieaschen

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Industrieaschen sind Produkte thermischer Abfallverbrennungsanlagen, die auf Grund ihres Schwermetallgehaltes, ihrer Salzfracht oder ihrer Gehalte an PCDD und PCDF häufig als „gefährlich“ einzustufen sind. Gegenstand der Untersuchungen ist die Bestimmung des qualitativen und quantitativen Phasengehalts solcher Industrieaschen mittels Röntgenpulverdiffraktometrie. Als besonders problematisch erweist sich der Abgleich der erhaltenen Resultate mit chemischen Analysen, da oft ein mengenmäßig großer Anteil röntgenamorph vorliegt. Somit steht dessen Bestimmung im Mittelpunkt des Interesses.

Apparativ erfordern die Messungen keine besonderen Vorkehrungen. In unserem Falle wurde ein Seifert XRD 7 mit $\text{CuK}\alpha$ -Strahlung genutzt (bei 40 kV, 40 mA und 6s Zählzeit). Aber: Die Phasenanalyse an Industrieaschen bedeutet immer eine Phasenanalyse an Vielphasengemengen im Nichtgleichgewicht. Abbildung 1 zeigt ein typisches Beispiel mit 22 nachweisbaren kristallinen Phasen.

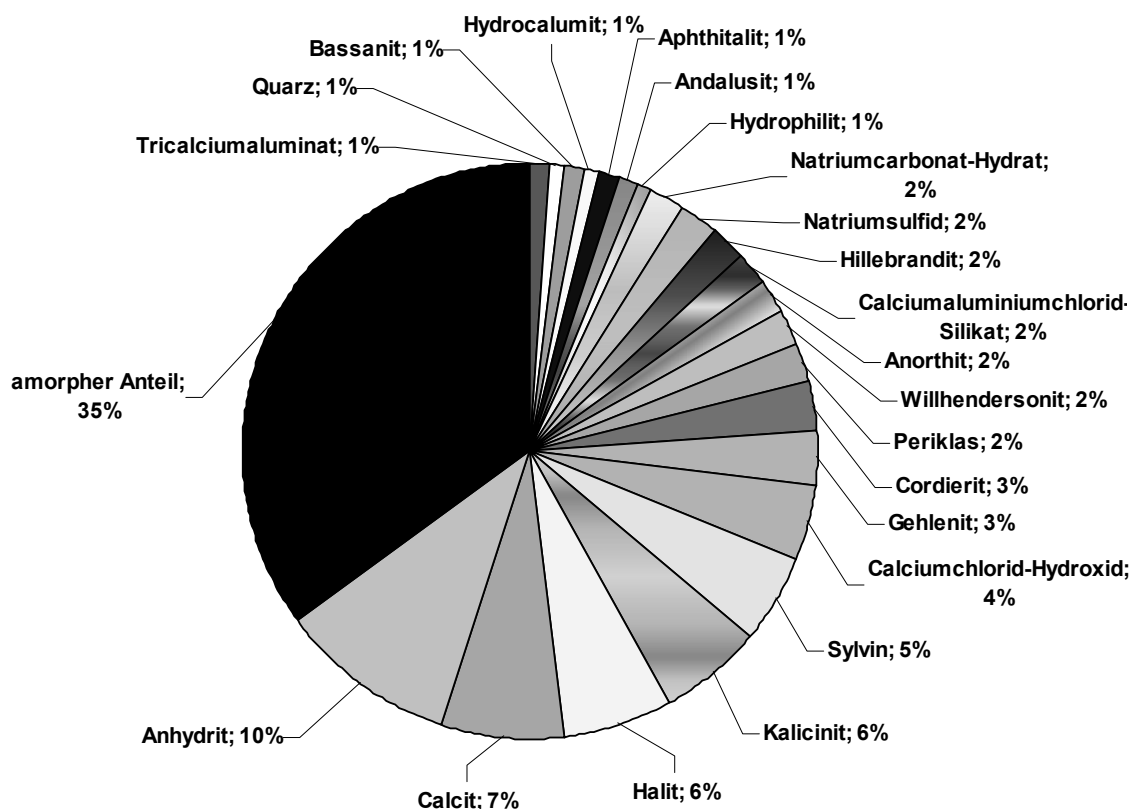


Abb. 1: Durchschnittlicher quantitativer Phasengehalt einer beispielhaften komplexen Industrieasche

Die Komplexität des Systems mit mehreren Phasen niedriger Symmetrie führt zu zahlreichen Koinzidenzen im Diffraktogramm. Häufig sind zudem seltene Minerale und anorganische Verbindungen, was zur Folge hat, dass die Kenntnis über die entsprechenden Kristallstrukturen, vor allem bei Hydratphasen, mangelhaft ist. Das wiederum bedeutet, dass die Rietveld-Methode kaum anwendbar ist, so dass die Faktoren-Methode, die auf dem Vergleich mit ICSD-Korund-Referenzintensitätsverhältnissen basiert, zum Einsatz kommen muss.

Ziel der Studie ist eine verlässliche Angabe der Reproduzierbarkeit bei der Bestimmung des amorphen Anteils solcher Proben.

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Metasomatic processes in eclogites: Evidence from radiogenic (Sr, Nd) and stable (O) isotopes

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High-pressure metamorphic rocks represent natural probes into the subducting lithosphere and can provide important information about subduction-related metasomatic processes. Element mobility and isotopic variations in these rocks are linked to fluid flow and recycling in the subduction zone and to magma genesis at active plate margins. Here, we report results from a geochemical and Sr-Nd-O isotopic study from the Raspas Complex (Ecuador), which represents a high-pressure ophiolite comprising serpentinites, eclogites, blueschists and metapelites. The Raspas Complex is the only eclogite occurrence in the Andes, and the eclogite-facies metamorphism occurred 130 Ma ago.

Based on field associations and trace element geochemistry, the Raspas eclogites can be subdivided into two groups: The first group is LREE-depleted relative to the HREE and has affinities to N-MORB, whereas the second group is LREE-enriched, zoisite-bearing, spatially associated with zoisite veins and characterized by relative enrichments in HFSE, Th and U. Oxygen isotope analyses of separated garnet, omphacite, amphibole, phengite and zoisite were carried out to determine the influence of metasomatic fluids on the O isotopic compositions inherited from the basaltic protolith. Garnet shows a considerable range in $\delta^{18}\text{O}$ values with a distinct difference between the MORB-type eclogites (+4 to +10) and the zoisite eclogites (+11 to +12). O isotope fractionation between omphacite and garnet and garnet and phengite reveals that the MORB-type eclogites are within or close to isotopic equilibrium ($\Delta^{18}\text{O}_{\text{omph-grt}} = 0$ to +2; Zheng et al., 1999), whereas omphacite-garnet and amphibole-garnet pairs from the zoisite eclogites have negative fractionations, indicating disequilibrium.

The large variations in $\delta^{18}\text{O}$ in the garnets of the MORB-type eclogites are interpreted to reflect heterogeneities of the basaltic precursor rock due to low-T alteration by seawater, as observed for eclogite-facies metabasalts from the Cyclades, Greece (Putlitz et al., 2000). However, there is evidence for fluid-induced metasomatic overprinting based on fluid inclusion and Li isotope data in these eclogites. These contrasting observations can be reconciled considering that O is a major mineral constituent with a lower diffusivity than Li, and hence not as easily affected by metasomatism, particularly in garnet. In contrast, the elevated and more homogeneous $\delta^{18}\text{O}$ values of garnets from the zoisite eclogites are most likely caused by metasomatic fluid-rock interaction (Baker et al., 1997). Preserved garnet-mineral disequilibria suggest that garnet cores preserve a pre-metasomatic stage, in contrast to omphacite and zoisite that re-crystallized during the metasomatic event.

Further insights into fluid-driven metasomatism can be gained from Sr-Nd isotope data, as the modification of Sr-Nd isotope systematics by subduction-zone metamorphism is a common feature linked to metasomatic processes. King et al. (2006) used Sr isotope data to identify a metasomatic fluid composition, which dominates Sr systematics in mélange rocks, whereas Nd isotopes were found to have a more conservative behavior. Analyses of Sr-Nd isotopic compositions of the Raspas eclogites are currently in progress and will be presented at the meeting.

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Nanometer-wide magnetite lamellae in mixed 4C/NC-type pyrrhotite from Bodenmais (Bavaria, Germany) – alteration or exsolution?

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Pyrrhotite is a magnetic iron sulfide of the general non-stoichiometric composition Fe_{1-x}S ($x < 0.125$) and is together with pyrite the most abundant iron sulfides in the earth's crust and significantly contributes to rock magnetization and the paleomagnetic record. Due to its variable Fe deficiency a large number of possible polytypes and superstructures arises from the ordering of vacancies within a NiAs-based substructure and concurrently leads to very different magnetic behaviors.

In monoclinic 4C pyrrhotite (Fe_7S_8) vacancies are ordered into every second Fe layer of the NiAs substructure and alternate along the *c*-axis with fully occupied Fe layers. Magnetic coupling within layers is ferromagnetic while coupling among layers is antiferromagnetic, resulting in a net magnetic moment and ferrimagnetic behavior of 4C pyrrhotite. In so-called "hexagonal" pyrrhotites (which are rather orthorhombic or monoclinic by symmetry) Fe deficiency and ordering sequences of vacant and filled Fe layers are different and commonly lead to vanishing net magnetic moments at ambient temperatures. TEM observations on such samples frequently show them to be of the NC-type in which the superstructure satellite reflections relate in a non-integral manner to the substructure periodicity. Despite the many studies on the structures and behaviors of pyrrhotites many aspects of the encountered complexity are poorly understood and present structural models do not fully explain the observed diversity or are poorly supported by sufficiently resolving observations. One phenomenon is the self-reversal of magnetization which was observed experimentally in pyrrhotites and may have large geophysical implications. Bina & Daly (1994) showed that the oxidation of hexagonal pyrrhotite to the monoclinic polytype and further on to magnetite at 500°C can result in a remanent magnetization antiparallel to an applied magnetic field.

Here we report the TEM observation of an assemblage of magnetite, 4C-, and NC-type pyrrhotite in a natural, untreated sample from the metasedimentary Bodenmais deposit (Bavaria, Germany). Intergrowths of the 4C polytype with host NC-type pyrrhotite ($N \approx 5.1$, forming the bulk material) are readily visible in cross polarized reflected light as lamellae parallel to the {001} planes in the direct vicinity of cleavage cracks. Darkfield TEM images reveal 4C lamellae in the same orientation down to sizes of a few 100 nm which are accompanied by {001} parallel 10 to 50 nm wide magnetite lamellae that are coherently intergrown with the host pyrrhotite and reach lengths of several μm . Magnetite octahedral planes {111} are aligned parallel to the pyrrhotite {001} basal planes of layer stacking, joining the two dense packed anion lattices as described by Bennett et al. (1972). The magnetite $\langle 110 \rangle$ directions coincide with pyrrhotite $\langle 100 \rangle$ axes and internally the magnetite lamellae are twinned according to the spinel law by rotation of 180° about $\langle 111 \rangle$ likely minimizing the lattice mismatch to bordering pyrrhotite. In consequence of the orientation relationship the easy axes of magnetization of the two minerals lie perpendicular to each other ($\langle 111 \rangle$ for magnetite, in the basal plane for pyrrhotite). The extreme high aspect ratio of magnetite lamellae may point to nucleation along defect structures like twin planes, stacking faults or boundaries between the different polytypes and indicates a very small interface energy.

Surprisingly, magnetite lamellae were found that share their interfaces with NC-type pyrrhotite instead of the expected 4C polytype given the proposed oxidation sequence $\text{NC} \rightarrow 4\text{C} \rightarrow \text{magnetite}$ of Bina & Daly (1994). Alternatively to an oxidative alteration the possibility of exsolution of magnetite from an oxygen-bearing pyrrhotite must be considered (e.g. Bennett et al. 1972, Graham et al. 1987), especially under the aspect of the coherent intergrowth of both phases. However, the observed assemblage is clearly related to alteration zones along fluid accessible pathways and Graham et al. (1987) were not able to detect magnetite exsolution in hexagonal (i.e. NC-like) pyrrhotites. Since both alteration and exsolution would involve diffusion of oxygen through the pyrrhotite over distances up to μm scale the formation of magnetite likely took place at elevated temperatures, bearing implications for possible magnetizations obtainable by the phase assemblage.

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Yttrium-Ytterbium interdiffusion along a grain boundary in YAG bicrystal

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Yttrium - Ytterbium interdiffusion in a synthetic Yttrium Aluminium Garnet (YAG) bicrystal with a single near $\Sigma 5$ grain boundary is investigated. The bicrystal with the grain boundary normal to the bicrystal surface was synthesized using the wafer bonding method. Yb:YAG thin-films were deposited as an Yb source on the bicrystal surface using Pulsed Laser Deposition (Dohmen, Becker et al. 2002). Diffusion anneals were carried out at 1450°C for run durations of 0.3 to 24 hours. Electron transparent foils were prepared using the Focused Ion Beam (FIB) technique. Analytical and Energy-filtered High-Resolution Transmission Electron Microscopy (ATEM, HRTEM) were used to analyze the bicrystal prior to and after the diffusion anneal. During the diffusion anneal, the initially amorphous thin-films crystallized and formed a homoepitactic layer within about one hour. The original grain boundary continues into the thin-film. The diffusion profiles of Yb along the grain boundary as well as into the volume of the bicrystal were measured using Energy Dispersive X-ray Spectroscopy (EDS) on the TEM applying beam scans over 40 nm by 20 nm analysis windows.

The Yb concentration profiles measured into the volume of the bicrystal substrate were fitted to the equation (Crank 1976)

$$C(x,t) = \frac{C_0^{film}}{2} \left(\operatorname{erf} \frac{x+h}{2\sqrt{Dt}} - \operatorname{erf} \frac{x-h}{2\sqrt{Dt}} \right),$$

where C_0^{film} is the initial Yb concentration in the thin-film. The initial concentration of Yb in the bicrystal is zero, and the thin film extends from $x=0$ to $x=h$. Note that this model implies that D is similar in the thin film and in the bicrystal substrate. This appears to be a feasible approximation, because the structural change of the thin film from amorphous to homoepitactic was rapid compared to the duration of the diffusion anneal. The coefficient of Yb/Y interdiffusion in YAG can then be extracted.

To capture the more complex situation along the bicrystal grain boundary, the system was modeled numerically using a finite element method. In particular, the model accounts for the successive decrease of component diffusivity in the thin film associated with its structural change during annealing. The modeling results are compared to the experimental data, allowing for an estimation of the volume and grain boundary diffusion coefficients.

Finally, we discuss our results with respect to previous studies, where diffusion data were obtained by using different experimental setups (Cherniak 1998; Jiménez-Melendo, Haneda et al. 2001).

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Kulturerbe mit Zukunft oder Last der Vergangenheit? – Die traditionsreichen naturkundlichen Sammlungen an der Martin-Luther-Universität in Halle (Saale)

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Die naturkundlichen Sammlungen der Martin-Luther-Universität – Anatomische Sammlungen, Botanische Sammlungen (Herbarium), Geiseltalmuseum mit Geiseltalsammlung, Museum für Haustierkunde, Geowissenschaftliche Sammlungen und Zoologische Sammlungen – haben nach einer mehr als 200-jährigen Sammlungsgeschichte, die von schwierigen Umbruchszeiten geprägt war, gewaltige Sammlungsbestände in die Gegenwart herüber retten können. Angesichts neuer Herausforderungen an den Universitäten soll skizzenhaft der Frage nachgegangen werden, ob es sich bei den reichen Sammlungsbeständen der Martin-Luther-Universität um ein Kulturerbe mit Zukunft oder doch eher um eine Last der Vergangenheit handelt. Im Focus stehen dabei die Geologisch-Paläontologischen Sammlungen, die innerhalb der Geowissenschaftlichen Sammlungen neben den Mineralogischen Sammlungen einen eigenständigen Sammlungskomplex bilden.

Die Geowissenschaftlichen Sammlungen wurden seit ihren Anfängen im 18. Jahrhundert ständig erweitert mit dem Ziel, Anschauungs- und Vergleichsmaterial für Forschung und Lehre verfügbar zu machen. Die Lehrsammlungen, vorrangig zur Allgemeinen Geologie, Regionalen und Historischen Geologie, Paläontologie und Mineralogie, spielen dabei in studentischen Lehrveranstaltungen nach wie vor als unverzichtbares Referenzmaterial eine wichtige Rolle. Das gilt auch für die umfangreichen Forschungssammlungen, die im Rahmen wissenschaftlicher Projekte international genutzt werden, wobei besonders häufig paläontologische Objekte (z. B. Typenmaterial) ausgewertet und auch ausgeliehen werden. Dabei ist von Bedeutung, dass das Material vorhanden und zugänglich ist. Die Frage, wie oft ein bestimmtes Objekt „begehrt“ wird, ist dabei falsch gestellt und zeugt von Unkenntnis.

Dennoch muss festgestellt werden, dass an modernen universitären Institutsstandorten oft kein Platz mehr vorgesehen ist für flächengreifende Ausstellungsareale, wie sie in Halle im alten Institutsgebäude noch existierten. Im neuen Institut sind die umfangreichen Sammlungen zwar nicht mehr öffentlich zugänglich, aber zum größten Teil sicher sowie trocken in Sammlungsschränken und einer Compactus-Anlage untergebracht. Dass Sammlungen der permanenten Betreuung und Pflege bedürfen, ist eine Binsenwahrheit, weshalb eine angemessene personelle Ausstattung und entsprechende Finanzmittel für die Sammlungen unerlässlich sind. Es sei in diesem Zusammenhang an ein Zitat von A. Seilacher (1975) erinnert: „Paläontologie erschöpft sich nicht in der Beschreibung und Klassifizierung von Fossilien und in der ständigen Verfeinerung ihres geologischen Aussagewertes. Sie ist zugleich eine biologische Wissenschaft, in der jede Forschergeneration mit neuen Fragen und Methoden an das alte Datenmaterial herantritt und damit ihren eigenständigen Beitrag liefert zum Verständnis biologischer Evolution“. Diese Aussage trifft in modifizierter Form gleichfalls auf die anderen Sammlungen der Martin-Luther-Universität zu. Auch wenn Universitätssammlungen heute nicht selten das Dasein eines vernachlässigten Erbes fristen und allzu häufig als Last der Vergangenheit empfunden werden, so ist ihr Wert als unbedingt schützenswertes Kulturerbe für zukünftige Forschergenerationen gar nicht hoch genug zu veranschlagen.

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Minerale mit inkommensurabel modulierten Kristallstrukturen

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Inkommensurable moduliert: So unaussprechlich der Name auch sein mag, so schön und faszinierend sind inkommensurable modulierte Kristallstrukturen sowie die unterschiedlichen Ursachen für die Modulation und ihre Reaktion auf Veränderungen im Chemiesmus, Druck und Temperatur.

Bereits zu Beginn des letzten Jahrhunderts fand man bei Calaverit, AuTe_2 , dass dessen Flächen nicht mit drei ganzzahligen Indices $\{hkl\}$ indiziert werden können und somit im Widerspruch zum klassischen kristallographischen Gesetz der rationalen Indizes stehen. Außerdem treten im Beugungsbild von Calaverit zusätzliche Reflexe im Beugungsbild auf, sog. „Gittergeister“^[1], oder Satellitenreflexe. Man kann aber sowohl die Flächen von Calaverit als auch die Satellitenreflexe mit vier ganzzahligen Indizes $\{hk\ell m\}$ indizieren, und die sogenannte inkommensurabel modulierte Kristallstruktur in einem höher-dimensionalen Superraum beschreiben^[2]. Heute kennt man eine große Anzahl von Mineralen mit inkommensurabel modulierten Kristallstrukturen^[3,4], wie Sylvanite, Nephelin, Mullite, Antigorit, Labradorite, Åkermanite, Lazurite, und Perovskit-verwandte Minerale wie Elpasolit oder Brownmillerit. Sogar SiO_2 zeigt inkommensurable Modulation: Die Umwandlung von α - und β -Quarz erfolgt nicht direkt, sondern über eine inkommensurabel modulierte SiO_2 -Phase mit einem Stabilitätsbereich von nur 1.3° ^[5]. Die meisten Minerale mit inkommensurabler Struktur weisen eine displazive Modulation auf, es sind aber auch Minerale mit Besetzungsmodulationen bekannt, wie etwa Labradorit, bei dem sowohl die Ca/Na-Positionen als auch die Al/Si-Positionen eine Besetzungsmodulation aufweisen^[6].

Die Mischkristallreihe der Brownmillerite $\text{Ca}_2(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_5$ zeigt modulierte Kristallstrukturen bei hohen Temperaturen. Die beiden Endglieder^[7,8], sowie einige Zusammensetzungen dazwischen wurden mittels Hochtemperatureinkristallröntgenbeugung untersucht und zeigen charakteristische Satellitenreflexe, die eine modulierte Abfolge verschiedener Tetraederketten beweisen. Die isotypen Hochtemperaturstrukturen lassen sich in der im (3+1)-dimensionalen Superraum beschreiben und unterscheiden sich nur durch die chemische Zusammensetzung und die Modulationsperiode. Die eisenreichen Proben zeigen am Phasenübergang einen Temperaturbereich in dem Domänen beider Strukturen (Tieftemperaturphase und modulierte Hochtemperaturphase) auftreten; dies kann mittels in-situ Dunkelfeldtransmissionselektronenmikroskopie direkt beobachtet werden^[9].

Bei genauen Einkristallbeugungsuntersuchungen von natürlichen Nephelinen, $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$, findet man in fast allen Fällen Satellitenreflexe^[10], deren Intensität sich sowohl unter Druck- als auch unter Temperatureinfluss verringert bis die Modulation bei etwa 2 GPa bzw. bei 173°C ganz verschwindet^[11]. Auch bei Calaverit verschwinden die Satellitenreflexe bei etwa 2.5 GPa^[12]. Lazurit, ein Glied der Sodalit-Gruppe $(\text{Na,Ca,K})_8(\text{AlSiO}_4)_6(\text{SO}_4,\text{S,OH,Cl})_2$, dessen Satellitenreflexe bei etwa 400°C verschwinden^[13], hat hingegen starke Satellitenreflexe bis zu mindestens 6.1 GPa^[14]. Lazurit hat die einzige bisher bekannte inkommensurabel modulierte Struktur die im (3+3)-dimensionalen Superraum beschrieben wird^[15].

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Petrology and geochemistry of orthogneiss of the Münchberg Massif/NE Bavaria

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A unit of three different types of orthogneiss – augengneiss, garnet-bearing gneiss, plagioclase gneiss – of the Hangendseries of the Münchberg Nappe pile was investigated by conventional geochemical and petrological methods. The outcrop is located in the NE of the Münchberg Massif, in the village of Oberkotzau, was well exposed in 1992, during construction work of the factory 'Viessmann' but is mostly destroyed now. According to the map description of Emmert et al. (1968) the sample locality is situated next to a fault, which separates the Hangend- from the Liegendseries.

The three gneiss varieties are closely associated and were exposed over a few m perpendicular to strike. Augengneiss and garnet-bearing gneiss are strongly foliated, the fine-grained plagioclase gneiss with a small amount of mica is only weakly foliated, visible in thin section. It consists of three parallel layers of an overall thickness of 0.5 m, folded together with all other units within the outcrop. Each layer has a central part and a light colored ≈ 1 cm wide rim.

Whole rock chemistry shows that augen- and garnet-gneiss are equivalent to granite-granodiorite. Several samples of the plagioclase gneiss are almost identical in their granitic composition, but central part (K-Ba-rich) and rim (Ca-Na-rich) differ significantly. Trace elements also allow to distinguish between the three rock types.

All three rock types contain garnet, however in different amounts and textures. In plagioclase gneiss and augengneiss, the garnets are almandine 80-60 mol%, grossular 20-40 mol% with up to 15 mol% spessartine and < 5 mol% pyrope. In the garnet-bearing gneiss pyrope content is between 15 and 20 mol% and grossular < 20 mol%. Feldspars are near-endmember K-feldspar and plagioclase An $\leq$ 20.

Although no clearly identifiable igneous mineral relicts could be found, textures and outcrop situation as well as whole rock major and trace element analysis indicate an igneous protolith for all three rocks. For the plagioclase gneiss felsic dikes as protolith are assumed. In these rocks abundant allanite (with coronas of epidote) might be igneous relicts. This demonstrates that in the Hangendseries, which is dominated by mafic to intermediate rock assemblages, also orthogneiss is present. The different varieties of orthogneiss underwent metamorphism at estimated 500-650 °C / 5 - 8 kbar. These results are in agreement with an amphibolite facies overprint of the eclogites of the Hangendseries by 600–650 °C / 8-10 kbar as proposed by Liebscher et al. (2007). No relics of HP metamorphism are preserved, which is indicative for the Hangendseries.

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200 Jahre Mineralogisch-petrographische Sammlung der Universität Leipzig

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Die Sammlung feiert in diesem Jahr ihr 200jähriges Bestehen und gehört damit zu den ältesten ihrer Art an deutschen Universitäten. Sie wurde 1809 anlässlich des 400. Universitätsjubiläums durch Schenkungen von Universitätsangehörigen begründet und in den Folgejahrzehnten beträchtlich erweitert. Damit verkörperte sie bald den Hauptfundus eines Naturalienkabinetts, das 1837 erstmalig der Öffentlichkeit zugänglich gemacht wurde. Sein reichhaltiger mineralogischer Teilbestand bildete die materielle Voraussetzung dafür, dass 1842 an der Universität Leipzig eine a.o. Professur für Mineralogie und Geognosie eingerichtet werden konnte, deren erster Amtsinhaber Carl Friedrich Naumann war. Während seiner Amtszeit gelang es ihm, allein den Bestand an Mineralen auf über 17.000 Nummern zu erweitern. Sein Nachfolger Ferdinand Zirkel bezifferte 1909 den gesamten Sammlungsumfang auf 51.280 Minerale, Gesteine und Fossilien. Am Leipziger Mineralogischen Institut, das damals zu den am besten eingerichteten seiner Art in Europa gehörte, lehrten und forschten auch in den Folgejahrzehnten zahlreiche namhafte Mineralogen, deren wissenschaftliche Leistungen u.a. durch 5 Mineralbenennungen nach ihrem Namen gewürdigt wurden: Naumannit, Zirkelit, Rinneit, Niggliit und Pauflerit.

1943 wurden das Institut und seine Sammlungen bei einem Bombenangriff nahezu vollständig zerstört. Vorsorglich ausgelagerte Bestände gingen am Kriegsende als Beutegut verloren. Herbert Pührer, ein zu dieser Zeit am Institut angestellter Assistent, bezifferte 1947 die Verluste u.a. auf über 39000 Minerale, 41000 Gesteine und 3600 lagerstättenkundliche Exponate. Wegen der 1945 erfolgten Übersiedlung des Institutsdirektors Karl Hermann Scheumann in die amerikanische Besatzungszone waren die Nachkriegsjahre bis 1960 geprägt durch die Vakanz des Lehrstuhles und einen mehrmaligen Wechsel der kommissarisch eingesetzten Institutsleitung. Weil die von der Zerstörung zunächst verschont gebliebenen Kellerräume des Institutsgebäudes vom Einsturz bedroht waren, erfolgte die provisorische Unterbringung der verbliebenen Geräte und Sammlungsteile im Haus gegenüber. Ungeachtet dieser widrigen Umstände wurde der heutige Sammlungsbestand, dessen Kernstücke u. a. die über 5000 Minerale aus aller Welt umfassende Sammlung von Karl Weikert und die Seidelsche Mineralsammlung mit über 600 Belegen aus Sachsen sind, überwiegend unmittelbar nach dem 2. Weltkrieg angeschafft. Er widerspiegelt einerseits das Bemühen der verbliebenen Institutsangehörigen um die Aufrechterhaltung der Lehre bis zu deren Einstellung im Sommersemester 1945, andererseits lassen sich in bestehenden Sammlungsstrukturen noch heute Lehranwendungen für Nebenfächler in den Jahren nach Wiederaufnahme des Lehrbetriebes 1949 erkennen. Seit 1963 befindet sich die Sammlung an ihrem jetzigen Standort Scharnhorststraße 20. Seit Mitte der 1960er Jahre bis in die Gegenwart wurde die Teilsammlung „Technische Produkte“ angelegt. Es handelt sich hierbei ausschließlich um synthetische Materialien. Diese Kollektion ist nicht nur die jüngste, sondern verkörpert darüber hinaus auch einen Beleg von über 40 Jahren erfolgreicher Lehr- und Forschungstätigkeit auf dem Gebiet der Technischen Mineralogie.

Der heutige Gesamtbestand umfasst im Einzelnen: die systematische Mineralsammlung mit ca. 12000 Belegen aus aller Welt, die lagerstättenkundliche Sammlung (1000 Belege), die petrographische Sammlung (3500 Belege), die Dünn- und Anschliffsammlung (2000 Belege), die Sammlung zur Technischen Mineralogie (200 Belege) und die Kristallmodellsammlung (130 Pappmodelle, 800 Holzmodelle, 80 Struktur- und Gittermodelle).

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Low temperature hydrothermal crystallisation of minerals in the system Cu-Zn-Cl-O-H-N

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The authors investigated a copper deposit NE of Almeria in southern Spain. Primary ore minerals are tetrahedrite with a high zinc content, pyrite and rarely bournonite as impregnations and fillings of small veinlets in a hydrothermally altered mica schist. Gangue minerals are barite and dolomite.

Oxidation of the primary ore minerals yielded a very peculiar paragenesis of secondary mineralisations: Though dolomite is a gangue mineral secondary carbonates (as e.g. Malachite) are nearly missing. On the other hand copper chlorides are very frequent and manifold. Most frequent are members of the atacamite group with clinoatacamite, atacamite and "paratacamite". Whereas atacamite is almost Zn-free, the clinoatacamites and "paratacamites" showed Zn contents up to 10 % Zn apfu. Whether the "paratacamites" from this deposit are a distinct mineral species or merely solid solutions of clinoatacamite and herbertsmithite is still debatable (Malcherek and Schlüter 2009).

Further copper chloride minerals in this paragenesis are Kapellasite, $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$, formerly known only from Lavrion, Greece, (Krause et al. 2006) and Claringbullite, $\text{CuCl}(\text{OH})$.

Buttgenbachite, $\text{Cu}_{36}(\text{NO}_3)_2\text{Cl}_8(\text{OH})_{62} \cdot 4-10\text{H}_2\text{O}$, is frequent as tiny blue balls on pyrite-impregnated micaschist. The nitrate is thought to be of biological origin, produced by bacteria oxidizing NH_3 originating from the reaction of nitrogen with altering pyrite.

Youngest formations are the sulfates chalkanthite, hexahydrite and gypsum which mainly have grown on the gallery walls after the end of the mining activities.

Water leaking from the deposit is relatively warm (about 50°C, pH 7,3) and shows high contents of chloride, sulfate and nitrate. This is in good agreement with the paragenesis of secondary minerals, which are mainly chlorides, sulfates and nitrates of copper, zinc, magnesium and calcium.

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Tiefhydrothermale Mo – V – Mineralisationen in der Betischen Kor-dillere, Südspanien

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Nordwestlich von Almeria, Südspanien befinden sich in den triassischen Dolomiten und Kalken der Sierra de Gador zahlreiche Blei-Zink-Vererzungen, die im 19. Jahrhundert in einer Vielzahl meist kleiner Gruben abgebaut wurden (Jacquin 1966, 1968). Einziges Bleierz ist Bleiglanz, der in Linsen und Putzen im Kalk eingelagert ist und häufig in situ in Cerussit umgewandelt ist. Auf Klüften im Gestein, als Hohlraumfüllungen in Brekzienzonen und in Oxidationsschlotten auf Limonit und Quarzstegen findet sich Wulfenit in Kristallen unterschiedlichster Habitusformen von dünn tafelig bis hin zu spitzpyramidal. Dabei lassen sich aufgrund der Habitusformen und Wachstumsverhältnisse mehrere unterschiedlich alte Wulfenitgenerationen bis hin zu subrezenten Bildungen unterscheiden.

Ein weiteres Vorkommen von Bleivererzungen liegt südlich von Granada bei Albunuelas (Gomez und Sola 2000). Dort findet sich Wulfenit, ebenfalls in mehreren Generationen auf Klüften im Kalk bis hin zu subrezenten Bildungen als Verkittung feinkörniger tonmineralreicher Kluft- und Hohlraumfüllungen. Die jüngsten Bildungen sind hier schuppenartige extrem dünne Kristallite, die meist nur einen unregelmäßigen Umriss zeigen. Auf Klüften im Kalk bzw. in Lösungshohlräumen tritt Wulfenit in dicktafeligen bipyramidalen Kristallen auf.

Daneben treten hier reichliche Vanadium-Vererzungen in Form von Vanadinit, Descloizit und Endlichit in Kristallen bis 5 mm Größe und Kristallkrusten. Begleitmineral als junge Bildung in Krusten nadeliger Kristalle ist der erst kürzlich als eigenständiges Mineral beschriebene Phosphohedyphan (Kampf et al. 2006).

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Die magmatische Entwicklung der Kommandeurinseln (westliche Aleuten)

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Die Entwicklung der Kommandeurinseln als westlichstes Segment des aleutischen Inselbogens erstreckt sich über nahezu 50 Mio. Jahre Erdgeschichte (LAYER et al., 2007) und ist rezent durch ein Strike-slip – Regime gekennzeichnet. Deshalb ist auf den Inseln gegenwärtig kein aktiver Magmatismus festzustellen. Untersuchungen im Rahmen des deutsch-russischen Forschungsprojektes KALMAR haben ergeben, dass alle magmatischen Komplexe der Inseln die Signatur einer Subduktionstätigkeit aufweisen. Zusätzlich zu den bisher bekannten vier mitteleozänen bis obermiozänen Komplexen (IVASCHENKO et al., 1984) kann die Existenz einer fünften magmatischen Serie nachgewiesen werden. Die Spurenelementsignatur dieser Serie weist einen Übergangscharakter auf, der einen Wechsel vom reinen Arc-Vulkanismus zur adakitischen Tätigkeit kennzeichnet. Dieser Magmatismus setzt ab der Wende Eozän/Oligozän ein und verstärkt sich bis zum Obermiozän. Die Bildung von Adakiten muss durch eine Veränderung des tektonischen Regimes bedingt sein. Hierbei sind auf den Inseln Low-SiO₂ – gegenüber High-SiO₂ – Adakiten vorherrschend. Low-SiO₂ – Adakite werden auf den Kommandeurinseln durch Basalte und basaltische Andesite repräsentiert, demnach muss eine Modifizierung der Schmelze auf dem Weg zur Erdoberfläche stattgefunden haben. Es ist denkbar, dass die aufsteigende High-silica Schmelze eine hoch reaktive Wechselwirkung mit Mantelperidotit eingegangen ist. Im Falle einer Infiltration von High-silica Schmelze in Peridotit kann Olivin in Pyroxen umgewandelt und so ein Olivin-freier Pyroxenit gebildet werden (LIU et al., 2005). Hohe Fe/Mn – Verhältnisse > 60 in Basalten lassen auf eine pyroxenitische Quelle schließen, während niedrigere Werte eine peridotitische Quelle nahe legen (LIU et al., 2008). Es zeigt sich, dass eine klare positive Korrelation zwischen dem, als Zeichen der starken Fraktionierung adakitischer Schmelzen dienenden, hohen Sr/Y – und dem Fe/Mn – Verhältnis vorhanden ist. Die basaltischen Adakite zeigen teilweise Fe/Mn – Werte ≥ 80 . Dies deutet auf eine Veränderung der Magmenquelle hin zu einem pyroxenitischen Ursprungsmaterial.

Als Auslöser für den adakitischen Magmatismus der Westaleuten wird auf der Grundlage von tomografischen Mantelmodellierungen ein möglicher Riss oder gar Plattenabriss (Slab Break-off) der Pazifischen Platte angenommen (z.B. LEVIN et al., 2005). Dieses Ereignis könnte dazu geführt haben, dass heißes Asthenosphärenmaterial die im Vergleich kalte pazifische Lithosphäre umflossen hat und diese Interaktion in eine partielle Aufschmelzung der subduzierten Platte mündete.

Die Ausführungen machen deutlich, dass die westlichen Aleuten ein komplexes geotektonisches Regime darstellen, dessen Entwicklung ein Schlüssel für die geologische Evolution des gesamten Aleuten-Kamtschatka-Systems ist.

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Bildung amorpher und polymerer Kieselsäure durch zyklisches Gefrieren verschiedener wässriger Lösungen

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In dieser Arbeit wurden wässrige Lösungen (100 mL) von monomerer Kieselsäure für 100 Tage einem Tauwechselversuch unterzogen (6 h bei +20 °C, 6 h Abkühlung von +20 °C auf -20 °C, 6 h bei -20 °C, 6 h Erwärmen von -20 °C auf +20 °C). Konzentrationen von monomerer Kieselsäure von ungefähr 1,79 mM wurden durch Zersetzung von Tetraethoxysilan in wässriger Lösung erhalten. Der initiale pH-Wert wurde durch die Zugabe von NaOH bzw. HCl eingestellt (3, 5, 7, 9, 11). Die Ionenstärke wurde durch die Zugabe von 5 mM NaCl in jeder Lösung angeglichen worden. Zusätzlich erfolgten bei bestimmten Versuchsreihen Zugaben von 0,1 mM Al (als $\text{AlNO}_3 \cdot 9 \text{H}_2\text{O}$), B (als H_3BO_3) und Ge (als GeO_2). Nach definierten Reaktionszeiten (20, 40, 60, 80 und 100 Tage) wurde jeweils eine Probe der Versuchsserie aus dem Klimaschrank entnommen und mittels 0,1 µm-Zellulosefilter filtriert. Die filtrierten Proben wurden mittels ICP-OES analysiert.

Die Ergebnisse zeigen während der ersten 40 Tage eine Ausfällung von amorpher Kieselsäure an. Die anderen Komponenten verblieben in der Lösung. Die Menge der gebildeten Festphase stieg mit der Anzahl der Frier-Tau-Zyklen an. Während der Gefrierphase präzipitierte amorphe Kieselsäure infolge fortschreitender Übersättigung der Lösung. Während der Tauphase ist die Wiederauflösung kinetisch gehemmt. Die Verarmung der Lösung an gelöster Kieselsäure war bei pH 5 am stärksten und nahm zu größeren und kleineren pH-Werten hin ab. In einer zweiten Phase von ebenfalls 40 Tagen lösten sich die Niederschläge teilweise wieder auf. Schließlich kam es in einer dritten Phase zu einer erneuten Ausfällung von amorpher Kieselsäure. Die Verarmung der Lösung an gelöster Kieselsäure war in der Gegenwart von Al und besonders von Ge deutlich stärker als in reinen Si- und in Si-B-Lösungen. Ein ähnlicher Effekt wurde in Gegenwart von Alkali- und Erdalkalitionen von Dietzel (2005) beschrieben.

Analysen des Polymerisationsgrades gelöster Kieselsäuren mit der β -Silicomolybdat-Methode zeigen, dass die Anwesenheit von Al und Ge zu einer nahezu vollständigen Polymerisation der ursprünglich monomeren Kieselsäure führt. Im Gegensatz hierzu blieb die Kieselsäure in den Referenzlösungen bei 25 °C in monomerer Form erhalten. Der komplexe Prozess der Bildung amorpher Kieselsäure durch zyklisches Gefrieren wird diskutiert. Dies kann zu einem erweiterten Verständnis der Auflösungs- und Ausfällungsprozesse von Kieselsäuren in aktiven Horizonten von Cryosolen und der diesbezüglichen Bildung von Sekundärmineralen wie Tonmineralen und Zeoliten beitragen.

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Ordered and disordered aluminum borates

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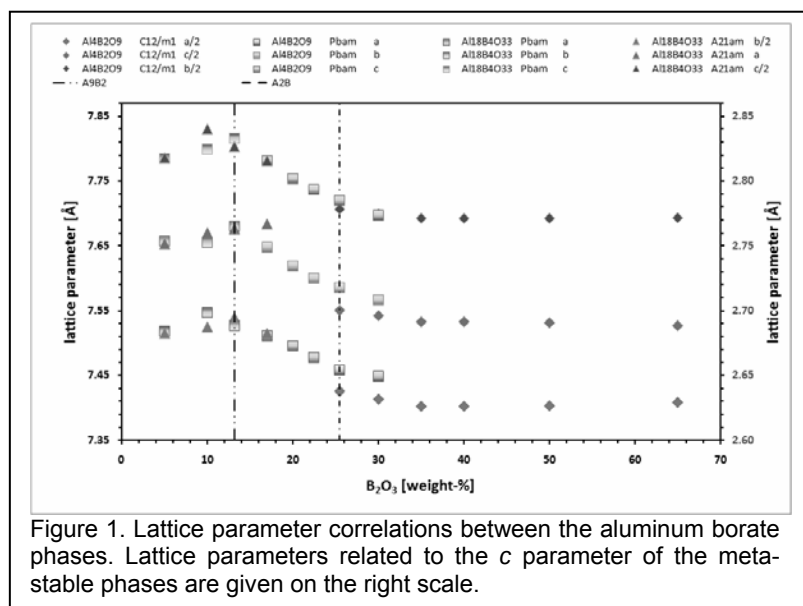


Figure 1. Lattice parameter correlations between the aluminum borate phases. Lattice parameters related to the *c* parameter of the meta-stable phases are given on the right scale.

In the binary phase diagram of the system $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ two phases are described to exist [1]. For either one of the binary phases, two different modifications are reported. $\text{Al}_4\text{B}_2\text{O}_9$, as the boron rich phase, was described in the orthorhombic space group *Pbam* with a pseudo-tetragonal metric [2] which is assumed to be meta-stable [3, 4] as well as with monoclinic symmetry in the space group *C2/m* in an enlarged unit cell with all lattice parameters doubled [5]. The aluminum rich phase $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystallizes in the orthorhombic space group *A21am* [6] as stable form, and analogously to $\text{Al}_4\text{B}_2\text{O}_9$ also in the space

group *Pbam* with a pseudo-tetragonal metric [2]. All compounds investigated here were synthesized from the corresponding ratios of aluminumnitrate nona-hydrate and boric acid solved in ten weight percent 1,2,3-propanetriol (glycerol) at 353 K, dried at 573 K and crystallized at 1223 K for three days right below the incongruent melting point of $\text{Al}_4\text{B}_2\text{O}_9$ at 1303 K [1]. Subsequently, the samples were washed with hot water to remove the amorphous and partially crystallized sassolite (H_3BO_3). The remaining powder was studied by means of X-ray powder diffraction refinements using the Rietveld method. For the fit of the stable monoclinic $\text{Al}_4\text{B}_2\text{O}_9$ ($\text{A}_2\text{B(s)}$) with lattice parameters of $a \approx 14.81 \text{ \AA}$, $b \approx 5.54 \text{ \AA}$, $c \approx 15.05 \text{ \AA}$ and $\beta \approx 91^\circ$ the atomic parameters were taken from ref. [5] and fixed in the refinements. The same procedure was applied to meta-stable $\text{Al}_4\text{B}_2\text{O}_9$ ($\text{A}_2\text{B(m)}$), $a \approx b \approx 7.61 \text{ \AA}$, $c \approx 2.83 \text{ \AA}$ and Al_5BO_9 ($\text{A}_9\text{B}_2(\text{m})$), $a \approx b \approx 7.62 \text{ \AA}$, $c \approx 2.83 \text{ \AA}$ [2] and the stable orthorhombic $\text{Al}_{18}\text{B}_4\text{O}_{33}$ ($\text{A}_9\text{B}_2(\text{s})$), $a \approx 7.69 \text{ \AA}$, $b \approx 15.01 \text{ \AA}$, $c \approx 5.66 \text{ \AA}$ [6]. To compare the resulting lattice parameters of the stable phases with those of the meta-stable ones they were divided by two in all three directions for $\text{A}_2\text{B(s)}$ and in *b* and *c* for $\text{A}_9\text{B}_2(\text{s})$. Deviating from the literature [2] the lattice parameters of the meta-stable phases $\text{A}_2\text{B(m)}$ and $\text{A}_9\text{B}_2(\text{m})$ studied here are clearly orthorhombic with $a \neq b$ as known for mullites and mullite-like compounds [7]. As shown in Figure 1, $\text{A}_2\text{B(s)}$ is present in the boron rich part of the diagram, obtained at room temperature after heating at 1223 K without significant changes of the lattice parameters. Close to the A_2B phase boundary, $\text{A}_2\text{B(m)}$ was found as second phase together with a slight increase of the $\text{A}_2\text{B(s)}$ values, probably correlated with a small replacement of boron by aluminum. In the phase field between A_2B and A_9B_2 the lattice parameters of the meta-stable phase increase approaching the values of the stable A_9B_2 . In the aluminum rich region, $\text{A}_9\text{B}_2(\text{s})$ is always observed to be accompanied by $\text{A}_9\text{B}_2(\text{m})$ (and Al_2O_3) but only slight changes of the lattice parameters of both phases are observed. Because of the continuous change of the lattice parameters from $\text{A}_2\text{B(m)}$ to $\text{A}_9\text{B}_2(\text{m})$ it is assumed that only one meta-stable phase exists in which boron is partially replaced by aluminum resulting in increasing lattice parameters and slight structural changes.

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Goldrausch im Museum? - Goldwaschversuche zur Standort-Bestimmung einer mittelalterlichen Pochmühle im Edergebiet

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Moderne Museumsarbeit lässt sich in die Teilbereiche Sammeln, Bewahren, Ausstellen/Vermitteln und Forschen aufgliedern. Gerade der letzte Aspekt erschließt sich jedoch dem eigentlichen Museumspublikum nur selten. Da es aber ein großes Anliegen ist, die „Institution Museum“ für die Öffentlichkeit auch als Forschungseinrichtung sichtbar zu machen, sollten wissenschaftliche Programme wirksamer nach außen präsentiert werden. Das Museum für Naturkunde in Dortmund knüpft genau hier an. Basierend auf der langen Tradition, in der sich das Haus einen Namen in der Goldlagerstätten-Forschung gemacht hat, werden wissenschaftliche Goldwaschversuche im Gelände durchgeführt, an denen auch interessierte Laien teilnehmen können.

Eine montanhistorische Fragestellung, die 2009 unter der Leitung des Erstautors bearbeitet wurde und deren Ergebnisse hier präsentiert werden, führte an den Korbacher Eisenberg (Hessen). Vor rund 500 Jahren befanden sich in diesem Areal mehrere durch Wasser angetriebene Pochwerke, in denen die Golderze des Eisenberger Bergwerkes zerkleinert, zur Gewinnung eines Gold-Konzentrates verwaschen und schließlich amalgamiert wurden. Hinweise dazu finden sich in Urkunden, Bergamtsberichten und Gerichtsakten. Die geographische Lage dieser Pochwerke ist jedoch nur ungefähr bekannt und sollte mittels systematischer Goldwaschversuche eingegrenzt werden. Als Schlüssel dient das gewaschene Gold: Beim Pochen der Erze geht ein gewisser Prozentsatz des Goldes verloren, daher enthalten die Waschkonzentrate dicht unterhalb dieser Pochwerke neben dem üblichen Waschgold auch Goldamalgam und kristallisiertes Berggold, das oftmals noch mit Gestein verwachsen und mit für die Region typischen Mineralarten vergesellschaftet ist – z.B. Clausthalit PbSe , Libethenit $\text{Cu}_2(\text{PO}_4)(\text{OH})$. Ein finaler, großer Waschversuch im Frühjahr 2009 (in Kooperation mit dem Deutschen Bergbau-Museum Bochum, dem Bonhage-Museum Korbach und dem „Verein Historischer Goldbergbau Eisenberg“), der auch in der Presse eine große Resonanz fand, brachte die erhofften mineralogischen Nachweise und es gelang, den Standort eines Pochwerkes bei Nieder-Ense an der Itter bis auf mehrere Meter genau zu lokalisieren.

Das Museum für Naturkunde in Dortmund wird derartige Geländearbeit (ergänzend zum klassischen Exkursionsprogramm) in Zukunft nutzen, um das interessierte Museumspublikum an aktuelle wissenschaftliche Fragestellungen heranzuführen und auch aktiv an deren Bearbeitung teilhaben zu lassen. Dies ist ein effektiver Weg, der Öffentlichkeit die verschiedenen Aufgaben der „Institution Museum“ näher zu bringen und Besuchern das interdisziplinäre, wissenschaftliche Arbeiten zu vermitteln.

Geologische Aufnahme und Charakterisierung tertiärer Basalte und ihrer Fremdgesteinseinschlüsse im Gebiet Marktredwitz – Mitterteich – Wiesau

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Die geologischen Untersuchungen fanden im südöstlichen Teil des Fichtelgebirges, in den Regierungsbezirken Oberpfalz und Oberfranken, statt (Abb.1). Die Eckpunkte des ca. 64 km² umfassenden Arbeitsgebietes bilden die Städte und Märkte von Marktredwitz – Mitterteich – Wiesau und Fuchsmühl. Die Morphologie ist gekennzeichnet durch flache Hügel, umgeben von Hochflächen mit starker anthropogener Nutzung. Inmitten von weitläufigen Feldern treten vereinzelt teils kegelförmige, teils ungleichmäßig regellose Basaltvorkommen zu Tage, die in der Vergangenheit als Baumaterial abgebaut und somit durch lokale, kleine Brüche gut aufgeschlossen vorliegen. Zudem befinden sich die zwei im Abbau befindlichen Basaltbrüche „Teichelberg“ und „Hirschentanz“ im Untersuchungsgebiet.

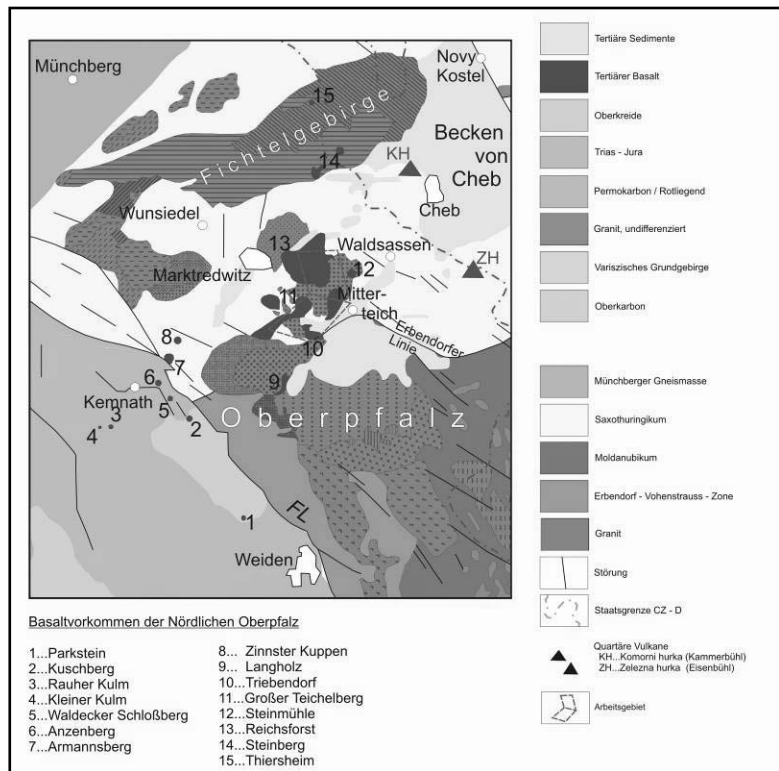


Abb1: Geologische Lage der Kartiergebiete in der Oberpfalz

Die Basalte des südöstlichen Fichtelgebirges sind als Teil des „European Cenozoic Rift System“ Produkt einer vulkanisch höchst aktiven Zeitspanne im Tertiär (K-Ar-Alter der Basalte: 19-26 Ma; TODT & LIPPOLT, 1975). Die mafischen Extrusiva sind gekennzeichnet durch Untersättigung an SiO₂ und einer damit verbundenen erhöhten Konzentration an Feldspatvertretermineralen. Neben Olivin xenolithen enthält das Gestein eine Vielzahl von sauren Fremdgesteinseinschlüssen, sowie sekundär gebildete Hohlraumfüllungen. Zudem zeigt der Basalt im Arbeitsgebiet spezielle Verwitterungsformen. Die Lage der Basalte und Tuffe zum angrenzenden variszischen, bzw. tertiären Nebengestein wurde erfasst und die basaltoiden Vorkommen der Effusiva zur Charakterisierung systematisch beprobt. Ein besonderes Augenmerk bei der Probenahme lag auf der Möglichkeit der Unterscheidung verschiedener vulkanischer Ereignisse und auf sekundären Reaktionen des Basalts mit Fremdgesteinseinschlüssen. Das Probenmaterial wird zunächst makroskopisch beschrieben. Zur weiteren Spezifizierung werden die Proben mikroskopisch, chemisch und physikalisch analysiert (→ RFA, XRD, REM, ICP, Druckfestigkeit). Die Clusterverteilung der ermittelten Haupt- und Spurenelemente können Aufschluss über die Beziehungen einzelner Basaltvorkommen geben und die Bestimmung der analysierten Sekundärminerale macht die posteffusive Entwicklung der Basalte und Tuffe nachvollziehbar. Ziel dieser Arbeit ist die Charakterisierung lokaler Vorkommen basaltoider Effusiva nach ihrem primären und sekundären Mineralbestand. Die sich dadurch ergebenden physikalischen Eigenschaften werden erarbeitet. Diese dienen als Auswahlkriterium zur möglichen Verwendung als Baumaterial.

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Amphibole chemistry in calc alkaline igneous rocks of the Natanz batholith, Central Iran

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Two magmatic belts dominated by calc-alkaline igneous rocks (Berberian and Berberian, 1981) run parallel to the Main Zagros Thrust (suture zone between Arabia and Eurasia) on the Eurasian upper plate and cut across central Iran. The magmatic activity was restricted to the Sanandaj–Sirjan magmatic arc during the Mesozoic and to the Urumieh–Dokhtar magmatic arc during the Tertiary. The Oligo-miocene Natanz plutonic complex is part of a series of intrusions in Urumieh – Dokhtar magmatic belt which is composed of gabbro, diorite, quartz-diorite, quartz monzonite, granodiorite and granite. Differentiation from diorite to granite is the main process in magmatic evolution of this area.

Amphibole is the most important mafic mineral in the intermediate rocks of this complex. All of the amphiboles have Ca + Na contents greater than 1.34, indicating that they are calcic amphiboles according to the classification of Leake et al (1987) with these parameters : $[(Ca + Na_B) \geq 1, Ca > 1.5, Na_B < 0.5, (Na + K)_A \geq 0.5, Ca > 0.5 \text{ and } Ti < 0.5]$. The amphibole analyses have oxide wt% totals of between 95.69 and 98.06 . Cation totals lie between 14.08 and 15.23 per 23 oxygen anhydrous formula unit. Most of amphiboles plot in the hornblende and magnesio-hornblende in the (Na + K) versus Si diagram (Leake et al 1987). The amphiboles in the granite have more Na contents than ones in other samples. Ti contents in all of amphiboles are less than 0.5 atoms per formula unit. Al^{IV} has a direct relation with Ti in these minerals which may show increasing of Si in crystal lattice with differentiation in melt. The composition of all of the amphiboles in gabbro to granite samples in the (Al^{IV}) versus $(A \text{ site} + 2Ti + Al^{VI} + Fe^{3+})$ diagram lie around the line with 1:1 ratio. So variation in composition of amphiboles from each unit is a function of Al^{IV} and replacement of Fe^{3+} , Al^{VI} , Ti and $(Na + K)_A$ in octahedral site.

Studying of Fe contents in different units of this complex show that mafic minerals (such as amphiboles) in complex have more Fe with increasing of SiO_2 in host rock.

As amphiboles in intraplate tectonomagmatic setting (I-Amph) have more Na_2O and TiO_2 than ones in subduction setting (S-Amph) (Coltorti et al, 2007), the amphiboles in Natanz plutonic complex plot in the "S-Amph" field in the diagram designed for this classification.

Is it possible to date the shear zone activity along the Andros detachment, Cyclades, Greece?

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The Attic-Cycladic crystalline belt (ACCB) in the central Aegean region is a major tectonostratigraphic unit of the Hellenides. The ACCB records a complex structural and metamorphic evolution which documents various stages of the closure of the Neotethys ocean, the collision of continental fragments and extension-related exhumation. Two major structural groups of tectonic units with contrasting metamorphic histories can be distinguished, that are separated by low-angle normal faults. A prerequisite to develop an improved tectonic history of the study area is dating of tectonic displacement along major shear zones. Such ages will provide important constraints for refining existing geodynamic models. On Andros, a notable detachment is exposed and we tested the possibility to date the time of shear zone activity by means of Rb–Sr geochronology.

The metamorphic succession of Andros can be subdivided into two tectonic units, the Makrotantalón Unit and the Lower Unit. The structural position and geochronological constraints suggest that the Makrotantalón Unit belongs to the upper group of units of the ACCB, which has not been affected by HP/LT metamorphism. The Lower Unit can be correlated with the Cycladic blueschist sequences. Biostratigraphic evidence suggests that the rocks of the Makrotantalón Unit are older than those of the structurally lower sequences, implying that the tectonic contact between both units originated as a thrust fault (Papanikolaou, 1978). During subsequent regional extension, the contact zone was reactivated as a low-angle normal fault (e.g. Avigad et al., 1997). The detachment is well-exposed along the NE coast of Andros (Mehl et al., 2007), but here the overlying sequences are either submerged below sea level or were completely removed by erosion. In the NW part of the island the tectonic contact is roughly outlined by serpentinites, but the exact position of the detachment is difficult to localize. During this study detailed field work focusing on the presumed contact zone revealed a key location that displays a weak angular unconformity with cohesive cataclasites and/or pseudotachylites.

Rb–Sr geochronology was carried out on 10 samples representing clastic metasediments, calc schists and greenschists that were collected within a distance of <5 to ~50 m on both sides of the detachment. To characterize the white mica populations used for geochronology, polished thin section were prepared from splits of the phengite separates. Electron microprobe analyses indicate variable compositions, suggesting the presence of mixed populations. Multigrain dating of such populations can not provide accurate and precise ages but can only provide an upper time limit for tectonic displacement. For samples interpreted to represent the Lower Unit, internal mineral isochrons indicate apparent ages between 42 and 25 Ma. Samples collected above the contact zone fall within the range from 73 to 35 Ma. All these dates are similar to previously reported Rb–Sr phengite ages for samples collected at greater distance from the tectonic contact, interpreted to indicate variable degrees of greenschist facies overprinting at c. 23–21 Ma (Bröcker & Franz, 2006). A higher degree of disturbance or a distinct younging trend towards the tectonic contact is not developed. The scatter in apparent ages can not specifically be linked to shear zone processes and instead is considered to record the influence of regional metamorphic overprinting that caused incomplete resetting of pre-existing mica populations in the hanging and the footwall of the fault zone. Due to the lack of complete recrystallization, the rock sequences exposed along the Andros detachment are not suitable for direct dating of deformation.

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Übertragung und Adaption der KAK-Methode aus der Bodenkunde auf Seesedimente aus Bergbauseen der Braunkohle

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Eine wichtige Kenngröße zur Einschätzung reversibel gebundener Ionen ist die Kationenaustauschkapazität von Böden. Die Methode (nach Lavkulich, 1981) mit Ammoniumacetat als Austauscher bei pH 7 findet in der Bodenkunde in ihrer Anwendung eine weite Verbreitung. Diese Methode, sowie die Methode der Messung der effektiven KAK (VDLUFA, 1993) auf Seesedimente aus Bergbauseen zu übertragen war Ziel dieser Arbeit. Dazu wurde das Seesediment von 3 Bergbauseen aus der Lausitz mit unterschiedlichen Eigenschaften untersucht. Das Sediment des Restlochs 111 (Probenahmestelle R11) mit einem pH Wert von ca. 3 repräsentiert einen, durch die Verwitterung von Pyrit, stark versauerten See. Die Sedimente des Restloch 1223 und des Restloch 111 (Probenahmestelle R12) liegen durch Ausprägung einer konstanten Schichtung des Wassers im reduzierten Milieu mit einem pH Wert von ca. 6 vor. Aufgrund der ganzjährigen Schichtung des Waldsees befindet sich auch das Seesediment dieses Bergbausees im reduzierten Zustand, wobei der pH Wert durch Sanierungsmaßnahmen aktuell im schwach alkalischen Bereich liegt. Diese Spannweite des pH Wertes umfasst auch in etwa den Anwendungsbereich der Messmethode der Kationenaustauschkapazität.

Bestimmt wurden potentielle und effektive Kationenaustauschkapazitäten, wobei auch austauschbare Schwermetalle mit berücksichtigt wurden. Unter Berücksichtigung des Einflusses auf die gemessene effektive Kationenaustauschkapazität wurden unterschiedliche Methoden der Probenaufbereitung des Seesedimentes gegeneinander verglichen. Ebenso ist der Zusammenhang zwischen Gesamtkohlenstoffgehalt und Höhe der potentiellen Kationenaustauschkapazität Teil der Untersuchung.

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A natural experimental petrology lab to study aspects of mantle metasomatism: the Heldburg phonolite, Thuringia

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The phonolite from Heldburg (Thuringia, Germany) is one of a handful of phonolites worldwide that are known to contain mantle xenoliths. They are often disaggregated to microxenoliths and xenocrysts, where magnesian olivine and orthopyroxene are by far the dominating phases. Both minerals are not stable in contact with the alkaline phonolite melt and are rimmed by reaction zones a few tens of micrometers wide. These complex reaction rims are too thin and microcrystalline to allow detailed investigation by optical microscopy, but can be studied with electron beam analytical and optical methods in great detail.

The reaction products are diverse and in some instances contain zircon together with a SiO_2 -phase, which is surprising in this SiO_2 -undersaturated environment and points to strong local deviations from overall equilibrium conditions in the reaction zones. The most frequent type of reaction rims consists of phlogopite rims between olivine and melt, and zoned amphibole-phlogopite rims between orthopyroxene and melt, where amphibole forms in the inner part of the reaction zones and phlogopite outward in contact with the melt. These reaction rims are typically well-organized regarding mineral composition, and within the mineral zones regarding chemical composition. Where orthopyroxene contains pigeonite lamellae they proceed as Ca-enriched stripes throughout the reaction zones on element distribution maps, indicating that (i) rim growth occurs totally by replacement of the magnesian silicates, and (ii) that the growth in rim thickness was much faster than the internal redistribution of compositional contrasts within the mineral zones, and (iii) that the chemical zonation of the rims records original growth zoning without significant later redistribution of elements.

The amphibole in the reaction rims is K-bearing richterite, that has chemical resemblances with the K-richterite occurring together with phlogopite in the MARID suite of xenoliths in kimberlites and K-richterites in metasomatized mantle xenoliths outside the kimberlitic context¹. It is compositionally almost identical with richterite that was synthesized by reaction of an aqueous fluid with model peridotite in a temperature gradient in an experiment designed to mimic mantle metasomatism^{2,3}. The Heldburg phonolite provides us with another mechanism to produce K-Richterite-Phlogopite aggregates by replacement of harzburgitic material in a chemical potential gradient. We therefore consider the Heldburg phonolite a natural experimental petrology lab devised to study aspects of mantle metasomatism.

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Preliminary experimental results on phase relations in the system K_2O - MgO - Al_2O_3 - SiO_2 - H_2O at pressures up to 10 GPa

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Observations on diamond-bearing rocks from the Erzgebirge in Saxony and the Kokchetav massif in Kazakhstan clearly demonstrate that rocks of pelitic composition can be buried to depths of 150 km and more. In addition, calculations of temperatures in inner crustal portions of downgoing slabs (Gerya et al., 2002; Stöckhert & Gerya, 2005) point to geotherms as low as 3°C/km. Thus, we performed experiments with different chemical bulk compositions in the system K_2O - MgO - Al_2O_3 - SiO_2 - H_2O (KMASH) to determine phase relations at pressures ranging from 5 to 10 GPa and temperatures between 600 and 1200°C in order to learn more about the metamorphic fate of pelitic material at great depths. These experiments were undertaken in a conventional piston-cylinder apparatus (only 5 GPa) and a Walker-type multi-anvil press using WC-cubes with 8 mm TEL. The run batches consisted of 8 mg dried KMAS gel and 1 mg H_2O each. The pressure in the multi-anvil press was calibrated by the Bi (II) – Bi(III) transition at room temperature and the coesite-stishovite equilibrium at high temperatures controlled with W-Re thermocouples.

According to investigations of the first run products with an X-ray powder diffractometer and an electron microprobe the SiO_2 excess products contained phengite and K-cymrite whereas phengite, enstatite and spinel appear in SiO_2 -undersaturated products. Coexisting phlogopite shows a considerable solid solution towards muscovite. Thermodynamic calculations with the computer software PERPLE_X (Connolly, 1990), using the data set by Holland & Powell (1998) augmented by phases such as K-cymrite, K-hollandite and slightly modified in regard of OH-topas etc., were undertaken parallel to the experiments. The calculated phase relations and the new experimental results are, so far, widely in agreement.

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STEM/EELS investigations of the mechanism of experimental ilmenite alteration in dilute acids

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Ilmenite (FeTiO_3) is an important mineral being the raw material for the production of titanium for the high-tech industries. The production process typically involves acid treatment, which oxidises and removes the Fe, leaving a TiO_2 -rich phase, generally rutile. In nature ilmenite initially undergoes weathering through oxidation and removal of Fe to form an apparently continuous series of compositions from ilmenite to pseudorutile (ideally $\text{Fe}_2\text{Ti}_3\text{O}_9$) as a transitional phase (Grey and Ried, 1975). In the second stage, pseudorutile undergoes incongruent dissolution, resulting in the formation of rutile, hematite, and goethite (Schroeder et al., 2002). However detailed information of the ilmenite alteration mechanism in acids is still not available. The understanding of structural and chemical relationships at the nanometre scale between ilmenite and the alteration products is essential because it can be help to understand the exact alteration mechanism of ilmenite, and hence optimise the industrial process¹

A hard rock ilmenite from the Manvers granite pegmatite dike (Canada) with starting composition $\text{Fe}_{0.94}\text{Mn}_{0.06}\text{Ti}_{0.99}\text{O}_3$ was used in this study. The mineral was cut into cubes with length of 1.6 mm. The dissolution experiments were carried out in sulphuric and hydrochloric acid solutions at 150 °C for 5 to 31 days. The resulting products are studied by electron microprobe, scanning and transmission electron microscopy.

The alteration begins at the original ilmenite crystal surface and has also taken place along fractures in the ilmenite. However, the fracture pattern did not exist before the reaction and appears to have been generated by the reaction. The fracturing provides pathways for fluid infiltration and enhances the alteration process. The fracturing is possibly driven by volume changes associated with dissolution of ilmenite and reprecipitation of a product phase from the interfacial solution. Element distribution maps and chemicals analysis within the fractures of the reaction products is rutile – no phases between the ilmenite and rutile were detected. The Fe is removed into solution. The chemical and structural changes induced by reactions with fluids at relatively low temperatures take place by discrete dissolution-reprecipitation mechanisms rather than by solid-state diffusion.

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Mineral Exploration in the Harz Mountains – Preliminary Results

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In 2008, Harz Minerals GmbH, a fully owned subsidiary of Scandinavian Highlands Holding A/S, was granted an approx 1250 km² exploration license (Erlaubnis) in the Harz Mountains. Well aware of the comprehensive exploration history, the company didn't expect to locate near surface ore bodies, but encouraged by experiences with modern helicopter borne EM technology it was decided to look for deeper targets.

With the aim to locate a Rammelsberg-like SEDEX deposit, a seven hundred line-kilometre TEM survey was initially conducted over the middle Devonian Goslar Basin in the West Harz.

The first results showed the presence of larger conductors in the Gosetal area, less than two kilometres west of the Rammelsberg deposit. Similar to the Rammelsberg deposit, the Gosetal anomaly lies on the south-eastern margin of the Middle Devonian Goslar Basin, at the shelf edge of the Mid Harz Rise.

Access to the mine archives enabled the construction of a detailed three dimensional model of the geology in the Gosetal area. The model has provided important constraints for the 3D inversion of the TEM data.

It is now evident that the TEM conductor occurs at the same stratigraphic position as the Rammelsberg deposit – located within the ore equivalent-horizon ("Lager Horizont"). Structurally the Gosetal anomaly fits with strike of an overturned fold limb between a syncline-anticline pair.

Geochemical vectoring as well as a recent soil gas survey supports the presence of an ore body at the position of the TEM conductors.

Despite the location adjacent to Rammelsberg, the Gosetal anomaly has previously not been intersected by exploration drilling. A drill hole east of the anomaly intersects the "Lager Horizont" where it contains 4% base metals over 2 m.

As only the conductance – the product of width and conductivity – can be modelled from TEM data, volume can't be predicted without assumptions. However, the anomaly holds the potential for a mineralisation comparable to Rammelsberg.

Diffusion-controlled growth of monomineralic Åkermanite reaction rims in the ternary system CaO-MgO-SiO₂

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We investigated the solid-state reaction between Monticellite (CaMgSiO₄) and Wollastonite (CaSiO₃) that produces a monomineralic Åkermanite (Ca₂MgSi₂O₇) reaction rim due to the reaction:



Starting materials were synthetic Monticellite single crystals provided by the "Institut für Kristallzüchtung", Berlin and natural wollastonite crystals from Ciclova-Romina, Banat, Romania. Crystal cylinders of both reactands were produced by drilling and dried at 800 °C for about 1 h. Both sides of the crystals were subsequently polished with diamond powder. A thin film of platinum markers was deposited on the Monticellite surface, acting as inert marker. The crystal-cylinders were dried at 110 °C for 30 minutes and assembled in an inner platinum capsule (diameter: 3.0/ 3.2 mm) that was closed by cold sealing. The inner capsule was subsequently transferred in an outer Platinum capsule (diameter: 4.0/ 4.4 mm), which was hot-sealed immediately. Throughout the preparation procedure special care was taken to keep the experimental setup as dry as possible. All experiments were performed in a Harwood-type IHPV at 5 kbar, varying temperatures between 1000°C and 1200 °C with durations of 5 min to 60 h. As pressure medium pre-dried Argon was used. After the experiments, samples were embedded in epoxy and polished perpendicular to the initial interfaces. Polished samples were examined by electron microprobe (JEOL JXA-8500F) and transmission electron microscopy (FEI TecnaiTMG2 F20 X-Twin transmission electron microscope). The inert platinum markers are always located in the centre of the Åkermanite rim. In combination with textural evidences this suggests that they trace the initial interface, implying that the rim grows symmetrically from the interface towards two directions. This indicates that CaO and SiO₂ are immobile relative to the MgO component. Consequently, rim growth is controlled by the mobility of MgO due to the partial reactions:



at the Monticellite-Åkermanite interface and:



at the Åkermanite-Wollastonite interface, respectively. We can therefore combine SiO₂ and CaO, treating them as one immobile component, so that the system becomes binary. Consequently, MgO mobilities were calculated according to the model of Abart et al. (2009). Effective bulk diffusion coefficients at 1200 °C are estimated at $\log D_{\text{MgO}} = -15.7 \pm 0.1 \text{ m}^2/\text{s}$ and at 1100 °C at $\log D_{\text{MgO}} = -16.2 \pm 0.1 \text{ m}^2/\text{s}$. This yields a preliminary Arrhenius law with the activation energy $E_a = 170.2 \pm 16.9 \text{ kJ/mol}$ and a pre-exponential factor of $\log D_0 = -9.67 \pm 1.28$ that describes the temperature dependency of the effective bulk diffusion coefficient. We also performed powder experiments in the IHPV, where Monticellite seeds (grain size: 100-200 µm) were embedded into a Wollastonite powder (grain size: < 20 µm). Åkermanite rims grown at 1200 °C and 5 kbar are significantly thicker, resulting in much higher MgO-mobilities at $\log D_{\text{MgO}} = -14.3 \pm 0.1 \text{ m}^2/\text{s}$. Powder experiments differ from single crystal experiments because the surface area of the starting materials is much larger. As minute amounts of water are always adsorbed even on pre-dried powders, the water activity, though still very low, is somewhat higher. This changes MgO-mobilities drastically. If so, metamorphic mineral coronas of a specific bulk composition do not only contain the P-T-time record of a particular rock, but also record the water content of a presumably dry system.

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Separating the twins: Nb-Ta fractionation by partial melting at the titanite-rutile transition

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Niobium and Ta are considered to be geochemical twins due to their equal valence (5+) and almost identical ionic radii. However, during the evolution of the Earth distinct geochemical reservoirs with different Nb/Ta have developed implying that fractionation of Nb from Ta may be a much more common process than hitherto assumed. The upper mantle and the continental and oceanic crust are both characterized by subchondritic Nb/Ta and the difference in Nb/Ta between the upper mantle (~14-16) and the continental crust (~12) requires a fractionation process during the formation of continental crust. Archaean granitoids of the tonalite-trondhjemite-granodiorite (TTG) suite represent Earth's early continental crust. These TTG's are, opposite to modern crust, characterized by sub- and suprachondritic Nb/Ta, indicating that Nb-Ta fractionation was already active during early crust formation. The nature of this early fractionation process, however, is not understood. Nb and Ta preferentially partition into Ti-minerals and processes associated with crust formation in subduction regimes occur at a depth where titanite and/or rutile are the dominant Ti phases. Although both minerals coexist along a certain depth range, titanite is more abundant at shallower depth, while rutile becomes more abundant at greater depths. Here we present a new model on how Nb may be fractionated from Ta during partial melting of titanite- and rutile bearing subducted oceanic crust in subduction zones. We argue, based on natural observations and on partitioning systematics, that titanite in equilibrium with rutile is characterized by relatively low Nb/Ta while rutile displays much higher Nb/Ta. During partial melting of a titanite- and rutile-bearing eclogite, melting relations prefer titanite over rutile which implies that titanite will dominate the Nb-Ta budget of the melt during partial melting of the subducting slab, whereas rutile is expected to control the residue as the slab continues to descend. As a consequence, the resulting melt has first a very high Nb/Ta at low degrees of melting due to the presence of titanite in the residue. If melting proceeds, titanite in the residue becomes successively less abundant, leading to decreasing Nb/Ta ratios in the melt at higher degrees of melting and with a residue, which is dominated modally by rutile. At even higher degrees of melting rutile is expected to be the only residual Ti phase, and consequently, Nb/Ta of partial melts will be high. The aforementioned mechanism successfully explains the observed extreme variation of Nb/Ta observed in TTG's and other rock series and may help to shed some new light on fractionation processes of Nb from Ta during the early evolution of the Earth.

Plagiogranitic melt impregnations in abyssal peridotites: their formation, alteration and influence on serpentinization

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Hydration of rocks of the oceanic lithosphere by interaction with seawater influences the physical and chemical properties of the lithosphere, and thus it is of importance for the rheological behavior as well as for chemical budgets. We examined Amph-Chl schists ("fault schists") and surrounding serpentinites from an ultramafic-hosted oceanic detachment fault at the slow-spreading Mid-Atlantic Ridge (ODP Leg 209, Site 1270; Jöns et al., 2009). These samples show evidence for both melt impregnation and intense hydration related to shearing, and thus they are an ideal subject to study the interrelation between magmatism, tectonism and fluid flow.

Fault schists occurring on shear zones consist of euhedral crystals of brownish magnesio hornblende ($X_{Mg} = 0.86-0.96$) situated in a matrix of chlorite ($X_{Mg} = 0.82-0.95$). Late-stage fibrous actinolite/tremolite ($X_{Mg} = 0.85-0.93$) rims the magnesiohornblende. Accessory minerals are zircon and apatite. The latter minerals indicate that shear zones developed where an evolved melt (i.e. plagiogranite) had impregnated the peridotites. This interpretation is confirmed by results of Ti-in-zircon thermometry ($T \approx 820$ °C). The ultramafic host rock of the fault schists is an almost completely serpentinized harzburgite (<10 vol.% of primary minerals preserved). Serpentine ($X_{Mg} = 0.88-0.97$) replaces olivine in mesh textures and orthopyroxene in bastite textures. Chromium-bearing spinel is the least altered primary mineral phase. In immediate vicinity of fault schists, serpentine and magnetite are secondary minerals, whereas brucite is generally absent.

Whole-rock geochemical measurements show that contents of rare earth elements of fault schists (10 to 100 times chondritic) and adjacent serpentinites (up to 10 times chondritic) are comparatively high, which is in general agreement with the interpretation of plagiogranitic melt impregnations. Reaction path models (calculated using EQ3/6) for interaction of a seawater-derived fluid with a 70:30 mixture of fresh harzburgite and plagiogranite are able to replicate the observed mineral assemblage of fault schists. Other models indicate that increased silica activity adjacent to former plagiogranitic melt impregnations inhibits brucite formation in serpentinites.

We conclude that detachment fault zones are major fluid pathways for hydration of the oceanic lithosphere. Such fluids could reach greater depths, where they promote partial melting of gabbroic intrusions and formation of plagiogranitic melts. When plagiogranitic melt impregnations are hydrated during cooling, chlorite forms at temperatures of ca. 500 °C, when olivine in the surrounding harzburgites is still stable. Thus high temperature shear zones preferentially follow pre-existing melt veins. Although it might be possible that fault schist lithologies form from an ultramafic protolith under conditions of extremely high fluid flux, conditions for fluid-related element transport are particularly favorable at interfaces between different lithologies, i.e. where high chemical potential gradients exist.

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From orogenesis to passive margin: the cooling history of the Bemarivo Belt (N Madagascar)

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During the Neoproterozoic, Proto-Madagascar was a micro-continent situated between the Congo Craton of East Africa and the Dharwar Craton of India. All these cratonic blocks collided in the Late Neoproterozoic/Early Cambrian and formed the central part of the supercontinent Gondwana. Details about the timing and character of related geodynamic events are unknown for many tectonic units of Madagascar. For unraveling the sequence of metamorphic events, a combined study of metamorphic reaction textures with precise in-situ geochronology of metamorphic minerals is necessary. We performed U-Th-total Pb dating of monazite and SHRIMP U-Pb dating of zircon in combination with pressure-temperature (P-T) path reconstructions of rocks from the Bemarivo Belt of northern Madagascar (Jöns et al., 2006; Jöns et al., 2009). The study is complemented by apatite and titanite fission-track dating, allowing also assess the Gondwana supercontinent breakup, involving crustal thinning, brittle deformation and denudation along the evolving sedimentary basins.

Metapelitic rocks show evidence for a clockwise P-T evolution. The prograde path in the kyanite stability field is documented by kyanite inclusions in garnet as well as GASP barometry (garnet core + plagioclase inclusion). Peak-metamorphic conditions of $T = 900\text{--}950\text{ }^{\circ}\text{C}$ and $P = 8\text{--}9\text{ kbar}$ are deduced from feldspar thermometry and GASP barometry (garnet rim + matrix plagioclase). In vicinity of charnockite massifs temperatures might have been slightly higher (ca. $970\text{ }^{\circ}\text{C}$), as evidenced by aluminous orthopyroxene (ca. 8 wt.%) in garnet-sillimanite-bearing metapelites. Peak-metamorphism was followed by near-isothermal decompression to 5-7 kbar, demonstrated by extensive formation of cordierite around garnet, and subsequent cooling.

Monazite shows a polyphase growth history, with an M_1 stage correlating with the prograde P-T path and an M_2 stage marking the high temperature period. M_1 is dated at ca. 540 Ma by both U-Pb zircon and U-Th-total Pb monazite geochronology. The M_2 stage is only found in monazite rims and dated at ca. 521-513 Ma. The deduced P-T-t evolution is supposed to reflect the attachment of the Bemarivo Belt to the Gondwana supercontinent. Metamorphic ages are comparable to geochronological data from Southern and Western India; however, evidence for an older metamorphic event, which is often observed in rocks from East Africa, has not been found in rocks from the Bemarivo Belt.

Titanite and apatite fission-track ages ranging between ca. 320-160 Ma indicate differential cooling of ca. $150\text{ }^{\circ}\text{C}$ within the Bemarivo Belt during the separation of Madagascar from East-Africa and India. Inverse thermal models show that the main cooling episode occurred from the Carboniferous to Early Triassic, probably related to rift shoulder denudation, correlating with the main episode of intracontinental basin development within Gondwana.

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X-ray computed microtomography in geoscience: two case studies

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X-ray computed microtomography (μ -CT) allows - expressed in simplified terms - the reconstruction of 3-dimensional images of bodies. The μ -CT technique therefore represents a powerful tool to study internal textures of rocks, e.g., the geometry of pore spaces within rocks. The geometry of pore space of rocks is interesting in many respects as it provides information about, e.g., (a) physical properties of quasi static pore space (e.g., the hydrodynamic behaviour of sandstones) or (b) the nature of dynamic processes that shaped the pore space itself (e.g., bubble formation and degassing of magmas studied on pumice rocks). Based on two case studies we will describe these two aspects in more detail below.

In both studies the X-ray computed microtomograph Skyscan 1172 of the Institute of Geosciences, Kiel, (in service since August 2008) was used. Specifications of the μ -CT device are as follows: maximum tube voltage 100 kV; maximum tube power 10 W; resolution per pixel 0.7 to 35 μ m (depending on the beam geometry).

Case study (a) physical properties of quasi static pore space (e.g., the hydrodynamic behaviour of sandstones): this study* focuses on the mesopore space of sandstones. These sandstones represent reservoir rocks for the geological storage of CO₂. In laboratory experiments we simulate chemical and mineralogical reactions at or near by sequestration sites of CO₂ in sandstone aquifers (see Beier et al., this volume). The changes of microstructures of the reservoir rocks due to geochemical processes associated with the geological storage of CO₂ are monitored using μ -CT by reconstructing the internal textures of the individual starting materials and the corresponding post-run charges. This is possible because μ -CT analyses are non-destructive. Due to the reconstruction of the internal texture of the same sandstone sample before and after the experiment we are able to localise and quantify the dissolution of carbonate cementation as well as the precipitation of halite caused by the drainage of brine during the injection of CO₂. Furthermore, we are currently exploring software to have the possibility to extract pore network models based on tomographic data. The pore network models can then be used to derive relative permeabilities of the bodies and residual saturation of the existing pore spaces.

Case study (b) dynamic processes that shaped the pore space itself (e.g., bubble formation and degassing of magmas studied on pumice rocks): to understand the processes of magma fragmentation and modes of eruption we investigate bulk vesicularity and vesicle texture (bubble shapes, bubble size distribution, impact of heterogeneous nucleation). Not only pore spaces (bubbles), but also 'simple' cracks can be detected using μ -CT. We might therefore be able to answer the question: Is the permeability of pumice rocks mainly based on the connectivity of the bubbles (i.e., is the permeability of magmatic origin), or do cracks significantly contribute to the permeability? Cracks usually develop later during the cooling of the pumice rock. Thus the permeability would not be only of magmatic origin.

In general, microstructural elements on the scale of the pore space or even with sizes below the detector resolution pose a challenge to pore space analysis. To estimate the uncertainties of determined pore space volume (due to classification of partially filled voxels as part of pore spaces or as part of the surrounding matrix) we currently compare images of 2D slices (μ -CT) with images based on photographs of 2D microsections (thin section photos - optical microscopy; BSE images - electron microprobe).

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Light elements as tracer minerals for hydrothermal or magmatic overprint in natural rocks

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The light elements Li, Be and B and their isotopes are important tracers for mass transfer in terrestrial systems. The mobility of Li, Be and B in hydrous fluids is strongly dependent on pressure and temperature. At moderate P and T, mineral/fluid partition coefficients increase in the order $K_B^{\text{min/liq}} < K_{\text{Li}}^{\text{min/liq}} \ll K_{\text{Be}}^{\text{min/liq}}$, but only if there are no significant amounts of F and Cl (Brenan et al., 1998a; Franz and Morteani, 2002; Kaliwoda et al. 2008).

At higher pressures (>3 GPa), the compositions of hydrous fluid and silicate melt converge along a miscibility gap, and in supercritical liquids $K_{\text{Be}}^{\text{min/liq}}$ may be similar to or even smaller than $K_B^{\text{min/liq}}$ (Tenthorey and Hermann, 2004; Kessel et al., 2005, Kaliwoda et al. 2008). The different behaviour of Li, Be and B in rock-melt and rock-hydrous fluid systems at moderate pressures offers the chance to use the relative abundances of these three elements for example in metasomatized mantle rocks to constrain the nature of the metasomatic agent (i.e. melt versus hydrous fluid).

In general every rock overprinted by melt displays an increase in all (Li, Be and B), but rocks overprinted with fluids show only an increase in the fluid mobile Li and B but hardly in Be, with the only exception of very F and Cl rich fluids.

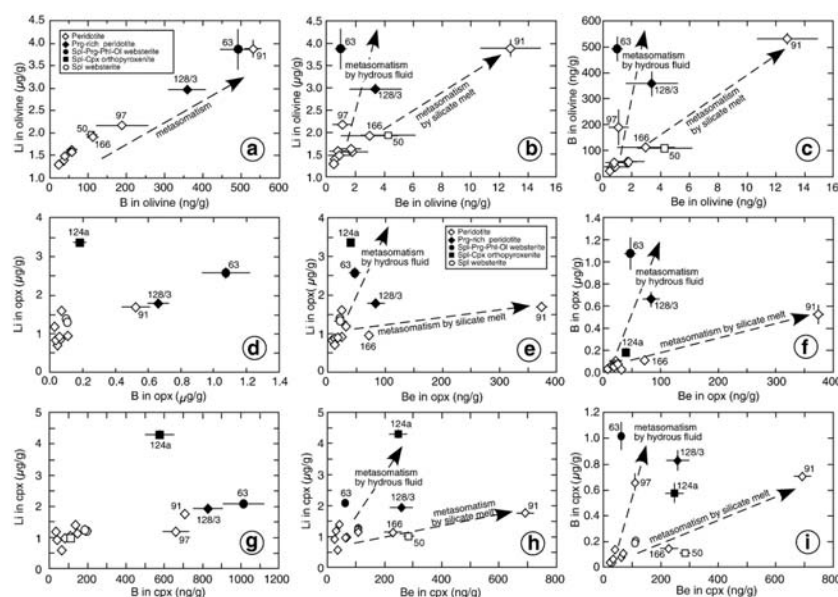


Fig.1: Behaviour of Li, Be and B in mafic minerals. The overprint via fluids or melts could be easily seen by the amount of Li and B versus Be.

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New Investigations on the Meteorite Neuschwanstein

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The meteorite Neuschwanstein, fallen in 2002 near the castle of Neuschwanstein (Bavaria), is classified as EL6-chondrite. A summary of its recovery is to be found in Hochleitner and Heinlein (2003). Neuschwanstein has a re-crystallized structure dominated by enstatite and plagioclase with kamacite, troilite, daubreelite, oldhamite, graphite, alabandite, cristobalite, schreibersite and sinoite [Bischoff and Zipfel 2002; Hochleitner et al. 2004]. Only a small number of chondrules are left. Optical features; i.e. undulatory extinction of plagioclase indicates, that the meteorite is weakly shocked (S2-3). The absence of maskelynite was proven by Micro-Raman-Spectroscopy (LMU, München). All feldspars showed sharp peaks indicating a high grade of crystallization. Graphite is found in form of elongated large phases often in contact with troilite and pyroxene and also identified by Micro Raman Spectroscopy. Electron microprobe (LMU, München) investigations revealed tiny crystals of a SiO₂ phase inter-grown with feldspar in a "myrmekitic" style. Raman spectra showed the phase to be cristobalite. There is no clear evidence within the sample for an impact melting event, but the existence of cristobalite points to a high temperature event in the mother body of Neuschwanstein.

The bulk chemistry of Neuschwanstein is characterised by lower La abundance, K and Na depletion, low Mn/Mg ratio and low Zn concentration compared to other EL-chondrites [Zipfel and Dreibus 2003].

Lithium measured by SIMS (Universität Heidelberg) along traverses in pyroxenes displays no clear zoning but scatters around 0.6 - 1.5 µg/g with a tendency to be lower at the rim of the crystals. Beryllium follows the trend of Li but the amount of Be in pyroxene is somewhat lower (0.01 – 0.09 µg/g). The boron content varies between 0.05 and 0.7 µg/g; partly increasing towards the rim.

In feldspars the Li content scatters around 1.1 µg/g, Be is in the range of 0.2 µg/g and the B content is about 0.6 µg/g.

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The complexity of replacement reactions: The calcium carbonate to calcium phosphate hydrothermal transition

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Aragonite and calcite single crystals can be transformed into hydroxyapatite (HAP) pseudomorphs by hydrothermal treatment with $(\text{NH}_4)_2\text{HPO}_4$ solution (Kasiopas et al., 2008). The preservation of morphology and the extended porosity present in the new phase are indicative of a coupled mechanism of dissolution and precipitation that takes place along a moving reactive interface (Putnis and Putnis, 2007). In this case, the replacement includes consumption of phosphate, release of carbonate and also affects the strontium that is present in the initial aragonite. Electron microprobe measurements showed that some of the strontium is incorporated in the apatite while the rest is released to the solution. Replacement reactions are quite complex processes that involve many variables. We have performed investigations using Raman spectroscopy in order to understand certain aspects of this replacement. We performed replacement experiments using phosphate solutions prepared with water enriched in ^{18}O (97%). The solution was not allowed to equilibrate before reaction, meaning that the ^{18}O for ^{16}O exchange which takes place between the oxygen atoms of the water molecule and oxygen in the PO_4 molecule of the solution would take place simultaneously with the replacement reaction. Raman spectroscopy of the HAP product was used to trace the ^{18}O from the shifts in the vibration modes in the PO_4^{3-} molecule due to the oxygen exchange. Apart from the main $\nu_1(\text{PO}_4)$ band located near 962 cm^{-1} , we observed four new bands near 945, 931, 919 and 908 cm^{-1} indicating species with increasing ^{18}O substitution. Our results indicate that the degree of ^{18}O equilibration in the solution is preserved by the solid during replacement. Differences in the intensity of the four vibration modes offer kinetic information on the replacement mechanism when compared with kinetic data of the $\text{H}_2^{18}\text{O}-\text{P}^{16}\text{O}_4$ exchange reaction in the solution obtained from in situ Raman investigations (Geisler et al., 2009). This method enables us to effectively trace the course of the replacement reaction and understand the meaning of the variations of oxygen isotopes in the resulting HAP. The current study aims to elucidate further some of the many complex aspects of replacement reaction mechanism that are observed in geochemical processes.

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Wasserumverteilung im System Salz - Bentonit

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Artgleicher Salzgrus ist das bevorzugte Versatzmaterial für die Resthohlräume in Strecken und Bohrlöchern in einem geplanten Endlager für hochradioaktiven Abfall in Salzformationen. Um die auf lange Sicht zugewiesene Barrierefunktion gegen potentielle Radionuklidträger erfüllen zu können, muss das lockere Material mit der durch den Gebirgsdruck ausgelösten Hohlraumkonvergenz kompaktiert werden. Nach Zhang & Stührenberg (1997), Stührenberg & Walter (2000) und Stührenberg (2007) kann eine deutliche Verbesserung dieser Kompaktierbarkeit durch die Zugabe geringer Mengen Ca-Bentonit (10 – 15 %) zum Salzgrus erreicht werden. Offensichtlich agiert der quellfähige Ton als eine Art Schmiermittel. Diese Wirkung lässt allerdings nach, wenn der Bentonit austrocknet, was üblicherweise bereits bei moderat erhöhten Temperaturen wie z.B. 60°C stattfindet. Aus diesem Grund wurde untersucht, ob dies in einem Gemisch aus Salz (im wesentlichen Halit) und Bentonit stattfinden kann. Setzt man ein bezüglich Wasser geschlossenes System voraus, das sich makroskopisch aus den abgedichteten Stollen und mikroskopisch durch geschlossene Poren ergibt, so stellt sich die Frage, ob a) der Bentonit innerhalb der Pore soviel Wasser abgeben kann, dass die schmierende Wirkung verloren geht und b) ob die innerhalb einer Pore generierte Luftfeuchtigkeit ausreicht, um eine Umverteilung des Wassers vom Bentonit auf das Salz zu ermöglichen.

Übliche Wassergehalte von industriellen Bentonitprodukten liegen zwischen 7 – 10 Gew.% (Wasser pro Einwaage), niedrigere und höhere Gehalte sind schwer zu gewährleisten, da sich das Material schnell den Umgebungsbedingungen anpasst und daher besondere Transportmaßnahmen ergriffen werden müssten. Die Wasserabgabe von Bentoniten ist insbesondere zur Erforschung der Wasserbindungsformen in den Smektiten (die quellfähigen Tonminerale, die die Eigenschaften des Bentonites bestimmen), intensiv untersucht; allerdings ausschließlich in offenen Systemen.

Die vorliegende Studie hat gezeigt, dass die relative Luftfeuchtigkeit in einer geschlossenen Pore, auch bei großem Porenvolumen (Bentonit/Porenvolumen bis 1:100), schnell derart steigt, dass keine weitere Wasserabgabe möglich ist. Das Austrocknen eines Bentonits in einem geschlossenen System ist daher nicht möglich. Andererseits ist bekannt, dass Salz (Halit) bei ca. 75 % r.L. große Mengen Wasser aufnimmt um einen gelartigen Zustand zu erreichen (Wise et al., 2008). Wenn also die relative Luftfeuchte in einer geschlossenen Pore 75 % übersteigt, dann wird die Umverteilung des Wassers vom Bentonit auf das Salz stattfinden, der Ton austrocknen und das Salz instabil werden. Die Faktoren, die die relative Luftfeuchte innerhalb einer geschlossenen Pore steuern, sind der Anfangswassergehalt des Bentonites sowie die Temperatur. Erwartungsgemäß wird bei Temperaturerhöhung Wasser vom Bentonit desorbiert, was die absolute Luftfeuchtigkeit erhöht. Die relative Luftfeuchtigkeit sinkt aber durch die Temperaturerhöhung. Da die kritische relative Luftfeuchtigkeit bei der Salz Wasser aufnimmt zumindest bis 80°C weitgehend unabhängig von der Temperatur ist, ist also keine Wasserumverteilung durch erhöhte Temperatur zu erwarten. Dies bedeutet aber andererseits, dass bei niedrigen Temperaturen eine Wasserumverteilung stattfinden könnte. Dies erfordert aber hohe Bentonit-Anfangswassergehalte von z.B. > 11 Gew.% im Fall der beiden Testmaterialien.

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Non-ideal behavior of Cu in core forming metal alloys. Implications for siderophile element contents of the Earth mantle.

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Siderophile elements are depleted in the Earth mantle compared to estimated bulk Earth compositions. This depletion is a consequence of core formation. The extent of removal of an element from the mantle is related to the metal-silicate partition coefficient ($D^{\text{met-sil}}$) of an element. The partition coefficients depend on the free energy of formation of the relevant oxide and the activities of the elements in metal and oxide in silicate. A similar formalism is used for sulfides. This often leads to a complex dependence of the partition coefficients on oxygen and sulfur fugacities, temperature, pressure, silicate melt and alloy composition. This study focuses on the influence of alloy composition on the $D^{\text{met-sil}}$ of Cu.

Fig. 1 shows the activities (a) of Ni, Co, Ge and Cu in binary iron-metallic element alloys (Fe-M, e.g., Fe-Ni) compared to the ideal behavior of the element ($a_M = X_M$; the diagonal in Fig.1). Ni and Co show a behavior very close to ideal, especially at low concentrations of Ni and Co in Fe-M alloys, whereas the activities of Ge and Cu are very different from ideality at these low concentrations: Ge has activity coefficients (γ) less than 1, implying higher siderophilicity than calculated from ideal behavior. The γ -values of Cu (γ_{Cu}) are larger than 1, leading to higher Cu concentrations in the silicate than expected (i.e. effective lithophilicity is higher). In general, this non-ideal behavior of metallic (siderophile) elements present as traces in iron alloys has to be taken into account when calculating the expected contents of these elements in the Earth mantle based on experimentally determined $D^{\text{met-sil}}$.

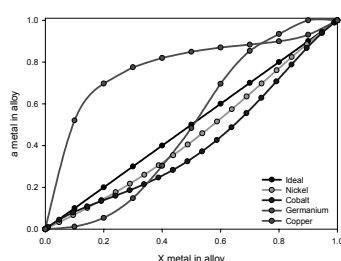


Fig. 1: Activity of Ni (green), Co (blue), Ge (green) and Cu (red) in binary iron alloys. The black line shows the ideal behavior of an element in an iron alloy.

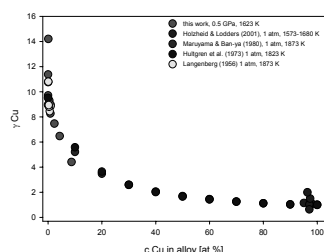


Fig. 2: Calculated γ_{Cu} values vs. Cu conc. in alloys.

Unfortunately literature data of γ_{Cu} are only available for Fe-Cu alloys with Cu concentrations above 1000 ppm whereas the estimated Cu content in core forming metal is ~ 190 ppm. The motivation of this present study was therefore to investigate γ_{Cu} in Fe-Cu alloys with relatively low Cu contents. Furthermore experiments with ternary Fe-Ni-Cu alloys were performed to test the influence of Ni. Metal-silicate partitioning experiments were performed in vertical gas mixing furnaces (1350°C) and piston-cylinder apparatus (0.5 GPa at 1350°C, Universität Kiel). The Cu content of the starting Fe-Cu alloys varied between 100 ppm and 12 wt. %. To test the influence of Ni, three experiments with Ni bearing Fe-Cu alloys were performed ($\text{Fe}_{94}\text{Ni}_5\text{Cu}_1$, $\text{Fe}_{90}\text{Ni}_9\text{Cu}_1$, $\text{Fe}_{84}\text{Ni}_{15}\text{Cu}_1$). The silicate starting material was a synthetic basalt komatiite. Major and trace element concentrations of all post run charges were analyzed using EMP (metal and silicate glass; Universität zu Köln) and LA-ICP MS (only silicate glass; Universität Münster). Activity coefficients of Cu were calculated using the molar fraction of Cu in the observed alloys (X_{Cu}) and the activity of Cu_2O in the coexisting silicate melt at known oxygen fugacity. The calculated γ_{Cu} values of this work and literature data as function of X_{Cu} are plotted in Fig. 2. The non-ideal behavior of Cu in Fe-Cu alloys is obvious. The calculated γ_{Cu} values are higher than expected based on literature data. Although the Cu concentration in alloy is as low as 100 ppm, Henry's law behavior of γ_{Cu} is not yet obeyed. Experiments with even lower Cu content of the Fe-Cu alloy are therefore in progress. Experiments with Ni-bearing Fe-Cu alloys show that Ni (0-15 wt.%) increases the lithophilicity of Cu. This is an important observation as meteoritic metal contains significant quantities of Ni (2 to 25 wt.%). Results of modeling the influence of the composition of core-forming alloys on expected Cu concentrations in the Earth's mantle will be presented at the meeting.

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Quantification of the ^{14}B -content in Synthetic Tourmaline: A Multi-methodical Study

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Olenitic tourmalines with different ^{14}B -content have been synthesized in an endloaded piston cylinder press at run conditions between 25 and 40 kbar, 600 and 750 °C and run durations of 120 to 215 h. The starting materials consisted either of oxide mixtures with Al-Si ratios for the ideal endmember olenite $\text{NaAl}_3\text{Al}_6[\text{Si}_6\text{O}_{18}](\text{BO}_3)_3\text{O}_3(\text{OH})$ or of a gel with the anhydrous composition $0.625\text{Na}_2\text{O} \cdot 4.5\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. To both starting materials different amounts of boron and sodium in excess were added. Comparatively, two samples of synthetic ^{14}B -containing olenite from a gel starting material of the above given composition of a previous work of SCHREYER et al. (2000) have been re-examined.

Within the investigated pressure interval olenitic tourmaline could be synthesised in all runs. Additionally AlBO_3 , quartz or coesite, ^{14}B -containing paragonite, kyanite or dumortierite occurred. The samples were investigated by X-ray powder diffraction, FTIR spectroscopy and electron microprobe. The data indicate that boron substitutes Si on the tetrahedral site via $\text{Si}^{4+} \leftrightarrow \text{B}^{3+} + \text{H}^+$. Rietveld-refinements show that the tourmaline samples have mean T-O-distances between 1.575(6) and 1.600(12) Å, indicating that B^{3+} ions ($\text{B-O} = 1.470$ Å) partly replace Si^{4+} ions ($\text{Si-O} = 1.620$ Å). Hence the ^{14}B -content varies between 1.0(4) and 1.8(2) pfu. The water content has been determined after LIBOWITZKY & ROSSMAN (1997) and confirms indirectly the ^{14}B -content in the tourmalines.

Our results indicate that the ^{14}B -incorporation in olenite increases with decreasing temperature within the investigated pressure interval. At 600 °C we observed a ^{14}B -content of more than 1.0 pfu. This is in good agreement with SCHREYER et al. (2000) and MARLER et al. (2002) who have suggested that ^{14}B in olenitic tourmaline is favored by low temperatures and high pressures. According to our results pressure has no effect on the ^{14}B incorporation at least - within the investigated pressure interval. This fits with the observations of ERTL et al. (2008) whose data base indicates that the ^{14}B -content in olenitic tourmalines does not change significantly with pressure at a given temperature. The pros and cons of the different analytical methods to study B^{3+} on the tetrahedral site of tourmalines will be discussed.

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Mineralogy of Bohemian porcellanites

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Rocks with a pyrometamorphic overprint caused by the combustion of coal-beds are a common observation in the neighbourhood of coal deposits (VENKATESH, 1952; MIYASHIRO, 1957; BENTOR et al., 1981; FOIT et al., 1987; COSCA et al., 1989; KALUGIN et al., 1991).

Pyrometamorphism results either in the generation of so-called clinkers or porcellanites or in the creation of paralavas. The formation of both is due to the exposure of the educts to a high temperature environment. But in difference to the generation of paralavas, the development of porcellanites is not dominated by fusing-processes.

Their generation is determined by a combination of the following factors (SOKOL et al., 1998):

- a) high temperatures, low pressures and a very short duration of thermal exposure
- b) extreme chemical heterogeneity
- c) aggressive gaseous atmosphere
- d) high and transient temperature gradients and oxidation-reduction potential gradients

The entirety of these factors results in the presence of a high number of different special minerals and mineral assemblages.

The investigated samples are from the coal basin of Most-Teplce in the Czech Republic. Aim of the study is the determination of the mineralogical, chemical and physical properties and the description of relations among each other. For this purpose analyses concerning the mineralogical composition were processed with XRD next to chemical investigation with the XRF and the microprobe. Furthermore colour values have been determined from VIS-spectra. They will be related with the metamorphic temperature estimated with the knowledge about the physicochemical and mineralogical properties of the porcellanites. It is assumable that the different colours of the porcellanites are also partly related to the different grain sizes in the specimens. An approach concerning the grain sizes will be made by so-called domain analysis with XRD which relates the size of the domains which show coherent X-ray reflects with the grain sizes. Typical minerals in the porcellanite are mullite, cordierite, cristobalite and hematite.

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Hydrothermale Stabilität von Nitrat – Cancrinit $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_3)_2(\text{H}_2\text{O})_2$

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Auf Grund ihrer physikochemischen und strukturellen Ähnlichkeiten mit Vertretern der Zeolithgruppe sind Cancrinite interessante Modellverbindungen für die Zeolithforschung. Cancrinite besitzen eine aus ε – Käfigen bestehende charakteristische Kanalstruktur. Die Kanäle sind dabei entlang der c-Achse der hexagonalen Struktur angeordnet. Das Strukturgerüst als Wirtsgerüst enthält Gastionen und Wassermoleküle, wobei Cancrinite mit verschiedenen Gastanionen synthetisiert werden können. Hier steht die Verbindung Nitrat Cancrinit (Idealzusammensetzung: $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_3)_2(\text{H}_2\text{O})_2$) im Vordergrund des Interesses. Für zukünftige Anwendungen wird die hydrothermale Stabilität dieser Verbindung untersucht. Die experimentellen Arbeiten zielen dabei sowohl auf die Möglichkeit des Abbaus der Gerüststruktur, als auch auf den Ersatz von Nitrat und Natriumkationen durch Wassermoleküle unter hydrothormaler Belastung.

Im Vergleich zu Sodalithen, bei denen bereits ähnliche Untersuchungen durchgeführt wurden [1], sollten die Gastanionen der Cancrinite auf Grund der Kanalstruktur mit einer entsprechend guten Zutrittsmöglichkeit für Wassermoleküle in die Struktur-Hohlräume eine geringere hydrothermale Stabilität aufweisen. Als Ausgangsmaterial der Untersuchungen diente hydrothermal synthetisierter Nitrat – Cancrinit [2]. Die Behandlungen erfolgten für die Intervalle von 4h, 8h, 12h, 24h, sowie 48h bei Raumtemperatur sowie unter milden hydrothermalen Bedingungen bei 353K. Vor und nach jeder Behandlung wurden jeweils das Probengewicht und der pH-Wert der fluiden Phase ermittelt. Veränderungen der Gerüststruktur wurden mit Hilfe von XRD-Messungen und mittels Rasterelektronenmikroskopie mit EDX-Analyse dokumentiert. Die in den Kanälen vorliegenden Nitratgruppen wurden mit der IR-Spektroskopie kontrolliert. Die Bestimmung des Nitrat- und Wassergehaltes erfolgte für ausgewählte Proben mit Hilfe der Thermogravimetrie. Das Thermische Verhalten wurde zusätzlich im Vergleich zum unbehandelten Cancrinit durch temperaturabhängige IR-Messungen (TIR) bestimmt.

Die Untersuchungsergebnisse belegen eine nur geringe hydrothermale Stabilität von Nitrat – Cancrinit. Die bereits erwähnte gute Zutrittsmöglichkeit für Wasser, bedingt durch die Kanalstruktur, ist hier als Hauptursache zu nennen. Im Unterschied zu den Sodalithen, die auf Grund ihrer Käfigstruktur und der Anordnung der Kationen vor den Käfigzutrittsöffnungen gut gegen Hydrolysereaktionen geschützt sind, ergibt sich somit für die Cancrinite eine wesentlich höhere Anfälligkeit gegenüber Reaktionen wie Hydrolyse oder Auslaugung. Besonders bei der Untersuchungsreihe bei 353 K konnte ein deutlicher Abbau der Gerüststruktur festgestellt werden. Das verbleibende Material zeigte dabei stets eine deutliche Abnahme des Nitratgehaltes und eine Zunahme des Wassergehaltes. Weiterhin konnte auch die Abnahme der Natriumgehalte nach intensiver Hydrothermalbehandlung festgestellt werden. Orientierende analytische Untersuchungen zeigten gleichzeitig eine Erhöhung des Si/Al-Verhältnisses der behandelten Cancrinite [3]. Weiterführende Untersuchungen sind notwendig, um die Möglichkeit einer „Dealuminierung“ der Cancrinitstruktur durch Hydrothermalbehandlung zu klären.

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The dissolution mechanism of sulphur in silicate melts with implications for the sulphur cycling in subduction zones.

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Understanding and modelling the volatile cycle in subduction zones still remains one of the most difficult tasks in order to understand the interaction of magmatic processes and climate change or to use volcanic gas emission as a tool to predict volcanic eruptions. Sulphur (S) is after H₂O and CO₂ the third most abundant volatile component in magmatic systems but compared to H₂O and CO₂ the incorporation mechanisms of S in silicate melts are poorly understood. The difficulties arise from great uncertainties of fundamental parameters that affect the S solubility such as the prevailing oxygen fugacity (fO_2). At subduction zone relevant fO_2 S can be dissolved as sulphide (S²⁻) and/or as sulphate (S⁶⁺; Carroll & Rutherford, 1988). This is important assessing the S flux because S is thought to be more soluble in natural magmas as S⁶⁺ than as S²⁻ (e.g. Jugo, 2009). Here we present the results of experimentally determined S solubilities in "simple" and analogues of natural melt compositions for various P-T- fO_2 conditions in combination with the S oxidation states in these glasses determined by various methods that are available ($\Delta\lambda$ S K α shift, S K-edge XANES, ³³S MAS NMR and RAMAN-spectroscopy). The results are used to deduce the dissolution mechanism of S in silicate melts.

In Fe-free glasses the total S solubility is a function of the degree of polymerisation and increases with decreasing NBO/T. At reducing conditions (QFM) highly depolymerised glasses dissolve twice the amount of S (up to ~2 wt. %) compared to oxidising conditions (QFM+4). Trondhjemitic glasses at 3 GPa have S concentrations up to 10000 ppm, which are at least one order of magnitude higher compared to results from lower pressures of 0.2 GPa (~500ppm). When determining the S oxidation state with $\Delta\lambda$ S K α shift or S K-edge XANES the glasses may experience significant beam damage (Wilke et al., 2008) resulting in deficient S⁶⁺/ΣS ratios. However, both methods are sufficient to determine reliable S⁶⁺/ΣS ratios by reducing the beam exposure time. S K-edge XANES also provides additional information on the local environment of S in the glass. In Fe-free reduced samples, a distinctive peak at 2466 eV and a small peak at 2472 eV are observed. In Fe-bearing samples these peaks are absent and replaced by a peak at 2468 eV. It is implied that the 2468 eV peak relates to direct Fe-S²⁻ bonding, which is also confirmed by RAMAN-spectroscopy. The 2466 eV peak suggested that a S-Si bond is involved. Both, RAMAN and ³³S MAS NMR show difficulties in determining reduced S species in the glass whereas sulphate appears detectable. Only in glasses that contain Fe the RAMAN spectra show a signal at ~400 cm⁻¹ indicating the presence of FeS in the glass.

The species dissolved in silicate glasses is S⁶⁺ as SO₄²⁻ at fO_2 > QFM+1.5. At fO_2 < QFM-1.5 S is dissolved as S²⁻. In Fe-free glasses S²⁻ is bonded with cations (e.g. Ca, Na) depending on glass composition. In addition direct bonding of S with Si occurs. With increasing Fe/S ratio in the glass direct Fe-S²⁻ bonding is observed, indicating that in natural systems S²⁻ may predominantly dissolve as FeS. At fO_2 between QFM-1.5 and QFM+1.5 S is dissolved as a mixture of S⁶⁺ and S²⁻. The relatively steep change of S⁶⁺/S²⁻ ratio with fO_2 is at lower fO_2 than previously reported for Fe-bearing systems (QFM+1; Jugo et al., 2009). Thus, for a fixed fO_2 at ~QFM S is dissolved as mostly S²⁻ in Fe-bearing systems and as S⁶⁺ in Fe-free systems. The oxidation state of S is therefore not only depending on the oxygen fugacity as previously assumed, but also depends on composition, in particular Fe.

In a subduction zone setting at high P partial melts from subducted MORB that are felsic and Fe-poor can carry an order of magnitude more S (close to 10000ppm) than previously determined for similar compositions at crustal pressures. Progressive melting of peridotite by slab liquids and increasing Fe/S may saturate the system in FeS. This could be important for ore-forming processes or the "excess sulphur" phenomena observed at several Arc volcanoes.

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Influence of clay microfabrics on the petrophysical properties of clays

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Claystones and bentonites are currently being investigated as potential host rock and geotechnical barrier, respectively, for radioactive waste disposal. For this application hydraulic conductivity, swelling properties, water uptake, rheological and mechanical properties are important. The most studied clays are the Opalinus Clay (Switzerland) and Callovo-Oxfordian clay stone (France). One of the goals is to develop a model being able to predict mechanical behaviour of clays under repository-like conditions.

The results of this study show that Opalinus Clay and Callovo-Oxfordian clay stone behave different with respect to the dependence of mechanical strengths on carbonate content. The failure strength of Opalinus Clay decreases with increasing carbonate content while the failure strengths of Callovo-Oxfordian clay stone increases. For the investigation of the microfabrics scanning electron microscopy of polished sections and image analysis were used. Opalinus Clay shows large elongated carbonate grains of shell fragments while Callovo-Oxfordian clay stones show a homogeneous distribution of fine-grained and more isometric carbonates. The most important result of this study is that not only the carbonate content but also the grain size distribution and shape and distribution of carbonates has an influence on the mechanical behaviour of the claystones.

In addition, the microfabric of 38 bentonites was investigated. During genesis bentonites undergo continuous maturation from glass to smectite. Almost all bentonites show glass relict structures. The microfabric of the bentonites, particularly the intergrowth with relict volcanic glass may have an additional influence on relevant geotechnical properties. Based on the optical characterisation a model of maturation was developed containing five alteration-classes. The following petrophysical properties of bentonites were determined and compared to the microstructural characteristics: density, porosity, BET-surfaces, abrasivity of bentonite suspensions, electrical conductivity, and water uptake capacity. The results show that all these properties are affected by the microfabric.

IR absorption coefficients for H₂O in nominally anhydrous minerals

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Infrared spectroscopy is a powerful tool to determine traces of OH and H₂O in minerals and glasses. The application is based on the Beer Lambert law $A = \epsilon \cdot c \cdot t$, where A is the absorbance, ϵ the absorption coefficient, e.g. in $\text{L mol}^{-1} \text{H}_2\text{O cm}^{-2}$, c the concentration in mol/L and t the thickness in cm. It has been shown in numerous experimental and theoretical studies, i.e. Paterson (1982) and Libowitzky and Rossman (1997) that ϵ generally increases with decreasing wavenumbers. However, this general trend seems to be valid only for hydrous minerals and glasses and should not be applied to water quantification in nominally anhydrous minerals (NAMs), which incorporate traces of water in their structures (e.g. Rossman 2006, Thomas et al. 2009). For example, Bell et al. (2003) showed that if the general IR calibration of Paterson (1982) is adopted, the water concentration of olivine is underestimated by about 25 %. A similar result has been obtained by Deon et al. (2009) for Mg-wadsleyite. Thomas et al. (2009) evidenced using a large variety of analytical methods that not using mineral-specific IR-calibrations for the OH quantification in NAMs (e.g. SiO₂ polymorphs and olivine) leads to either underestimation as for olivine or overestimation of the water content as for stishovite and coesite. Thus, to quantify the water content of NAMs mineral specific absorption coefficients are needed but unfortunately only for a few minerals available.

In this study we synthesized hydrous ringwoodite samples different in composition and ranging from $x_{\text{Mg}} = 0.0$ to 0.6. We analyzed the samples by electron microprobe, Fourier-Transform IR spectroscopy and Secondary Ion Mass Spectrometry. For water quantification we integrated the area under the broad absorption band which shifts with increasing Mg content to lower wavenumber from 3386 cm^{-1} for the Fe-endmember to 3244 cm^{-1} for the ringwoodite with $x_{\text{Mg}} = 0.6$. The OH concentration expressed as water increases with increasing Mg-content from 0.2 to 0.35 wt%. These data allow us to calculate absorption coefficients. The values of the four different ringwoodite samples plot well below the general calibration curves of Paterson (1982) and Libowitzky and Rossman (1997) but follow the same trend, i.e. they increase with decreasing wavenumbers of the OH bands from 59000 ± 6000 for the Fe-endmember to $85800 \pm 10000 \text{ L mol}^{-1} \text{H}_2\text{O cm}^{-2}$ for the Mg-richest sample. Our values allow us to predict an absorption coefficient for the iron-free Mg-endmember as $100000 \pm 7000 \text{ L mol}^{-1} \text{H}_2\text{O cm}^{-2}$. Within a polymorphic mineral series of the same composition we observe a positive correlation of ϵ with density and a negative correlation with the molar volume. This allows us to predict absorption coefficients for some minerals, where coefficients for one or better two of their polymorphs, either high- or low-pressure, are available.

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Investigations for the quantification of microorganisms in sulfidic mine waste dumps

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In three different mine waste tailings forming acidic, heavy metal enriched effluents called acid mine or rock drainage (AMD/ ARD) the microbial communities were quantitatively analyzed using the molecular quantification techniques catalyzed reporter deposition – fluorescence in situ hybridization (CARD-FISH), FISH and quantitative real-time PCR (Q-PCR) in comparison with SYBR Green direct counting and most-probable-number (MPN) cultivation.

Depth profiles of these cell numbers showed that the composition of the microbial communities is highly different at the three sites, and also strongly varied between zones of oxidized and unoxidized tailings. Maximum cell numbers with up to 10^9 cells g⁻¹ dry weight were determined in the pyrite or pyrrhotite oxidation zones whereas the cell numbers were significantly lower in the zones of unoxidized tailings. Bacteria dominated over Archaea and Eukarya at all tailings sites. Among the Bacteria, the acidophilic Fe(II)- and sulfur-oxidizing *Acidithiobacillus* sp. dominated over the acidophilic Fe(II)-oxidizing *Leptospirillum* sp. at two sites, while both genera were equally abundant at the third site. The acidophilic Fe(II)- and sulfur-oxidizing *Sulfobacillus* sp. was generally less abundant and the Fe(II)-oxidizing *Acidimicrobium* and relatives were not detected at all. The acidophilic Fe(III)-reducing *Acidiphilium* sp. could only be found at one site while the neutrophilic Fe(III)-reducing Geobacteraceae as well as the *dsrA* gene of sulfate reducers were quantifiable at all three sites. FISH analysis provided reliable data only for tailings zones with high microbial activity but CARD-FISH, Q-PCR, SYBR Green direct counting and MPN were suitable methods for a quantitative microbial community analysis of tailings in general.

In situ LA-ICP-MS U-Pb dating of rutile from the Pikwitonei Granulite Domain, Canada: implications for Pb diffusion and the closure temperature

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Rutile (TiO₂) is a common accessory mineral in many metamorphic rocks and is a stable phase over a wide range of *P-T* conditions. It is very robust in sedimentary environments and therefore also used for provenance studies. Rutile may contain up to 200 ppm U, allowing U-Pb dating with an excellent analytical precision, and has been used as a geochronometer that provides important constraints on the cooling history of metamorphic terranes (e.g. Mezger et al., 1989). For a reliable interpretation of the U-Pb ages knowledge of the closure temperature for Pb diffusion is essential. In this context various studies have been done, but there is a discrepancy of closure temperature estimates, both from nature (ca. 400 °C; Mezger et al., 1989, ca. 620, Vry & Baker, 2006) and experiment (ca. 600 °C; Cherniak, 2000). To provide further constraints on Pb diffusion and the closure temperature in rutile we analyzed U and Pb isotopes in rutiles from granulite facies metapelitic rocks of the Archean Pikwitonei granulite domain (Manitoba, Canada). These rocks cooled slowly from high grade conditions (Mezger et al., 1989), which is ideal for the present study, since age uncertainties are small relative to the duration of cooling.

Laser ablation ICP-MS was applied to resolve possible age heterogeneity within single rutile grains. This technique is very suitable for rutile dating, because it allows analysis of multiple small spots on single grains as well as in situ measurements in thin sections preserving textural information. We selected 17 rutile grains in thin sections from 4 different samples. These were analyzed using a Thermo Fisher Element2 ICP-MS coupled to an ArF Excimer laser system. Transects of 35 µm spots were measured across rutiles with grain sizes ranging from 100 to 350 µm. A ²⁰⁸Pb-based common Pb correction was applied where necessary. The rutiles yielded concordant ages with core ages of ca. 2450 Ma and core-to-rim younging towards 2280 Ma. Analytical uncertainties are on the order of 20-30 Ma (2σ). These results agree with the range of U-Pb ages obtained by conventional ID-TIMS analyses on bulk rutile samples (Mezger et al., 1989).

As postulated by Dodson (1986), the closure temperature of slowly diffusing species in a volume of matter depends on the distance from the rim and hence may develop a closure temperature profile. The age profiles, which represent diffusion profiles that originated from volume diffusion during slow cooling, were used to reconstruct a closure temperature profile. Although the weighted mean of this profile agrees well with the closure temperature of the whole grain as calculated using Dodson's equation (1973), the profile indicates that the absolute closure temperature at which Pb diffusion became insignificant in the rim is significantly lower. This approach allows the determination of cooling rates and –ages from the analysis of single grains, and provides constraints for the cooling history of the metamorphic terrane.

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Sequestration of rare metals from seawater by ferromanganese oxides – implications from sorption experiments and XANES/EXAFS studies

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Marine ferromanganese oxide crusts (Fe-Mn crusts) cover thousands of square kilometers of seabed throughout the global ocean, containing significant concentrations of rare metals such as Te, Ti, Zr, Pt, Mo, W, and others. The sorption of some of the metals onto Fe-Mn crusts controls their dominant redox species and concentrations in the global ocean. Understanding the geochemical processes that govern the interactions of these rare metals with natural Fe-Mn oxides have far reaching implications that span the range from global-ocean geochemical balances to the development of new techniques for extractive metallurgy for these economically interesting high-tech metals.

To investigate the bonding forms of the trace metals in the Fe-Mn oxide phases, sorption experiments with trace metals in seawater and different natural and artificial Mn and Fe oxides were carried out. First investigations with EXAFS and XANES at the SSRL beamline in Stanford were carried out on natural Fe-Mn crust material and Te sorbed artificially on different oxides. The most striking result is that the EXAFS spectra for all the Fe-Mn crust samples are virtually identical, regardless of location within the global ocean, depositional conditions, or chemical and mineralogical compositions (Hein et al., 2007). This uniformity indicates that the mode of incorporation of Te into the Fe-Mn crusts does not vary despite varying environments of formation. This conclusion implies that a common set of processes applies throughout the global ocean to the incorporation of Te into Fe-Mn crusts. The XANES data show that >85% of the Te occurs as Te(VI) in all the crust samples. Te is sequestered via surface oxidation and inner-sphere sorption, predominantly on FeOOH, which is confirmed by Te-O and Te-Fe bonds.

Other strongly enriched elements in marine Mn-Fe crusts that we focus on in this study include Pt, Ti, Pb, Zr, Bi, Mo, and W. Most highly enriched rare metals are sequestered predominantly by inner-sphere adsorption on FeOOH. For redox-sensitive elements, such as Pt, Mo, and W, redox processes on the Fe-Mn oxide surface, similar as found for Te, are possible enrichment mechanisms. XANES and EXAFS spectra for Mo in Fe-Mn crust samples indicate sorption of a polymolybdate complex. This was not expected because polymolybdate was found as the dominant phase in hydrothermal Mn oxides that have a different Mo source and different environment of formation (Kuhn et al., 2003).

A further metal of interest is Pb, for which sequential leaching indicated that Pb is transferred from the oxide phase to the phosphate phase during diagenetic phosphatization. Pb isotopic studies show that the ratios of the various Pb isotopes do not change during phosphatization (Christensen et al., 1997). This is a significant geochemical process in which there is a wholesale transfer of an element without isotopic exchange. The final data from these investigations will allow us to determine a set of mechanisms by which metals are sequestered from seawater by marine Fe-Mn oxides and formulate first-order principles by which these important geochemical processes operate.

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A very special collection for teaching

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Today the mineral collection of the Friedrich-Schiller-University of Jena – belonging to the Institute of Geoscience – is open to the public and is one of the worthwhile instruments for teaching mineralogy. As every mineralogist knows typical characteristics, physical properties etc. of minerals are used to identify minerals. But what happened before about 200 years in this collection? Okay, let's start a little bit earlier.

Carl August (1757-1828), Duke of Saxony-Weimar, bought a typical natural history collection in 1779. To this collection he added parts of his private mineral and gem collection and so he laid the foundation for the today's Mineralogical Museum of the Friedrich-Schiller-University of Jena /Germany. But Carl August didn't only found the museum, he took an interest in the development of the collection in all the time and subsidized the first curator and later director of the museum, Johann Geog Lenz. Duke Carl August kept on sending a few suites of minerals and rocks to the collection in Jena. J. G. Lenz had been employed by J.W. von Goethe who had been in position of a minister at the court of Carl August. Lenz got into mineralogy as an autodidact after the system of Abraham Gottlob Werner. Because of his publications and his work in the museum he became the first professor of mineralogy in Jena in 1794. In the same year he published his famous "*Mustertafeln der bis jetzt bekannten einfachen Mineralien*" with 400 coloured specimen of the collection. Three years later, in 1797, Lenz founded the "*Societät für die gesammte Mineralogie zu Jena*" - the first association belonging especially to geoscience. Thousands of minerals, rocks and fossils from all over the world arrived in Jena as presents from the members of the association. Duke Carl August kept on sending a few suites of minerals and rocks to the collection in Jena. The son of Carl August married Maria Paulowna, a daughter of the Russian tsar Paul I. Later on two grandsons and two granddaughters were born. This both - Marie and Augusta - obtained a real good education and in the same way they got well schooled in mineralogy. For this reason Carl August bought and compiled under the guidance of Goethe in 1820 a collection of minerals, mostly polished objects. Predominantly the collection contained a lot of quartz and a large variety of chalcedonies. Furthermore there are some topaz, beryl, feldspars and oxides contained. In the first years of existing this collection was really used only for teaching. This assemblage belonged to the family in Weimar till the beginning of the 20th century. Then under the professorship of Gottlob Eduard Linck (1859 - 1947) this famous collection went to the mineralogical museum in Jena. After 1945 this collection for teaching had been assigned to the traditional grown up collection of gems in Jena. In 2007 the author hit by fluke on the origin of parts of the today's gem collection and kept tracks in the archive.

Radiohaloes in feldspar group minerals

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External irradiation of minerals with alpha-particles emitted from radionuclide bearing inclusions may lead to significant alteration of the physical and chemical properties of the host material. These altered regions are commonly referred to as radiohaloes. In the vast majority of reported cases, haloes can be detected using an optical microscope, because they show significantly changed optical absorption and birefringence behaviour in comparison to the unaltered host (e.g. Ramdohr, 1960). However, there are minerals which commonly show no change in optical absorption upon alpha-irradiation. One well known example is quartz, where radiohaloes can only be revealed by cathodoluminescence (CL) imaging, as they show an intensified, orange emission (e.g. Götze et al., 2001). In the course of CL-studies on radiohaloes in quartz (cf. Krickl et al., 2008), hitherto unreported alpha-induced alteration effects in alkali-feldspars and plagioclases were discovered and characterised.

In contrast to quartz, the newly discovered “negative CL-haloes” in feldspars exhibit lower emission intensity as compared to the unaltered host. Cathodoluminescence spectra show, that this decrease is mainly caused by a strong intensity loss of bands attributed to the $O^{-27}Al$ centre. In some cases a new, probably radiogenic band at ~570–600 nm can be observed.

Radiohaloes in feldspars seem to be quite common and were detected in a number of rocks from different localities. Haloes are not only found around radioactive inclusions but also along cracks, indicating the former circulation of radionuclide bearing solutions. The radioactive origin of the reported features is confirmed by several observations: Haloes are only found at the contact zones to radionuclide bearing phases like for example monazite. Measured outer radii of haloes (and sometimes rings within haloes) are in very good agreement with penetration depths of natural alpha-particles calculated by Monte-Carlo-simulations. Finally, micro-Raman spectroscopic investigations indicate the presence of structural damage which increases with decreasing distance from the radionuclide bearing inclusion, thus correlating with the presumed point defect density distribution in radiohaloes. Amorphised regions within haloes are rare, though they exist in some cases. Glassy feldspar seems to be unstable against secondary alteration and is most often found to be recrystallised and chemically altered. Evidence on different resistance against secondary alteration within different feldspar minerals will be discussed.

The results on natural radiohaloes are confirmed by artificial irradiation experiments: Implantation of a sanidine single crystal with 8.8 MeV He^{2+} ions (corresponding to alpha-particles produced in the decay of ^{212}Po) results in analogous decrease in CL-intensity, showing systematic dependence on irradiation dose. Raman spectroscopic investigations show significant broadening of vibrational bands, indicating significant disturbance of the short range order in the crystal structure. However, crystalline long range order seems to be preserved up to doses of $10^{16} He^{2+}/cm^2$. The measured extent of broadening correlates very well with calculated point defect distribution curves resulting from Monte-Carlo-simulations. In the case of natural and artificial alpha-irradiation no change in optical absorption could be detected. However, irradiation with electrons and gamma-rays resulted in a markedly yellow-brown colouration of the same sample material that was subjected to He-implantation. For these treatments obviously induce different effects, they are not adequate methods to simulate alpha-particle haloes in these minerals.

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Petrology of Pyrometallurgical Slags from the Prehistory: a indispensable tool for unravelling archaeometallurgical processes

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In most of the larger mining districts of the Eastern Alps prehistoric metal mining activities are known (Schwaz-Brixlegg, Mitterberg, etc.). The earliest pyrometallurgical activities verified at the Mariahilfbergl (Brixlegg, Tyrol) date from the younger Neolithic 4500-3650 BC. In Bronze Age especially in the middle Bronze Age times mining-and smelting activities are commonly known in the Eastern Alps. Besides montan-archaeological work in the last few years mineralogical-petrological research became important to examine metallurgical artefacts and hence provide data to reconstruct smelting processes. These results will then be consulted for the archaeological interpretation and reconstruction of prehistoric mining activities. In the following, the applications of petrological methods are discussed with reference to artefacts from the early Bronze Age Kiechlberg fahlore smelting site near Innsbruck, Tyrol. It is to expect, that pyrometallurgical artefacts contain complicated and probably uncommon phases/phase chemistry and textures compared to natural rock samples. Due to oxidation- and reduction processes metallic-, sulfidic- and oxidic melts can coexist in one sample and specific elements show varying affinity for one of the melts, depending on the atmospheric conditions. In a first step, optical microscopy studies (transmitted and incident light mode) must be applied for a first phase identification and textural studies of the phase relations present. It is noteworthy that slags from one site and the same time also show strongly varying oxidic mineral assemblages. This phase assemblage as well as its metallic- and sulphidic inclusions are a first qualitative manifestation of the charge composition present during smelting. But it is still controversially discussed if the charge was intentionally mixed with special additives or if the charge is a mixture of ores and gangue minerals and thus only reflects the different nature of the host rocks by containing varying amounts of the components. Phase characterization using XRD and Raman spectroscopy as well as EMPA analyses are important tools to describe reaction textures, crystallization sequences and the chemical composition. In the case of pyrometallurgical copper slags from Kiechlberg, slags can not be reduced to a simple Fe-rich system with fayalite + magnetite + glassy melt present but have to be described with the components Fe-Mg-Ca-K-Al-Si-Zn-O-(Ba), metallic Cu-Sb-As-Ag compounds and Cu-Fe-S sulfide droplets. All listed elements are major elements and lead to the formation of complex zoning-, exsolution, and crystallization patterns. This chemical/structural complexity bears assets and drawbacks, such as the possibility of application of thermodynamic calculation (thermometry, fugacity calculations etc.) but makes it also difficult to interpret textures and recognise disequilibrium. Since oxygen fugacity controls the affinity of elements for metallic melts and/or oxide melts, the presence and absence of elements in these two coexisting melts can be used to estimate the oxygen fugacity of the process and to

Synthese und Charakterisierung von zinkhaltigen Layered Double Hydroxides mit organischen Zwischenschichtanionen

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Layered Double Hydroxides (LDHs) sind aufgrund ihres chemischen Aufbaus und der Fähigkeit verschiedenste organische und anorganische Anionen in die Schichtstruktur einzubauen schon lange von großem Interesse für den Einsatz als katalytischer Werkstoff, Speichermineral, Antacidum oder Adsorbermaterial (Lee *et al.*, 2006, Pöllmann, 2007). Aufgrund der großen Variabilität in der Zusammensetzung der Haupt- und Zwischenschichten können auch deren spezifischen Eigenschaften stark variieren. LDHs sind Schichtstrukturen, die aus chemisch und strukturell verschiedenen, alternierenden Schichten aufgebaut sind. Alternierend zu den positiv geladenen Hauptschichten liegen negativ geladene Zwischenschichtanionen und nicht strukturnotwendige reversibel austauschbare Wassermoleküle. Von großer Bedeutung für die Mehrzahl der Anwendungsmöglichkeiten von LDHs ist ihre Fähigkeit des Anionenaustausches. Natürliche LDHs bauen bevorzugt Karbonat in die Zwischenschicht ein. Untersuchungen an synthetischen Verbindungen der Hydrotalkit-Gruppe haben gezeigt, dass eine Vielzahl an anorganischen und organischen Anionen in die Zwischenschicht eingebaut werden können (Anbarasan *et al.*, 2005, Kopka *et al.*, 1988, Meyn *et al.*, 1990).

In dieser Arbeit wurde die Substitution verschiedener organischer Moleküle unterschiedlicher Kettenlänge und funktioneller Gruppen in eine zinkhaltige LDH-Precursorphase in Abhängigkeit von den Syntheseparametern und die strukturellen Eigenschaften nach Ausheizen der Zwischenschichtwassermoleküle untersucht. Sämtliche synthetisierten ZnAl-Verbindungen kristallisieren in der für LDHs typischen Form als hexagonale Plättchen mit wenigen Mikrometer Durchmesser. Im Vergleich verschiedener Synthesemethoden und unter Variation der Syntheseparameter Zeit, Temperatur und pH-Wert erweist sich Nitrat als optimales Precursoranion für Austauschreaktionen mit organischen Anionen. Der Schichtabstand von ZnAl-LDHs ändert sich in Abhängigkeit von der Größe und der Anordnung des Zwischenschichtanions. Anhand der Zunahme der Schichtabstände mit steigender Kettenlänge, wurden die Inklinationwinkel der substituierten organischen Anionen bestimmt. Dicarboxylate und Alkylsulfonate ordnen sich in monomolekularen Schichten in der Zwischenschicht an, wobei der Schichtabstand linear mit der Anzahl der Kohlenstoffatome der organischen Kette steigt. Monocarboxylate bilden in Abhängigkeit von der Kettenlänge und den eingestellten Syntheseparametern monomolekulare oder bimolekulare Strukturen bzw. Überstrukturen aus beiden Anordnungen aus. Durch Trocknung bei unterschiedlichen relativen Luftfeuchten verändern sich die Gitterparameter nur geringfügig. Dicarboxylate, Aminosäureanionen und Verbindungen mit kurzkettigen organischen Molekülen sind gegenüber Trocknung instabil. Eine Änderung des Schichtabstandes tritt bei der Remobilisierung des nicht strukturnotwendigen Zwischenschichtwassers auf. ZnAl-LDHs mit stabilen kurzkettigen organischen Anionen bilden durch Aufheizen auf Temperaturen bis max. 150°C eine zwischenschichtwasserfreie Hydratstufe aus, wobei der Schichtabstand abnimmt. Langkettige Sulfonatketten richten sich dagegen bei Temperaturerhöhung auf, ohne das Zwischenschichtwasser dabei vollständig abzugeben. Dadurch kommt es zu einer Aufweitung der Zwischenschicht. Erst bei höheren Temperaturen werden die OH-Gruppen der Hauptschichten entwässert und die Kristallstruktur wird zerstört.

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Anthropogenic Gadolinium as Micropollutant in Drinking Water in Berlin

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Due to their coherent behavior, rare earth elements (REE) can be used as tracers in hydrogeochemical studies, provided that the system under investigation is free from anthropogenic impact. An ever increasing number of reports, however, show that anthropogenic REE are becoming progressively more relevant for the dissolved rare earths content of surface waters, especially in urban areas. The application of Gadolinium-based contrast agents in magnetic resonance imaging (MRI) has been documented in Germany, Japan, U.S.A, France, Italy, Czech Republic, Netherlands and Australia, and also in coastal seas, such as the southern North Sea.

Gadolinium-based contrast agents are designed not to interact with the human body, which is achieved by binding Gd in water-soluble highly stable chemical complexes. Nevertheless, a link has been shown between nephrogenic systemic fibrosis (NSF) and the administration of anthropogenic Gd to patients suffering from renal failure. While the absolute number of cases is relatively small, the severity of this fatal disease was enough to prompt the U.S. Environmental Protection Agency to force the pharmaceutical companies to issue a warning, informing patients about the risk of NSF development.

The anthropogenic gadolinium is not only present in surface waters, but has also been found in groundwater that is affected by natural bank infiltration or by controlled groundwater infiltration performed to improve water quality or to replenish groundwater resources. The City of Berlin is an example for an area (among others in Germany) where this is of importance.

In this study we report on the REE geochemistry of tapwater from several districts within the City of Berlin, that shows different characteristics, depending on the waterworks by which it is distributed, i.e. depending on the location of the groundwater wells within the city. Even 20 years after reunification, there exists a remarkable difference between the former districts of East-Berlin and West-Berlin: tapwater from districts in West-Berlin show significant amounts of anthropogenic gadolinium, while this micropollutant is largely absent from drinking water in East-Berlin. The geogenic background concentrations of gadolinium (which is the total dissolved gadolinium load in tapwater from East-Berlin) are below 1 ng kg^{-1} , while drinking water in West-Berlin that is dominated by anthropogenic gadolinium (>90% of total gadolinium) shows concentrations of up to 11 ng kg^{-1} , i.e. concentrations well-below the suggested limits for freshwater. Among the well-known sampling sites are "Zoologischer Garten", "Museumsinsel" and "Reichstag", all of which carry significant amounts of anthropogenic gadolinium. The presence of anthropogenic gadolinium in Berlin drinking water is confined to areas where groundwater is affected by bank infiltration from Lake Tegel and from the Havel River or where it is artificially recharged with surface water. The Havel River is heavily contaminated with anthropogenic gadolinium introduced with the clear water effluent from the waste water treatment plant at Ruhleben.

While Berlin drinking water shows elevated levels of gadolinium, its uranium concentrations fall in a range between $0.1 \text{ } \mu\text{g kg}^{-1}$ and $0.5 \text{ } \mu\text{g kg}^{-1}$ (i.e., below the $2 \text{ } \mu\text{g kg}^{-1}$ Federal limit set for water used to prepare baby food) with no significant differences between the eastern and western districts of Berlin.

REE - distribution between basalt and seawater at “supercritical” conditions: an experimental approach

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Extremely hot vent fluids have recently been discovered at 5°S on the Mid Atlantic Ridge (SMAR). These fluids are characterized by extreme temperatures (>400°C), very high concentrations of transition metals, and peculiar rare earth element pattern (see Figure 1: 5° SMAR fluid). All processes during phase separation, up-welling, and final venting of the hydrothermal fluids at 5° SMAR run entirely under “supercritical” conditions [1]. So far, our understanding of fluid-rock interaction, pressure-temperature regimes, and temporal variability of hydrothermal systems has been dominated by studies of natural fluids at the EPR in more shallow water depth [2]. As a consequence, most hydrothermal experiments studying basalt-seawater interaction have been conducted mainly under p, T conditions prevailing at the EPR (150-400°C, 250-500 bar) [e.g. 3]. These p, T conditions are different to the condition at SMAR (>400°C, 300 bar). We therefore started a systematic experimental investigation to determine the element distribution behavior between coexisting basalt and seawater at the p, T conditions similar to those of the SMAR venting site. In addition our focus is on REE distribution between basalt and seawater as previous studies concentrated on major (and minor) elements. In a first set of experiments under “supercritical” conditions (500°C, >1.7 kbar) we used original MORB glass fragments and bottom seawater from the SMAR and conducted cold seal pressure vessel (CSPV) experiments using Au as container material. Chemical compositions of the post-run charges have been analyzed by analytical techniques available at the Institute of Geosciences, Universität Kiel: major and trace elements have been determined by electron microprobe and laser ablation ICP-MS (solid phases) and ICP-OES/-MS (fluid phases). Figure 1 shows first results of the REE pattern of the experimental post-run fluids. We were able to reproduce the high Fe concentrations (not plotted in the Figure) and REE pattern with LREE depletion and without Eu-anomaly, i.e. characteristics of the “supercritical” SMAR hydrothermal fluids. The REE pattern of SMAR fluids might therefore reflect “simple” water-rock interaction at “supercritical” conditions. However, we are aware of the fact that the experimental run pressure is about a factor of 6 too high compared to SMAR. The focus of the presently performed experiments is on the pressure influence of REE distribution between MORB and fluid. The results of this second set of experiments will be presented at the meeting.

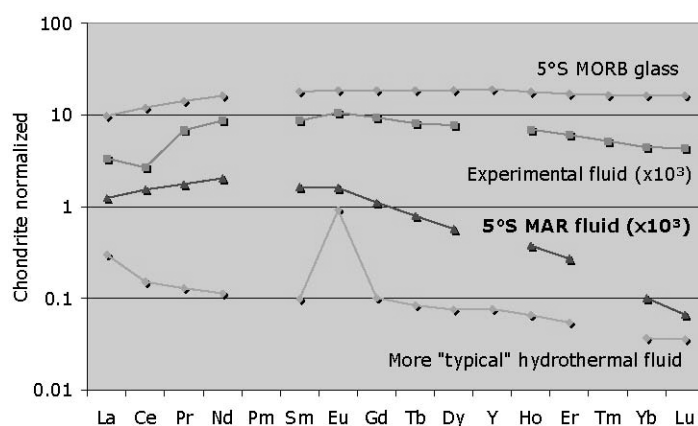


Figure 1: Chondrite-normalized rare earth element concentrations of MORB glass (3ROV-8) and black smoker fluid (20ROV-5, 412 °C, $\times 10^3$) from 5°S MAR in comparison to our experimental fluids (500°C, $\times 10^3$). Note that these high-temperature hydrothermal fluids do not display a positive Eu-anomaly. A more “typical”, subcritical hydrothermal fluid REE pattern exhibits a positive Eu anomaly and a continuous increase of REE concentrations towards La (67ROV-5, 365°C, $\times 10^3$).

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Solid state NMR spectroscopic investigations of Al-rich phlogopites synthesized at 873 K

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Our research project is part of the ORION-project (Ordering of Ions in Minerals) in the EuroMinSci programme of the ESF which aims the elucidation of ionic ordering in three exemplary systems by combining experimental investigations and theoretical calculations. One of the systems to be investigated is phlogopite, a trioctahedral 2:1 layer silicate.

Our main interest focuses on the order/disorder of the Al/Mg cations and F/OH anions in the octahedral sheets, and the amount of aluminum being incorporated into the structure. Solid state NMR investigations on phlogopite samples synthesized at 1073 K already showed that fluorine-rich compositions indicate a decreased Al-content in the tetrahedral sheets suggesting a destabilizing effect on the formation of Al-rich phlogopite (Fechteltord et al. 2003a, b). This leads to extensive formation of Al-rich impurity phases like corundum ($\alpha\text{-Al}_2\text{O}_3$), kalsilite (KAlSiO_4), and potassium aluminum hexafluoride ($\text{K}_3\text{AlF}_6 \cdot 0.5 \text{H}_2\text{O}$).

The latest results of our solid state NMR spectroscopic investigations of Al-rich phlogopites synthesized at 873 K confirm the destabilizing effect of fluorine-rich compositions on the amount of Al incorporated into the phlogopite structure. However, we observed less extensive formation of impurity phases. Corundum was always present after the synthesis runs, but in lower amounts compared to the samples synthesized at 1073 K. Potassium aluminum hexafluoride was only formed in samples with Al-rich nominal gel compositions. The formation of kalsilite has not been observed in our samples. Moreover, these results show that even low amounts of F-content decrease the ability for Al-incorporation drastically compared to pure hydroxyl-phlogopites. In fact, the increase of fluorine content in phlogopites already containing fluorine does not affect the ability of Al-incorporation so much.

It can be concluded that the two parameters synthesis temperature and F-content of the initial gel composition have a strong influence on the formation of Al-rich phlogopites, with higher temperatures and higher F-contents decreasing the incorporation of Al into the phlogopite structure.

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Bestimmung von Phasenbeziehungen und thermodynamische Berechnungen im System Li-Ti-O-H mittels in-situ XRD-Messungen

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In Zukunft werden erneuerbare Energiequellen eine immer wichtigere Rolle spielen und die Nachfrage nach modernen Möglichkeiten Energie zu speichern wird steigen. Die Entwicklung neuartiger Elektrodenmaterialien für Lithium-Ionen-Akkumulatoren mit hoher Energiedichte und einer guten Zyklenbeständigkeit bei hoher Kapazität und hoher Eigensicherheit können es ermöglichen, Bleibatterien in Fotovoltaik- oder Windkraftanlagen zu ersetzen und Automobile mit Verbrennungsmotor auf Hybridelektro- oder Elektroantrieb umzustellen.

Die Verbindungen $\text{Li}_4\text{Ti}_5\text{O}_{12}$ und $\text{Li}_2\text{Ti}_3\text{O}_7$ aus dem System Li-Ti-O werden als Elektrodenmaterialien diskutiert und auch teilweise schon als solche eingesetzt. Auch andere wirtschaftliche Anwendungen wie die der Phase Li_2TiO_3 als Brütermaterial in Kernfusionsreaktoren sind vorgesehen. Die Bildungsbedingungen der einzelnen Phasen und die thermodynamischen Beziehungen zwischen den Phasen sind jedoch erst wenig beschrieben.

An den Synchrotroneinrichtungen ESRF in Grenoble (Frankreich) und MAX-lab in Lund (Schweden) wurden Synthesen im System Li-Ti-O-H mit hoher zeitlicher Auflösung bei verschiedenen Temperaturen durchgeführt. Durch Rietveldverfeinerung wurden die Abhängigkeit zwischen Reaktionszeit und Reaktionstemperatur in Bezug auf das Kristallwachstum, sowie der Zusammenhang zwischen Reaktionsgeschwindigkeit und Temperatur analysiert.

Es hat sich gezeigt, dass Synchrotron-Pulverdiffraktometrie eine gute Methode ist, um in-situ Messungen zur Bestimmung der Phasenbeziehungen und der Reaktionsbedingungen im System Li-Ti-O-H durchzuführen. Dadurch könnten neue Wege gefunden werden, Lithium-Titan-Verbindungen verbessert und wirtschaftlicher herzustellen, so dass die Entwicklung erneuerbarer Energiequellen vorangetrieben wird.

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Diamondiferous kimberlites in central India synchronous with Deccan flood basalts

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India is known for its historic diamonds from alluvial gravels. The source rocks for these diamonds are thought to be among the so far nearly 100 identified kimberlitic/lamproitic pipes and dikes which occur mostly in the Dharwar craton (Andhra Pradesh) and the Bundelkhand craton (Madhya Pradesh), and which all have Mesoproterozoic ages with a peak at 1.1 Ga (Kumar et al. 1993). However, diamondiferous kimberlite pipes in the recently discovered Mainpur kimberlite field in central India have surprisingly young $^{40}\text{Ar}/^{39}\text{Ar}$ whole-rock ages of 66.5 ± 2.0 and 62.4 ± 2.9 million years (2σ), confirmed by more precise laser ablation ICP-MS $^{206}\text{Pb}/^{238}\text{U}$ perovskite data of 65.1 ± 0.8 and 62.3 ± 0.8 Ma (2σ). These ages overlap with the main phase of the Deccan flood basalt magmatism at 65 million years, and suggest a common tectonomagmatic control for both flood basalts (including carbonatite-alkaline rock variants) and kimberlites. The kimberlites were studied in drill core (Mainkar and Lehmann 2007) and have textural, bulk and mineral chemical composition typical of orangeite (African kimberlite Group 2), confirmed by Sr and Nd isotope data. The Mainpur kimberlite field is in the Archean Bastar craton with felsic rocks as old as 3.6 Ga (Rajesh et al. 2009). The presence of macrodiamonds in the pipes implies that Central India had a cool and thick lithospheric mantle root at the Cretaceous/Tertiary boundary, significantly different from the modern Indian lithosphere of about 80-100 km thickness only (Kumar et al. 2007). The loss of India's cratonic roots must have taken place in the Tertiary, i.e. after much of the superfast northward motion of the Indian plate from Gondwana break-up at about 130 million years until the collision with Eurasia at about 50 million years ago. India's unique plate-tectonic behaviour in the Cretaceous cannot be related to a plume-eroded lithosphere. About one third of the Indian lithosphere was lost during or after the Deccan flood basalt event.

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Texture investigation of forsterite (Mg_2SiO_4) - enstatite (MgSiO_3) - thin films

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The preferred geometrical arrangement of polycrystalline aggregates has direct influence on the mobility of element species and is fundamental to various physical and chemical processes in the Earth's crust and mantle. The texture of MgSiO_3 pyroxene layers within silicate thin films with total thickness $<1\ \mu\text{m}$ was studied experimentally at 0.1 MPa total pressure and temperatures from 900 to 1150°C.

The starting samples were produced by pulsed laser deposition of amorphous thin films with compositions of forsterite (Mg_2SiO_4) and enstatite (MgSiO_3) on polished slices of quartz oriented normal to the [00.1] crystallographic axis. The layer thickness before and after the experiments and the layer composition as well as microstructures, grain size and shape of the interfaces were determined by transmission electron microscopy. It has become obvious that the forsterite film and the quartz crystal are continuously consumed to form enstatite. The investigation reveals that the pyroxene consists of twinned lamellar intergrowths of orthoenstatite and clinoenstatite with grain boundaries oriented almost perpendicular to the pyroxene-quartz reaction front. Annealing of the thin film setting leads to fairly homogeneous grain sizes, increasing with annealing time. After the pyroxene layer has increased in width during annealing, chains of strain contrast centers are present in quartz along the pyroxene reaction front, typically reaching about 200 nm into the quartz substrate crystal.

The geometrical orientation of the enstatite crystallites has been investigated with an X-ray diffractometer using the grazing incidence setup, with an incident beam angle of 0.5°. The texture index was applied to the relative intensities of selected enstatite Bragg peaks to provide a quantitative texture analysis. A preferred orientation of the enstatite crystallites in the direction of the crystallographic b-axis almost normal to the pyroxene-quartz reaction front was revealed.

To investigate the textural growth correlation of an amorphous enstatite thin film deposited on an amorphous silicon dioxide substrate, another sample has been prepared by pulsed laser deposition. The experimental study is carried out with grazing incidence X-ray diffraction and scanning transmission electron microscopy. Short annealing for 20 minutes at 1000°C lead to a still highly amorphous sample with coherent scattering regions of about 60 nm in size, resulting in extensive peak broadening. Further annealing will solve this problem, making it possible to quantify the potentially occurring textures.

Archaeometric studies of ceramic materials from Amazon Dark Earth (ADE)

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The Amazon region covered by deep rain forest and cross cut by a large river and lake drainages and a nursery of uncountable biodiversity is rich on archaeological ceramic artifacts mostly potteries, which indicate the region has been already intensive occupied by prehistorically peopling. Anywhere in the Amazon region you can touch a ceramic-bearing archaeological site. This is more impressive where the terrains are plenty of the so called Amazon dark earth (ADE) soils. The ADEs are rich on ceramic fragments inside of its A's horizons. The majority of the ceramic fragments represent daily use potteries with simple finishing but such ones with fine decoration can be found and represent records of Marajoara, Tapajós and/or Konduri cultures. 20 years ago we started to carry out archaeometric studies of the ceramics found in the ADE in order to identify their raw materials and provenience and to recognize the process they were made, contributing to archaeology in the Amazon, where the deep biochemical weathering has input in short time a severe decomposition of the archaeological artifacts. The ceramic fragments seem to resist to weathering agents, fortunately. We used thin section optical microscopy, XRD, FTIR, TDA/TG, SEM/EDS, electron microprobe, thermoluminescence (TL) dating and bulk chemical analysis. Ceramic fragments coming from distinct sites from several areas of the Amazon have been analyzed thanks to increasing field campaigns of archaeologists for mapping and excavations carried out in the last decades in the Amazon region by Museu Goeldi and Scientia Consultoria, mainly, who provided the ceramic samples. The results already obtained led concluding the ceramic fragments although showing a common basic clayey raw material, they display distinct tempers of organic and inorganic origin, rough or treated by fire, crushed rocks, quartz sand, coal and ashes. In fact the most impressive aspects of these ceramic fragments in the Amazon are the phosphor contents, they may reach as much as 10 wt. % of P_2O_5 . They rarely form a phosphate mineral phase; here phosphor looks like to be amorphous to XRD. Locally variscite-strengite, crandallite-goyazite and sometimes rhabdophane have been identified by XRD and SEM/EDS as crystallites or just fine massive material. The contents of phosphor vary strongly, meanwhile they come close to 1 up to 2 wt.% P_2O_5 . Phosphor has been found in several ceramic fragments in many regions outside Amazon as components of painting, enamel, fusion flux or bone fragments. But this is not the case of the archaeological Amazon ceramics. Some analyses have shown phosphor related to some surficial painting, but in general phosphor looks like to be well distributed in ceramic masse. The data show phosphor may be a contamination caused by phosphor-rich foods (fishes, meat, and so on) during cooking and storage. The relatively high contents of phosphor inside of ADE (600 to 2,000 ppm) could be a contribution of the ceramic weathering liberating it to the soils. Finally phosphor can be a very exciting fingerprint of the ADE-ceramics in Amazon.

The high phosphor ceramics from archaeological Dark Earth (ADE) in Amazon Region

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Ceramic fragments are most conspicuous artifacts found in the Archaeological Dark Earth (ADE) soils in Amazon region; they represent daily using potteries. The majority of the fragments are part of simple and few decorated potteries occurring in the A horizons of the ADE soil profile, i.e., from soil surface up to 2 m depth. Normally they exhibit phosphor contents ranging from 0.5 to 3.0 wt. % of P_2O_5 . However at site Jabuti near to Bragança city in the Eastern Amazon on Atlantic coast line a very interesting ADE site has been found and archaeologically prospected. The site is ceramic-rich represented by fragments of pots and plates exhibiting a simple decoration. The ceramic fragments found here show the highest phosphor contents ever have been identified in archaeological ceramics

In the Amazon region, as much as 6 to 10 wt. % of P_2O_5 . They also constitute the first ceramics we identified phosphor mineral by XRD and at the same time we got SEM good images of nice micron-scale crystals of crandallite-goyazite. Additionally SEM/EDS chemical analyses at several points and rhombohedral crystals confirm the mineral. Quartz, metakaolinite, kaolinite, mica and feldspars have been identified and they constitute the common minerals of the most ceramics in Amazon region.

The crandallite-goyazite crystals occupy the small voids inside the ceramics well distributed in the ceramic matrix. The too high phosphor contents indicate a peopling occupation based on labeled phosphor-rich foods, for examples fishes and sea-foods. The formation of crandallite-goyazite, an

Ca-Sr-bearing aluminum phosphate bearing suggests that a hydrothermal reaction took place inside of the pots during preparation and cooking of foods. Crandallite-goyazite is a typical mineral of this environment, and cooking in the pots can well represent this environment. The low-ordered

aluminum clay rich walls of the potteries in contact with the high temperature solution rich in phosphor by comminuting of meat and fishes promote the formation this mineral. The presence of Ca and Sr indicates the disposable of these elements either in foods (bones and shells) as well as in sea water, since the sites are close to Ocean coast line (Atlantic Ocean).

Non destructive X-ray tomographical studies will be presented revealing the 3D-dimensional micro-structure and mineral distribution within the objects down to voxel of ca. 10 micron. These results will be correlated with locally high resolved chemical analytics due to corresponding thin sections using microprobe technique and with X-ray diffraction data.

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REE and U systematics in secondary fluorites, goethites and Mn oxides from a hydrothermal ore deposit

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The trace element concentration of several generations of fluorite, goethite and different manganese oxides from the Clara mine (Schwarzwald, SW Germany) have been analyzed by LA-ICP-MS. Most samples have formed through secondary processes in a fluorite-barite vein system, and have precipitated from fluorine-rich solutions at close to ambient conditions. Additionally, primary fluorites were analyzed for comparison. In particular, rare earth element (REE) patterns have been obtained in order to shed light on redistribution processes of these elements in this type of system.

REE patterns of secondary fluorites are very similar to those of the primary fluorites they have grown onto, although their overall REE content is much lower. This suggests that dissolution of old fluorites was the essential source of REE for the young ones. The uranium contents in the younger fluorites are much higher than in the primary fluorites. This is most likely explained by highly oxidizing conditions during formation of the secondary fluorites, and possibly also by inclusions of a uranium-rich mineral phase in the dissolved primary fluorite. The secondary fluorites show variable crystal morphologies and pronounced growth and sector zoning. This indicates strong dependence of REE and U incorporation on surface complexation and composition of the solution. This also points out the necessity to carefully consider crystal shape and zoning effects when calculating apparent fractionation coefficients between fluorite and a fluid phase.

Goethite and manganese oxides which are co-genetic with the fluorites display much more variable REE patterns. They act as sinks for REE along with several distinct REE minerals (e.g., rabdophane) which are also found in the same veins. Differences in Y/Ho ratios between those minerals do also point to complexation controlled redistribution behavior. The manganese oxides show pronounced Ce anomalies, which appear to depend on the oxidation state of Mn. This is probably due to catalyzed oxidation of Ce(III) to Ce(VI) on the mineral surface during growth.

Variations of HFSE (Nb, Zr) contents in rutile after partial replacement by titanite

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Titanite growth at the expense of rutile and the formation of titanite rims around rutile during retrograde hydration of eclogite into amphibolite is a common phenomenon. We investigated an amphibolite sample from the Tromsø eclogite facies terrain in Northern Norway to gain insight into the trace element behaviour during a metamorphic mineral reaction. High field strength elements (HFSE) were determined by laser ablation ICP-MS and electron microprobe analyses. HFSE systematics of rutile rimmed by titanite indicate a pronounced enrichment of these elements in the rim (Nb up to 700 ppm; Zr up to 400 ppm) that decreases towards uniform HFSE contents in the core (Nb ~300 ppm; Zr ~100 ppm). The uniform core composition is interpreted as the initial HFSE signature of the large rutile. Ta, Hf, and W show a similar distribution pattern. HFSE contents vary with the size of the rutile crystals. In a large single rutile crystal (~ 8 mm) we observed the above mentioned concentrations; in smaller rutile grains (~ 0.5 mm) and rutile inclusions (< 100 µm) in the titanite overgrowth they are similar or higher than in the large rutile's rim. The mechanism of the HFSE enrichment in the large rutile is diffusion. Modelling of Zr and Nb diffusion in rutile during titanite growth indicates that diffusion coefficients in fluid dominated natural systems must be considerably faster than those determined experimentally at 1 bar in dry systems. Diffusion of HFSE into the crystals is also inferred for small HFSE-rich rutile where no differences between core and rim are preserved. HFSE ratios in diffusion-altered rutile show variable but systematic variations (e.g., average Nb/Ta ~18.6; Zr/Hf ~36.1; Zr/Nb ~0.59) compared with the uniform core composition of the large rutile (average Nb/Ta ~16.4; Zr/Hf ~20.1; Zr/Nb ~0.30).

HFSE contents of the newly formed titanite are variable but always substantially lower (e.g.; Nb ~100 ppm; Zr ~100 ppm) than in the rutile's rims. The comparably small compositional variations along individual profiles in titanite show no systematic distribution, e.g. related to possible diffusion or a growth pattern. HFSE ratios in titanite (e.g., average Nb/Ta ~12.2; Zr/Hf ~20.8; Zr/Nb ~0.95) and the rutile's rims are systematically different, indicating different solid/fluid distribution coefficients in these minerals.

Element fractionation by diffusion into the relict rutile and during fluid-mediated growth of new titanite substantially changed the HFSE budget of these minerals. If applicable to other locations of rutile-titanite, this observation would significantly affect the use of HFSE-contents for geochemical tracing and other applications, e.g., Zr-based geothermobarometry.

U-Pb geochronology of zircons from the South Eastern volcanic Province (SEVP), Spain

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Tuffs samples from three localities of pliocene (~2.6 Ma) alkali basalts in south-eastern Spain (Alto de Las Cutandas, Cabezo Negro de Tallante, San Isidro) were collected for zircon dating. The basaltic edifices contain mantle (plagioclase peridotite) and crustal xenoliths (medium to high grade metamorphic rocks). Zircon separates from the heavy mineral concentrates could enable us to obtain statistically meaningful age spectra of the crust underlying the volcanoes. The results were compared with SIMS U-Pb analyses (Zeck and Williams, 2002) on zircons from a dacite (6-7 Ma) and its crustal xenoliths to the south west (Cerro del Hoyazo). The two volcanic localities are set within the same geological unit.

More than 150 zircon grains for each sample were analysed by laser ablation magnetic sector field ICP-MS in Frankfurt. The obtained age spectrum ranges from 2.5 Ma up to 3 Ga. Clear, fairly large sized zircons with oscillatory zoning yielded ages of 2.5 – 2.8 Ma, i.e. the eruption age of the volcanics. Xenocrystic zircon show major age clusters at around 300 Ma, 450 - 500 Ma, 550 - 650 Ma, 1 Ga, and 1.8 - 2 Ga in all three sample localities; while two have an additional age peak at around 2.9 - 3 Ga.

Our zircon age pattern is very similar to that obtained from the dacite locality of Zeck and Williams (2002) except for the ages around 3 Ga which are also missing. It is unclear as yet whether the crust underneath Tallante contains older components (up to 3 Ga) than the crust underneath Cerro del Hoyazo (up to 2.5 Ga) or if the Tallante volcanoes are underlain with sediments containing older zircon grains than at Cerro del Hoyazo.

We are presently in the process to analyse zircons from directly underlying metasediments (mica shists) to clarify this question. In addition, we plan in-situ Hf isotope analyses of the different zircon age domains. This will allow us to estimate the average crustal residence time of the crustal material involved at the distinct age clusters and to evaluate the proportion of old recycled versus juvenile crust. Furthermore, we are trying to obtain age information on mantle events from the determination of the Sm-Nd- and Lu-Hf isotopic composition of clinopyroxene separates from the mantle xenoliths.

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Ca and K exchange in Zeolite A

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Zeolites, especially Linde Type A zeolites ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$, Na-A), have a high potential as cation exchangers with high selectivities. These properties are due to their uniform network of channels and pores, formed by the aluminosilicate framework, occupied by exchangeable cations and water molecules.

Cation exchanges of K and Ca were performed as a function of duration and temperature on powdered samples of Na-A. Single crystals of Na-A were fully K exchanged. The degree of exchange was determined by energy dispersive X-ray spectroscopy (EDX) attached to a scanning electron microscope (SEM), and for a subset of powdered samples by X-ray fluorescence analysis (XRF). The water content was determined by thermal analysis (Bähr STA 503). The cation exchanged samples were characterized by X-ray powder diffraction methods including Rietveld refinements in space group $Pm\bar{3}m$. Single-crystal data collection for the crystal-structure refinement were performed with a STOE imaging plate diffractometer system (IPDS I).

Rietveld refinements for the Ca exchanged samples revealed the dependence of lattice parameter a on temperature and duration of exchange. For high degrees of exchange, a is significantly smaller for Ca-A than for Na-A, which is in accordance with De Roy & Vansant (1980). A trend towards bigger values for a can be observed with decreasing degree of exchange. At very low Ca contents, a tends to become even larger than for Na-A. The K exchanged samples show a similar behavior. However, variation of a is distinctly smaller than for Ca-A. We observe a linear relationship between a and the degree of exchange.

Single-crystal structure refinements of K-A ($\text{K}_{10.5}\text{Al}_{10.7}\text{Si}_{13.3}\text{O}_{48} \cdot 23\text{H}_2\text{O}$) were performed on the superstructure in space group $Fm\bar{3}c$. The occupancy refinement yielded 10.6(4) K atoms and 17(1) water molecules calculated for the primitive unit cell for comparative purposes. The superstructure was first described by Gramlich & Meier (1971) for hydrated Na-A and by Pluth & Smith (1979) for dehydrated K-A. Up to now, the crystal structure of hydrated K-A has been described by Leung et al. (1975) only. However, these refinements were performed in the primitive unit cell. Thus, we present the first refinement of hydrated K-A in space group $Fm\bar{3}c$. Refinement of the framework positions yielded virtually ideal T-O distances, indicating a strong ordering of Si and Al. There are three K positions, two of them on the threefold axis displaced by 0.23 and 1.6 Å off the 6-ring into the large grc cage, occupied by 0.7(1) and 6.0(1) K atoms per primitive unit cell, respectively. The third K position has 3.9(2) K Atoms and is linked to the 8-ring opening of the grc cage, slightly displaced off its centre and about 1 Å into the grc cage. Six water molecules occupy the small (toc) cage and another 11 are found to be within the large (grc) cavity. Crystal structure refinement was in full accordance to the chemical analysis.

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Spurenelementchemische und bleiisotopische Untersuchungen an frühbronzezeitlichen Metallfunden aus Mitteldeutschland

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Mitteldeutschland wird für Herkunft und Entwicklung der frühbronzezeitlichen Metallurgie eine zentrale Bedeutung zugesprochen, da dieser Raum besonders reich an frühbronzezeitlichen Metallfunden ist. Schon erste analytische Untersuchungen durch Otto und Witter (1952) in der dreißiger und vierziger Jahren befassten sich mit diesem Thema und stellten erstmals der Formentypologie eine Materialtypologie gegenüber. Weitere Studien folgten in den 1950er und 1960er Jahren am Württembergischen Landesmuseum in Stuttgart im Rahmen der "Studien zu den Anfängen der Metallurgie" (SAM; Junghans et al. 1960, 1968, 1974) und in den 1990er Jahren mit dem von der Volkswagenstiftung geförderten Projekt "Frühe Metallurgie im zentralen Mitteleuropa" (FMZM; Daten in Krause 2003). Der reiche Bestand an frühbronzezeitlichem Fundmaterial des Landesmuseums in Halle blieb aber bei den jüngeren Studien weitgehend unberücksichtigt. Diese Forschungslücke machte sich gerade für die Untersuchung und Bewertung des kulturhistorischen Umfeldes von Nebra und seiner regionalen Ressourcen empfindlich bemerkbar. Im Zuge der DFG Forschergruppe "Die Funde von Nebra, Sachsen-Anhalt, und ihre Bedeutung für die Bronzezeit Europas" wurde diese Lücke nun geschlossen und der Bestand des LM Halle an neolithischen und frühbronzezeitlichen Metallfunden nahezu vollständig analysiert. Ziel dieser Untersuchung war es, einen Überblick über die in den frühbronzezeitlichen Hortfunden auftretenden Metallsorten zu gewinnen und diese dann in das System der prähistorischen Metallgruppen aus Mitteleuropa einzubinden. Durch Vergleich mit Erzanalysen mitteleuropäischer Lagerstätten sollte auch die Herkunft des Metalls untersucht werden.

Insgesamt wurden 718 frühbronzezeitliche Metallfunde des LM Halle beprobt. Alle Proben wurden zunächst mittels Röntgenfluoreszenzanalyse (RFA) gemessen. An einer Auswahl von Funden wurden zusätzliche spurenelementchemische Analysen durchgeführt (Neutronenaktivierungsanalyse) und die Bleiisotopenverhältnisse gemessen. Im frühbronzezeitlichen Fundbestand aus dem LM Halle dominieren die Fahlerzmetalle. Rund 90 % der Metallfunde bestehen aus verschiedenen Sorten Fahlerzkupfer, die allgemein relativ hohe Anteile an Ni, As, Sb und Ag aufweisen. Besonders häufig ist Nickel-Fahlerzkupfer, das gerade in den frühen Hortfunden gehäuft auftritt und dem offensichtlich für den Aufschwung der Metallurgie am Beginn der Frühbronzezeit besondere Bedeutung zukommt. Die zweite wichtige Fahlerzgruppe am Beginn der Frühbronzezeit ist das "klassische Ösenringmetall", das kein oder nur wenig Nickel enthält. Später kommen im weiteren Verlauf der Frühbronzezeit noch weitere Fahlerz-Metallgruppen hinzu. Eine weitere wichtige Materialgruppe ist Arsenkupfer mit Gehalten um 5 % As, aber ansonsten nur geringen Spurenbeimengungen. Dieses Material wurde aufgrund seiner besonders guten Gießeigenschaften vorzugsweise für Dolch- und Stabdolchklingen eingesetzt.

Die Funde von Nebra – Himmelsscheibe wie Beifunde – sind sich in ihrer chemischen Zusammensetzung sehr ähnlich. Das Metall enthält nur geringe Anteile an Begleitelementen. Sucht man nach Funden ähnlicher Zusammensetzung in den Datenbeständen Mittel- und Ostdeutschlands, so ergeben sich nur wenige Treffer. Das Material war gemessen an der Gesamtzahl der Funde in der Frühbronzezeit in dieser Region eher selten. Es erscheint daher unwahrscheinlich, dass die Nebrafunde aus Kupfer hergestellt wurden, das in der Region aus lokal vorkommenden Erzen erschmolzen wurde. In diesem Fall wäre eine größere Fundhäufigkeit dieser Materialgruppe in Mitteldeutschland zu erwarten.

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Minerals as Sb and As reservoirs and vectors in the mining waste from the Pezinok Sb-Au deposit (Slovakia)

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The Pezinok deposit was mined between 1905 and 1992 and has produced ~380000 m³ of waste. Beside the rock-forming silicates, the waste contains mostly Fe oxides enriched in Sb and As. Our bulk chemical analyses and integration of the concentrations over the volume of the waste suggest that several thousands tons of As and Sb have been left behind. The secondary minerals in the waste occur in two forms, as rims on the primary minerals and as newly-precipitated (authigenic) grains. In the former case, the core of a primary sulfide mineral is usually preserved. In the latter case, these grains probably precipitated directly from aqueous fluids which percolate through the waste pile.

We have amassed a large data set with bulk chemical analyses of the waste, ochres that are discharged from the waste, and electron microprobe analyses of the rims and grains in the waste. The chemical analyses show that As and Sb fractionate within the body of the waste impoundment. Arsenic is more mobile and is released, antimony, on the other hand, is retained in the waste to a larger extent.

X-ray microdiffraction on the grains was carried out at the SUL-X beamline at the ANKA synchrotron radiation source to identify the mineral phases present in the waste. The most common phase is goethite, very often with elevated Sb content. Interestingly, Fe oxides with higher As content appear to be X-ray amorphous. The grains where Sb dominates over Fe are poorly crystalline; Rietveld refinement of our patterns hints that this material is structurally close to the mineral tripuhyite (FeSbO₄). The presence of poorly crystalline iron oxides (ferrihydrite) is likely but was obscured by intense background from the supporting glass.

X-ray fluorescence spectroscopy confirmed the close association of Fe and As in the studied samples. X-ray absorption near-edge structure (XANES) spectra measured on multiple weathering grains showed that arsenic is always present in its highest oxidation state, i.e., as As⁵⁺. The collected extended X-ray absorption fine-structure (EXAFS) spectra can be interpreted in terms of tetrahedral coordination of As by oxygen (as (AsO₄)³⁻); the weaker features in the second coordination shell correspond probably to the bidentate-binuclear complex that has been postulated on the iron oxides in previously published studies. Interestingly, the EXAFS spectra on the As *K* edge are identical for the grains where Sb is subordinate and where Sb dominates. This observation indicates that arsenic associates almost exclusively with iron on atomic scale.

The invisible gold in arsenopyrite from the Sb-Au deposit Pezinok (Slovakia)

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Arsenopyrite is the most common sulfide host of invisible gold. Yet, despite many studies, the position of such gold in the structure of arsenopyrite has not been resolved conclusively. The abstract reports a multitechnique study of arsenopyrite (FeAsS) samples from the Pezinok deposits (Slovakia) with moderate gold concentrations of 7-10 µg/g. The gold-bearing arsenopyrite is a component of ore mineralization in Variscan basement in the Malé Karpaty Mountains. A stratiform and metamorphosed pyrite-pyrrhotite (FeS₂-FeS) mineralization was followed by hydrothermal ores with pyrite, gold-bearing arsenopyrite, and a varied assemblage of primary Sb minerals stibnite (Sb₂S₃), berthierite (FeSb₂S₄), gudmundite (FeSbS), antimony (Sb), kermesite (Sb₂S₂O), and valentinite (Sb₂O₃).

Arsenopyrite in the studied sample contains has an average formula of FeAs_{0.98}S_{1.06}. The As concentration in pyrite is somewhat variable but averages FeS_{2.01}As_{0.01}, close to the ideal composition. Back-scattered electron (BSE) images show little variation in the sulfide minerals in this sample, marked by occasional patchy zones that are not easy to recognize even in BSE images. Inspection of the samples from this deposit, either within this work or within studies conducted at this deposit during the last 30 years, did not reveal the presence of metallic gold particles. Secondary ion mass spectrometry (SIMS) measurements were conducted at the GeoForschungsZentrum Potsdam with a mass filtered, nominally 10 kV ¹³³Cs⁺ primary beam. These experiments showed that gold occurs as either (1) almost uniform, low-concentration of "dispersed" gold, or as (2) hot spots along fractures.

X-ray absorption spectra at the Au L edge were collected from hot spots in one of the samples. The X-ray absorption spectra were collected at the 13-ID beamline of the Advanced Photon Source (Argonne National Laboratory, Chicago, USA). The fluorescent radiation was collected by an Oxford wavelength dispersive spectrometer (WDS) equipped with a LiF crystal. The use of the WDS was absolutely necessary because the As K and Au L absorption and emission lines have very similar energies. The X-ray absorption near-edge structure (XANES) spectra document metallic character of gold although no discrete gold particles were seen even after careful re-examining in back-scattered electron images. Despite the low gold concentration, we were able to collect an extended X-ray absorption fine-structure (EXAFS) dataset which also confirms that the measured spot contains metallic gold. Such occurrence is most readily explained by the presence of gold nanoparticles. We suggest that the dispersed gold is the chemically-bound gold previously detected in these deposits by ¹⁹⁷Au Mössbauer spectroscopy (András et al. 1995). Unfortunately, the concentration of this dispersed gold is too low for X-ray absorption spectroscopy. In the future studies, we should focus particularly on this type of gold to explain the nature of the invisible gold in arsenopyrite or other sulfides.

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The crystal structure of keyite, revisited

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Keyite is a complex Cu-Zn-Cd-arsenate described from Tsumeb/Namibia. The crystal structure of keyite has been determined by Cooper & Hawthorne (1996). According to this study keyite is monoclinic, with space group symmetry $I2/a$. The most unusual feature of the crystal structure is the disordered population at the Cu(1)-site. Cu(1) is coordinated by four oxygen and two water molecules, forming a distorted octahedron. The water molecules are nominally shared between two adjacent Cu(1) sites. However, realistic Cu-OH₂ distances can only be achieved if water occupies a split position, with adjacent Cu(1) sites being alternately filled and unfilled.

Here we report on a new structure refinement of a keyite crystal from the type locality. The structure model differs in two major aspects from that proposed by Cooper & Hawthorne (1996): (i) the space group symmetry is $C-1$ with the effect that the two Cu(1) sites of the monoclinic structure model become inequivalent. One of these sites is preferentially occupied by Cu, while the other one is nearly empty. (ii) excess electron density close to the assumed water position of the Cooper and Hawthorne structure model is associated with Pb. Approximately 0.1 Pb p.f.u. have been analyzed by Cooper & Hawthorne (1996), which is confirmed by our own microprobe analysis. If the Pb-content is neglected, the split water-site appears overpopulated.

With these two modifications and the assumption of two twin domains related by a diad along [010], the residual significantly improves relative to the monoclinic structure model. Implications of this new structure model for the stoichiometry of keyite and its true water content are discussed. While keyite retains a monoclinic metric, stronger triclinic distortion is expected if more Ca substitutes for Cd.

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Anwendung der Nah-Infrarot (NIR)-Spektroskopie zur quantitativen Bestimmung von Portlandit

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Ziel dieser Untersuchung ist die Entwicklung eines Messverfahrens zur quantitativen Bestimmung von Portlandit unabhängig von seiner Kristallinität und Korngröße, um die Qualität des Zementsteins in Mörteln und Betonen zu prüfen. Portlandit ist neben den Calcium-Silikat-Hydraten eine wichtige Phase, die bei der Hydratation von Portland-Zement entsteht. Die quantitative Bestimmung von Portlandit ist nicht unproblematisch. Die bisher verwendeten Methoden zur Quantifizierung sind QXRD (Quantitative X-Ray-Diffraktometrie) und Themogravimetrie. Durch Röntgendiffraktometrie können nur kristalline Phasen erfasst werden. Es ist aber bekannt, dass Anteile von Portlandit durchaus als röntgenamorph vorliegen können. Thermoanalytische Messungen erlauben die Portlanditbestimmung anhand des Gewichtsverlustes durch Wasserabgabe um 420°C (Taylor, 1997); liegen allerdings Portlandite unterschiedlicher Korngrößen vor, weitet sich dieser Temperaturbereich von unter 420°C bis 510°C und sogar bis 580°C auf (Taylor, 1997). Zusätzlich ist eine eindeutige Zuordnung der thermischen Effekte in heterogen zusammengesetzten Proben nicht mehr möglich. Deshalb wird eine Messmethode zur direkten Portlandit-Bestimmung dringend benötigt.

Die NIR-Spektroskopie ist eine zuverlässige Methode zur Bestimmung des Wassergehalts in diversen Stoffen. Gemessen wird im Spektralbereich 4000 – 10000 cm⁻¹. In diesem Bereich treten Obertöne- und Kombinationsschwingungen von OH-Gruppen und H₂O auf. Ridi et al. (2006) verwendeten die NIR-Spektroskopie, um die verschiedenen Wassertypen, die bei der Hydratation von C₃S (Zementklinker Alit Ca₃SiO₅) vorkommen, zu bestimmen. Die Methode wurde von Weckler und Lutz (1996) benutzt, um die OH-Bindungen in verschiedenen Hydroxiden wie Ca(OH)₂, Mg(OH)₂ zu untersuchen.

Wir zeigen, dass die NIR-Spektroskopie im Routineeinsatz zur Bestimmung des Portlanditgehalts, und damit zur Qualitätssicherung des Mischgutes sehr gut geeignet ist. Im Verlauf unserer Untersuchungen wurde eine Kalibrierkurve erstellt, indem wir Portlandit und Quarzmehl in verschiedenen Mischungsverhältnissen zwischen 0-100% präpariert und gemessen haben. Die Proben wurden homogenisiert, indem wir die Mischungen in einer Kugelmühle für 5 Minuten vermahlen haben. Die NIR-Messungen wurden mit einem MATRIX-F-Spektrometer und tragbarer Sonde an kleinen Probenmengen (5 g) in Küvetten durchgeführt. Durch eine Kreuzvalidierung der Messergebnisse wurde eine multivariate Quantifizierungsmethode mit der Software OPUS V6.5 (Bruker-Optics) entwickelt. Zum Vergleich wurden an den gleichen Proben die Portlandit-Gehalte mit der Rietveld-Methode bestimmt. Wie erwartet lieferte die Röntgendiffraktometrie niedrigere Portlandit-Gehalte. Dies liegt darin begründet, dass die NIR-Spektroskopie Portlandit unabhängig von Kristallinität und Korngröße erfasst. Andere Vorteile der NIR-Spektroskopie sind die schnellen, automatisierbaren, zerstörungsfreien und gut reproduzierbaren Messungen. Dieses spektroskopische Messverfahren stellt eine für die Zukunft viel versprechende analytische Messmethode bei der Quantifizierung von Hydroxiden dar.

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The behaviour of CO₂ and CO₂ mixtures during the storage in deep geological formations

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Industrial CO₂ sequestration with competitive technologies produces CO₂ fluids or gases in various degrees of purity, depending on the method used. These CO₂ mixtures contain between 85 and 99.9 % CO₂ and additional further components as O₂, N₂, NO_x, SO_x, Ar, H₂O in different concentrations. The storage of these CO₂ mixtures effects some fluid (gas)/rock interactions which may have extensive consequences to the deep geological formations. These include alteration and mineralogical transformations of the reservoir rocks which may influence the storage capacity and long-term safety and stability of the storage formation.

Geochemical reactions are highly rock-specific and time dependent. To determine the degree of reactivity between (impure) CO₂ and minerals, long-term laboratory experiments under simulated in-situ P-T conditions will be performed with different rock types and variable fluid (gas) compositions. For this purpose experiments in autoclave systems will be conducted in one autoclave as batch methods in a closed system, or in 2-3 connected autoclaves as coupled trials in a closed or an open system. A set of rock samples such as silicate sandstones and claystones, carbonates and sulphate rocks reacting with fluids and gases of 4 different well-defined compositions of CO₂ with impurities in well-controlled autoclave experiments. The duration of these experiments will range from 3 to 8 weeks. Subsequently, geochemical and mineralogical analyses in combination with geomechanical investigations will be executed to determine parameters like deformability, strength, effects of pore fluid pressure of the reservoir rocks. Several geomechanical tests in a computer-controlled triaxial load cell where carried out in the past to investigate rock stability and resistance (fig.1).

The results of the experiment with CO₂- and Ar-saturated pore fluid in crystalline rocks and pore fluid pressure of 40 MPa (fig. 1) show clearly that even in the case of crystalline rocks with their minimal pore space mechanical reactions occur. Appropriate reservoir rocks such as sandstones offer a much larger effective pore space, therefore a distinct higher rock mechanical differencing can be expected in those materials. Although limited in scale and time, laboratory experiments have the advantage that they can help to identify geochemical and geomechanical key reactions on actually for CO₂-storage considered rock material under simulated reservoir conditions. This knowledge is important as such reactions are supplied to be highly site-specific. They are also helpful to test whether there is an ability to reproduce geochemical and geomechanical codes in experimental observations before using them to make long-term predictions over timescales of up to thousands of years.

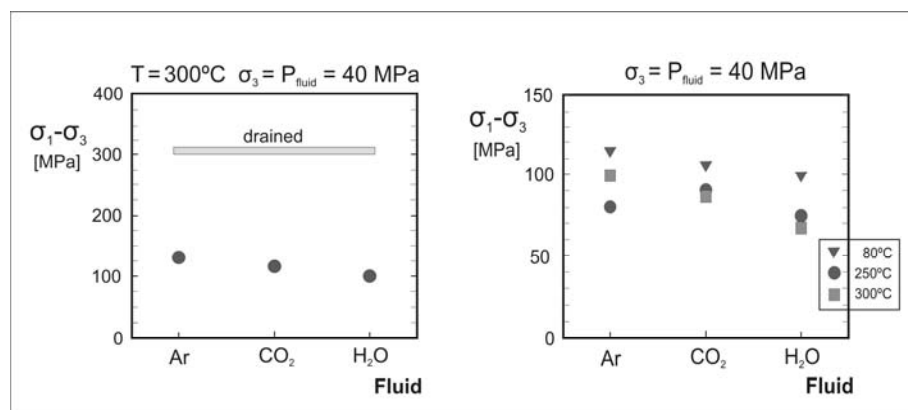


Fig. 1: Different pore fluids reducing the compressive strength of the Granit to about one third compared to drained conditions (left). Different fluids showing significant effects on the fracture strength also depending on the temperature used (right) (Lempp, 1994).

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Aqueous silicate solutions in metamorphic rocks at high pressures: What do we still need to know and how do we get the data?

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Aqueous fluids rich in dissolved silicate material play an important role both for the rheological behaviour of rocks as well as for the transport of elements during rock-forming processes at depth. However, the physico-chemical nature of such fluids at high pressures is not well understood. Primary data such as the composition of aqueous fluids coexisting with specific mineral assemblages as a function of pressure, temperature, etc., are sparse. The actual atomistic structure of such fluids and the speciation of the dissolved components are still largely conjectural. Experiments are difficult. Although straightforward in terms of experimental method, weight-loss techniques are *post-mortem* examinations of complex *in situ* processes in the experimental capsule. Without a theoretical template, uncertainties are difficult to gauge. *In situ* techniques such as with the diamond-anvil cell have so far not produced much data on solutions rich in the lighter elements typical of rock-forming minerals. Although pertinent data sets and geochemical work-benches exist at low pressures and have been successfully used to model settings in which reactive flow is important, this treatment of aqueous silicate solutions is difficult to extrapolate beyond 0.5 GPa. Polynomial descriptions of various types allow available data to be fitted up to 1 GPa, and extrapolations based on the isothermal linearity of equilibrium constants of dissociation reactions have proven useful, but fit parameters generally have no physico-chemical significance. Such extrapolations also assume that speciation does not change markedly with pressure. Polynomial fits are thus generally restricted to the pressure-temperature range and solution chemistry of the experimental data base. We suggest that a viable alternative approach is to treat H₂O in terms of a statistical thermodynamic model of water (e.g., Gerya *et al.*, 2005), which allows experimental data to be fitted to a realistic solution formalism with fit parameters representing conventional thermodynamic parameters. This approach was first successfully tested on simple SiO₂-H₂O fluids (Gerya *et al.*, 2005), and, using the extensive available data set for wollastonite, can be extended to arrive at an explicit model for CaO-SiO₂-H₂O fluids. This model can yield macroscopic thermodynamic data on dissolved components and their interaction parameters, but cannot identify the intrinsic atomistic nature of the species themselves. Spectroscopic data of aqueous solutions rich in silicates are still problematic. A viable alternative is represented by complementary *ab initio* molecular dynamics (AIMD) simulations. Such calculations have the added advantage that the diffusivities of specific dissolved species can be determined. Pertinent calculations have been carried out for the SiO₂-H₂O (Doltsinis *et al.*, 2007) as well as CaO-H₂O and Ca²⁺-H₂O systems (Adeagbo *et al.*, submitted). Combining these atomistic results with the macroscopic Gerya-type model above allows a realistic thermodynamic model for aqueous fluids in the CaO-SiO₂-H₂O system up to 900°C and 4 GPa to be obtained. The above example can only be a very first step toward modeling more complex rock-forming fluids involving additional cations, additional fluid components and additional ligands such as Cl⁻. More basic data on the solubilities of minerals and mineral assemblages are required. We suggest that *ex situ* and *in situ* methods can be effectively combined by monitoring mass changes of crystal fragments in diamond-anvil-cell experiments to allow more complex systems to be investigated with high precision. Introduced by Wang *et al.* (2004), these methods have been systematically refined by Gross (2009). Using basic geometrical principles, *in situ* determination of the habit and measurement of the relative development of faces of an idiomorphic crystal under the microscope can be used to calculate the crystal mass as a function of pressure and temperature. For irregular crystal fragments, mass can be determined via classical techniques of optical crystallography by mapping out crystal birefringence.

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Fluid-mineral interaction during weathering of hydrothermal ore deposits deciphered from supergene mineral assemblages in the Schwarzwald area, SW Germany

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The Schwarzwald in SW Germany hosts more than 400 hydrothermal veins. These veins contain a wealth of ore mineral assemblages of e. g. Pb, Zn, Cu, Ag, Bi, U, Co, Sb, As, Fe, Mn in barite, fluorite, quartz or calcite gangue minerals.

Weathering and reaction surface-derived fluids in oxidation zones produced a large number of supergene mineral assemblages which have been investigated in detail in the recent years, the most prominent being the Clara mine near Wolfach with up to now more than 400 described mineral species. The talk will shed light on a few examples to show how the combination of mineralogy, isotope geochemistry and hydrochemistry allows to reconstruct reaction processes in great detail.

Iron-isotope studies both of whole mineral grains using bulk techniques and of zoned minerals using a femtosecond laser system showed that measured iron isotope fractionation combined with known fractionation factors and careful textural observations allow the quantification of mineral reactions e. g. during redistribution of Fe from dissolved siderite by re-precipitation as botryoidal hematite or goethite.

Detailed REE studies both in fluids and in minerals revealed that the main source of REE in secondary REE minerals such as rhabdophane or agardite from mineralized veins is not related to dissolved primary fluorite (which contains some hundreds ppm of REE), although secondary fluorite has much lower REE concentrations, but is probably derived from the country rocks. The interplay between fluid, primary minerals in vein and host rocks, secondary Fe and Mn hydroxides and secondary REE minerals is a complex one which offers, however, the hope to trace fluid pathways in unprecedented detail. Further investigations are currently underway, but a review of the present results will be given.

A third group of studies concerns secondary minerals of transition metals such as copper, lead or zinc arsenates. Their stability relationships are poorly understood, but clearly reflect changing fluid conditions in terms of redox, pH or various ion activities. The talk will present a few examples how the careful investigation of mineral assemblages can be related to changing fluid chemistry during weathering of a mineral deposit.

Bildungsangebote im Konzept der neuen mineralogischen Ausstellung terra mineralia im Freiburger Schloss Freudenstein

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Im Oktober 2008 öffnete die neue mineralogische Dauerausstellung terra mineralia im Freiburger Schloss Freudenstein ihre Pforten. Etwa 3.500 Minerale aus der Sammlung von Frau Dr. Pohl-Ströher, die der TU Bergakademie Freiberg am 30. Juni 2004 als Dauerleihgabe zur Verfügung gestellt wurden, werden hier gezeigt. Die wunderbare Mineralsammlung der Frau Dr. Pohl enthält Minerale aus der ganzen Welt. Sie wurden nach ästhetischen Gesichtspunkten und privatem Geschmack zusammen getragen. Deshalb lag es nahe, als roten Faden durch die Ausstellung eine Mineralogische Weltreise zu schaffen. Die Ausstellung stellt jedoch nicht nur eine Mineralienshow dar, sondern bei Absteuern von der großen Weltreise kann man in jedem Raum etwas Interessantes erfahren. Die so genannte Aussichtsplattform bietet einen Einblick in die Ausstellung. Per GoogleEarth kann der Besucher zu bekannten Mineralfundpunkten fliegen und erleben, unter welchen Umständen die ausgestellten Minerale geborgen wurden. Der Nutzen bzw. die Verwendung von wichtigen Industriemineralen wird an den Beispielen Diamant, Quarz und Fluorit mit beeindruckenden Exponaten demonstriert.

In der Forschungsreise können die Besucher die Eigenschaften von Mineralen und Gesteinen kennen lernen. Moderne Mikroskope bieten Einblick in unbekannte Welten. Das gipfelt in einem Rasterelektronenmikroskop, unter dem sogar mitgebrachte Mineralfunde analysiert werden können. Diese Angebote richten sich insbesondere an junge Leute. In den Schulferien und an Aktionstagen, wie der Nacht der Wissenschaft, werden spezielle Programme angeboten, von denen zahlreich Gebrauch gemacht wird. Dafür können zusätzlich der moderne Vortragssaal oder in den Sommermonaten auch die Außenanlagen genutzt werden.

Weiterhin bietet auch jeder Kontinentraum eine Kurzreise. In Amerika gibt es die Reise ins Licht. Die Faszination lumineszierender Minerale hält hier alle Besucher im Bann. Die Zeitreise in Afrika zeigt, wie sich die Bedeutung wichtiger Minerale im Laufe der Menschheitsgeschichte verändert hat. Einige erstaunliche Eigenschaften, die an Mineralen entdeckt wurden, können selbst im Experiment ausprobiert werden. Dazu zählt die Fotovoltaik, die Pyro- und Piezoelektrizität, die optische Doppelbrechung und die Radioaktivität. Im Europa-Saal gibt es eine Reise zum Ursprung, bei der die wichtigsten geologischen Bildungsräume der ausgestellten Minerale erläutert werden. Mit Gulliver kann man im Asien/Australien-Saal vom Makro- in den Nanokosmos reisen. Die meisten Besucher stellen immer wieder die Fragen: „Wo kommen denn die schönen Kristalle her? Wie werden sie gefunden? Wer hat die glatten Flächen so kunstvoll geschliffen?“ So wurde die Idee geboren, die untertägige Situation nachzugestalten und dem Besucher zu zeigen, wie die Bergleute auskristallisierte Drusen vorfinden. Mit Gulliver kann man nun durch einen Gang schreiten, in dem drei große Fluoritdrusen installiert worden sind. Während einer abenteuerlichen Reise zum Bergwerk und zu chinesischen Händlern im Sommer 2007 konnten die Verhältnisse untertage dokumentiert und das erforderliche Material erworben werden. Ein 3D-Film erlaubt es im Anschluss, sich vom Maßstab 1:1 bis zu 360.000.000facher Vergrößerung in Fluoritkristalle hinein zu zoomen. Ein 3D-Monitor, der von der Dresdener Firma SeeReal entwickelt und gesponsert wurde, macht dies möglich. Wem das noch nicht reicht, der kann sogar in einen Fluoritkristall hinein klettern, der im Maßstab 1:1.400.000.000 gebaut wurde. Das Thema Fluorit wird weiterhin durch die Erläuterung der häufigsten Farbursachen und der wichtigsten Kristallformen ergänzt. Letztendlich kann man sogar Kristallen beim Wachstum zuschauen. Zum Abschluss erfährt der Besucher in der Schatzkammer etwas über Meteoriten und die Entstehung von Meteoritenkratern.

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The way towards engineering cement hydrate phase assemblages

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Until recently cement science was often considered to be too complex to fully understand the nature of the material. One of the main reasons for this is the often practiced detachment of cement/concrete science from natural sciences, e.g. physics, chemistry, geology etc. and the trend to only consider it as an engineering discipline. As a consequence concrete was/is often treated as macroscopic material only and structural engineers tend to rely on received wisdom, based on field experiences and accelerated standard tests with often unrealistic test conditions. Though always questioned due to a high degree of uncertainty this empirical approach so far had to be applied in practice as there is a general lack of more reliable experimental test methods. The relevant criteria of these test methods are often based on physico-mechanical properties e.g. strength, expansion, etc. leaving the hydrated cement system as untouched "black box". So far the approach was accepted, as many binder systems were Portland-cement based or dominated by Portland cement in blended cements.

With growing urbanization and population the worldwide cement demand is expected to grow significantly in the next decades, whereas on the other hand at the same time the cement industry has to take great efforts to reduce the CO₂ emissions considerably. Cement production alone accounts for ~5% of the worldwide CO₂ emissions. New approaches to lower energy consumption and reduce GHG emissions are therefore of major ecological significance. This can be done in three fields:

1. Product development as the key lever
2. Improvement of thermal energy efficiency and process technology
3. Optimization of fuel composition

In Portland cement production about 1/2 of the emitted CO₂ can be attributed to the raw materials, mainly due to the energy intense calcination of the used limestone. Thus beside process optimization (points 2 and 3 above) the main driver to lower CO₂ emissions is the partial substitution of Portland cement by alternative supplementary cementitious materials (SCM), e.g. limestone, fly ash, slag, natural pozzolans etc. In the Holcim Group, composite cements today account for more than 80% of products compared to 30% in 1990.

As we move more and more away from Portland cement based systems, the variety of cementitious binders increases and the chemistry of these materials will be undoubtedly become more complex. As a consequence we cannot rely anymore on experiences that were mainly gained on Portland cement systems. The uncertainties regarding existing test methods and their interpretations increase. However at the same time more capable techniques and methods became available in order to design and optimize new composite binder solutions.

For example predictive modeling based on thermodynamic concepts is one method which will gain more importance in future cement research. The idea behind this approach, however, is not new - most of the people working in cement science or industry still apply thermodynamics on a daily routine while frequently using Bogues equations [1] to estimate the mass balance of cement clinkers based on a high temperature equilibrium of the quaternary system CaO-SiO₂-Al₂O₃-Fe₂O₃. Although many people argued cement hydration is a "non-equilibrium" process, experimental works on cement systems (Kuzel et al. [2][3]; Pöllmann [4][5], etc) benchmarked by thermodynamic calculations of the phase constitution of hydrated cement paste [6] were in close agreement showing the applicability of thermo-dynamics to cement hydration. Pioneering works, by Damidot and Glasser [7], as well as from other groups e.g. Reardon [8] and Berner [9] proved that cement hydration follows the basic principles of physical chemistry by minimization of the free energy of an isochemical system.

Based on the outcomes of these calculations and with the availability of a complete dataset [10] which is able to accurately describe the phase constitution of hydrated cements the next step is to use these tools to tailor-made cementitious binder compositions in order to obtain maximum performance. First attempts on limestone blended systems are promising and show that the hydrate chemistry can be in principle controlled via thermodynamics [6]. Missing links are the coupling of chemical models to powerful generic kinetic models and to combine these approaches with mechanic concepts in order to

close the historically grown gap between natural disciplines and structural engineering in cement/concrete science.

To overcome these basic challenges, nanocem (www.nanocem.org), an industrial-academic research network, was founded in 2004 as a platform for interdisciplinary cement research. Nanocem brings together more than 120 researchers who manage about 60 PhD projects in fundamental cement research. Holcim is one industrial partner, amongst others, in this network, which also underlies Holcim's commitment to sustainable development and research. In 2008, for the fourth year running, the Dow Jones Sustainability Index acknowledged the company as the "leader of the industry". Consequently typical research issues being currently addressed in Holcim's own research department but also partly by nanocem are:

- development of blended cements with Portland cement like performance
- maximum utilization of alternative fuels and raw materials (AFR)
- development of low energy or alternative binders
- end of life and recycling concepts
- service life prediction of concrete.

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Roter Turm in Halle/Saale - Provenienzbestimmung der Bausteine

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Das mit 84 Metern höchste Bauwerk der mittelalterlichen Stadt ist bis heute ihr Wahrzeichen. Der in der Zeit von 1418 bis 1506 in mehreren Bauabschnitten errichtete Rote Turm besteht aus einem massiven, rechteckigen, viergeschossigen Unterbau und einem achteckigen, mehrgeschossigen Oberbau, der durch große Maßwerkfenster gegliedert ist (Krause & Voss 1986). Im 19. Jahrhundert wurden diverse Reparaturmaßnahmen vorgenommen, die zum Teil auch mit einem Steinaustausch verbunden waren. Nach der Kriegszerstörung, deren charakteristische Brandschäden stellenweise noch heute in Form von konkaven Abplatzungen und einer Rotfärbung der Steine im Unterbau nachvollziehbar sind, ist er 1975 in alter Form restauriert worden. Diese lange Baugeschichte des Objektes macht die Verwendung verschiedener Baumaterialien bzw. Sandsteinvarietäten zur Errichtung und Reparatur des Mauerwerkes sehr wahrscheinlich. Im Rahmen der gelungenen Gesamtanierung des Turmes in den Jahren 2008/2009 war es möglich, alle Bereiche zu inspizieren und an auszutauschenden Quadern entsprechende Proben zu nehmen, an denen die Provenienz durch mikroskopische und infrarotspektroskopische Untersuchungen ermittelt werden konnte. Die Anwendung der IR-Spektroskopie wurde durch die Zusammenarbeit mit der Bundesanstalt für Geowissenschaften und Rohstoffe in Berlin möglich. Die Untersuchungen erfolgten mit Hilfe des transportablen Gerätes PIMA, das die Proben zerstörungsfrei im nahen Infrarotbereich spektroskopisch untersucht. Anschließend wurden die so erhaltenen Infrarotspektren mit einer umfassenden Referenzdatenbanken verglichen und Sandsteinprovenienzen zugeordnet (Bowitz & Ehling 2008). Zerstörungsfreie Messungen sind von erheblichem Interesse für Untersuchung im Denkmalbereich, obgleich die hier verwendeten Proben an Ausbaumaterial vorgenommen worden sind. Zum Bau des Roten Turms wurden fast ausschließlich helle, gelblich-graue Sandsteinvarietäten verwendet. Vereinzelt sind auch rote Sandsteine und rhyolithisches Material im Mauerverband zu erkennen. Bis zu dem Zeitpunkt der Sanierung waren die Oberflächen durch dicke dunkle Krusten belegt. Eine Differenzierung insbesondere der hellen Gesteine war oft unmöglich. In einer früheren Arbeit von Beeger (1971) wurden die Sandsteine als Buntsandsteine angesprochen und eine Herkunft aus Steinbrüchen im Saaletal bei Wörlitz für wahrscheinlich gehalten. Das konnte für einen Teil der Baumaterialien auch bestätigt werden. Bei den rötlichen Sandsteinen handelt es sich im Gegensatz zu früheren Annahmen zum Teil um Material der relativ stadtnah (Saaletal) liegenden Brüche des Rotliegendesandsteins. Die detaillierten Untersuchungen an Ausbausteinen und gereinigten Oberflächen haben allerdings auch weitere Varietäten aufgezeigt, womit wesentliche Informationen für die Bau- und Restaurierungsgeschichte des Turmes bzw. entsprechende Handelsverbindungen und Transportwege gegeben werden können.

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Discriminating “coltan” from African rare element pegmatites on the basis of mineralogy and geochemistry

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Since about the year 2000, the African continent has developed into a major exporter of “coltan” – heterogeneous concentrates of niobium-tantalum ore. A probable link between raw material exports (i.e. tin, tantalum, tungsten, gold and diamonds) and continuing violent conflicts, especially in the Democratic Republic of the Congo, is widely discussed. In many African countries, tantalum ore is mined from rare-element pegmatites and their weathering products (placers) by mainly artisanal, small-scale mining operations.

On behalf of the German Federal Ministry for Economic Cooperation and Development (BMZ), the Federal Institute for Geosciences and Natural Resources (BGR) commenced a pilot project on the analytical fingerprint of coltan ores. Reference samples from known locations are studied using a variety of methods, accompanied by regional pilot studies in selected mining areas in Africa. The combined mineralogical and geochemical information is used to discriminate between ore provinces, even down to the deposit scale, especially in east and central Africa (Melcher et al. 2008a, b).

Methods employed include automated scanning electron microscopy (mineral liberation analysis), electron microprobe analysis, laser ablation plasma-source mass spectrometry, X-ray fluorescence spectroscopy, X-ray diffraction analysis and thermal-ionisation mass spectrometry.

In a first step, determination of mineral formation ages using the U-Pb isotope system traces the origin of a concentrate to one out of five “age provinces” known from African tantalum-bearing pegmatites. In a second step, mineralogical parameters such as modal mineralogy, grain size distribution and intergrowth relationships are determined. Coltan is a mixture of a large number of minerals, commonly dominated by columbite-tantalite group minerals. In some cases, their compositions and textural relations already provide diagnostic proofs of origin. In a final step, the concentrations of major and trace elements are measured in a representative number of columbite-tantalite grains of a given sample. Some elements, e.g. the rare earth elements, are suitable for fingerprinting. Finally, statistical and mathematical methods are applied to classify samples objectively and to validate the results.

So far, our data show that a discrimination of “coltan provinces” is possible using age determination. Mineralogical and geochemical attributes of coltan concentrates and columbite-tantalite group minerals further allow the distinction of single deposits within certain age provinces.

The analytical fingerprint of coltan may assist in the establishment of a control instrument in an envisaged certification of the production and trade chain of coltan.

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Platinum-group element potential of chromite ores from southern Iran

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With an annual production of 225,000 tons of chromite concentrate in 2006, Iran ranks number ten among the World's chromite producers. Four important chromite mining areas are distinguished: north and northeast Iran (Sabzevar), south Iran (Kerman with important mining areas at Faryab and Esfandagheh), southwest Iran (Neyriz, Fars) and east (Birjand) and southeast Iran (Baluchestan-Makran). Chromite is exclusively associated with ultramafic rocks of the upper mantle and the lower cumulate sequences of ophiolite complexes. The platinum-group element (PGE) potential of Iranian chromitites is poorly known. Highest concentrations were reported in chromitite from Sikhoran / Esfandagheh area (435 ppb Pt and 277 ppb Pd; Alinia & Facherabadi, 2005). Rajabzadeh (1998) identified inclusions of platinum group minerals (PGM) in chromite ores from the Neyriz and Faryab ophiolite complexes, mainly minerals of the laurite-erlichmanite series (RuS_2 - OsS_2). The goal of the reconnaissance study was to improve the poor data base on PGE concentrations in Iranian ophiolites, and to develop a concept aimed at regional PGE exploration.

Chromite samples were collected from more than 20 chromite orebodies in four ophiolite complexes in southern Iran - Neyriz, Abdasht, Sikhoran, and Faryab. All are areas of active chromite mining. Host rocks vary from harzburgite and dunite to pyroxenite, websterite and wehrlite. Textures range from disseminated, nodular, schlieren-type to dense, massive ores. Ages are disputed (i.e. for Faryab and Esfandagheh), but mostly considered Mesozoic, with a Cretaceous obduction history. Analyses of PGE concentrations in 58 samples of chromitite and sulphide-bearing dunite yield a variation from 57 to 5183 ppb total PGE with an average of 456 ppb. In general, PGE concentration patterns normalized to primitive upper mantle (PUM) of Iranian chromitites are characterized by negative slopes from the IPGE (Os, Ir, Ru) to the PPGE (Rh, Pt, Pd). A few chromitite samples, however, display elevated Pt + Pd, and PGE totals may exceed 5 ppm in cases.

Most interesting is a group of sulphide-rich chromitites with visible interstitial pentlandite from Sikhoran which have Pd_n/Ir_n from 4 to 15, and Pt_n/Ir_n from 1 to 5, respectively. These chromitites are part of a banded dunite sequence with chromitite interlayers (Cr numbers 75-80, Mg numbers 30-65). Sulphide-bearing chromitite also has elevated concentrations of Au (up to 0.5 ppm) and Re (up to 3.5 ppm). Sulphide-poor chromitite samples from Sikhoran carry from 100 to 400 ppb PGE only. This indicates a close association of Pt and Pd with interstitial sulphides. At Faryab, all but one sample have low Pt+Pd; this sample from the Dovais orebody has Pt, Pd and Re concentrations similar to those from associated sulphide-bearing dunites. In the Neyriz ophiolite, small pods of massive chromite (Cr numbers 65-70, Mg numbers 45-60) carry up to 2 ppm PGE, with Pt_n/Ir_n close to 0.5.

$^{187}\text{Os}/^{188}\text{Os}$ ratios of all chromitites vary within a narrow range, i.e. from 0.125 to 0.134. Samples are characterized by low Re/Os (<0.1); More radiogenic Os isotope values and higher Re-Os ratios are restricted to sulphide-rich samples. The inventory of PGE carriers was evaluated using reflected light and electron microscopy and electron microprobe analysis. Major PGM in all areas investigated is laurite with considerable substitutions of Os and Ir for Ru; in addition erlichmanite, cuprorhodsite, cuproiridsite, Ni-Cu-Ir-Rh sulphides, irarsite, hollingworthite, Pt-Fe alloys, Os-Ir-rich alloys, Ru-rich alloys, Ru-rich oxides, stibiopalladinite, unnamed RhNiAs , tolovkite [IrSbS], and poorly defined As-rich phases were identified. Pentlandite is not a major carrier of Pd and Rh (<50 ppm) in sulphide-rich samples.

In conclusion, areas of elevated sulphide concentrations in chromitite and dunite, especially in the Esfandagheh district of southern Iran, may be regarded as targets for future PGE exploration.

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Germanium in sphalerite and willemite at the Tres Marias mine, Mexico: An EPMA, CL, LA-ICP-MS and synchrotron study

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The Tres Marias carbonate-hosted Zn-Ge deposit in Chihuahua, Mexico contains sphalerite with the highest average Ge (960 ppm), and willemite with the highest reported Ge contents of Mississippi Valley-type (MVT) deposits worldwide (Saini-Eidukat et al. 2009). This has prompted recent exploration efforts to focus on the deposit as a high-grade source of germanium. The Tres Marias deposit has hybrid characteristics consisting of a primary low temperature Mississippi Valley Type Ge-rich Zn-Pb sulfide ore body, overprinted by Ge-rich hemimorphite, willemite and Fe-oxide mineralization. The sulfide-rich ore type (> 125,000 t @ 20 % Zn and 250 g/t Ge) contains Fe-rich botryoidal sphalerite (Type I) associated with solid hydrocarbons. This type exhibits distinctive, intimately intergrown lamellar texture, of high-Fe sphalerite (average 9.9 wt% Fe and 800 ppm Ge), and a somewhat less Fe-rich sphalerite phase (average 5.5 wt% Fe and 470 ppm Ge). Reddish-brown, banded sphalerite (Type II, average 5.7 wt.% Fe and 1320 ppm Ge) is subordinate followed by galena and pyrite. Highest Ge concentrations (>3000 ppm) are detected in small (<100 µm) isolated sphalerite crystals interstitial to calcite. Further trace elements in sphalerite as detected by electron microprobe and LA-ICP-MS analysis include high (>2000 ppm) Cd and Pb, intermediate (20-2000 ppm) As, Sb and Tl, and low (<20 ppm) Ag, Bi, Co, Cu, Ga, In, Mn, Mo, Ni, Se and Sn (Cook et al. in press). Trace element X-ray mapping using synchrotron radiation indicates zoning patterns in "schalenblende"-type sphalerite with highest concentrations of Ge close to the contacts with calcite matrix.

The sulfide-poor, "oxidized" zinc ore (up to 50 wt% Zn; 250 to 300 ppm Ge) is a fine-grained, often friable alteration product of the sulfide ore and associated limestone and breccia host. While some areas are dominated by carbonates and sulfates, others are enriched in hemimorphite, fraipontite, muscovite-illite, halloysite, or willemite. Minor wulfenite, greenockite, cinnabar and descloizite occur as late-stage phases. Willemite [Zn₂SiO₄] occurs as two types, (1) veinlets of several hundred µm width filled with zoned willemite displaying oscillatory zoning, and (2) smaller, but also zoned grains in the matrix. Willemite carries unusually high concentrations of minor and trace elements (e.g., Pb, Ge, As, P, V); Pb concentrations are as high as 2 wt%, and Ge may reach 4000 ppm (average 900 ppm) making willemite an interesting target of future Ge extraction. In cathodoluminescence (CL) images (Neuser hot cathode CL microscope), those areas of willemite having high trace element concentrations have no, or low CL intensities, whereas zones low in trace elements (except for P) display bright blue CL colours. Microprobe analyses and synchrotron X-ray maps show that Zn and Ge, as well as Zn and Pb are negatively correlated, whereas Ge and Pb are positively correlated across zoned willemite crystals. Oscillatory zonation reflects trace element incorporation into willemite from the oxidation of primary Ge-bearing sphalerite and galena by siliceous aqueous fluids. The nature of trace element substitution in sphalerite (Ge) and willemite (Ge, Pb) was investigated by X-ray absorption fine structure (XAFS) spectroscopy, focussing on the XANES part of the Pb L₃ edge (Pb L₃ edge at ≈ 13.035 keV) and Ge K edge (≈ 11.103 keV) absorption spectra. A comparison to reference spectra of natural and artificial substances points to the presence of Ge⁴⁺ in willemite, and to a chemical environment of Ge in sphalerite similar as in briartite, argyrodite and GeS₂; the best match is with briartite [Cu₂(Fe,Zn)GeS₄]. Lead seems to be present as Pb²⁺ in willemite. These results will allow the determination of substitution mechanisms for minor elements in the willemite structure.

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Applicability and limitations of Raman mass-spectroscopy on CO₂ inclusions

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The ratio of ¹³C-¹²C in carbon dioxide is dependent on the carbon dioxide's origin. Biogenic derived CO₂, for example, is relatively depleted in ¹³C, while carbon from the mantle is relatively rich in ¹³C. The determination of the isotopic carbon composition of CO₂ trapped as inclusions in minerals can therefore provide important information on the origin and global circulation of CO₂ in the Earth's lithosphere. Conventional mass spectrometric methods allow a precision of less than 1 ‰ and a high accuracy, but it is not possible to measure small single CO₂ inclusions. We investigated the limitations and possibilities to determine the ¹³C-¹²C ratio of CO₂ inclusions in minerals by micro-Raman spectroscopy, a non-destructive tool that allows the analysis of small, single inclusions.

The Raman spectrum of natural CO₂ is characterised by intense bands near 1286 and 1389 cm⁻¹ and 1265 and 1370 cm⁻¹ of ¹²CO₂ and ¹³CO₂, respectively, which result from Fermi resonance. The intensity and area ratios of the ¹³CO₂ and the ¹²CO₂ bands are directly related to the isotopic composition. Although the ¹³CO₂ bands of natural CO₂ are hardly detectable at atmospheric pressure, the upper ¹³CO₂ band can be measured precisely in dense CO₂ inclusions, if long counting times are used. Pressure and the temperature inside the inclusion can be obtained *in situ* by measuring the frequency difference between the upper and lower Fermi diad, respectively, by the relative scattering intensity of the hot bands and the Fermi diads.

We used two CO₂ gasses as standards with known ¹³C-¹²C ratios (ranging from -36 ‰ ¹³C to -3 ‰ ¹³C values) which were obtained by conventional mass spectrometry. To investigate the dependence of the intensity ratio between the ¹³CO₂ and ¹²CO₂ band on the CO₂ density and various instrumental parameters, we conducted Raman measurements in an in-house made gas pressure cell at pressures up to 500 bar at about 295 K. We will show that for the most precise and accurate results, it is necessary to measure the standard and inclusion gas with identical instrumental settings and, importantly, at equal density. Currently, we are able to measure the carbon isotopic compositions of the standard gasses with an internal precision of about ± 6 per mil (2σ).

Internal temperature appears to be the major factor contributing to larger scatter of intensity ratios. Therefore measurements of CO₂ inclusions in natural zircons did not yield reasonable results, yet. We are currently investigating the relationship between internal inclusion temperature and intensity ratios of ¹³CO₂ and ¹²CO₂ bands.

Sources and sinks of colloids in a weathering profile

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Colloids play an important role in weathering processes because of their high specific surface area and the resulting potential to adsorb heavy metals or trace elements. In contrast to dissolution/precipitation processes, the processes of colloidal transport, their contribution to the total geochemical mass balances, as well as their interaction with mineral surfaces are still not well understood. Here we present results about the occurrence of natural colloids in a weathering profile. After migration through the regolith profile the colloids may adsorb on mineral and rock surfaces at high-permeability zones (FISCHER et al., 2008).

We studied material from a weathering profile of slates, well-known from previous investigations. We sampled in-situ weathered material from the upper layers of weathered slates (source of colloidal material) as well as from the deeper layers of the profile (sink for colloidal material).

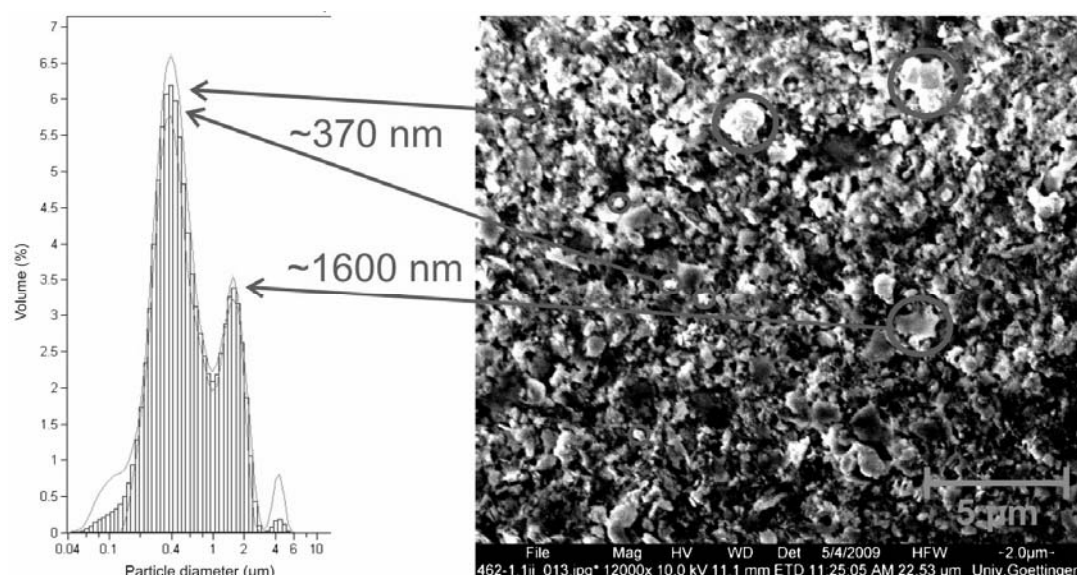


Fig. 1: A bimodal grain size distribution (mean diameters of 370 nm and 1600 nm) were found for both, the samples from the regolith and the encrustation. The SEM image gives an impression about the common grain size distribution.

Particle fractions < 2 μm were separated from regolith samples as well as from encrustation samples. The separated particles (< 2 μm) were characterized for grain size, shape and mineralogical composition.

We will apply the here investigated natural colloids as well as artificial analogues (well defined surface charge, well defined shape and diameter) for experiments about the interaction of colloids with rough mineral surfaces.

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Ore-mineralogy and genesis of vein-type Cu ores at Saalfeld-Kamsdorf, Thuringia

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In the context of a bachelor-thesis, copper samples from narrow hydrothermal veins of the Christian-Zeche near Könitz (Thuringia/Germany) were macro- and microscopically analysed to identify the ore-paragenesis and to determine the metallogenetical sequence of formation. The work forms part of the research project "Geochemische und archäometallurgische Untersuchungen zur prähistorischen Buntmetallgewinnung in Europa" (Geochemical and archaeometallurgical investigations on prehistoric base-metal mining in Europe), which is sponsored by the Deutsche Forschungsgemeinschaft. Within this project, potential copper mining sites of the Bronze Age are registered and geochemically analysed. From lead-isotope- and trace-element data, conclusions are drawn to compare Bronze-Age artefacts, especially the hoard find of Nebra, with ore deposits of Europe. Initial studies show a distinct Pb-isotopic and moderate trace element similarity of the Kamsdorf ores with hoard finds from Dieskau/Kanena, Sachsen-Anhalt (Frotzsch in prep.) The Saalfeld-Kamsdorf ore deposit is part of a historical mining district in Thuringia, Central Germany. The deposit is situated near the eastern-most border of the Thuringian basin, where Zechstein strata, mainly Zechstein-carbonates, outcrop against an older basement. The rocks overlie discordantly the folded strata of the Thuringian Schiefergebirge, which neighbors the Thuringian basin to the East and which strata continue under the basin sediments. The mineralisation is tectonically bound to the intersection of the Eichenberg-Gotha-Saalfelder and the Remdaer fault-zones with the East-Thuringian monocline, a marginal flexure of the Thuringian Schiefergebirge. The analysed samples

consisted mainly of chalcopyrite and the gangue mineral calcite. Chalcopyrite is altered along the rims to covellite and digenite. Chalcopyrite and calcite were partially replaced by supergene iron- and manganese-hydroxides. The latter have been identified by energy-dispersive X-ray spectroscopy (EDX) and only occur in subordinate amounts. Calcite shows unusual pleochroism in thin section and locally microscopic banding of brownish to whitish colours. EDX-analyses have identified iron-bearing calcite with 3-4 wt-% iron, explaining the colour and unusual pleochroism. In some specimen, intra-crystalline cavities were found, in which hydroxides precipitated. Besides the common secondary ore-minerals malachite and (less) azurite, baryte is also found in one sample neighboring the hydroxides. Malachite and azurite usually occur as a fringe between chalcopyrite and calcite. Locally, small veinlets of malachite occur within the calcite. Triangular growth of calcite, directed towards the sulphides, indicates that calcite existed before sulphide-precipitation. After Meinel (1993), calcite was replacing barite; the calcite shows REE-signatures of a carbonate built by microbiological redox-procedures. The corresponding release of CO₂ led, besides the mixing of deep, saline waters with sulphate-bearing meteoric waters, to an alkaline setting. The coupled sulphur-ion concentration led to an overgrowth of chalcopyrite on calcite (Meinel, 1993). The Cu was potentially mobilized from the Rotliegend and precipitated in the area of the reducing Zechstein-barrier. Fe and Mn of the hydroxides originate from metasomatic ankerite, although a barite-related siderite-placement should also be considered as a potential origin (Meinel, 1993). The vein-type ores represent near-surface, Cu-rich, massive, mixed sulphide and carbonate ores with an excellent potential for pre-historic exploration, mining and metallurgical processing. Additional geochemical and Pb-isotopic analyses are currently carried out to broaden the statistical data base of indications that copper from Kamsdorf was the raw material for artefacts of the hoard finds of Dieskau/Kanena.

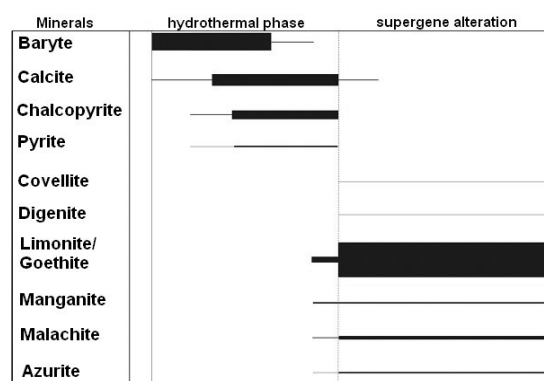


Diagram showing the sequence of formation of the ore paragenesis. Thickness of bars represents relative abundance of minerals.

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Carbonate-bearing metaperidotite from Gorgona (Xanthi area, Central Rhodope, Greece): An example of mantle-crust interaction in a subduction zone

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In the Central Rhodope terrain of NE-Greece a carbonate-bearing metaperidotite lense ~200×500 m in size, is found within the Jurassic high- and ultrahigh-pressure Kimi Complex ~ 500 m SE of the Gorgona Village, north of Xanthi. It is composed primarily of coarse grained (3-20 mm in size) olivine and orthopyroxene, medium grained clinohumite and medium to fine grained tremolite, chlorite, dolomite, magnesite, talc, antigorite, and spinel-group minerals.

Whole-rock chemistry, mineral textures and compositions, and P-T, P/T- X_{CO_2} phase diagram calculations show that the metaperidotite underwent prograde HP metamorphism, isofacial with the surrounding gneisses and eclogites. The prograde character of metamorphism is demonstrated by inclusions of talc, antigorite, chlorite, dolomite, magnesite and Ti-clinohumite in ferrit-chromite, olivine, and orthopyroxene, and of olivine in orthopyroxene, and by the chemical composition of zoned spinel minerals from Cr-magnetite in the core to ferrit-chromite and high Al-spinel at the rim.

The prograde path is characterized by successive growth of amphibole, Ti-clinohumite, olivine and orthopyroxene, followed by the breakdown of Ti-clinohumite to olivine + Mg-ilmenite and of chlorite to olivine + spinel during exhumation. The P-T path is clearly constrained by the absence of clinopyroxene.

The X_{CO_2} in the fluid phase increased with increasing grade of metamorphism as magnesite consuming and olivine forming reactions produced much more CO_2 than H_2O . The increase in X_{CO_2} in the fluid phase was responsible for the orthopyroxene formation at the peak metamorphic conditions. Decomposition of Ti-clinohumite to olivine and Mg-ilmenite and of chlorite to olivine and high Al-spinel occurred during decompression and further increase of X_{CO_2} in the fluid.

The retrograde matrix assemblage chlorite (chl-2) + magnesite (mgs-2) + talc + tremolite (tr-2) replacing olivine, high Al-spinel, orthopyroxene and dolomite may have alternatively formed during a second metamorphic event at moderately high-pressures in the Eocene. In that case, the re-volatilisation of the assemblage could have been triggered by fluids liberated from the underlying Albite-Gneiss Series that underwent metamorphism during this period.

Trace element data indicate that the carbonate-bearing metaperidotite from Gorgona represents a fragment of the hydrated mantle wedge as the REE compositions differ from those of ophiolitic peridotites and resemble those of spinel or garnet peridotites of sub-continental origin, of which a fragment was incorporated into the subduction channel by tectonic erosion in the Early Jurassic.

A Synchrotron Microscope for pressure-dependent Far-Infrared Measurements in Diamond Anvil Cells under vacuum at BESSY

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Infrared spectroscopy is one of the most powerful tools in identifying minerals and provides many different applications for examining the local structure of materials and detecting even very small amounts of impurities. Combined with experiments in diamond-anvil-cells (DAC) it provides important insights in pressure-induced structural changes such as phase transitions, cation order and disorder etc. Mid-Infrared-measurements (wavelength 10 – 20 μm) in DAC can easily be performed with an aperture diameter of about 100 μm or smaller using a conventional IR source (e.g. Koch-Müller et al. 2005), which allows reaching pressures up to 50 GPa and even more. Problems arise in the Far-Infrared (FIR) region as with increasing wavelength of the light (20 – 200 μm) the insitu DAC experiments would require an aperture of at least 1 mm to overcome the loss of light due to diffraction. That would limit the applied pressure to about 1 GPa. However, when investigating pressure-induced structural changes the FIR region provides important information as in this region the vibrations, in which the metal cations are involved, occur and it would be desirable to investigate the FIR region also at high pressures.

Synchrotron light sources like the Berlin electron storage ring for synchrotron radiation BESSY II (Berlin - Adlershof, Germany) provide light of extreme high brilliance ranging from the Terahertz long wavelength to the hard x-ray region. The intensity of synchrotron IR light compared to a standard global can counterbalance the described effect of longer wavelengths. Thus a big advantage of synchrotron radiation is that the generated light is much more intense and is highly collimated such that spectroscopy with synchrotron radiation can be done at the diffraction limit of the light, that means with a very high spatial resolution, e.g. an aperture diameter of 5 μm at 3.3 – 2.5 μm wavelength (Koch-Müller et al., 2003) or 400 μm in the far infrared (FIR) to a wavelength of 200 μm . Furthermore the very weak absorption of far infrared bands for instance of silicate minerals is a difficulty that also can be dealt with by means of the high intensity of synchrotron light.

We therefore developed an FIR microscope adapted to a Bruker IFS66v - Fourier transform infrared spectrometer (FTIR) operating under vacuum at the BESSY infrared beamline IRIS. The microscope is equipped with a Cassegrain-objective with a numerical aperture of 0.28 and a movable sample holder with external adjusting screws. All parts of the assembly (mirrors, sample holder, objective) are mounted on a ground plate that easily can be set into the spectrometer. Synchrotron FIR spectroscopy was successfully carried out at pressures up to 20 GPa with aperture diameters of about 300 μm .

We will introduce the new FIR-microscope and its application by presenting three examples on pressure-induced structural changes in silicate minerals such as feldspar, olivine and wadsleyite detected in the MIR – FIR region.

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Tonminerale in Lagerstätten und Böden: die Rolle von Eisen und Titan

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Eisen und Titan sind die häufigsten Übergangselemente in der festen Erdkruste. Sie sind ebenfalls Haupt-, Neben- oder Spurenbestandteile der meisten Tone und Tonminerale. Als Bestandteile kommerzieller Tone, insbesondere des Kaolins, wirken Eisen und in geringerem Maße Titan (insbesondere wenn sie in oxidischer Form vorkommen) störend und müssen soweit möglich im Zuge der industriellen Aufbereitung entfernt werden. Im Gegensatz dazu ist die Rolle des Eisens bei landwirtschaftlich genutzten Böden eher ambivalent: während Eisenoxide eine positive Funktion als aggregierende Komponenten haben können, konkurrieren sie mit den Pflanzen um Nährstoffe (insbesondere Phosphat). Dabei sind Faktoren wie Mineralart und Teilchengröße von entscheidender Bedeutung. Eisen kommt ferner zwei- und/oder dreiwertiger Form als struktureller Bestandteil von Tonmineralen vor und kann die physikalischen Eigenschaften mancher Tonminerale (z.B. eisenreicher Smectite, s. Stucki, 2006) entscheidend beeinflussen.

Aus diesen Gründen kommt der analytischen Bestimmung der Eisen- und Titanmineralogie in Tönen eine erhebliche Bedeutung zu. Probate Verfahren hierzu sind die Röntgenbeugung und, vornehmlich für Eisen, ^{57}Fe Mössbauerspektroskopie, bzw. speziell für Titan Ramanspektroskopie. Die ^{57}Fe Mössbauerspektroskopie ermöglicht einerseits die Unterscheidung von zwei- und dreiwertigem Eisen, andererseits eine Unterscheidung zwischen oxidisch gebundenem und strukturell in Tonmineralen eingebautem Eisen. Unbekannte Phasen können somit anhand ihrer Mössbauerparameter (dem sog. "Fingerabdruck", s. Abb. 1) gekennzeichnet werden. Im Gegensatz dazu reagiert die Ramanspektroskopie besonders empfindlich auf Verbindungen des Titans und hier insbesondere auf den Anatas (Murad, 1997). Dies macht die genannten Techniken zu geeigneten Verfahren um die Eisen- bzw. Titanmineralogien von Tonmineralen und Tönen zu kennzeichnen, sowie die Veränderungen der Eisen- bzw. Titanmineralogien von Tönen im Zuge deren industrieller Aufbereitung (Murad & Köster, 1999; Mussel et al., 2008).

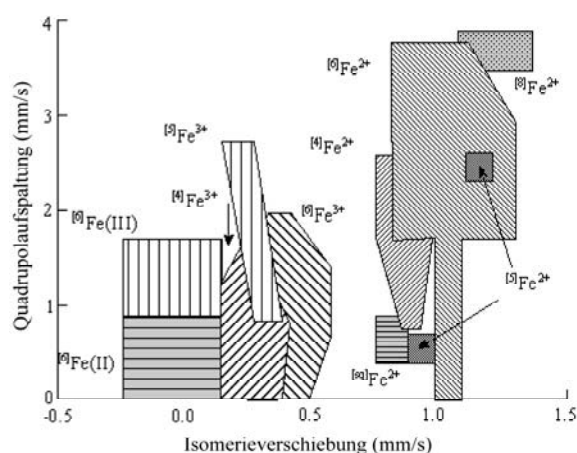


Abb. 1. Mössbauer-Parameter Paarungen für unterschiedliche Fe Oxidationszustände und Koordinationen (nach Murad & Cashion, 2004).

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Internal structure parameters of crystals and their morphological influence: A bond-valence approach

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The aim of our research is to provide a methodology, which can be applied to predict various mineral surface reactions. The bond-valence theory of Brown (2002) was enhanced, and we are able to calculate and describe mineral interfaces via their surfaces terminations, in terms of bond-valence deficiencies. Further, our model not only considers the surface states of the mineral interface to be important to forecast crystal morphologies, but additionally considers different internal structure parameters influencing the crystal habit. Thus, our approach is able to account for both internal and external factors controlling the reactions at mineral-water interfaces. In this context the internal structural parameters lattice density, reticular density and surface symmetry are used to predict an ideal crystal morphology, which is used as a profitable initial crystal shape to forecast growth morphologies, mainly influenced by external parameters such as foreign ions present in solution.

Broken bonds and thus unsaturated bond-valences around an ion are natural for atoms at mineral surfaces, and to a large extent these unsaturated bonds control the readiness of a crystal surface to participate in chemical reactions. The number of unsaturated bonds can easily be calculated and is called the bond-valence deficiency of either an atom, ion, molecule or crystal surface. Further, bond-valence deficiencies of differently oriented crystal surfaces are comparable and can be used to predict crystal morphologies. With respect to its destination, this approach is similar to computer simulations, which likewise use surface energy minimization models to predict the equilibrium form of crystals and the stability of different crystal surfaces. Two examples, magnetite and sphalerite, are presented, and the results of the bond-valence deficiency approach will be compared with the results obtained by computer simulations. While in the example of magnetite (Barbieri et al., 1994) both models obtain similar results for the octahedral {111} terminations, the findings differ significantly considering the prediction of the equilibrium forms of sphalerite. Wright et al. (1998) and Rohl et al. (2003) predict the {110}-surfaces, which exhibit the lowest surface energy, to be the morphological dominant faces of sphalerite, in contrast the bond-valence deficiency model predicts the tetrahedral {111} surfaces. The later are well known to occur as dominant faces of sphalerite, and are more abundant in natural occurring crystals than the {110}-surfaces. These differences in predicting the equilibrium forms of sphalerite are due to the disregard of internal structural parameters in the most commonly applied computer simulations. In return the bond-valence deficiency model is able to include internal structural parameters such as lattice density, reticular density and surface symmetry in its calculations, and therefore its predictive power on the morphology of sphalerite crystals is in good agreement with the habit of natural crystals. Because of its simplicity and its rapid application, the authors suggest the BVD-model as an additional continuative tool to computational simulations, if one is interested in predicting the morphology of crystals having low surface energies.

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Stable isotope and dissolved inorganic carbon analysis of the CO₂-H₂O system at various pressures and temperatures

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Isotope and geochemical data, in conjunction with mass balance calculations, can be used as a monitoring technique to quantify ionic trapping of CO₂ in water. Monitoring the fate of injected CO₂, for instance, is of great importance in geological storage or enhanced oil recovery projects. Mixing injected CO₂ with water is expected to change the isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) values in the CO₂-H₂O system, as well as to increase dissolved inorganic carbon (DIC) concentrations. Furthermore, $\delta^{13}\text{C}_{\text{DIC}}$ data can be used to distinguish between already present and to be injected inorganic carbon. Because injected CO₂ is formed from hydrocarbon combustion, it is expected to have a more negative $\delta^{13}\text{C}$ value than the DIC already present in water. Also, when large amounts of CO₂ are injected into water, a shift in the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is expected.

Depending on the carbonate composition of the water, enhanced carbonate dissolution processes due to CO₂ injection can also further influence the isotopic composition. Such interactions between dissolved CO₂ and carbonates depend on the temperature and pressure regimes applied. Using isotope analysis with mass balance calculations, the effects of varying temperature and pressure conditions on CO₂ and carbonate dissolution are currently tested with laboratory experiments. Additionally the effects of CO₂ injection on the oxygen isotope ratios of the CO₂-H₂O system will be analysed. Laboratory experiments should therefore provide further information in understanding stable isotope behaviour at various temperatures and pressures applied in the CO₂-H₂O system.

Sodium exchange between alkali feldspars and salt melts – the effect of different barium contents

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Ion exchange experiments between potash rich alkali feldspars and sodium chloride rich salt melts were done in order to investigate sodium diffusion in feldspars. For these experiments, feldspar grains (size fraction $100\text{ }\mu\text{m} < x < 200\text{ }\mu\text{m}$) were directly reacted in salt melts of various compositions ($\text{NaCl}:\text{KCl} = 1; 0.95; 0.90; 0.85; 0.8$) at $850\text{ }^{\circ}\text{C}$ and 0.1 MPa in evacuated and sealed quartz glass tubes. Experimental durations varied from one day up to four weeks. The reaction is believed to take place in a dry environment due to the highly hygroscopic nature of the salt mixture. Starting materials were homogeneous, natural gem-quality crystals of sanidine from the Eifel (Or85), orthoclase from Madagascar (Or95) and a synthetic pure sanidine (KAlSi_3O_8). Apart from Na/K compositions, electron probe microanalyses showed significant amounts of Ba in Eifel sanidine (0.6 wt% BaO) and Fe in Madagascar orthoclase (1.6 wt.% FeO). In contrast, the synthetic sanidine is free of any minor and/or trace elements. XRD analyses revealed that both sanidines are highly disordered with respect to Si/Al, whereas T-O distances in the orthoclase indicate a higher degree of tetrahedral order.

During the exchange reaction a system of parallel cracks with a regular spacing is developed in all experiments. The spacing of the cracks depends on the composition of the salt and ranges from 5 to $40\text{ }\mu\text{m}$. Additionally, a second generation of cracks perpendicular to the first generation is formed. Along these newly formed pathways, sodium migration into feldspar grains is enhanced. In the case of pure NaCl melt, this results in a continuous transition between pure, triclinic high albite near the crack surface to the original composition of the starting material in the interior of the grains. With decreasing NaCl content in the salt mixture the resulting feldspar composition becomes increasingly intermediate with regard to Na/K. After four weeks feldspar grains are completely exchanged, leading to a homogeneous distribution of sodium and potassium in the orthoclase and the synthetic sanidine. In contrast, ion exchanged Eifel sanidine still shows small potassic rich domains in grain centers after 4 weeks. In addition, the transition zone around cracks is wider in orthoclase and synthetic sanidine than in natural sanidine from the Eifel after shorter run durations. However, all three sample materials approximate the same equilibrium compositions during our experiments.

We suggest, that the different trace element compositions play an important role in the diffusivity of sodium in feldspars. Sanidine from the Eifel contains large amounts of barium, whereas the orthoclase specimen from Madagascar contains more than one magnitude less BaO. WDX – maps of the run products show, that barium is completely immobile during the dry exchange process. Furthermore, barium is known to be related to potassium due to their large ionic radii. Different diffusion velocities of sodium observed in our experiments indicate that barium stabilizes a feldspar lattice, that is more favorable for potassium ions than for sodium. Consequently, high Ba contents seem to effectively inhibit sodium diffusion through a coherent lattice since it requires Ba diffusion along with K. This, on the other hand, is only possible if Si and Al migrate within the tetrahedral framework, which is known to be very sluggish at experimental conditions used in this study. This fact is supported by the fact that XRD analyses of run products only revealed significant changes during run durations exceeding two weeks.

Microstructure evolution during hydrothermal replacement of potassium-rich alkali feldspars by high albite/high sanidine in aqueous NaCl/KCl solutions

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The mechanisms of metasomatic replacement of two near-endmember potassium-feldspars in contact with sodium-rich aqueous chloride solutions were investigated at 750 °C and 500 °C, and 200 MPa. Run durations varied from 6 to 768 hours. Starting materials were homogeneous, gem-quality megacrysts of Eifel sanidine from Volkesfelde, Germany and Fe-rich Madagascar orthoclase. Starting materials and run products were subject to a detailed characterization using XRD, dual-beam FIB-SEM (equipped with EBSD detector), FEG-EMP, Raman and photoluminescence (PL) spectroscopy, as well as HR-TEM. In order to provide “quasi-infinite” cation reservoirs, aqueous NaCl and Na_{0.75}K_{0.25}Cl solutions and feldspar were mixed at a molar ratio of 20:1. In addition, a bulk composition of $(\text{Na}_{\text{fluid}} + \text{Na}_{\text{fsp}}) / (\text{Na}_{\text{fluid}} + \text{Na}_{\text{fsp}} + \text{K}_{\text{fsp}}) = 0.7$ representing a cation reservoir changing with time was used.

SEM and EMP investigations of run products revealed very complex microstructures in grain areas where sanidine and orthoclase were replaced by triclinic high albite (Ab₉₈₋₁₀₀) and monoclinic, sodium-rich sanidine (Ab₄₀), respectively, depending on fluid composition and/or temperature. Experiments using mm-sized, oriented single crystal fragments revealed that the observed replacement reaction is pseudomorphic and highly anisotropic, showing much faster progress along [h0l]. Pristine and replaced regions are separated by an extremely sharp chemical reaction front that penetrates the crystals surprisingly fast, producing highly porous replacement rims or patches by a coupled dissolution-reprecipitation process (Putnis, 2002). This secondary porosity partly is the result of an average loss in unit-cell volume of 8 %, which occurs especially during the initial stages of pseudomorphic replacement. In addition, an overall porosity clearly exceeding the predicted volume difference, the occasional appearance of amorphous SiO₂ spheres (quench products) as well as crystal surfaces and shapes of run products, indicate significant dissolution without immediate precipitation during the experiments. TEM investigations show a high defect concentration close to the approximately 20 nm wide reaction front, resulting in an almost complete loss of coherency across this boundary. EMP and laser-induced PL spectroscopy (Fe³⁺) revealed that apart from changes in Na/K, minor elements such as Ba, Fe and Ti were also heavily affected by this fluid-driven alteration. Barium for example, is known to be coupled to K. Therefore, the data show a strong dependence on X_{Ab} of the exchange product, resulting in a continuous omission of Ba from the feldspar lattice at a X_{Ab} exceeding 0.90 [apfu]. In contrast, the partitioning of tetrahedrally incorporated cations such as Fe³⁺ and Ti⁴⁺ depends on temperature and their initial concentrations in the starting material. Remobilization of these elements during hydrothermal exchange resulted in inclusions of rutile and ilmenite forming within pores in the replacement rim.

In contrast to diffusion-controlled exchange of alkali feldspars in salt vapours or melts (e.g. Laves, 1951), textures and chemical changes observed in this study support an exchange mechanism mainly controlled by dissolution coupled with simultaneous reprecipitation of a thermodynamically favoured phase. The release of framework-related Fe³⁺ and Ti⁴⁺ along the sharp replacement front, indicates that nearly every bond is broken during this process, which has also been shown by similar experiments utilizing $\delta^{18}\text{O}$ enriched aqueous chloride solutions (Niedermeier et al., 2008). However, long term experiments, especially at 750 °C indicate an increasing importance for alkali diffusion across the reaction front over longer periods of time.

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Archäometrical analyses of pottery fragments from Cameroon

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Some hundred pottery fragments from three different excavation sites in Cameroon were investigated archaeometrically with respect to the phase and chemical composition, fabric, and decoration. The sample material comes from Zamala (Delneuf et al. 1998) in the far North province, from Mombal (Lako 2005) in the East province, and from Mfomakap (Elouga 2001) in the central province. Together with the sherds regional clay material which is supposed to have been used by the potters was collected. The aim of the study is to relate the characteristics of the sherds to the raw materials and the production technologies. First the phase composition of selected sherds was determined by X-ray diffraction and optical microscopy. Their chemical compositions with respect to major and minor constituents were investigated by X-ray fluorescence spectroscopy. Physical properties related to the firing process such as density, porosity, pore size distribution, and BET surface area were measured by mercury injection porosimetry and nitrogen adsorption, respectively. Fabric and porosity studies were carried out by X-ray micro computer tomography. The clay material was characterised with respect to the chemical and phase compositions. Furthermore, temperature-dependent reactions were monitored by X-ray diffraction investigations of samples heated up in the temperature range from 200 – 1200 °C in progressive temperature steps of 100 - 200 °C and checked by differential thermal analysis.

Special attention was paid to graphite and iron oxide red coatings and decorations on the surface of most of the sherds (Drost 1967). The coatings were investigated by X-ray diffraction techniques while the decorations were discussed with respect to the fabrication and the complexity of patterns (planar symmetry groups). Temperature-dependent X-ray phase analysis of the raw material yielded three important temperature intervals between 400 – 500 °C, 900 – 1000 °C, and 1000 -1100 °C marked by the disappearance of kaolinite and illite, respectively, and the formation of mullite. The absence of kaolinite and the presence of illite in sherds from Mfomakap point out to a firing temperature between 500 – 900 °C, whereas the absence of illite and mullite in sherds from Zamala indicate a firing temperature around 1000 °C. In the case of sherds from Zamala a second clue to the firing temperature is given by the partial melting of potassium feldspar grains. The incongruent melting point of potassium feldspar in the pure binary system leucite – SiO₂ is 1150 °C. The presence of kaolinite in sherds from Mombal indicated by X-ray diffraction and thin section microscopy points out to a firing temperature just below 500 °C.

The sherds from the three locations differ not only in the firing temperature but also in the composition and grain size of the temper. Apart from quartz grains which are present in all sherds the temper of sherds from Mfomakap is characterised by plagioclase and hornblende, whereas the temper of sherds from Zamala contains a lot of microcline. Biotite flakes and heavy minerals (zircon, rutile) are typical in sherds from Mombal. While the different mineral compositions of the temper are related to the regional geology providing the raw material for the ceramics, the grain size distribution of the temper and the firing temperature are connected to the production technology and reflect cultural differences. Stylistic comparisons of decorated sherds with type material in museum collections (Grassi Museum of Ethnology Leipzig; Royal Museum of Central Africa Brussels) and radiocarbon dating of charcoal pieces from the strata from which the samples were taken will assist to determine the age and the cultural background of the pottery production (Gosselain 2002).

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Zircons from kimberlite pipes – drilled cores through the continental crust? A case study from the Ekati mine (Canada)

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The evaluation of the grain size distribution of micro diamonds is an important tool in the evaluation of the economic value of diamond deposits. For this large volumes of kimberlite material from individual localities are subjected to the so-called caustic fusion process. Only diamonds, zircons and the occasional rutile survive this intense chemical process. We have analyzed such zircons from different kimberlites. of the Ekati-mine district in the Slave Province, Canada. We consider kimberlite diatremes as drill cores through the continental crust which may provide us with information from the deeper continental crust. The age distribution together with the Hf isotopic composition of the zircons should give us constraints on the timing of the formation of continental crust.

Three main age groups can be distinguished: The youngest ages are between 55 and 60 Ma which correspond to the kimberlite emplacement ages at Ekati in several episodes at ~48, 51–53, 55–56 and 59–61 Ma (Creaser et al., 2004). Their Hf isotopic ratios are fairly primitive.

A second age group lies between 95 and 108 Ma, ages so far unknown in this area. Their Hf isotopic composition is highly variable and ranges from juvenile (initial ϵ_{Hf} of +11) up to Palaeoproterozoic crustal residence times ($T_{\text{DM}} \sim 2.0$ Ga; initial ϵ_{Hf} of -18) of the protoliths.

The third most abundant group is defined by Archean zircon with ages of 2.54 to 2.87 Ga. The majority of them have early Archean depleted mantle model ages (average crustal residence time) of 3.2 to 3.6 Ga, with maxima at 3.3 and 3.5 Ga. Others are more juvenile, pointing to Mesoarchean crust formation of around 2.9 Ga

A minor group of zircons with ages around 1.8-2.0 Ga suggests Palaeoproterozoic recycling of this Mesoarchean crust. Furthermore, some zircons, with concordant Jurassic to Palaeoproterozoic (1.9 Ga) ages and positive initial ϵ_{Hf} , point to minor addition of juvenile crust between Cretaceous to Archean times.

In summary, the crust of the Ekati-mine district in the Slave province was predominantly formed during Archean times in two phases: Mesoarchean (3.2 - 2.8 Ga) and Neoarchean (2.8 – 2.5 Ga). In addition, minor amounts of juvenile crust formed through dikes or smaller intrusions sporadically until Eocene.

Novel mineralogical methods applied to platinum mineralisation: Examples from pristine ores (Great Dyke, Bushveld) and placers

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The study of noble metal ores is generally hampered by comparatively low grades of the ores (1-10 g/t) and the "nugget effect". Consequently, laborious and time-consuming studies are necessary in order to obtain statistically sound data on gold and PGM ores and, finally, to advance the genetic understanding and metallurgical treatment of ores. Combinations of novel and "classic" methods, namely electric pulse disaggregation (EPD), hydroseparation (HS), and mineral liberation analysis (MLA) were employed here to study platinum-group element (PGE) mineralization of the Great Dyke, Zimbabwe, ores from platinum pipes (Bushveld Complex, South Africa), and gold/PGM placer deposits. – The EPD technique liberates mineral grains without any visible destruction and provides isolated grains for the study and analysis of rock-forming and ore minerals (e.g. Cabri et al., 2008), in our case platinum-group minerals (PGM). The HS method effectively concentrates heavy minerals by factors up to 10,000 fold. Near-total recoveries of grains >10 µm are achieved (Cabri et al., 2006, 2008). The MLA technique combines BSE images with EDX spectra and is a fast tool to detect and characterize mineral phases in ores and ore processing products (Gu, 2003).

(1) In the Main Sulfide Zone of the Great Dyke at Hartley Mine, PGM observed in numerous polished sections have apparent grain diameters in the range < 5 to 50 µm and only exceptionally reach 200 µm in the longest dimension. In the search for larger grains, an ore sample (ca. 1 kg) was treated by EPD. This procedure released altogether 75 PGM grains larger than 50 µm with max. diameters up to 480 µm for (Pt,Pd)-bismuthotellurides, 85 µm for sperrylite, 195 µm for cooperite/braggite, and 300 µm for Pt-Fe alloy grains.

(2) Ten polished sections of a sample from the Driekop pipe (34.9 g/t Pt) revealed 9 PGM grains only. Therefore, a combination of EPD, HS, preparation of monolayer polished sections, and MLA was used in order to obtain more information on the PGM. In five EPD size fractions, more than 500 PGM grains (15 different PGM species) were recovered using HS. PGM grain sizes range up to 330 µm (mostly ~100 µm). In the 63-125 µm fraction, which contains most PGM grains, a total of 6611 grains were classified in the following proportions (vol.%): silicates (65 %), chromite and magnetite (25%), pentlandite (2.4 %) and PGM (2.4 %). The 152 PGM grains are sperrylite (78 %), Pt-Fe alloy (16 %), Rh-Ir-sulfarsenides (3 %), stibiopalladinite (2 %) and rarer phases (1 %).

(3) Application of the MLA method to PGM-bearing heavy mineral concentrates proves highly successful, as the classified MLA images obtained provide rapid overviews on mineral proportions and assemblages, and in addition they provide parameters of individual grains. Exotic mineral grains are easily depicted. Differences between various localities are obvious at first sight, and grain selection for further studies (microprobe or isotope analysis) is substantially eased. For example, in a gold/PGM concentrate from Colombia, the MLA system defined 342 particles at the following proportions (vol.%): Pt-Fe alloy (~ 63 %), gold (24.5 %), and about 2.5 % of rarer PGM (mostly Ir-Os alloys). In a gold/PGM concentrate from the Philippines, 1851 particles were defined at the following proportions (vol.%): Gold (44.5 %), erlichmanite [OsS₂] (29.3 %), Ir-Os alloys (5.4 %), Pt-Fe alloy (~ 4 %), and some rare PGM. The remaining minerals are mainly chromite and silicates.

In summary, the results show that the techniques employed, either on their own or in combination, provide a wide range of additional information especially on platinum ores which is beneficial to both the researcher and the metallurgist. Examples and further details will be presented at the conference.

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Methoden zur Charakterisierung historischer Ziegel aus Wien

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Die Erforschung der Wiener Ziegelgeschichte wurde in der Vergangenheit zu Unrecht sehr stiefmütterlich betrieben. Wien hat eine zumindest 2000 Jahre alte Tradition in der Ziegelherstellung und Ziegelarchitektur. Die ersten Ziegelöfen wurden vermutlich von den Römern errichtet, um für die Befestigung ihrer Lager Carnuntum und Vindobona Baumaterial zur Verfügung zu haben. Es wird vermutet, dass diese Öfen an den Ufern des Alserbaches errichtet wurden, wo eine sehr gute Tonqualität für hochwertige Ziegelprodukte vorzufinden war (Koller, K. 1989).

Im gesamten Mittelalter waren für die Befestigung der Stadt und deren Ausbau große Mengen an Baumaterial – vor allem Ziegel – notwendig (Gaál 1989). Insbesondere die Stadterweiterung im 19. Jh. und die Bautätigkeit während der Gründerzeit sind Höhepunkte in der Wiener Ziegelgeschichte. Den guten historischen Kenntnissen des Ziegeleiwesens stehen sehr geringe Material Kenntnisse der historischen Ziegel gegenüber. Erst Schirnböck begann etwa 1950 mit einer systematischen Sammlung historischer Ziegel aus dem Großraum Wien. Diese Tätigkeit gipfelte in der Gründung des Wiener Zieglmuseums im Jahre 1978 (Schirnböck, A. 1978).

Seit der Gründung des Museums ist der Bestand an Ziegeln von ursprünglich 1.000 Exemplaren auf etwa 25.000 angewachsen. Diese Sammlung dokumentiert die Ziegelgeschichte Wiens über einen Zeitraum von über 2.000 Jahren. Viele Exemplare sind sowohl zeitlich als auch geografisch bestimmten Epochen bzw. Regionen zuzuordnen, bei einer bedeutenden Anzahl ist dies aber nicht möglich. Ein wissenschaftlicher Bedarf der Wiener Ziegelforschung liegt darin, durch Kenntnis von Materialparametern Rückschlüsse auf deren Herkunft, Produktionszeitpunkt und Herstellungstechnologie ziehen zu können. Wie eine Reihe von Vorversuchen gezeigt hat, können die angeschnittenen Fragen durch die Erfassung von mineralogischen, geochemischen und physikalischen Parametern in vielen Fällen zu einer Zuordnung der Ziegel führen. Sehr wertvoll hat sich auch die aus der Gesteinskunde übernommene petrografischen Dünnschliffmikroskopie mit polarisiertem Licht erwiesen. Aus dem Bestand des Wiener Zieglmuseums und aus der eigenen Sammlung wurde nach regionalen Aspekten eine bestimmte Anzahl an Ziegeln entnommen und folgendermaßen vorbereitet, bearbeitet und analysiert: Durch 2 Parallelschnitte mittels einer Diamantsäge in der Mitte der Längsachse wurde ein plättchenförmiges Stück aus dem Ziegel herausgeschnitten und sowohl für die Herstellung eines Dünnschliffes als auch für die geochemisch/mineralogischen Analysen herangezogen. Die Schnittflächen der Ziegel wurden anschließend fein geschliffen und mit farblosem Mattlack lackiert, um das vorhandene Gefüge und die Struktur visuell und mittels Auflichtmikroskopie studieren zu können.

Folgende Analysen wurden zur Erfassung einer maximalen Anzahl an Parametern an den Objekten durchgeführt:

- Petrografischen Dünnschliffmikroskopie in polarisiertem Licht
- Gesamtmineralanalyse mittels XRD zur Bestimmung der mineralogischen Zusammensetzung
- Simultane Thermoanalyse (STA) zur Bestimmung des thermischen Verhaltens bei der Aufheizung
- Infrarotspektroskopie (FTIR)
- Spurenelemente und Seltenen Erden mittels ICP MS. Die Rohmaterialien verschiedener Lagerstätten zeigen diesbezüglich signifikant unterschiedliche „Fingerprints“
- Gesteinsdichte und Porosität geben gute Hinweise auf die Rohstoffe und Brenntechnologie
- Festigkeitseigenschaften

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Microbiological alkylation and volatilization of inorganic selenium immobilized by LDH and ferroselite

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Selenium under reducing cement-bearing near field conditions of nuclear waste repositories is preferentially precipitated in the oxoanionic form of selenite with the cement mineral hydrotalcite (Se-LDH), in the more reduced selenide form with iron as ferroselite, FeSe_2 , or in the more oxidized form of selenate with the Fe-oxide goethite. Se sorbed by these solid phases is considered as of low mobility and thus of benefit for long-term stabilization of the fission product ^{79}Se . We will show, however, that sulfate-reducing bacteria (SRB) including the common *Desulfovibrio gigas* are capable to volatilize the Se from all these solid phases. We used a standardized nutrient broth for sulfate reducers and incubated with 10 g L^{-1} suspension under strictly anaerobic conditions. For sampling we gently purged the head space of the culture flasks with nitrogen into Tedlar bags. Volatile organic selenium (VOSe) species were measured by a cryotrapping cryofocussing gaschromatographic system with ICP-MS detection. VOSe species thus found at the tens to hundreds ng m^{-3} level above the Se-LDH were the common dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) but also ethylated forms (Figure 1). Species concentrations found during the FeSe_2 incubation were by 1-2 orders of magnitude lower, but two more yet unknown compounds with peaks at retention times in between those of DMSe (150s) and DESe (300s) were found to occur within a few days (Figure 1). In conclusion, microbe mediated VOSe formation cannot be neglected but must be considered as a potential fission product mobilization pathway, which may lead to onsite accumulation of highly mobile ^{79}Se through evapoconcentration. The same conclusion was previously found with goethite in aerobic microfungal cultures (Peitzsch et al., 2009).

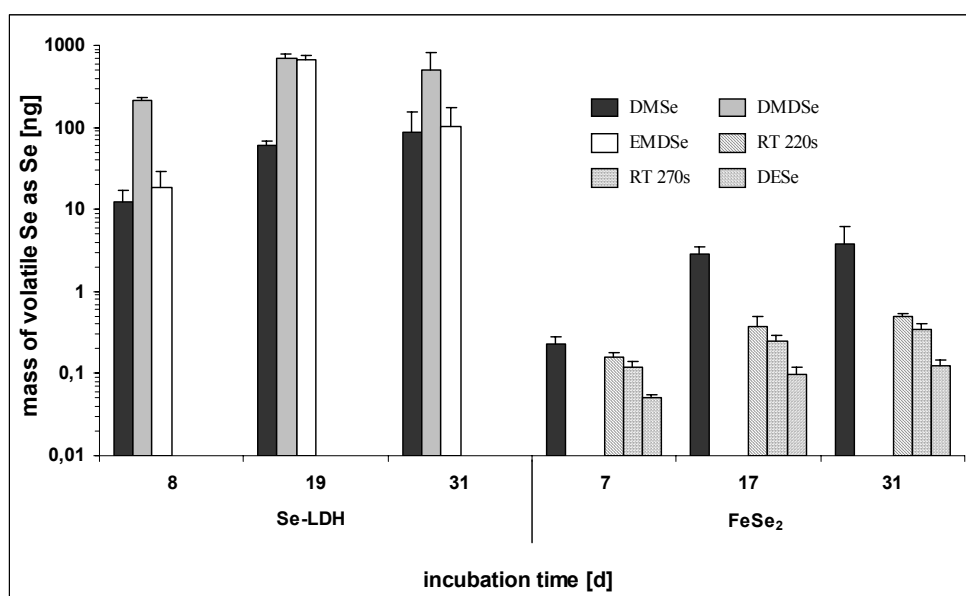


Figure 1: Time-dependent volatilization of alkylated selenium from two different inorganic selenium sources (error bars represent standard deviation, $n = 3$).

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Hydrothermal replacement reactions of calcium carbonate polymorphs

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Replacement reactions commonly involve a dissolution-precipitation mechanism and take place along a moving reacting interface (Putnis & Putnis, 2007). While in many cases the product is a perfect pseudomorph of the initial crystal (Kasiopas et al., 2008), there are cases in which the new phase contains extended cracks and pores (Jamtveit et al., 2009; Perdikouri et al., 2008).

The aragonite to calcite transition has been studied extensively over the years because of its wide spectra of applications and of its significant geochemical interest. While studies of kinetics (e.g. Topor et al., 1981), thermodynamics (e.g. Wolf et al., 1996) and behaviour of ions such as Sr and Mg (e.g. Yoshioka et al., 1986) have been made there are still unanswered questions regarding this reaction especially in the cases where the effects of fluid composition are considered. We have performed hydrothermal experiments using both biogenic (coral and cuttlebone) and inorganic aragonite as the starting material. In the case of inorganic aragonite, small individual calcite domains were observed within the aragonite crystal, surrounded by cracks that were induced from stress resulting from the calcite formation. Additionally, calcite overgrowths were observed around the crystal. Depending on solution composition, the replacement was pseudomorph or almost pseudomorph. We observed differences in the case of biogenic aragonite due to the presence of organic material and to differences in structure.

We performed experiments using solutions prepared with water enriched in ¹⁸O (97%) in order to study the behavior of the CO₃²⁻ molecule during replacement. The exchange of ¹⁶O for ¹⁸O in the carbonate was traced using Raman spectroscopy. Additionally, we investigated the structural relationship between the two solid phases by determining the crystallographic orientation of the calcite replacements in relation to the aragonite. Our observations have produced new insight in the fluid-mediated replacement reaction of aragonite by calcite.

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The Nonsulfide Zn-Ag Mineralization in Wiesloch, SW Germany

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The nonsulfide Zn-Ag ores in Wiesloch (SW Germany) were the historical basis for the prosperity of the towns Worms and Speyer (SW Germany) in medieval times. Artefacts and coins were made from silver mined from the nonsulfide Zn-Ag ores known as "Galmei" in which Ag occurs as native silver. The formation of this nonsulfide deposit also caused strong environmental pollution with respect to As and Tl and is the product of the supergene oxidation of the primary carbonate-hosted Mississippi Valley-Type deposit – mainly consisting of silver-bearing sphalerite, As- and Tl-rich pyrite and galena - during tectonic uplift, karst development, changes in the level of the water table, and weathering.

The nonsulfide paragenesis mainly consists of (Cd-) smithsonite, native silver, quartz, kaolinite and goethite with minor amounts of hemimorphite, anglesite and cerussite. With smithsonite to be the least soluble Zn mineral and the occurrence of goethite, it is obvious that this secondary mineralization suffered extensive supergene oxidation and comprises both, direct-replacement and wall-rock-replacement ore bodies.

The nonsulfide mineralization was investigated by microscopy, electron microprobe, and whole rock XRF analyses. Interestingly, abundant elements in the primary mineralization as As, Sb, and Tl lack completely in the oxidized orebody and silver occurs as native silver within a smithsonite matrix. After Large (2001) the process of supergene oxidation can be subdivided into 3 parts: (1) generation of H₂SO₄ during the oxidation of primary sulfide (in particular pyrite) and therefore a decrease in pH; (2) dissolution of sphalerite which is soluble under acid conditions; and (3) precipitation of insoluble zinc carbonate (smithsonite), which may replace calcite and/or dolomite in the host rocks, as the pH of the zinc-bearing solution increases through reaction with the carbonate host rocks. As a matter of fact, trace elements which were incorporated in sphalerite and pyrite in the primary mineralization - e.g. Ag, As, Sb, Tl - cannot be incorporated in Zn-carbonates and are highly soluble under acid, oxidizing conditions. However, Ag solubility is more sensitive to changes in pH and therefore, Ag precipitates as native silver due to a shift in pH towards more alkaline conditions during stage (3). On the other hand, the high solubility of especially As and Tl under oxidizing conditions caused a strong environmental impact as soil and water pollution with respect to these elements occurred.

However, the nonsulfide Zn-Ag deposit in Wiesloch was attractive for medieval smelting activities as silver occurs as native silver within carbonates and was therefore easy to extract. But even nowadays, nonsulfide zinc deposits are becoming attractive exploration targets as they are easy to mine and thus, they could again become an important source of metallic zinc and silver.

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Herstellung von Wasserglas durch hydrothermalen Aufschluss von Opal, Quarz oder Kieselglas in Natronlauge

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Unter der Anforderung einer nachhaltigen Entwicklung und der Notwendigkeit des Energie- und Rohstoffwandels in der chemischen Industrie muss auch die Rohstoffsituation für Silicate neu betrachtet werden. Rohstoff für viele Silicate ist meist thermodynamisch stabiler Quarz, somit sind heutige Aufschlussverfahren sehr energieaufwändig. Der hydrothermale Aufschluss von Quarzsand mit Natronlauge ist eines der Standardverfahren zur Herstellung von Wasserglas (Vail 1952), jedoch ist der zu realisierende Zusammensetzungsbereich eingeschränkt. Infolgedessen bedarf es einer Optimierung des Hydrothermalverfahrens hinsichtlich der Energetik und mit alternativen Rohstoffquellen. Alternativ wurde versucht Wasserglas mit möglichst hohem SiO₂-Gehalt (molares Verhältnis von SiO₂ zu Na₂O (R_M) ≥ 3 und SiO₂ Gehalt ≥ 25 M.-%) aus brasilianischem Opal oder amorphem Kieselglaspulver mit wässriger Natriumhydroxidlösung bei unterschiedlichen Reaktionstemperaturen und Verweilzeiten hydrothermal herzustellen. Diese Rohstoffe sind zwar wirtschaftlich irrelevant, jedoch sollte das Löseverhalten von amorphen und krypto-kristallinen Rohstoffen untersucht werden.

Die Hydrothermalsynthese nach Gleichung (1)



wurde in mehrteiligen Edelstahl-Autoklaven mit Tefloneinsatz durchgeführt. Die Beheizung und Durchmischung erfolgte auf beheizbaren Magnetrührern oder durch einen umgebauten Trockenschrank mit einer rotierenden Welle, auf der die Autoklaven fixiert waren. Als Rohstoffe wurden neben gemeinem Opal (Fundort: Minas Gerais, Brasilien, Dr. F. Krantz, Bonn/Deutschland), amorphes Kieselglas (Fa. Saint Gobain Quartz S.A.S, Nemours Cedex/Frankreich), Quarzsande und 50 %-ige Natronlauge (Fa. Akzo Nobel, Wurzen/Deutschland) eingesetzt. Die Reaktionstemperatur wurde zwischen 30 und 220 °C variiert, die Verweilzeiten im Autoklaven betrugen ohne Aufwärm- und Abkühlphasen 2 bis 20 h. Neben stöchiometrischen Versätzen wurden auch Versuche mit einem Überschuss an SiO₂ durchgeführt.

Nach der Synthese wurden die Wassergläser chemisch analysiert (SiO₂-Gehalt durch Glühverlust, Na₂O-Gehalt durch Titration mit 0,5 N HCl). Darüber hinaus wurden Röntgenbeugung (XRD), Rasterkraftmikroskopie (AFM), Lichtmikroskopie, Thermogravimetrie (DTA/TG), Rasterelektronenmikroskopie mit energiedispersiver Röntgenanalyse (ESEM/EDX), Refraktometrie, Viskosität, Dichtebestimmung, Dynamische Lichtstreuung (DLS), Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS), Röntgenfluoreszenzanalyse (RFA), Infrarot-Spektroskopie, Korngrößenanalyse und Porositätsmessungen (Stickstoff-Tiefemperatur-Adsorption) zur Charakterisierung von Edukten und Produkten angewandt. Mit stöchiometrischen Ansätzen wurden unter Verwendung von Quarz keine hinreichend hohen SiO₂-Gehalte in Lösung gebracht. Auch bei Verwendung von Überschüssen an SiO₂ näherte sich die Konzentration an SiO₂ einem Grenzwert an, der bei etwa 20 bis 22 M.-% lag. Ursache ist vermutlich eine metastabile Sättigungsgrenze, die eine Folge des kolloidalen SiO₂ ist, das sich in der wässrigen Phase bildet. Bei Verwendung amorpher (Kieselglas) oder kryptokristalliner (Opal) Rohstoffe werden höhere Konzentrationen erreicht, die aber nach einer längeren Zeit wieder auf den Wert abfallen, der schon mit Quarz als Rohstoff erreicht wurde. Dies entspricht dem von La Mer beschriebenen Verhalten von kristallisierenden Lösungen mit Keimbildung (La Mer 1952). Ursache des Verhaltens ist die Ausfällung von Tief-Quarz, der im Falle des Opals noch von Analcim begleitet wird. Auch dies lässt sich über eine metastabile Sättigung der wässrigen Phase erklären. Das hydrothermal synthetisierte Wasserglas aus Opal wurde nach (Weber 1960) erfolgreich zum Zeolith A umgesetzt.

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Phase formation on typical pipe steels in CCS-technology

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Carbon dioxide corrosion, which can cause failure of pipelines and wells, is a well acknowledged problem in the oil and gas production [1] and will become an issue when compressing emission gasses from combustion processes in deep geological layers (CCS Carbon Capture and Storage) [2]. In geothermal energy production the CO₂-corrosion is sensitively dependent on environmental conditions like temperature, CO₂ and H₂S partial pressure, flow conditions and protective corrosion scales [3]. But very little experience of the corrosion behaviour and mechanism is available for saline waters such as aquifers with the given conditions at the geological site Ketzin, Germany, the first on-shore CO₂-storage (CO₂-SINK) established starting October 2007, with T=60 °C / p=80 bar.

To determine the low temperature, low pressure behaviour the corrosion testing is carried out using samples of a heat treated steel with 1% Cr (42CrMo-4) and a high alloyed 13% chromium bearing martensitic stainless steel (X46Cr13). These are kept in a synthetic Aquifer environment similar to the Stuttgart Aquifer. The saline aquifer water is saturated with technical CO₂ at a flow rate of 2 l/h to keep stable environmental conditions. Microstructures were characterized by X-ray diffraction XRD, light microscopy LM, scanning electron microscopy SEM, and energy dispersive x-ray EDX, after a series of heat treatments (60 °C, 750 h - 17520 h). A short incubation time is followed by the constitution of a multi-layered continuous carbonate/oxide scale with a thickness twice as high as the residual base metal after 2 years of exposure. Main phase is siderite FeCO₃ and goethite α -FeOOH in both types of steel depending of the environment: gas, liquid or intermediate phase with a gas/liquid phase boundary. A complicated layer structure reveals hematite Fe₂O₃, lepidocrocite γ -FeOOH and spinelphases of various compositions. Also mackinawite FeS and akaganeite Fe₈O₈(OH)₈Cl_{1,34} are present and in the high chromium bearing alloy carbides are found. While the formation of the carbonate phases is relatively clear, the precipitation of the multilayered oxid-salt-carbid scale may be related to a natural hydrothermal process but is subject to be investigated in future.

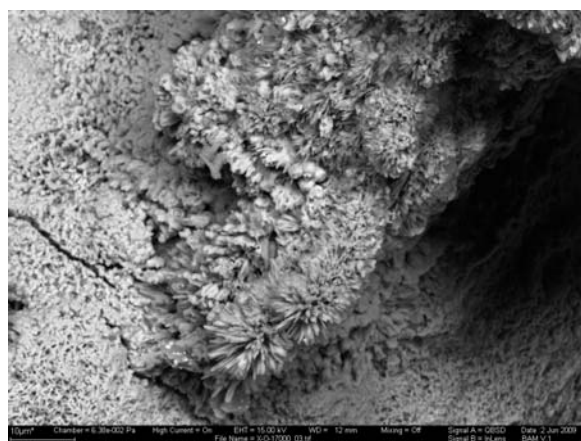


Figure 1: surface of X46Cr13 after 2 years of heat treatment in CO₂ saturated saline aquifer brine. The needle shaped precipitates are Fe-O rich phase, mainly hematite

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Design of a new multifunctional diamond anvil cell for high-pressure high-temperature applications

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The limitation in achieving homogeneous and uniform high-pressure high-temperature conditions exceeding 1000°C, together with the requirements multipurpose use applicable to various analytical techniques (e.g. Miletich et. al. 2000, Burchard et. al. 2003), lead us to consider a new design for a heatable diamond anvil cell (DAC).

We developed a new DAC suitable to various spectroscopic and diffraction applications (Fig. 1) based on the principles of exchangeable modules. The new DAC has a cylindrical shape of 52 mm in diameter and 24.4 mm in height. According to these dimensions it is sufficiently small enough for using a standard goniometer head. The guidance works comparable to a dog clutch that provides optimal radial access to the diamond anvils, both optically and mechanically. The diamond anvils are completely adjustable in all space coordinates in addition to a pre-adjustment system in radial direction. For high-pressure generation a new adaptive gas-membrane has been developed, which enables us to keep the pressure by bolts independent of the gas pressure on the membrane. In the current configuration level we have developed three exchangeable inner modules, for high pressure X-ray diffraction, HP-HT single-crystal diffraction and HP-HT spectroscopy, respectively. The HP-HT modules contain a large-dimensioned compatible liquid cooling system for heat removal close to the diamond anvils simultaneously providing sufficient mechanical stability. For heat generation we suggest a heatable composite gasket (Miletich et al. 2009), which is supposed to exceed temperatures up to 2000 K.

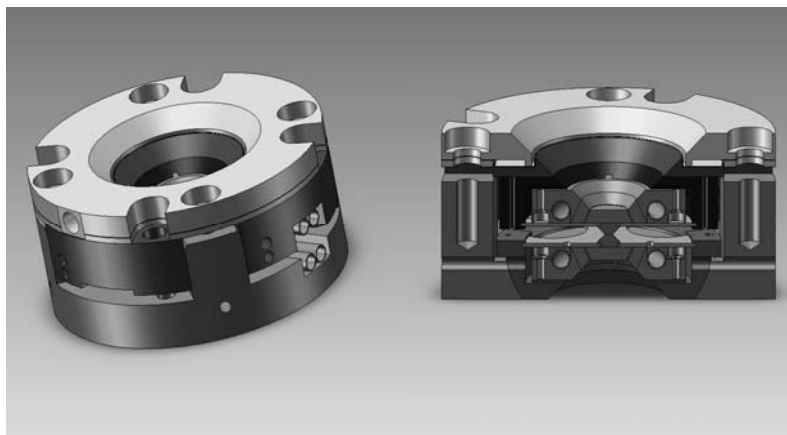


Figure 1: Isometric view and cross section through the new HPHT-DAC design. The modular design consist of following components: Gas membrane system (yellow), base plates with dog clutch (red, light blue), adjusting devices (dark blue, purple), HP-HT single-crystal X-ray diffraction module

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Development of well cements for CO₂-underground storage

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Ordinary Portland cements as they are used in cementation tend to carbonate rather rapidly due to their reaction with CO₂, CO₂-gas, CO₂-gasmixtures, water solutions and salinar solutions. First results for reactions under supercritical conditions at 90°C show some reduced stability due to carbonation reactions combined with chemical differences and increase in porosity. There are almost no data available for the use of alternative cementitious products. Quantitative results for a long term exposure provide data which seem to follow a formula to the square root of time. The extrapolation of present data seem to show only a stability of OPC's to several hundred years. Chemical degradation reactions are based mainly on calcium ions and carbonation combined with dissolution reactions as they occur in classic Portland cements at low pressure and temperature conditions. Therefore it seems to occur a lack on data for increased depth (450 bar, 130°C) which occurs of about 3500 m. Also insufficient data are available for replacing classic Portland cements with other optimized cements. Reaction behaviour of materials used for wells under aspect of stability with reaction of CO₂-gas mixtures. Cement materials to be used and their stability against carbonation effects

- Characterization of well materials, casings on a time scale
- Characterization of abandoned wells under aspects of material characterization
- Tech. development of special cementitious materials for well cementing replacing OPC
- Study of existing materials in wells
- Development of alternative materials as stable materials against CO₂-corrosion
- Characterization of relevant chemical, mineralogical processes and kinetic effects
- Risk assessment on the basis of local facts, how fast can CO₂ develop a reaction to leak a well: a) Materials, b) Mechanical state, c) Microstructure, d) Geometry
- Determination of cement degradation rate
- Development of pH, free water solubility of products, reaction products
- Influence of self-healing effects
- Degradation of materials in CO₂-brines, can a thermodynamic approach be considered
- Development of effective sealing materials based on:

a) CAC carbonated, b) CAC c) Sorel cement (MgO, chlorinated, phosphated, carbonated) d) Alinite cement, e) Manganese cement

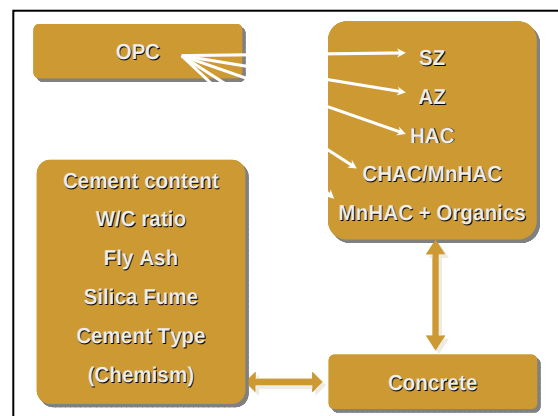


Figure 1. shows schematically probable replacement strategies of OPC by different new cementitious materials to form a gas-tight and resistant material against corrosion.

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Nano-defect structures in the mineral bixbyite

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The Thomas Mountain range in Utah, USA is a well known location where cubic bixbyite ($\text{Fe,Mn}_2\text{O}_3$) single crystals can be found. Bixbyite crystals normally have dimensions of a few millimeters in edge length, but on the Thomas Mountain range samples with greater dimensions up to 1 cm in length can be found. On the large bixbyite crystals linear parallel structures that run along the surface of the crystal are visible. These structures form re-entrant flat faces when they reach the edges of the crystal. An examination of the small bixbyite single crystals using a scanning electron microscope did not reveal the existence of such parallel structures on the crystal surface. An analysis of the chemical composition of the interlayers showed an increased silicon content that corresponds with braunite $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$ or braunite II $\text{CaMn}_{14}^{3+}\text{SiO}_{24}$. The lattice parameters of the tetragonal braunite match nearly perfectly with the lattice parameters of two superimposed bixbyite crystals and the lattice parameters of braunite II have only a four time elongation of the c-axis and therefore the intergrowth of the phases bixbyite and braunite or braunite II is possible.

The existence of the interlayers in the large bixbyite single crystals led to the first assumption that the interlayers work as fast diffusion paths and promote the exaggerated grain growth. The specimens were examined under a transmission electron microscope and the existence of silicon containing interlayers that run along the (100) planes of the bixbyite host crystal was revealed in the large crystals, as well as in the small ones. Besides the polytypic faults small precipitations of a second generation of bixbyite were found, which were grown epitactically along the interlayers.

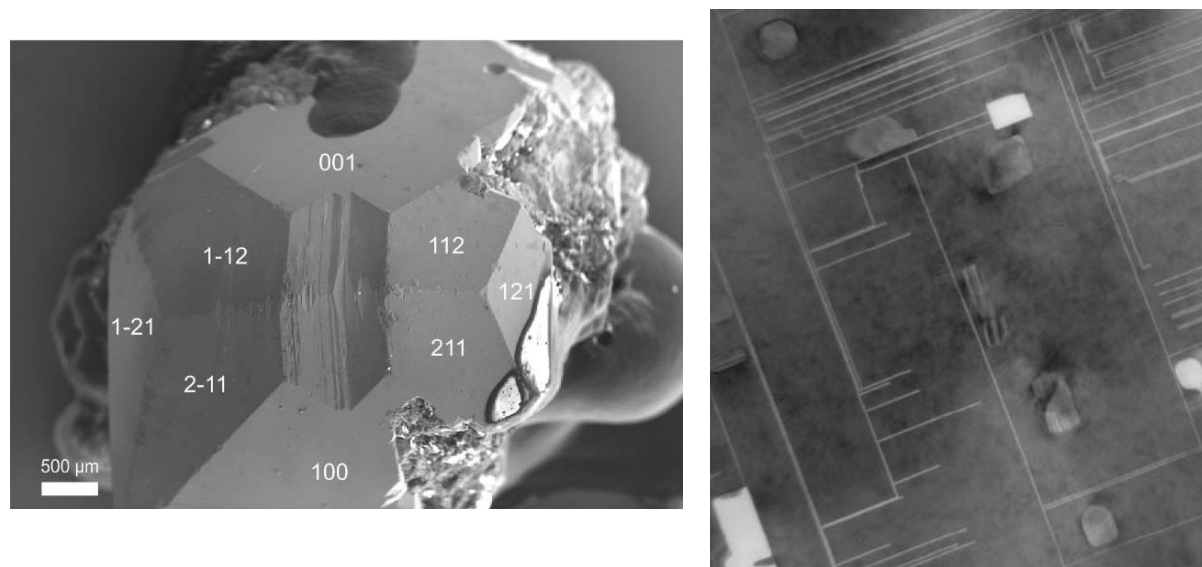


Figure 1.1 SEM-picture of an enlarged bixbyite single crystal with re-entrant faces (left) and TEM-image showing the typical lamellae and small precipitations of a second generation of bixbyite.

The results of the TEM studies showed, that the determining factor for exaggerated grain growth was not only the existence of the interlayers, but also the fact that if the interlayers reach the surface of the crystal and form re-entrant faces, which promote a preferential crystal growth. These faces are areas that provide more atomic steps where new building units can be attached and a 2D nucleation is supported (Lee et al., 2002).

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Die Hessenberg-Sammlung am Institut für Geowissenschaften der Universität Halle/Saale

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Die Mineralogische Sammlung der Universität Halle zählt mit zu den bedeutendsten Sammlungen in den neuen Bundesländern. Leider wurden durch widrige Umstände (z.B. Lagerbedingungen) Teile der Sammlung zerstört.

Ein Bestandteil der Mineralogischen Sammlung sind Kristallmodelle und Mineralstufen von Friedrich Hessenberg (1810 – 1874). Hessenberg, ein Juwelier aus Frankfurt am Main, eignete sich als Autodidakt ein umfangreiches mineralogisches und kristallografisches Wissen an. Die Ergebnisse intensiver reflexionsgoniometrischer Vermessungen von Kristallen zahlreicher Minerale – die Grundlage für die Ableitung der Symmetrieverhältnisse – publizierte er in einer Reihe von Arbeiten. Für mehrere Minerale konnte Hessenberg erstmals Kristallformen beschreiben, ebenso fand er zahlreiche neue Formen an bekannten Mineralen. 1867 wurde Hessenberg für seine Verdienste die Ehrendoktorwürde der Universität Berlin verliehen.

Nach seinen reflexionsgoniometrischen Untersuchungen fertigte Hessenberg Kristallmodelle an. Die außerordentlich sorgfältig gearbeiteten Modelle bestehen aus mit Wachs getränktem Gips. In die Modelle eingraviert sind der Mineralname sowie auf den Kristallflächen die Symbole nach dem heute nicht mehr verwendeten Naumannschen System. Daneben legte Hessenberg eine recht umfangreiche mineralogische Sammlung an. Seine besondere Vorliebe galt dabei den Mineralen Calcit und Titanit. Auffallend sind die Etiketten Hessenbergs zu den Exemplaren. In einer sorgfältigen Handschrift finden sich hier sehr detaillierte Beschreibungen der Minerale, ihrer Paragenese und der Kristallformen, oft noch ergänzt durch Kristallzeichnungen und Angabe der Kristallformen. Neben dem Mineralnamen ist auch meist die chemische Formel des Minerals in der Schreibweise nach J.J. Berzelius vermerkt.

Die Sammlung von Friedrich Hessenberg gelangte nach dessen Tod 1874 über den Geologen Karl von Fritsch nach Halle, der ein guter Bekannter Hessenbergs war und 1873 von Frankfurt am Main an die Universität Halle wechselte.

Die Kristallmodelle und Zeichnungen sind ein wertvolles Zeugnis kristallografischer Arbeiten aus der Mitte des 19. Jahrhunderts. Daneben faszinieren sie heute durch ihre außerordentliche Präzision und Ästhetik.



Hessenbergs Modell von einem Humit-Kristall.



Hessenbergs Modell von Bournonit.

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Biotic and abiotic alteration and formation of sulfides: differences and commonalities

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The oxidative alteration of sulfides and its reversal process, the formation of sulfides in marine and fresh water sediments as well as in remediation, are important redox reactions, which exert an important control the elemental cycles of sulfur, iron and other elements. These redox reactions are well known to occur on both biotic and abiotic pathways which are intimately connected to the electron transfer at mineral surfaces and/or microorganisms.

In this contribution we combine results from different studies in order to discuss common aspects and evident differences among the reaction pathways in low temperature environments: 1. Natural alteration of pyrrhotite (Fe_{1-x}S) from Dalnegorsk, Russia, 2. microbially assisted dissolution of pyrrhotite from Tysfjord, Norway, 3. experiments on the reactions of dissolved sulfide and iron hydroxides (lepidocrocite, ferrihydrite) under anoxic conditions to form iron sulfides, 4. experimental formation of nickel sulfide by sulfate reducing prokaryotes (SRPs) extracted from contaminated soil of the former uranium mining area of Ronneburg, Germany. TEM has been used as a central analytical tool accompanied by Raman spectroscopy, XPS, AFM, SEM, and XRD.

Amorphous, disordered and nanocrystalline phases are commonly observed. Many of these phases are transient, i.e. they only form at a certain stage/time of the reaction and can only be detected using TEM but not by XRD. These include nanocrystalline magnetite in pyrrhotite alteration, disordered and nanocrystalline mackinawite (FeS) as well as magnetite in the abiotic iron sulfide formation, and amorphous and crystalline nickel sulfide formed by SRPs. The abiotic experiments show both a number of metastable phases (iron (oxyhydr)oxides, elemental sulfur, sulfides) but reach a (pseudo-) equilibrium state consisting of pyrite and an iron oxyhydroxide. Structural differences of the reacting phases (different polymorphs of FeOOH , different structure types of pyrrhotite) significantly influence reaction rates and pathways in dissolution and formation experiments. The biotic formation of nickel sulfide results in a high temperature polymorph in contrast to the thermodynamically favored phase which is formed in the abiotic control experiment.

The description and comparison of the processes involving nanoparticles and their connection to redox reactions, microbial forcing and mineral surfaces will be discussed in spite of their relevance to the local cycling of elements which in turn has important implications to larger scale processes.

Reaction Induced Fracturing During Fluid-Rock Interaction

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Mineral replacement processes occur commonly in the Earth whenever minerals are in contact with fluids with which they are not in equilibrium. The underlying mechanisms are poorly understood but both mechanical and chemical processes are thought to be important. Replacement of leucite (KAlSi_2O_6) by analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) is common in silica-poor igneous rocks. A 10% increase in molar volume is associated with the dissolution-precipitation replacement process and this generates stresses that eventually cause fracturing of the reacting leucite (Putnis et al., 2007). Experimentally reacted leucite crystal grains display characteristic fracturing patterns on a micron – millimetre scale, that includes both spalling of concentric “onion-skin” like layers near the reacting interface and the formation of cross-cutting, often hierarchically arranged, sets of fractures that divide the remaining leucite into progressively smaller domains. These structures may explain many textural characteristics of replaced minerals, such as so-called mesh-textures associated with serpentinization of olivine grains during hydration of mafic or ultramafic rocks. They are also strikingly similar to larger scale patterns formed during spheroidal weathering processes. A simple discrete element model can illustrate the mechanics that control the development of such systems and shows how fluid-induced replacement processes may be accelerated due to the generation of new reactive surface area by hierarchical fracturing (Jamtveit et al., 2009).

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Synthese und Hydratation von Mayenit $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$

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Mayenit $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7) ist eine der hydraulisch reaktivsten Phasen in Tonerdezementen und daher sind Synthesebedingungen und Hydratationsverhalten von großem Interesse. Die Synthese von C_{12}A_7 erfolgte neben der herkömmlichen Festkörper-Synthese, mittels Polymer-Synthese und einer Combustion-Methode (GNP) [RAAB ET AL.]. Dabei sollte gezielt das Kristallisationsverhalten bei einer verbesserten Homogenisierung der Ausgangsprodukte in Abhängigkeit von der Temperatur untersucht werden. Im Anschluss an die Synthese der Reinphasen soll das Hydratationsverhalten in Abhängigkeit von Zeit und Temperatur untersucht werden.

Bei den Untersuchungen zur Phasenbildung von C_{12}A_7 konnte gezeigt werden, dass es beim Sintern von den über die Polymer- und Combustion-Methode hergestellten amorphen und gut homogenisierten Precursorphasen, bei 900°C (2h) zur Bildung der metastabilen Verbindung $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$

(C_5A_3) kommt. Die Kristallitgröße beträgt bei dieser Sinter-temperatur ca. 50 nm. Anschließend

wurde die Sintertemperatur schrittweise erhöht (2h je 100°C -Erhöhung), dabei kommt es bei 1200°C zur vollständigen Umkristallisation zum stabilen C_{12}A_7 . Mittels der Festkörperreaktion sind mehrere Sinter- und dazwischliegende Homogenisierungsschritte notwendig, um eine Reinphase zu erhalten. Das Hydratationsverhalten von C_{12}A_7 wurde bereits detailliert von EDMONDS ET AL. untersucht. Dabei entsteht neben amorphen gelartigen Phasen als kristalline Hydratationsprodukte unterhalb von 20°C $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ (C_2AH_8) und $\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ (CAH_{10}); darüber nur C_2AH_8 . Oberhalb von 30°C wird die Umwandlung zum stabilen Hydrogranat $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ (C_3AH_6) und Gibbsit $\text{Al}(\text{OH})_3$ (AH_3) beschleunigt. Zusätzlich kann nach SCHELLER ET AL. abhängig von Temperatur, Luftfeuchte und Druck das C_2AH_8 durch Abgabe von Wasser aus der Zwischenschicht zum $\text{C}_2\text{AH}_{7,5}$ dehydrieren. Die röntgenographischen Untersuchungen von hochreaktivem C_{12}A_7 bei 25°C zeigten eine wesentlich höhere Kristallinität des Haupthydratationsprodukts $\text{C}_2\text{AH}_{(8\pm x)}$. Dies stimmt mit den Beobachtungen von SCHELLER ET AL. überein, der bei der Hydratation von Calcium-Aluminat-Gläsern eine erhöhte Kristallinität der Hydratationsprodukte feststellte. Mittels *in-situ* XRD Untersuchungen (25°C)

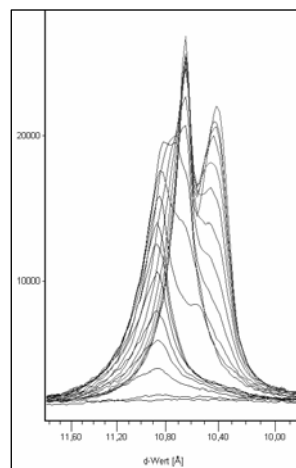


Abbildung 2: Verlauf des 00l-Reflexes von $\text{C}_2\text{AH}_{8\pm x}$ bei der Hydratation von hochreaktivem C_{12}A_7

ist es möglich die einzelnen Modifikationen bzw. Hydratstufen des C_2AH_8 und deren Übergänge zu verfolgen. Unmittelbar nach dem auskristallisieren des hochreaktiven C_{12}A_7 entsteht eine bis dahin unbekannte Hydratstufe des $\text{C}_2\text{AH}_{(8\pm x)}$ mit einem Basisabstand von $10,87\text{\AA}$ (hexagonal $a=5,775\text{\AA}$; $c=65,274\text{\AA}$). Über eine lineare Extrapolation des Wassergehalts gegen den Schichtabstand kann ein ungefähre Wassergehalt von 8,2 angenommen werden ($\text{C}_2\text{AH}_{8,2}$). Diese Hydratstufe geht in die stabileren Hydratstufen mit den Basisabständen von $10,73\text{\AA}$ (C_2AH_8 , hexagonal: $a=5,787\text{\AA}$; $c=64,609\text{\AA}$) und $10,42\text{\AA}$ ($\text{C}_2\text{AH}_{7,5}$, monoklin: $a=9,927\text{\AA}$; $b=5,724\text{\AA}$; $c=42,226\text{\AA}$; $\beta=98,2^\circ$) über. Folglich existieren 3 Hydratstufen (Abb. 2) mit ähnlichem Wassergehalt, die bei weiterer Reduzierung der Luftfeuchte oder Erhöhung der Temperatur in C_2AH_5 bzw. C_2AH_4 übergehen. Mit Hilfe der isoperibolen Wärmeflusskalorimetrie konnte zudem die erhöhte hydraulische Reaktivität bei den mittels Niedrigtemperatur-Synthesemethoden hergestellten Proben und die Erhöhung der hydraulischen Reaktivität bei höheren Temperaturen zeitlich verfolgt werden.

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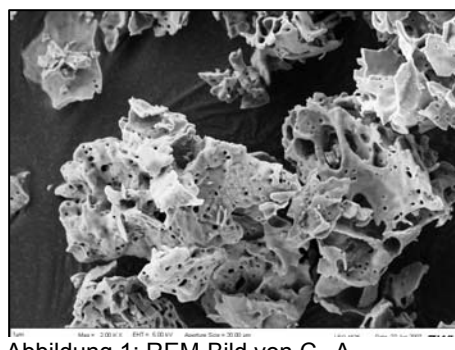


Abbildung 1: REM-Bild von C_{12}A_7 hergestellt mittels einer Combustion-

Synthese von Monocalciumaluminat mittels Sprühtrocknung und Zersetzung von Formiaten

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Ziel der Arbeit ist es zu untersuchen, ob sich hydraulisch hochreaktives und feinkristallines Monocalciumaluminat $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA) mittels Sprühtrocknung, aus einer stöchiometrischen Calciumaluminiumformiat-Lösung und deren anschließenden Zersetzung, herstellen lässt. Hochreaktives CA kann auch mittels anderer Niedrigtemperatur-Synthesemethoden hergestellt werden [RAAB ET AL.], jedoch sind diese Synthesemethoden nur bedingt für eine großtechnische Produktion geeignet. Bis jetzt wurden in der industriellen Produktion für die Sprühtrocknung oder Sprühtrocknung oder Sprühtrocknung meist Chloride oder Nitratre verwendet [KODAS ET AL.], die das Problem einer aufwendigen Abgasreinigung zur Folge haben. Zusätzlich wurde das reine Calcium- und Aluminiumformiat sprühtrocknet, um die Produkte der Sprühtrocknung und deren Zersetzungsverhalten genauer zu charakterisieren. Für die Sprühtrocknung wurde ein kommerziell erhältlicher Sprühtrockner B-191 der Firma BÜCHI verwendet. Abbildung 1 zeigt den schematischen Aufbau des verwendeten Gerätes. Die Parameter der Sprühtrocknung wurden so gewählt, dass möglichst kleine Partikel, bei gleichzeitig akzeptablem Mengendurchsatz hergestellt werden können und die Partikel eine möglichst enge Korngrößenverteilung aufweisen (Abb. 1). Die Untersuchungen zeigen, dass es beim Versprühen der stöchiometrischen Calciumaluminiumformiat-Lösung zur Bildung von nicht agglomerierten sphärischen Partikeln kommt (Abb. 2). Die äußere Gestalt der Partikel bleibt auch nach dem zweistündigen Sinterprozess bei 1000°C erhalten, wobei die metastabile orthorhombische Modifikation des Monocalciumaluminats ($a=8,6433\text{Å}$, $b=8,0775\text{Å}$, $c=15,1213\text{Å}$) auskristallisiert. Bei höheren Sintertemperaturen kommt es zu einer Umwandlung zur stabilen monoklinen Modifikation. Bei der Sprühtrocknung von reiner Calciumformiat-Lösung wird eine Mischung aus $\beta\text{-Ca}(\text{HCOO})_2$ und $\gamma\text{-Ca}(\text{HCOO})_2$ stabilisiert. Diese Modifikationen sind metastabil und kristallisieren innerhalb von einigen Tagen komplett zum stabilen $\alpha\text{-Ca}(\text{HCOO})_2$ um. Das Sprühtrockgut des Aluminiumformiat ist röntgenamorph; mittels IR-Spektroskopie konnte dies jedoch als ein Gemisch aus $\text{Al}(\text{OH})(\text{COOH})_2$ und amorphem Al_2O_3 identifiziert werden. Zusammenfassend konnte somit gezeigt werden, dass sich mittels der Sprühtrocknung und der anschließenden Zersetzung von Metallformiaten, die bei niedriger Temperatur metastabile orthorhombische Modifikation des Monocalciumaluminats herstellen lässt. Zudem konnte gezeigt werden, dass auch das reine Calcium- und Aluminiumformiat aufgrund deren Löslichkeit und deren Zersetzungsverhalten gut für die Sprühtrocknung geeignet sind. Die Partikelgrößenverteilungen sind bei allen Sprühversuchen sehr klein und charakteristische Eigenschaften wie die Partikelgröße können über die Konzentration der Lösung variiert werden.

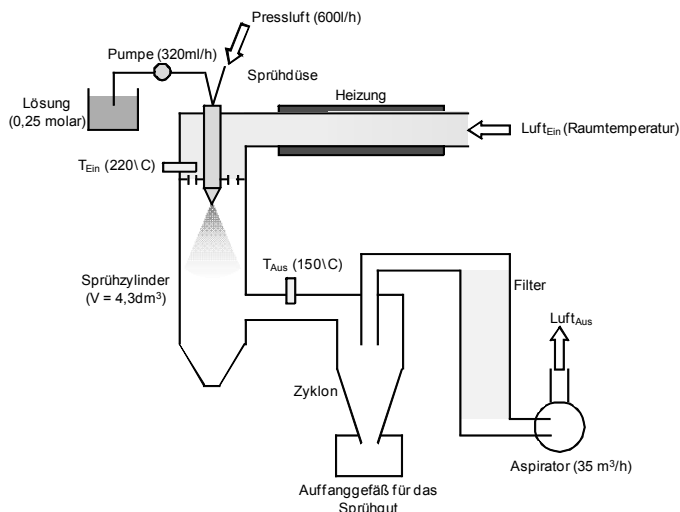


Abb. 1: Schematischer Aufbau des Sprühtrockners B-191 (BÜCHI)

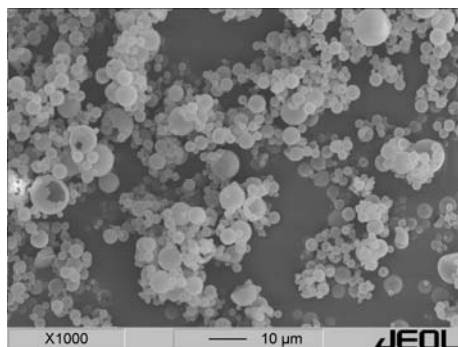


Abb. 2: REM-Bild von sprühtrocknetem Calciumformiat

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Sodalite-like layer structures in the series $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ — $4\text{CaO}\cdot 3\text{Ga}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, and their three-dimensional sodalite-type dehydration products: The first gallate–sodalite established.

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Aluminate sodalites have been known for quite a long time, and received some attention because of their wealth of structural phase transitions and modulated phases. The preparation of gallate sodalites remained a challenge. We have now succeeded in the preparation, and characterization, of mixed aluminate-gallate and of pure gallate sodalites. In order to do so we had to employ a three-step procedure. First, oxide precursors were prepared in the right stoichiometry which were then transformed hydrothermally into members of the solid solution series $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ — $4\text{CaO}\cdot 3\text{Ga}_2\text{O}_3\cdot 3\text{H}_2\text{O}$. Finally, three-dimensional sodalites were obtained by careful dehydration. The intermediate products formed were studied by X-ray powder diffraction, electron microprobe analysis and FTIR spectroscopy, and it was found that they all have structures which can be described as interrupted sodalite structures, or perhaps more appropriately as layered sodalites. No miscibility-gaps were observed in the series of eleven compounds, and the IR-spectra, lattice parameters and bond lengths in the solid solution series vary smoothly with composition. The volume increase from the Al- to the Ga-endmember is ~5.4 %, the average T—O-bond length increases linearly from 1.75(1) Å for the aluminate to 1.84(1) Å for the gallate.

Careful dehydration of the layered sodalite structures at 600-650°C leads to the formation of sodalite-type $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ — $4\text{CaO}\cdot 3\text{Ga}_2\text{O}_3$ mixed crystals. These have been studied by the methods as mentioned above. The end-member $[\text{Ca}_8\text{O}_2][\text{Ga}_{12}\text{O}_{24}]$ -SOD is the first pure gallate sodalite prepared to date.

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The origin of sapphirine-cordierite intergrowths in an iron/alkali-free Mg-Al granulite from the Eastern Ghats Belt (India)

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In this contribution, we document sapphirine–cordierite bi-phase intergrowths, some mantling coarse plates of corundum, in an iron/alkali-free Mg-Al granulite from the northwestern part of Eastern Ghats Belt whose composition can be described by the model system $\text{MgO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{H}_2\text{O}$. The Mg-Al end-member compositions of the coronal phases are explained by Al-conserved grain boundary-controlled discontinuous reactions promoted by intergranular diffusive transport and substitution of Mg and Si, without the masking influence of interfering cations.

The cm-wide layering of the studied Mg-Al granulite sample is composed of corundum (Crn) – sillimanite (Sil) – cordierite (Crd) layers alternating with corundum – cordierite layers. The well aligned coarse plates of corundum in a polygonized cordierite dominated matrix define the planar fabric of the rock. Sapphirine (Spr 7-9-3) occurs in three textural modes. Type-A intergrowths of idioblastic sapphirine crystals with cordierite occur as discrete elongate bi-phase aggregates in the sillimanite-free layers. Type-B intergrowths of randomly-oriented idioblastic sapphirine with cordierite form thin rims around strongly embayed margins of the coarse corundum porphyroblasts in both sillimanite-free and sillimanite-bearing layers. Type-C fine-scale intergrowths of short prismatic to acicular sapphirine with cordierite occur within sillimanite aggregates of the sillimanite-bearing layers.

The occurrence of sapphirine (65-66 wt% Al_2O_3) along margins of corundum and within sillimanite (~67 wt% Al_2O_3) aggregates in the cordierite (~33.5 wt% Al_2O_3) matrix indicates stabilization of sapphirine was dictated by the local availability and short diffusive length scales of Al (cf. Ashworth, 1993). The fluid-deficient nature of the rocks endorses sapphirine-cordierite intergrowths to have formed largely as consequence of grain-boundary controlled closed-system reactions. The compositions of the bi-phase intergrowths plot close to the MAS composition of natural and synthetic kornerrupine (Krn) (Schreyer & Abraham, 1976; Wegge & Schreyer 1994), albeit with lower MgO. The overlapping effective compositions of the intergrowths bracketed by the intersection between the Crd-Spr and the Krn-Sil, Krn-Crn tie lines suggest a formation of intergrowths by closed-system grain-boundary controlled reactions, $\text{Krn} + \text{Sil} \rightarrow \text{Crd} + \text{Spr}$ in sillimanite-bearing layer, and $\text{Krn} + \text{Crn} \rightarrow \text{Crd} + \text{Spr}$ in sillimanite-free layers. Alternatively and more likely, the intergrowth textures in the sillimanite-free layers may be explained by open-system reactions in which kornerrupine decomposed to sapphirine-cordierite and a small fraction of “Mg component” to produce type-A intergrowths. The migration of this excess Mg via intergranular diffusion to corundum-cordierite (matrix) interfaces, and its active participation produced type-B sapphirine-cordierite intergrowths at the expense of corundum and matrix cordierite.

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Ferrian clinopyroxene-wollastonite-melilite slags from lignite-fired steam generators: an analogue of pyrometamorphic melt-rocks of natural coal-fire sites.

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This contribution presents the results of a mineralogical study of slags deposited in lignite-fired steam generators. The majority of slag samples exhibit oxidized bulk compositions that can be represented in the system CaO-MgO-Fe₂O₃-SiO₂. Al₂O₃ and Na₂O constitute additional minor components. The bulk analyses define a linear array extending from calcic (32 wt.% CaO, 34 wt.% SiO₂) to highly siliceous (80 wt.% SiO₂, 32 wt.% CaO) compositions, and in which almost constant CaO:MgO:Fe₂O₃ ratios (60:20:20) indicate a common source of these components, while the variation in SiO₂ reflects mainly the varying incorporation of detrital quartz and, coupled with Al₂O₃ a minor contribution of clay minerals. The slags show viscosity-dependent crystallization behaviour: high glass fractions characterize the viscous siliceous slags; whereas low-viscosity calcic slags underwent almost complete crystallization. Phase assemblages correlate with bulk compositions, in agreement with the liquidus diagram for the model system CaO-MgO-SiO₂-(5 wt% Al₂O₃): (1) clinopyroxene+glass (SiO₂ = 80-60 wt%; CaO/(CaO+SiO₂) = 0,09-0,20); (2) clinopyroxene + wollastonite + melilite + glass (SiO₂ = 60-50 wt%; CaO/(CaO+SiO₂) = 0,25-0,32); (3) clinopyroxene + melilite + glass; monticellite + melilite ± glass; merwinite + monticellite (SiO₂ = 50-30 wt%; CaO/(CaO+SiO₂) ~0.45). Magnetite, magnesioferrite and di-calciumferrite are the typical accessory phases. Quartz, though thermally shocked and corroded, persisted as metastable phase in all slag-types. The stable polymorphs tridymite and cristobalite formed either as reaction wreath (Trd) on quartz grains through interaction with the glass or as polycrystalline reaction domains (Crs) progressing into the interiors of quartz grains. Devitrification phenomena are widely developed.

Clinopyroxenes exhibit significant compositional variation along a join connecting diopside with the ferrian endmember CaFe³⁺[Al_{0.5}Fe³⁺_{0.5}SiO₆] which reflects the oxidizing milieu of slag formation in dry-bottom boilers. The extensive chemical variation from almost pure diopside to ~70 mol% of the ferrian endmember occurs on the scale of zoned grains, micro-domains and samples, and is controlled by the coupled substitution (Mg)^[6]+(Si)^[4] ↔ (Fe³⁺)^[6]+(Al,Fe³⁺)^[4]. Individual grains show oscillatory zoning, commonly characterized by diopsidic core domains and extremely ferrian outer rims. Minor contents of Na (<0.15 a.p.f.u) and Ti (0.06 a.p.f.u.) are incorporated by the coupled substitution Ca+½Mg ↔ Na+½Ti^[6]. Melilites are solid solutions of the endmembers åkermanite (90-57 mol%), Na-melilite (10-28 mol%) and gehlenite (0-15 mol%). Significant substitution of Al by Fe³⁺ (Fe³⁺/(Fe³⁺+Al) up to 0.60) is evidence of the oxidizing milieu. Ferrites show extended solid solution along the magnesioferrite-magnetite and magnesioferrite-spinel joins.

The paragenetic and mineral chemistry features of the studied slags resemble those reported for unusual pyroxene-melilite-iron oxide-glass assemblages of natural coal-fire melt-rocks (Foit et al., 1987; Cosca et al., 1989; Zazek et al., 2005). This indicates that the physico-chemical conditions of their formation (1bar, ≤1400°C, fO₂ close to the hematite-magnetite buffer) were comparable to those prevailing in the slagging zone of pulverised lignite-fired steam generators.

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Suche nach Uranothorianit – Lagerstätten im SE Madagaskars Aus der Praxis der Exploration. Problematik der U-Th-Bestimmung

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Im Rahmen der spät-kambrischen Panafrikanischen Orogenese wurden proterozoische Formationen von regionaler Metasomatose erfasst. Aus Ca-Mg-reichen Sedimenten bildeten sich Pyroxenite (vor allem Diopsid) mit Skapolit, Feldspat, Hornblende, Spinell etc. Diese sind von Si-Al-reichen Gneisen, Graniten und Leptiniten umschlossen. Die Metasomatose fand bei ca. 750° C und 5 kb Druck statt. Im Bereich des Skarns bildete sich u.a.a. Uranothorianit.

Von 1956 bis 1964 wurde vom Commisariat à l'Energie Atomique in über hundert kleinen und mittleren Tagebauen im SE Madagaskars Uranothorianit gewonnen. 40 Jahre später begann erneut eine intensive Suche nach weiteren Vorkommen. Dabei werden neben den ,üblichen' Explorationsverfahren, angefangen vom Herstellen und Auswerten von Luftbildern, über Radiometrie, Kartierung, Messpunkt-Netzen erstellen bis hin zu Bohrungen auch Bestimmungen von U, Th und anderen Elementen mit Hilfe eines Hand-XRF Gerätes durchgeführt. Das so bereits im Gelände bestimmte Th/U-Verhältnis erlaubt schnelle Entscheidungen für die weitere Explorationsarbeit.

Gesteinsproben und Bohrkerne wurden bisher nass-chemisch mit HF-HNO₃-HClO₄ aufgeschlossen, mit HCl behandelt und dann mit ICP-MS bzw. ICP-AES auf Th, U und 48 andere Elemente analysiert. Beim Vergleich mit radiometrischen Messungen und XRF-Analysen ergaben sich starke Abweichungen. Letztere Verfahren zeigen wesentlich höhere Th- und U-Werte. Dies hängt vermutlich mit der schlechten Löslichkeit des Uranothorianits zusammen und der Tatsache, dass auch Zirkon bei diesem Verfahren eben doch nicht vollständig gelöst wird.

Ungeklärt sind aber noch die starken Schwankungen bei den ,Abweichungen': chemische und XRF-Werte stimmen bei niedrigen U-Th-Gehalten besser überein als bei hohen Gehalten.

Charakterisierung und Untersuchung der primären und sekundären Minerale der Kupferschieferschlacke bei Helbra/Mansfeld, Südharz

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Der primäre und der sekundäre Mineralbestand der Kupferschieferschlacke vom Standort der ehemaligen August-Bebel-Hütte bei Helbra wurde untersucht und beschrieben. Der Schwerpunkt der Arbeit lag auf primär aus der Schmelze auskristallisierten Pyroxenen, die den überwiegenden Teil der kristallinen Kupferschlacke aufbauen. Die Untersuchungsmethoden umfassten Auflicht- und Durchlichtmikroskopie, Rasterelektronenmikroskopie mit EDX sowie Röntgendiffraktometrie. Darüber hinaus wurde ein Teil der Proben mittels Röntgenfluoreszenzanalyse untersucht, um Aussagen über den Gesamtchemismus zu erzielen.

Tab.1: Durchschnittliche Zusammensetzung der Kupferschlacke der Rohhütte Helbra (in Gew.%).

Hauptkomponenten	Nebenkompontenten	Spuren
SiO ₂ 42 - 47 %	TiO ₂ 0,7 - 0,8 %	Cl, Co, Ni, Rb, Sr, Zr, Mo, U, Pb, Y
CaO 17 - 21 %	BaO 0,2 - 0,8 %	
Al ₂ O ₃ 12 - 15 %	ZnO 0,1 - 0,6 %	
MgO 5 - 7 %	V ₂ O ₅ 0,1 - 0,2 %	
Fe ₂ O ₃ 3 - 9 %	MnO 0,4 - 0,6 %	
K ₂ O 3 - 4 %	P ₂ O ₅ 0,3 - 0,4 %	
Na ₂ O 1 - 1,5 %	SO ₃ 0,3 - 0,4 %	
	Cr ₂ O ₃ 0,1 - 0,2 %	
	CuO 0,1 - 0,2 %	

Es konnte gezeigt werden, dass die kristalline Kupferschlacke hauptsächlich aus Augit und untergeordnet aus Diopsid aufgebaut wird. Die Pyroxene sind durch die rasche Abkühlung der Kupferschlacke beim Abkippen auf der Halde durchweg skelettartig kristallisiert. Neben den primären Silikaten kommen auch verschiedene Sulfide und ein Elementmineral vor. Bei den Sulfiden handelt es sich vorwiegend um Bornit, Chalkopyrit und Sphalerit, die meist als 5 - 10 µm große Tröpfchen in der Kupferschlacke verteilt sind. Als einziges Elementmineral wurde gediegenes Kupfer identifiziert, das sowohl primär als auch sekundär auftreten kann. Die Verwitterung der Metalle und Metallverbindungen führt zur Entstehung einer sehr großen Anzahl sekundärer Minerale, die oft als grüne bis blaue Krusten die Oberflächen der Schlacke überziehen. Es konnten Sekundärminerale mit den Kationen Cu²⁺, Ca²⁺, K⁺, Pb²⁺, Fe³⁺ und den Anionen SO₄²⁻, CO₃²⁻, OH⁻ und Cl⁻ nachgewiesen werden.

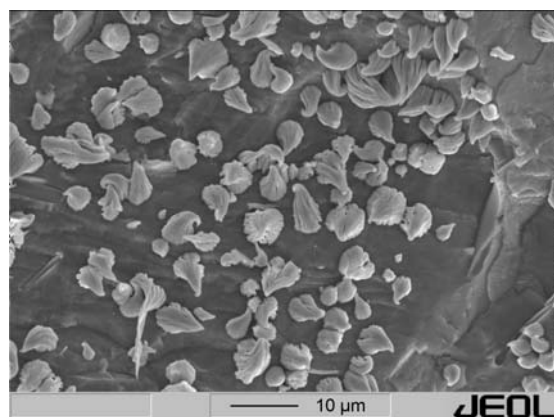


Abb.1: REM Bild. Gediegenes Kupfer als Kupferlocken auf auf Bornit.

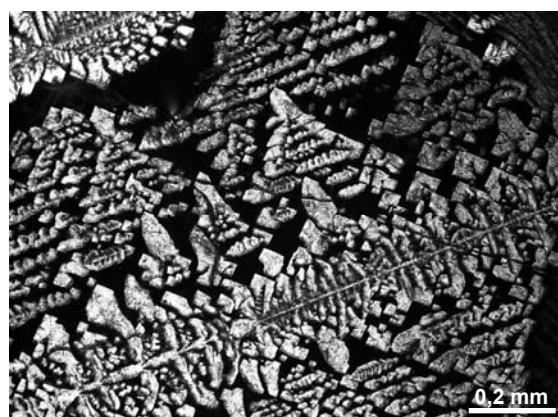


Abb.2: Augit-Skelettkristalle in glasiger Matrix. Dünnschliffphoto, gekreuzte Polarisatoren.

Geochemical characteristics of U-bearing minerals

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Uranium bearing minerals of two distinct conglomerate Reefs from the Archean Dominion Group underlying the Witwatersrand Supergroup are characterized. The Reef conglomerates compose of quartz pebbles and heavy minerals hosted in a sericitic-chloritic matrix.

The main purpose was to distinguish between primary mineralization versus alteration of uranium bearing minerals using various whole rock geochemical (XRF)-, petrographic (SEM)-, and electron microprobe analyses (EMPA).

Petrographic and SEM observations provide discrimination of different U-bearing minerals present in the Reefs. The main U-bearing phases are uraninite, Th-U and U-Ti phases, coffinite and pitchblende. Uraninite distribution can be described as patchy and isolated with oval to rounded, and subhedral shape. The inner part is often partially dissolved and replaced by sulphides (pyrite, pyrrhotite, chalcopyrite) or phyllosilicates. The replacement material can form fracture fillings within the uraninite grains. Most of uraninite crystals appear in different degree of alteration. Th-U and U-Ti mineral phases appear as "ghosts" around more or less altered uraninite with inclusions of pyrrhotite, and galena grains. Coffinite is present as a microcrystalline, relatively heterogeneous phase filling the interstices between the quartz pebbles. Pitchblende is rare distributed appearing around uraninite grains or along fractures.

Whole rock analysis reveal U contents up to 7524 ppm and Th contents up to 3210 ppm. Varying Th/U ratios, indicate the existence of primary uraninite, and secondary uranium bearing mineral phases within the Dominion Reef conglomerates. The decrease in U and Th in sedimentary rocks through geological time is explained by separation of U from repeated cycles of weathering and re-sedimentation (McLennan and Taylor 1979).

Electron microprobe analyses of uraninite grains reveal moderate to high Th contents (up to 9.30 wt% ThO₂) supporting the detrital hypothesis. The majority of U mineralization is represented by detrital uraninite crystals within the Dominion Reefs. Uraninite alteration occurred, evidenced by the U and Th leaching in secondary uranium-bearing phases (e.g. coffinite, U-Ti phases). Increasing Si-content of secondary uraniferous mineral phases during alteration, characterize coffinitization of detrital uraninite. The geochemical and mineralogical study suggest that several uranium-bearing phases occur in different generations in the Dominion conglomerate Reefs. The secondary U mineralization is represented by re-crystallized phases as pitchblende without Th, coffinite, U-Ti and Th-U phases occurring with the uranium redistribution by later hydrothermal processes.

Several studies show that U and Th are mobile during hydrothermal alteration under specific conditions. In clastic sediments, uraniferous mineral phases can be altered by low-grade metamorphism (McLennan and Taylor 1979). Consequently, determinant arguments resulting from this research support the modified paleo-placer theory for the Dominion Reefs mineralization.

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Fractal roughness as classifier for tektite substrewn fields

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Tektites are natural glasses generated by impact events in four major different strewn fields. The distinction of tektites from different sub-strewn fields is reported within the literature. Apart from geochemistry (Koeberl 1994), and physical properties (refractive index, density e.g. Kloess 2000) a classification with numerous diverse parameters is possible.

Tektites occurring in sub-strewn fields differ significantly in their morphology. Quantitative analyses of surface textures have not been reported yet. Therefore, the categorization of tektites from different sub-strewn fields with the help of the multi-scale roughness R_t and the fractal dimension D is of importance. D and R_t as classifier are used as discrimination factors of tektites from different strewn and sub-strewn fields.

To obtain a data set of the multi-scale roughness R_t of several random samples X-ray computer tomography (3D μ -CT) at the IZFP FhG Dresden and at the Leipzig University was used. Within the tomograms different densities are displayed in different grey values. The contrast depends on the X-ray radiation properties. The original obtained measurement categories (grey values and pixel numbers) have been calculated with the resolution to achieve surface profiles (Fig.1). The roughness R_t and the median roughness R_a have been calculated from the deviation of the base line within a profile. Ten different measure intervals were chosen by interpolation to compare the roughness values. Based on the assumption that tektites differ locally in their shape, numerous generated cross sections and profiles of each sample have been investigated.

The fractal dimension D as qualitative measurement of the surface condition was obtained using a modified Box counting and a "Wurstzähl" method. Within this investigation a mix of both methods was used. Representative cross sections have been reworked with digital image processing as comparison with well known geometric figures (e.g. circle, square, Koch snowflake).

As main result it can be proposed that the received data for R_t and D yield comparable results. Both impact trajectory and transport within the geological setting (including alteration processes) influence the tektite roughness demonstrable. Increasing distance from the impact location (e.g. Australites and Philippinites) and subsequent geological transport (e.g. Moldavites from Cheb basin) reduce the roughness and the fractal dimension.

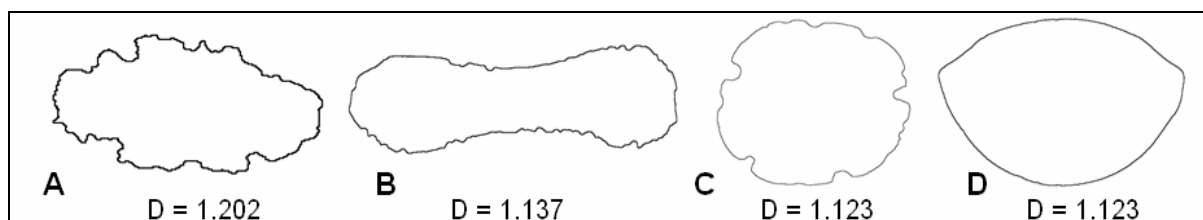


Fig.1: typical 3D μ -CT surface profiles and fractal dimension D of A: Moldavite, (Ločenice, Bohemia), B: Chinite (Guangdong, China), C: Rizalite (Luzern, Philippines), D: Australite (Nullabor Plain)

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Simultaneous monitoring of changes of both electrical conductivity and water saturation in column experiments

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Column experiments were used to obtain information on long term phenomena such as mineral alteration, dissolution, transport and precipitation.

Column experiments are almost black boxes regarding processes taking place at individual levels in site the column. In general only the final stage of alteration can be observed at the end of the experiment when the column is opened for further analyses.

The aim of our investigation was to develop methods which are able to document individual stages of the physicochemical changes taking place while the column experiments are running. Monitoring the change in chemistry by repeated EDXRF line scans over time has been shown (Rammlmair et al, 2006) to elucidate transport phenomena even the outermost portion only of the column provides the signal. Monitoring of multilevel electrical resistivity has been applied on 20 levels showing successfully changes related to transport at the individual levels (Furche et al. 2007). Both methods have been combined (Graupner et al., 2007)

Since results from resistivity measurements are the product of minerals, ion concentration of the fluid, and concentration of the fluid itself, etc. the ambiguity can be reduced by estimating an additional parameter by an independent method. In a first step water concentration was measured by applying NMR Method at the LIAG (former GGA) institute in Hannover. This method provides valuable information on the water content of about 5 cm height in the column. This method is time consuming, restricted to 5 cm diameter, and the column has to be disconnected from the experimental setting. Since the diameter of the columns was increased to 7 cm, another method, x-ray absorption was applied to quantify the water content down to a few percent.

The measurement was performed with the vertically operating EDXRF geoscanner from COX AB Sweden equipped with Mo tube, a flat beam guide, an EDXRF drift chamber detector and a line camera with 1024 pixel of 10 µm resolution. The column is stationary, and the scanning device moves. The Mo tube was operated at 60 kV, 45 mA. The absorption camera acquisition time was 2000 ms.

The experiments were performed for 6 defined grain size distributions in a number of steps such as measuring the empty PVC (polyvinylchloride) column to obtain information on the absorption of the two 50 µm PVC foil windows at the entrance and the exit of the beam. Then the columns were filled with water to derive the thickness of each 250 µm step of the vertical profile, and for deriving the k-factors for the 20 levels for the resistivity measurements. The columns were filled with dry sand of specified grain size distribution to estimate the porosity changes corrected by the thickness. Then stepwise imbibition from below till saturation and finally stepwise draining to achieve stable conditions was performed. Each step was monitored by the amount of water added or extracted, by x-ray absorption and resistivity measurements.

The results show some interesting features for the unsaturated zone, differently expressed for each step and grain size.

The experiments will now be extended to tailings materials to monitor material changes with all three methods, EDXRF, x-ray absorption and electrical resistivity.

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Quantitative Environmental Mineralogy

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Quantitative mineralogy is a fundamental requirement in the mining industries. The mineral processing accompanying quantification of mineral intergrowth and liberated phases of economic interest for each individual step of processing provides a powerful tool for tuning each step to obtain maximum liberation of required phases at minimal possible costs. In the mining industries fastest possible turn around is needed to manipulate the individual steps such as milling, gravity sorting, flotation etc. within the running process. MLA from JKTech and QEMSCAN[®] from FEI (since December 2008) are the leading software packages linked to SEM and widely used in the mining industries of SA and Australia.

BGR holds a MLA licence linked to a FEI Quanta FEG ESEM. We applied the MLA software for an extremely complex system, the Davidschachthalde tailings dam in Freiberg, Germany. A sample from the rim showing alternating hardpan layers and little altered primary material was cut and polished dry through all steps providing insight into a system of primary and secondary highly soluble to less soluble crystalline and amorphous phases.

The aim of the investigation was to obtain quantitative 2D information of primary minerals and porosity as well as secondary phases and clogging of pores, for individual layers of the tailings. The grain size distribution of all primary minerals, related to the mineral processing, such as quartz, feldspar, hornblende, sulphides, barite, cassiterite etc. for individual layers provides information of mineral and grain size sorting in the course of deposition. Secondary crystalline and amorphous phases are related to accessibilities of individual reactive phases and mineral assemblages such as sulphides, carbonates, and silicates. The reconstruction of the primary porosity, and the amount of pore clogging related to individual layers by secondary minerals and gels provides a new insight into processes and transport phenomena taking place at individual positions in the heap.

A database was created for all phases based on BSE-images, EDXRF-spectra evaluation and identification of phases by optical microscopy.

The bulk results obtained were evaluated by image analysis according to regions of interest (ROI) related to individual layers, changes in porosity, changes in alteration.

The future goal is to embed the obtained relationships in FLOTRAN reactive transport modelling of hardpan formation.

Petrogenesis of dunite-wehrlite and websterite xenoliths from Kimberley, RSA: Constraints from Sr-Nd-Hf isotopes

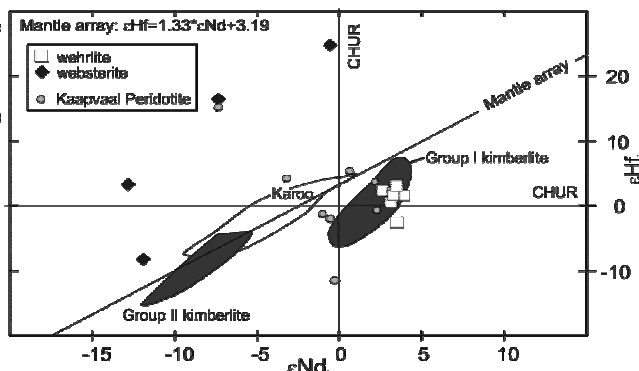
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Dunite-wehrlite and websterite xenoliths are rare members of the mantle xenolith suite found in Kimberley kimberlites of the Kaapvaal Craton in southern Africa. They document spatial differences in metasomatism in strongly depleted upper mantle (Rehfeldt et al. 2008). Websterites have high modal orthopyroxene, while in dunite-wehrlites orthopyroxene is rare. It is coarse-grained and replaces olivine. Additionally, amoeboid clinopyroxene and garnet crystallized along grain boundaries, replacing olivine and orthopyroxene. Textural evidence and olivine major element compositions (e.g. low CaO) indicate dunitic to harzburgitic protoliths. Mg-rich mineral compositions, high spinel Cr/(Cr+Fe) and depletion in Al₂O₃ indicate melt depletion prior to metasomatism. According to Re-Os systematics melt depletion occurred 3.2-2.9 Ga ago. High incompatible trace element contents and enrichment in SiO₂ reflect later metasomatic re-enrichment. The first metasomatic overprint is related to subduction of oceanic crust ~2.9 Ga ago. Partial melting of eclogite produced silica-rich melts that reacted with surrounding mantle, changing olivine into orthopyroxene. Later, percolating basaltic melts induced clinopyroxene and garnet crystallization and enriched the mantle in CaO, FeO and high field strength elements. Websterites have experienced silica-enrichment and clinopyroxene and garnet crystallization, while dunite-wehrlites have only experienced clinopyroxene and garnet crystallization. We report Sr-Nd-Hf isotope data for clinopyroxene in dunite-wehrlite and websterite xenoliths. In ϵNd_i versus $^{87}\text{Sr}/^{86}\text{Sr}_i$ all xenolith types overlap with Karoo basalts. Dunite-wehrlite clinopyroxenes plot within the 'depleted mantle' quadrant and overlap with Group I kimberlites, while websterite clinopyroxenes extend into the 'enriched mantle' quadrant towards Group II kimberlites. In ϵNd_i - ϵHf_i space websterite clinopyroxenes lie above the mantle array, while dunite-wehrlite clinopyroxenes lie in a small area below the mantle array overlapping the field for Group I kimberlites (Fig. 1). Kaapvaal peridotites plot between dunite-wehrlite and websterite clinopyroxenes that seem to represent end members of metasomatism. Nd model ages for clinopyroxene in dunite-wehrlite and websterite xenoliths yield 1.2 ± 0.1 Ga and may represent the age of clinopyroxene crystallization. ϵNd_i and ϵHf_i ratios can be modelled involving three steps, (i) 3.2-2.9 Ga melt depletion of primitive mantle, (ii) followed by evolution through time until 1.5 Ga, (iii) 1.5-1.2 Ga mixing with kimberlite or picrite melt inducing clinopyroxene crystallization and development until the time of kimberlite eruption. While the silica-enrichment seen in websterite xenoliths seems not to be reflected in Sr, Nd, Hf isotopes, these isotopic compositions do support the petrogenetic model of clinopyroxene and garnet crystallization in depleted peridotites developed from major and trace elements, as well as oxygen and Re/Os isotopes.

Fig. 1: ϵHf_i vs. ϵNd_i (calculated to 86 Ma, the time of kimberlite eruption) of clinopyroxene in dunite-wehrlite and websterite as well as Kaapvaal peridotite xenoliths compared to Karoo basalts (Jourdan et al. 2007) and Group I and Group II kimberlites (Nowell et al. 2004).



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Preliminary mineralogical results on tin- and germanium-rich chalcopyrite from the Barrigão Remobilised Vein Deposit, Iberian Pyrite Belt, Portugal¹

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The Barrigão copper mine is located in southern Portugal, about 10 km southeast of the Neves Corvo mine, in the Iberian Pyrite Belt. The ore deposit, surrounded by Viséan shales and greywackes of the Mértola Formation, consists of two converging metric thick vein structures of late-Variscan and/or eo-Alpine age, extending approximately 1800m along NE-SW strike (Mateus et al. 2003). Whole-rock analysis through ICP-MS for trace elements of 10 Barrigão ore samples revealed an average germanium (Ge) content of 61 ppm, with a range of 4 to 280 ppm and tin (Sn) contents mostly exceeding the upper detection limit of 200 ppm. The brecciated copper ore consists of chalcopyrite and tennantite, with accessory arsenopyrite, pyrite and gudmundite in gangue of quartz and carbonates. Minute (~1µm) and very rare sphalerite has been observed as marginal inclusions in chalcopyrite. Alteration took place along small carbonaceous veins and cracks, which often also host covellite, digenite, malachite and rare bornite. EPMA analysis revealed Ge (up to 0.64 wt%) and Sn (up to 1.88 wt%) to be restricted to chalcopyrite, averaging 0.19 and 0.57 wt% in 80 analysis points, respectively. High contents of Ge and Sn seem to be linked to disequilibrium phases of chalcopyrite, showing an irregular patchy zoning in backscattered electron images as well as in EPMA element maps. Textural evidence suggests that chalcopyrite occurs in two successive generations. Early chalcopyrite possibly formed in equilibrium with tennantite. A second chalcopyrite generation partially replaces tennantite. Additional Particle Induced X-ray Emission (PIXE) analysis confirmed the Ge contents in chalcopyrite with a measured range of 0.27 to 0.62 wt%. Germanium and tin occasionally show positive correlation but more often opposing behaviour. Elevated Sn seems to be correlated to lower Fe contents in chalcopyrite. The average composition of chalcopyrite corresponds approximately to a structural formula of $\text{Cu}_{(1.01)}\text{Fe}_{(0.97)}\text{Ge}_{(0.01)}\text{Sn}_{(0.01)}\text{S}_2$. Our ongoing research focuses on the question how Ge and Sn entered second generation chalcopyrite. A favourable explanation is that Ge and Sn are covered in submicroscopic phases, e.g. in stannite, known to be able to incorporate trace amounts of Ge in the crystal structure (Bernstein 1985). The potential detection of minute (<1 µm) stannite grains still has to be confirmed by further microanalysis. High Sn contents in chalcopyrite could also potentially be the result of Sn entering the chalcopyrite structure as a solid solution towards stannite, e.g. through coupled substitution of $\text{Sn}^{4+} + \text{Fe}^{2+}$ for $\text{Fe}^{3+} + \text{Fe}^{3+}$ (Kase 1987). The crystal structure of chalcopyrite, which is a sphalerite-derivate and closely related to stannite, suggests that Ge could potentially enter for Fe resulting in lattice expansion (Kamona & Friedrich 2007). The observed replacement texture also suggests highly that Ge, previously contained in tennantite or in inclusions of other Ge-bearing phases therein, has been somehow adopted by or incorporated into the second generation chalcopyrite.

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Stabilität und Kristallchemie von $\text{CaYAlAl}_2\text{O}_7$ – einem Ca-Y-Al-Gehlenit

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Werkstoffe mit lumineszierenden Eigenschaften werden in vielen Bereichen der Technik eingesetzt. Jeder Festkörperlaser verwendet Kristalle, die zur Strahlung im sichtbaren Wellenlängenbereich angeregt werden können. Um für spezielle Anwendungen definierte Wellenlängen erzeugen zu können wird nach neuen lumineszierenden Werkstoffen gesucht.

Dotierter Gehlenit $\text{Ca}_2\text{Al}_2\text{SiO}_7$ zeigt in Untersuchungen ein vielversprechendes Lumineszenzspektrum, aber eine geringe Quanteneffizienz [1-3]. Aufgrund struktureller Überlegungen ist der Ca-Y-Al-Gehlenit $\text{CaYAlAl}_2\text{O}_7$ als Wirtsgitter für Aktivatoren geeignet. Eine Dotierung mit Ce^{3+} erzeugt unter UV-Licht Phosphoreszenz [4]. Die Ca-Y-Gehlenit-Struktur leitet sich durch gekoppelte Substitution von Ca^{2+} durch Y^{3+} und Al^{3+} anstelle von Si^{4+} ab.

Der Y-Gehlenit kann im ternären Phasendiagramm $\text{CaO-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ dargestellt werden. Im thermodynamisch berechneten Phasendiagramm [5] hingegen sind keine Aussagen über Mischkristalle der auftretenden Phasen angegeben.

Für den Einsatz als Leuchtstoff muss das Material einphasig vorliegen und gute optische Eigenschaften aufweisen. Der Ca-Y-Al-Gehlenit sollte demnach als Kristall gezüchtet werden können. Zur Erzeugung der lumineszierenden Eigenschaften muss der Kristall dotiert werden. Ein gängiges Dotierelement und Aktivator ist Neodym

In dieser Arbeit wurde das Phasendiagramm $\text{CaO-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ bei 1400°C und 1500°C experimentell untersucht. Das bekannte aus thermodynamischen Daten berechnete Phasendiagramm [5] konnte so um Mischkristallreihen erweitert werden. Für die inkongruent schmelzende Verbindung Ca-Y-Al-Gehlenit wurden Kristallzuchtversuche nach dem Zonenschmelzverfahren unternommen. Das Ergebnis der Züchtung ergab einen nahezu phasenreinen Kristall mit klaren transparenten Bereichen. Das quaternäre System $\text{CaO-Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-Nd}_2\text{O}_3$ wurde im Bereich um den Ca-Y-Gehlenit untersucht.

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Einfluss der Werkstoffzusammensetzung auf die Prozesssignale beim Trennschleifen von Beton

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Bei der Bearbeitung von natürlichen und künstlichen Gesteinen ist das Trennschleifen mit diamantbesetzten Segmenten eines der am weitest verbreiteten Fertigungsverfahren. Für die Wirtschaftlichkeit dieses Verfahrens ist der Werkzeugverschleiß eine entscheidende Kenngröße. Diese hängt maßgeblich von der Abstimmung des Werkzeugs und der Maschinenparameter auf den Werkstoff ab. Bislang ist es nicht gelungen, ein System zu entwickeln, welches eine Werkstoffklassifizierung an Hand von Kennwerten in der Weise ermöglicht, dass ein geeignetes Werkzeug sowie geeignete Prozessparameter ausgewählt werden können. Die Abstimmung von Werkzeug und Werkstoff erfolgt überwiegend auf Basis von Erfahrungswerten oder arbeits- und kostenintensiven Schleifversuchen [1].

Lokale Härteunterschiede des heterogenen Betongefüges wirken sich unterschiedlich stark auf den Verschleiß des Werkzeugs aus. Dieser wird zugleich durch die Wahl der Prozessparameter (Schnitttiefe, Vorschubgeschwindigkeit, Schnittgeschwindigkeit) beeinflusst. Hieraus ergibt sich die Möglichkeit, auf werkzeugüberlastende Gefügephasen mit einer Anpassung der Maschinenparameter zu reagieren und so den Verschleiß zu reduzieren. Um die Parameter gezielt zu verändern, ist der Aufbau eines Regelkreises notwendig, bei dem die lokale Betonzusammensetzung das Steuersignal bestimmt.

Zur Regelung und Überwachung von Fertigungsprozessen kommt heute häufig der im Prozess entstehende Körperschall (Acoustic Emission – AE) zum Einsatz [2]. Aber auch andere Signale sind für die Regelung geeignet. Hier ist insbesondere der Luftschall zu nennen. Luftschallemissionen bei technischen Prozessen sind zwar dafür bekannt, dass sie dem Techniker oder Maschinenführer deutliche Hinweise auf Probleme im Verfahren geben, werden in der Praxis aber selten für Steuerungsaufgaben eingesetzt [3]. In vorherigen Arbeiten konnte gezeigt werden, dass die Luftschallemission guten Aufschluss über die Prozessstabilität [4] und lokale Werkstoffeigenschaften [5] gibt.

Im vorliegenden Posterbeitrag wird auf die Körper- und Luftschallsignale eingegangen, welche in Trennschleifversuchen mit unterschiedlichen Betonprobekörpern gewonnen wurden. Die Betonwerkstoffe werden dabei hinsichtlich der Härte und Verteilung der zugesetzten Gesteinskörnungen mineralogisch charakterisiert. Die im Trennschleifversuch aufgenommenen Prozesskräfte, Körper- und Luftschallsignale werden mit der lokalen Betonzusammensetzung in Beziehung gesetzt. Diese Vorgehensweise ermöglicht die Herausarbeitung von Signalcharakteristika, welche als Steuersignale für eine automatisierte Regelung der Maschinenparameter dienen können.

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Die Mineralogischen Sammlungen der Bergbauschule (*Escola de Minas*) der Bundesuniversität Ouro Preto, in Minas Gerais, Brasilien.

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Die *Escola de Minas* in Ouro Preto, Minas Gerais, Brasilien wurde am 12. Oktober 1876 von dem französischen Mineralogen Claude Henri Gorceix gegründet. In der Folge entstand eine erste mineralogische Kollektion, in welche zunächst Proben aus privaten Beständen der Dozenten eingingen. Diese Sammlung erfuhr im Laufe der Zeit viele Erweiterungen und Verbesserungen, bei denen 2 im vorigen Jahrhundert besonders hervorrangen. 1984 wurde für die besonders schönen Mineralstufen ein vollklimatisierter *showroom* mit indirekter Beleuchtung der einzelnen Vitrinen eingerichtet, der fortan vor allem das Besucherziel zahlreicher Touristen sein sollte. In 1995, die mineralogischen Bestände waren inzwischen um Gebiete, wie Bergbau, Metallurgie, Vermessungskunde, Astronomie u. a. m. erweitert worden, wurden alle Kollektionen unter dem Namen *Museum für Wissenschaft und Technik der Escola de Minas* im alten Hauptgebäude der Bergschule, dem ehemaligen Gouverneurspalast im Stadtzentrum zusammengelegt.

Bis zur Mitte des 20. Jahrhundert nahmen Leihsammlungen aus dem Mineralogischen Museum der *Escola de Minas* an vielen Ausstellungen im Ausland teil, u.a. Italien, USA, Deutschland, Chile, wo zahlreiche Prämien gewonnen wurden. Hierbei sind besonders die 2 Goldmedaillen und ein „Gran Prix“ bei der Weltausstellung in Paris -1989 zu erwähnen.

Heute gilt das Museum für Wissenschaft und Technik mit seinen ca. 30.000 Exponaten als eines der besten seiner Art in Südamerika. Mit 7 von 40 Räumen in denen ca. 20.000 Mineralproben gezeigt werden, bildet die Mineralogie das Herzstück des Museums.

Neben zahlreichen Exponaten aus aller Welt wird ein Überblick über die reichhaltige regionale Mineralogie geboten. Gleich am Eingang des Schauraums sieht der Besucher Proben vom schwarzen Gold (*ouro preto*), das der Stadt ihren Namen gab, und als *pretiosum tamen nigrum* (wertvoll wenn auch schwarz) ins Stadtwappen einging. Entgegen der leider bis heute in manchen Fachartikeln verbreiteten Meinung, hat die Farbe allerdings nichts mit den Pd-gehalten des Goldes zu tun. Weitere Stücke aus dem Eisernen Viereck, einem klassischen brasilianischen Bergbauggebiet, so Fe- und Mn-erze und Edelsteine aus dem ostbrasilianischen Pergmatitgürtel vervollständigen das Bild. Eine Vitrine ist den weltbekannten Imperial-Topasen, honiggelber bis weinroter Farbe, aus dem Raum Ouro Preto gewidmet. Als - ebenfalls lokale - Kuriosität kann ein *Itacolomit*, ein flexibler Quarzit, vom Besucher zum Wackeln gebracht werden.

Jährlich besuchen ca. 50.000 Personen aus aller Welt das Museum, darunter viele brasilianische Schulkassen. Für sie insbesondere interessant sind die didaktischen Ausstellungen zur nationalen Bergbaugeschichte und zu den brasilianischen Mineral- und Rohstoffvorkommen.

U.a. erfahren die Schüler in der Sektion „Anwendung der Mineralogie im täglichen Leben“ auch, dass alleine beim Bau eines Eigenheims mehr als 50 Minerale zum Einsatz kommen.

The Importance of the Mineralogical Museum at the Mining School in Ouro Preto as a Research Resource: The Au – Pd Minerals of Central Brazil

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The Mineralogical Museum of the School of Mines (Federal University) in Ouro Preto keeps about 200 gold and noble metal samples (silver, platinum, palladium) from 5 South American countries and 8 Brazilian states.

Included in this collection are very rare samples, such as PtPd nuggets and the famous unique dark coloured grains of „placer gold“ from which the name of the city of Ouro Preto (=black gold) derives. Additional important specimens are the Pd-containing gold grains from the Iron Quadrangle region. The element palladium was first discovered by Wollaston in 1805 and the first analysis of palladium-gold (mineral name: porpezite) was given by Berzelius in 1836.

We had the opportunity to investigate a large number of these samples during the last years. Moreover we found in the collection extremely rare mineral specimens such as atheneite (Pd,Hg)₃As, which previously had been known only from 2 nuggets of the British Museum in London. We could also identify electrum (Au,Ag) and Pd-electrum.

The results of our investigations provide valuable information about the cause of the dark colour around the „black gold“ nuggets (= Fe₂O₃) and the formation environment of AuPd in the region of Minas Gerais in Central Brazil.

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Korrosion von Natriumdisilicatgläsern in wässrigen Lösungen als Funktion des pH-Wertes

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Ergebnisse zur statischen Korrosion von Natriumdisilicatgläsern in neutralen bis basischen wässrigen Lösungen wurden in (Böschel 2003) vorgestellt. Statische Korrosion bedeutet Korrosion in einem geschlossenen System ohne Stoffaustausch. Nach diesen Untersuchungen war

- die Korrosionsrate ($= \partial m / \partial t$; m: Masse, t: Zeit) deutlich zeitabhängig,
- hing von der Zusammensetzung der Gläser und des Korrosionsmediums ab
- und nahm mit steigenden pH-Werten ab.

Bei mittleren und sauren pH-Werten verspricht der dynamische Korrosionstest, bei dem eine Probe einem ständigen Lösemittelfluss ausgesetzt wird, aussagekräftigere Ergebnisse als der statische, da durch die Nachlieferung frischer Korrosionslösung konstantere pH-Wertbedingungen erreicht werden. Diese Methode wurde in der Folge auf die Korrosion angewandt. Zudem können solche Ergebnisse nicht durch Säure-Base – Puffer beeinflusst werden.

Natriumdisilicatgläser $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ wurden wie in (Böschel 2003) beschrieben erschmolzen. Aus den Glasblöcken wurden unter wasserfreien Bedingungen Proben der Größe $15 \times 12 \times 1,5 \text{ mm}^3$ gesägt. Die Oberflächenstruktur war rau und entsprach einer Behandlung mit Schleifpapier der Körnung 600. Jeweils drei Proben wurde bei 30°C 4 d unter dynamischen Bedingungen in folgenden Medien korrodiert:

- 0,0002 M bis 0,3 M HCl - Lösung,
- H_2O (entionisiert),
- 0,001 M bis 0,3 M NaOH – Lösung.

Die Korrosionsmedien waren Maßlösungen (Carl Roth GmbH & Co. KG, Karlsruhe) oder wurden durch Verdünnen dieser Maßlösungen (für höhere Konzentrationen: 2 mol/l, ebenfalls Carl Roth GmbH & Co. KG, Karlsruhe) mit entionisiertem H_2O hergestellt. Die Konzentrationen der Ausgangslösung wurde durch Titration überprüft. Die Proben befanden sich in einem Polypropylenbehälter mit einem Volumen von 65 ml, durch den mittels einer Schlauchpumpe etwa $1 \pm 0,1 \text{ l}$ Korrosionslösung pro Tag durchgepumpt wurden. Probenbehälter und Korrosionslösung wurden in einem Wasserbad auf 30°C temperiert. Die durchtransportierte Korrosionslösung wurde für die chemische Analytik und zur Bestimmung des Durchflusses aufgefangen. Der Korrosionsfortschritt wurde gravimetrisch, durch pH-Wert-Messungen und chemische Analysen (UV/VIS – Spektroskopie, Molybdänblaumethode; Titration) ermittelt. Die Probennahme erfolgte alle 24 h. Zum Wiegen wurden die Proben in Äthanol getaucht und mit einem Heißluftgebläse getrocknet. In einigen Versuchen wurde der Na_2O – Gehalt der Korrosionslösung mit einer Ionensonde (Ionenmeter pMX 3000/ION, WTW GmbH, Weilheim) gemessen.

Durch den Durchflussversuch wurden in den meisten Fällen konstante pH-Werte erreicht. Das Korrosionssystem Natriumdisilicatglas in HCl – oder in NaOH – Lösungen erwies sich dabei als eine Art Puffersystem, da die Glasauflösungsprodukte den pH – Wert der Korrosionslösungen in Richtung neutralerer Werte verschoben. Die Versuche konnten meist durch ein lineares Zeitgesetz ausgewertet werden. In einigen Fällen, besonders im sauren und neutralen pH – Bereich, wurden auch Abhängigkeiten von einem Wuzel-Zeitterm beobachtet. Insgesamt konnten die Korrosionsraten für Natriumdisilicatgläser über einen weiten pH-Bereich ermittelt werden.

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Interactions between organophosphonates and calcite cleavage surfaces

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Many current problems in geology and engineering would benefit from a knowledge of the interaction between organic molecules and calcite. The application of additives which modify the growth process has made it possible to control the crystallization of calcite and other sparingly soluble phases which pose significant problems in the oil industry and in water treatment. Among the most widely employed crystallization additives are phosphonates (Ruiz-Agudo et al., 2006), which have been used as scale and corrosion control additives, as well as dispersants, cleaning agents, chelating agents, and crystal growth modifiers. They also appear naturally in plants, animals and soils, but synthetic phosphonates are entering the environment in increasing amounts as chelating agents, herbicides and crystallization additives (Jonasson et al., 1996). Phosphonates released in the environment may interact with minerals in the soil or in porous oil reservoirs. Mechanisms of phosphonate interaction with mineral-water interfaces may involve different types of processes, including adsorption and surface precipitation. The ability of phosphonates to adsorb on minerals such as silica and clays, barite, cassiterite, aluminum oxides, iron oxides and calcite is well documented (Nowack, 2003 and refs. therein). However, very little is known about the mechanisms of precipitation of multivalent metal ions (Ca^{2+} , Fe^{3+} and Al^{3+}) by phosphonates, which leads normally to the formation of sparingly soluble crystalline compounds (Jonasson et al., 1996). The purpose of this research is to study the interaction between HEDP-bearing solutions and calcite surfaces, using *in situ* Atomic Force Microscopy (AFM). The study aims to provide a better understanding of the mechanisms of phosphonate uptake by calcite, using *in situ* observations of the process at the nanoscale.

Contact of calcite surfaces with HEDP aqueous solutions results in the dissolution of calcite by formation and propagation of elongated, tear-shaped etch pits on calcite cleavage surfaces, in contrast to regular rhombohedral pits formed upon contact with deionized water. Slower etch pit spreading rates are observed in the presence of HEDP in comparison with pure water. These effects seem to be related to preferential adsorption at obtuse etch pit steps by binding to calcium pairs, inhibiting the movement of the kinks and anti-kinks along such steps. When calcite dissolution results in enough calcium release from the substrate, dissolution is followed by nucleation of a new phase on $(10\bar{1}4)$ surfaces. From thermodynamic considerations as well as from previously reported observations, the composition of this phase is considered to be Ca_2HEDP . Independently of the initial HEDP concentration in the initial solution, the nuclei reach a thickness of 3.5 ± 0.25 nm. The growth of these nuclei or 3D islands occurs mainly by lateral spreading, without significant increase of their height. The islands show initially a characteristic elongated shape, and straight edges which defined hexagonal morphologies on the islands were frequently observed. The growth of the islands seems to be crystallographically controlled by the underlying substrate. They appear oriented with respect to the calcite $(10\bar{1}4)$ surface, with their long axis parallel to $[42\bar{1}]$. In general, our observations are in agreement with a "Stranksy-Krastanov" mechanism of epitaxial growth (Chernov, 1984). Growth of the Ca-phosphonate layer avoids the areas where etch pits previously existed, leading to the formation of a surface almost identical to the original calcite surface. This effect is known as *template effect* (Astilleros et al., 2003). At high HEDP concentrations, nuclei growth leads to their coalescence. Then a nanometre layer completely covers the calcite surface, determining the end of the process.

The knowledge gained through this study may have implications for a wide range of fields where the presence of organic molecules may result in epitaxial growth of sparingly soluble crystalline phases within porous calcitic materials, including the oil and cement industry and biomineralization.

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Entwicklung des Austragsverhaltens von Kippenböden, am Beispiel der Lysimeter der Kippe Espenhain

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Die drei Bodenmonolithe 12/1, 12/2 und 12/3 stammen von der landwirtschaftlich genutzten Kippe des ehemaligen Tagebaus Espenhain. Seit 1995 werden die ungestörten Sickerwasserlysimeter von der Staatlichen Betriebsgesellschaft für Umwelt und Landwirtschaft (BfUL) in Brandis betrieben. Um das Austragsverhalten von Kippenböden unter wassergesättigten Bedingungen zu beobachten, wurde ab 2001 das Sickerwasser bis auf einem Meter unter der Geländeoberfläche (GFO) angestaut. Ab November 2006 wurden 12/1 und 12/3 vollständig eingestaut. Gesättigte Verhältnisse lösen reduzierende Prozesse aus und sollen Acid-Mine-Drainage (AMD) verringern. Reduktionsreaktionen sind mit einem Protonenverbrauch verbunden, deshalb ist charakteristisch für einen Übergang von aeroben zu anaeroben Verhältnissen, dass der pH-Wert steigt. Damit kann der Versauerung des Grundwassers bzw. angrenzender Restseen entgegengewirkt werden. Die Probennahmen erfolgten in 0,5 m (1. Ebene), 1,5 m (2. Ebene), 2,5 (3. Ebene) und 3 m (Sickerwasserauslauf) Tiefe.

Die Auswertung der Lysimeterdaten hatte folgende Zielsetzung: (1) Veränderung der Stoffkonzentrationen/ Milieuparameter der einzelnen Ebenen nach dem Sickerwasserstau, (2) Entwicklung des Austragsverhaltens der Lysimeter im langjährigen Mittel, (3) Reduktionspotential durch Wassersättigung, (4) AMD-Potenzial bzw. Entwicklungsprognose der Lysimeter.

Das Lysimeter 12/1 unterscheidet sich durch deutlich erhöhte Werte der elektrischen Leitfähigkeit, Sulfat, Eisen- und Aluminiumkonzentrationen und geringere pH-Werte, im Vergleich zu 12/2 und 12/3. Der im Jahr 2001 erfolgte Sickerwasserstau hat bei 12/1 und 12/3 eine Abnahme der elektrischen Leitfähigkeit in 3 m Tiefe (21% bzw. 15%) zur Folge. Nach dem Einstellen von vollständig gesättigten Bedingungen (12/1, 12/3) im November 2006 erfolgte keine statistisch signifikante Reduzierung der elektrischen Leitfähigkeit. Die Einstellung von wassergesättigten Verhältnissen geht mit geringeren Schwankungen der Sulfatwerte beim Lysimeter 12/1 und 12/3 einher. Die mittleren pH-Werte (2000-2008) von 12/1 und 12/2 sind ab der Tiefe 1,5 m extrem sauer (2,3 bzw. 2,5). Nach dem ersten Sickerwasserstau ist der pH-Wert in drei Meter Tiefe bei 12/1 angestiegen (2001: 2,17, 2003: 2,37) und weiter nach dem vollständigen Einstau (2006: 2,67, 2007: 2,81). Das ergibt einen mittleren jährlichen Anstieg von 0,11. Dennoch sind die pH-Werte in 3 m Tiefe nach mehr als sieben Jahren Wassersättigung im Jahr 2008 extrem sauer. Die Sulfatkonzentration von 12/1 hat sich mit Beginn des Sickerwasserstaus in 3 m Tiefe verringert (2001: 6,7 g/l, 2003: 6,1 g/l). Sie verbleibt dennoch auf diesem hohen Niveau bis 2008. Bei 12/3 ist die Sulfatkonzentration in 3 m Tiefe nach dem ersten Sickerwasserstau um 65% gesunken. Keine Reduzierung ist in 2,5 m Tiefe zu erkennen. Werden die Sulfatkonzentrationen mit den Messwerten von 1996-99 vs. 2004-08 verglichen, ist eine deutliche Reduzierung der Sulfatkonzentration von 12/1 und 12/2 in einer Tiefe von 2,5 m erkennbar (32%, 51%, Knappe et al., 2004). Die Eisenwerte in 3 m Tiefe sind nach dem ersten Sickerwasserstau, im Gegensatz zu den Sulfatwerten, in allen drei Lysimetern 12/1, 12/2, 12/3 deutlich gestiegen (z.B. 12/1: 2001: 1,5 g/l, 2003: 2,2 g/l). Die höchste Aluminiumkonzentration wurde bei 12/2 in 2,5 m Tiefe gemessen (2001: 1409,1 mg/l). Diese ist nach dem Sickerwasserstau deutlich gesunken (2003: 251 mg/l). Die Schwankungen der Aluminiumkonzentration haben mit dem Sickerwasserstau deutlich abgenommen. Das Lysimeter 12/3 hat die geringste Aluminiumkonzentration (2001: 48,6 mg/l), die nach dem ersten Sickerwasserstau weiter gesunken ist (2003: 8 mg/l).

Im Vortrag stehen folgende Fragen und Schwerpunkte im Mittelpunkt: (1) wie wirksam ist das Einstellen von wassergesättigten Verhältnissen, (2) Entwicklungsprognose/ Trendanalyse der Kippenböden, (3) räumlich, zeitliche Heterogenität, (4) Wassersättigung als Sanierungsmaßnahme?

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Normalization of trace metal for sediments samples along Wadi Al-Qilt, Jordan Valley, West Bank, Palestine

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The concentrations of Co, Cr, Ni, B, Mn, Cu, Zn, Ba, Sr, Pb, Cd, Ag, Hg, Al, Fe, TOC and LOI in surface sediments were measured (ICP-MS) from 10 sites along Wadi Al-Qilt (Jordan Valley, West Bank, Palestine) after microwave digestion with Aqua Regia. Sampling was carried out on June and October 2008. Inter-element correlation showed high correlation factors for most trace metals with iron and aluminium. Consequently, normalization of most trace metals to Fe or Al, respectively, showed similar results. Although correlation of trace metals with loss on ignition (LOI) or total organic carbon content (TOC) showed in numerous examples good correlations normalization either to LOI or TOC was not in good agreement. Therefore, normalization of trace metals of all 10 sites along Wadi Al-Qilt were performed to Fe and Al (for example see Fig. 1).

The paper will discuss the anthropogenic contamination which can be classified after normalization in the context of accumulation with respect to background values.

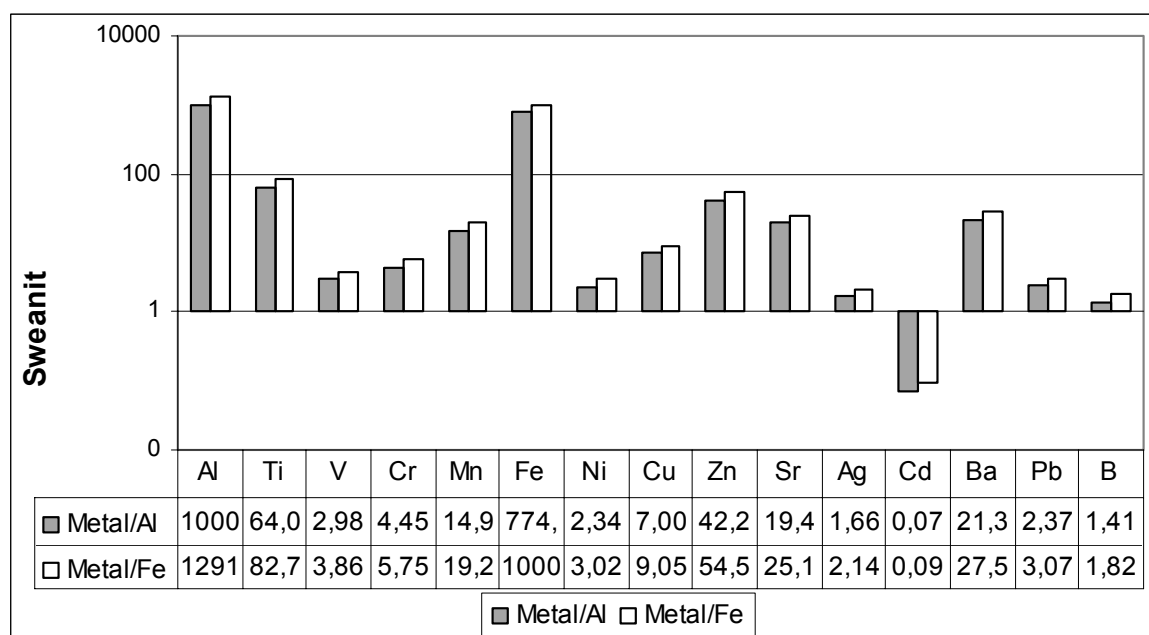


Figure 1: Normalization of trace metals to Al and Fe, respectively for the sampling site "Sweanit"; note values were multiplied by a factor of 1000 for better visualization

Geochemical and mineralogical processes in the pit lakes of the Iberian pyrite belt (SW Spain)

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The physical and chemical properties of pit lakes formed in flooded open-cast mines are strongly determined by a number of climatic, hydrogeological, geochemical, mineralogical and biological factors. Among these, hydrogeochemical and mineralogical processes are of major importance for the water quality evolution of these artificial lakes.

The example of the Iberian Pyrite Belt massive sulphide district in SW Spain is a clear example of how mineralogical factors might determine the water quality evolution of these lakes. From the very beginning, the existing imbalance between acid-producing minerals (mainly pyrite, which always constitutes the dominant phase) and acid-neutralizing phases (such as carbonates, which are very scarce in the mining district) is responsible for a rapid acidification of the pit lake waters. Further, the highly fractured and very low grain-sized nature of pyrite has favoured the dissolution processes, and the polyminerale character of the mineralization (with abundant chalcopyrite, arsenopyrite, sphalerite, galena, and diverse sulphosalts) is responsible for a high concentration of many different metals and metalloids, most of them highly toxic for aquatic biota.

The water quality of these pit lakes is also strongly influenced by the formation of a number of poorly crystalline solid phases which are typical for these acidic environments. A classical example is that of schwertmannite, an iron (oxy)hydroxysulphate formed after the oxidation and hydrolysis of Fe at pH 2.5-4.0. Its formation releases acidity and represents an efficient buffering system, but also generate colloids which represent efficient sorbents for a number of toxic elements such as As and Pb, due to the high specific surface area of this mineral. Similar cases of Fe(III) precipitation with associated trace metal sorption are those of jarosite at pH~2.0 and/or of ferrihydrite at pH>5.0.

Although less important, the formation of Al (oxy)hydroxysulphates at pH>5.0 (e.g., hydrobasaluminite, alunite) and/or Mn oxides (e.g., birnessite, todorokite) at pH 7-8, may also take place under certain conditions, thus representing additional buffering mechanisms and a temporal sink for a number of trace metals (Cu, Zn, Cd, Ni, Co). An important implication of the Fe(III) phases is that, after they settle and accumulate in the sediment cover of the (commonly anoxic) pit lake bottom, they can be either recrystallized (most of them are metastable with respect to goethite) and/or reduced and redissolved by consortia of anaerobic, Fe(III)-reducing bacteria. In both cases, previously adsorbed metals may be again released to the aqueous phase by desorption and/or direct redissolution, thus contributing to the cycling of many elements (mostly Fe, but also As, P, C or S).

Besides these dissolution/precipitation and sorption/desorption reactions, a major geochemical control of the pit lake chemistry is represented by the oxidation-reduction reactions. Specifically, the redox chemistry of iron clearly determines the stratification pattern, vertical structure and hydrogeochemical dynamics of the pit lakes (in this sense, they represent a clear example of "*iron meromixis*"). The oxidation of pyrite and dissolved Fe(II) dominates in the upper layer (*mixolimnion*) of the lakes, which is oxygen-saturated and regularly circulated throughout the year, whereas the reversed situation (Fe(III) reduction) is observed in the anoxic and reducing environment of the bottom layer (*monimolimnion*), which is perennially isolated from the rest of the water column, and in which reduced species and/or gases resulting from the bacterial metabolism (e.g., H₂S, CH₄, NH₄⁺) may accumulate with time. Solar (mainly UV) light may also cause the photo-reduction of Fe(III) and the photo-oxidation of organic matter, thus representing an additional control on the Fe and C cycling.

Untersuchung der Korrosion von Kalk-Natron-Silicatgläsern als Funktion des pH-Werts

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Das Auflösungsverhalten von Natronsilicatgläsern und Kalk-Natron-Silicatgläsern ist ein Standardthema der Glaskorrosion (Scholze 1985; Sinton u. a. 2001; Chopinet u. a. 2009). Mechanismen wie Netzwerkauflösung, Ionenaustausch und Gelschichtbildung sind bekannt aber noch nicht vollständig verstanden. Eigene Arbeiten befassten sich überwiegend mit leicht löslichen Natriumsilicatgläsern (Böschel u. a. 2003). Einige der dort angewandten Methoden sollten verfeinert und auf Kalk-Natronsilicatgläser übertragen werden. An dieser Stelle werden erste Ergebnisse berichtet.

Es wurden drei Kalk-Natronsilicatgläser der Zusammensetzung $(26-x)\text{Na}_2\text{O} \cdot x\text{CaO} \cdot 74\text{SiO}_2$ mit $x = 0, 6, 10$, bei 1500°C erschmolzen. Die Gläser wurden als Glasplättchen (jeweils drei Proben für jede Parametervariation) der Größe $16 \times 14 \times 1 \text{ mm}^3$ (Oberfläche mit Niedertourensäge erzeugt) und bei 30°C bis zu 120 d unter statischen Bedingungen korrodiert. Das Lösemittelvolumen betrug 50 ml. Als Korrosionsmedien dienten

- H_2O (entionisiert),
- sowie NaOH- (purum, Roth, Karlsruhe; mit H_2O verdünnt auf 1 M NaOH, 0,1 M NaOH und 0,01 M NaOH),
- und HCl-Lösungen (Maßlösung, Roth, Karlsruhe, mit H_2O verdünnt 0,1 M HCl, 0,01 M HCl und 0,001 M HCl).

Die Versuche wurden durch chemische Analysen (UV/VIS – Spektroskopie, Molybdän-Blau-Methode, ionenselektive Elektroden), Nachwiegen sowie Charakterisierung der korrodierten Proben im atmosphärischen Rasterelektronenmikroskop (ESEM; Philips XL 30 FEG, Philips Eindhoven, Niederlande) bewertet. Im ESEM wurden Elementprofile mittels energiedispersiver Analyse (EDX) der charakteristischen Röntgenstrahlung gemessen. Für die Bildgebung wurden rückgestreute Elektronen genutzt, so dass eine Verarmung an Na durch Ionenaustausch durch dunklere Färbung hervortritt.

Die korrodierten Glasplättchen wurden üblicherweise in Ethanol gespült und nach Antrocknen mit einem Heißluftgebläse im Trockenschrank bei 30°C 24 h lang weiter getrocknet. Einige der Proben wurden nach Austausch des Wassers gegen Aceton und des Acetons gegen CO_2 überkritisch getrocknet und dann mittels Hg-Porosimetrie charakterisiert. Die Überkritische Trocknung wurde in einem Autoklaven durchgeführt. Die Massenverluste der Gläser folgen in der Regel einem Zeitgesetz der Form: $q = mt + n\sqrt{t} + a$. Dabei ist q der auf die Oberfläche normierte Massenverlust, m und n sind die Ratenkonstanten des linearen Zeiterms und des Wurzel-Zeiterms, a eine additive Konstante und t die Korrosionszeit. Die calciumhaltigen Gläser haben sehr geringe Korrosionsraten, was deren Auswertung erschwerte. Mittels ESEM und EDX konnten Elementprofile senkrecht zur Oberfläche vermessen werden. Diese hatten bei den calciumfreien Gläsern, die unter neutralen und sauren Bedingungen korrodiert wurden, Tiefen von bis zu $50 \mu\text{m}$, bei den calciumhaltigen Gläsern allerdings nur bis zu $5 \mu\text{m}$. Die Form der Elementprofile stimmte mit dem bisher in der Literatur berichteten überein, die z. B. in [1] veröffentlicht wurden.

An überkritisch getrockneten Proben konnte mittels Hg-Porosimetrie die Porosität der der korrosiv veränderten Oberfläche charakterisiert werden. So wurden für ein calciumfreies Glas, das 4 d in 0,01 M HCl korrodiert wurde, ein mittlerer Porenradius von 22 nm ermittelt. Schätzt man den Volumenanteil der veränderten Oberflächenschicht aus ihrer Dicke ab, so ergibt sich ein Porenvolumenanteil von $45 \pm 5 \%$.

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Effect of bound H₂O layers on diffusive transport in compacted clays

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In water saturated pores of clays there is vicinal to the surface less mobile water which is arranged in so called "bound H₂O layers". The solid surface significantly modifies the structure of this water and the mobility of these adsorbed molecules is reduced by more than one order of magnitude (Michot et al., 2002). Bound H₂O layers have a thickness of several nanometers (Ichikawa et al., 2001). Their presence is important for transport processes as self diffusion and random walk of water is fastest in unbound H₂O and is slowed down in bound H₂O (Marry et al., 2008). An additional effect is the increase of the apparent volume of platelets which act as obstacles to diffusion (Duval et al., 2001).

Diffusion is an important in many geological processes. In geotechnical practice, the effective diffusivity, D_{eff} , is used to evaluate the design of barriers for waste disposal (Shackelford, 1991; Bourg et al., 2006). The advantages of compacted clays as engineered barriers are their unique physicochemical properties, plasticity and fracture self-sealing characteristics. The use of organo-clays is considered in geotechnical barriers in order to improve the adsorption capability for anionic and uncharged compounds.

The effect of surface properties on diffusive transport in compacted bentonites was determined in H₂O→D₂O exchange experiments at two different bulk density ranges and water saturation degrees. A cell adapted to the ATR-unit of a FTIR-spectrometer, allowing the quantification of the effective diffusion coefficient (D_{eff}) of H₂O was used. Diffusion experiments were accomplished on modified bentonite samples with three different organic cations (hexadecylpyridinium (HDPy), benzethonium (BE) and tetraphenylphosphonium (TPP)) in amounts of 0-400 % of the cation exchange capacity (CEC). Surface charge (SC) and wettability was determined for tracing the bound H₂O layers. SC of all three organo-clay combinations increases by the addition of organic cations from -100.1 for the original bentonite to 270.0 mmol_c/kg in maximum for HDPy-montmorillonite. The point of zero charge (PZC) of all three organo-clay was reached when the uptake of organic cations is at 75 % of the CEC. Hydrophobic surface properties with contact angles up to 110° were analysed only for HDPy-montmorillonite samples. In this case the formation of bound H₂O layers is suppressed. Here highest D_{eff} with 7.59×10^{-11} m/s² were observed at the high bulk density (1.0-1.5 g/cm³). At low bulk density (0.6 to 0.9 g/cm³) this effect is strongly weakened, as with increasing pore size the effect of bound H₂O layers is diminished. At high bulk densities and partially saturation, diffusion transport is decreased by a low connection degree of water saturated pores. For hydrophilic samples at the high bulk density and saturated state, D_{eff} was 1.5×10^{-11} m/s² for original bentonite and $\leq 1.1 \times 10^{-11}$ m/s² for all hydrophilic organo-clays, which is quite lower than for the hydrophobic sample. At higher loadings of organic cations the formation of bilayer structures (and more) at the montmorillonite-water interface might also contribute to low D_{eff} . In hydrophilic organo-clays slowing factors for D_{eff} up to a magnitude of 0.5 are (i) an increase of bulk density and (ii) a decrease in water saturation degree. In the saturated state at high bulk densities hydrophobic surface properties are suppressing the formation of bound H₂O layers can increase D_{eff} by one order of magnitude.

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Chalkophile Elemente in der Ozeankruste von ODP Hole 1256D

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Hydrothermale Prozesse an mittelozeanischen Rücken verursachen beträchtliche Umverteilungen einer Reihe von Elementen, darunter auch von chalkophilen Elementen wie Cu, Zn, Sb und den Elementen der Platingruppe. Diese Umverteilung kann potentiell Stockwerksvererzungen von Sulfiden erzeugen, z.B. in einer Übergangszone zwischen massiven Laven und den Sheeted Dikes. Quelle der Mineralisationen könnte der Bereich der unteren Sheeted Dikes und der Gabbros darunter sein. Eine komplette Bilanzierung der chalkophilen Elemente in der oberen ozeanischen Kruste konnte bislang noch nicht durchgeführt werden, weil geeignete Profile durch den oberen Teil der Ozeankruste nicht verfügbar waren. Seit einigen Jahren liegt ein derartiges Profil jedoch vor (ca. 15 Ma alte Kruste der Cocos-Platte im östlichen Pazifik, erbohrt in ODP Hole 1256D, Wilson et al., 2006). Davon stehen uns Proben jeder belegten stratigraphischen Einheit zur Verfügung aus einer Tiefe zwischen ca. 300m und 1500 unter Meeresboden: massive Laven, Übergangszone, Sheeted Dikes, Gabbros. Der Grad der Alteration steigt mit der Tiefe an (Wilson et al., 2006): In den Laven herrschen bei unter 150 °C entstandene Phyllosilikate und Fe-Oxihydroxide vor, während in den Sheeted Dikes grünschieferfazielle Paragenesen (Chlorit, Aktinolith) dominieren. Die untersten 60m der Sheeted Dikes sind teilweise oder völlig rekristallisiert (granoblastische Gänge) als Folge der Kontaktheizung durch die Intrusion der Gabbros darunter (Koepke et al., 2008).

Ziel unserer Studie ist eine Bilanzierung der postmagmatischen Mobilität der chalkophilen Elemente in der oberen Kruste und die Aufschlüsselung der Prozesse für die Mobilisierung. Die Ergebnisse weisen darauf hin, dass die Elemente Zn, Pb und Cu während der hydrothermalen Überprägung der oberen Kruste unabhängig voneinander fraktionieren. Zum Beispiel zeigt Cu keinerlei Korrelation zu Spurenelementen, welche für die Fraktionierung basaltischer Magmen stehen (z.B. Cr, Ni, Sc, Zr). Insgesamt variiert der Cu-Gehalt innerhalb der oberen Kruste (bis zur Basis der granoblastischen Gänge ca. 1400m unter Meeresboden) nur sehr wenig. Selbst in der Übergangszone zwischen Sheeted Dikes und Laven zeigt Cu – im Gegensatz zu anderen Lokalisationen wie ODP-Hole 504B – keine signifikante Anreicherung. Dagegen werden deutliche Verarmungen und Anreicherungen an Cu in der Übergangszone zwischen oberer und unterer Kruste beobachtet, also in den granoblastischen Sheeted Dikes. Da die Cu-Mobilität bei hydrothermalen Prozessen primär von der Bildung von Cu-Komplexen in den hydrothermalen Fluiden abhängt und deren Stabilität eine Funktion z.B. der Cl-Konzentration in den Fluiden und weitestgehend temperaturabhängig ist (Robb 2006), kann die Cu-Mobilität im unteren Bereich der oberen Kruste folgendermaßen erklärt werden: Cu wird durch Cl-reiche Fluide lokal aus den Sheeted Dikes herausgelöst und ortsnahe wieder abgelagert, wenn der Cl-Gehalt regional in den Fluiden durch die Bildung von Cl-reichen Mineralen sinkt. In der Tat finden sich in der Übergangszone zwischen oberer und unterer Kruste vermehrt sekundäre Cl-haltige Amphibole (Hornblende und Aktinolith – Wilson et al., 2006, Koepke et al. 2008) und erhöhte Cl-Gehalte (Sano et al., 2008). Im Gegensatz zum Cu zeigt das mäßig chalkophile Zn die größte Variation und die höchsten Gehalte im Top der Sheeted Dikes und kaum Variationen in der Übergangszone zwischen oberer und unterer Kruste. Ob das dem Einbau in sekundäre Spinellphasen (Magnetit) zuzuschreiben ist, ist bisher ungeklärt.

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Cathodoluminescence (CL) microscopy of HP- and UHP-metamorphic rocks: New avenues for petrological applications

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During the last 50 years the technique of cathodoluminescence (CL) microscopy has become a standard tool in mineralogy. First investigations mainly focused on sedimentary ($\pm$ magmatic) rocks and on zircon zonations in connection with ion probe dating (SHRIMP). Within the last decade, this technique has also been applied to various metamorphic rocks (e.g. Schertl et al, 2004; Harlow & Sorensen, 2005).

We would like to demonstrate here the great advantages of a "hot cathode" CL microscope, in particular in conjunction with EMP-studies on HP- and UHP-metamorphic rocks, just using normal polished thin sections. The compilation of data presented includes samples from Dora Maira/Italy, Kokchetav/Kazakhstan, Sulu/China, Western Gneiss region/Norway, Pohorje/Slovenia, the Rio San Juan Complex/Dominican Republic, Motagua Valley/Guatemala, NE-Corsica. Among other features, we introduce here: 1) oscillatory zoning patterns of garnet, jadeitic clinopyroxenes, kyanite, and zircon; 2) regular and irregular - in some cases very complex - growth structures of garnet, jadeite, omphacite, carbonates, and clinopyroxenes; 3) dolomitic exsolution patterns in calcite and K-feldspar exsolution patterns in clinopyroxene. We illustrate the effects of the change of crystal morphology during growth (e.g. on garnet and jadeite) and dissolution and deformational effects (garnet). Distinguishing features of different silica phases like coesite (bluish-green luminescence), quartz (dark red to violet), chalcedony (yellow), as well as those of calcite (yellow), aragonite (green), Mg-calcite (orange), and dolomite (red) are presented, as are the characteristics of different quartz and also carbonate generations. The CL-investigations introduced also contribute to the understanding of mineral reactions, particularly considering the formation of symplectites and pseudomorphs. Further studies focus on interstitial phases and different annealed crack systems of rock matrices; accessory luminescent minerals like diamond (greenish blue and partly zoned), zircon (blue), apatite (green), and bearthite (green) are easily identified in thin section, even when they occur in very small abundance.

It is important to note that CL-microscopy is far from a simple descriptive method only. Using high-resolution spectroscopy of the CL-emission, it is possible to evaluate the spectra of different minerals. Narrow bands of e.g. Cr^{3+} , Dy^{3+} , Sm^{3+} , Tb^{3+} and broad bands caused by Mn^{2+} and Fe^{2+} can be easily distinguished, even in different zones of the same mineral (e.g. as in garnet, clinopyroxene, kyanite, carbonates).

In essence, CL enables colour images of important but otherwise invisible growth features and internal structures of minerals to be obtained, easily and quickly achieved within seconds. Knowledge of the detailed structural characteristics of rock-forming minerals has an invaluable impact on more precise and detailed derivation of PT-paths, and thus on the evolution of geodynamic processes with any metamorphic rocks involved. Thus we propose the CL-technique to be used more intensively for routine investigations of thin sections as a pathfinder prior to chemical characterization by EMP.

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From the early magmatic to the post-magmatic stage: Approaching the source characteristics and tracking the post-magmatic evolution of the alkaline Mont Saint-Hilaire complex, Canada, using stable and radiogenic isotopes

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The Cretaceous Monteregian Hill intrusions form an East-West-trending magmatic alkaline province in South Quebec, Canada. Mont Saint-Hilaire is one of these intrusive complexes roughly 40 km east of Montreal. It consists of a progression from alkaline gabbros and diorites/monzonites to peralkaline foid syenites, each of which forming a distinct melt batch. In the most evolved peralkaline foid syenites the world-famous mineral collecting site of Poudrette Quarry is located. To date, nearly 400 minerals are described from Mont Saint-Hilaire, amongst them more than 40 type minerals. In all, Mont Saint-Hilaire consists of a wide range of magmatic rocks that formed under highly different conditions, covering a range in temperature from ~1150°C to presumably ~200°C.

Stable isotopes of O and H of mafic mineral separates are applied to trace potential heterogeneities between the different rock units present at Mont Saint-Hilaire. First results in $\delta^{18}\text{O}$ reveal values in the range of 3.9 to 4.8 (relative to VSMOW) for mineral separates from the most primitive gabbroic unit whereas mineral separates from the more evolved rock units display values from 4.8 to 6.3 (relative to VSMOW). QUIF (Lindsley & Frost, 1988) and two-oxide thermometry yield the highest temperatures for the samples in which the lowest $\delta^{18}\text{O}$ values of all samples are found, arguing against alteration effects. Therefore, systematic changes in $\delta^{18}\text{O}$ indicate either heterogeneities in the mantle source or are indices for variable degrees of crustal contamination. Isotopes of Nd and H are used to shed light on the problem of contamination and fluid-rock interaction, respectively, the different melt batches are affected by.

As Mont Saint-Hilaire is known to have developed its mineral-richest zones during late- to post-magmatic stages in highly evolved foid syenites and as carbonate minerals are present in some of these assemblages, C and O isotopes of carbonates from rocks that presumably have formed during late- to post-magmatic conditions are analyzed as well. The results are compared to the C and O isotopic composition of the sedimentary carbonate host rock.

A special focus is put on fluid inclusions from all rock units that are analyzed by microthermometry and Raman spectroscopy. The conditions of formation of the fluid inclusions are well-constrained in terms of temperature and pressure which are <600°C and <1kbar, respectively. As CO₂ is a major component in most of the fluid inclusions, the C isotopic composition of the CO₂ captured and preserved in the fluid inclusions is analyzed. To conclude with the post-magmatic processes, this allows for tracing the source of the CO₂ and is set into relation to the late-stage carbonates and the sedimentary carbonate host rocks.

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Comparison of crystal structure refinements of mordenite based on single-crystal and powder diffraction data

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Natural mordenites from Chimchvad, India, with the composition $\text{Ca}_{2.3}\text{Na}_3\text{Al}_{7.6}\text{Si}_{40.4}\text{O}_{96} \cdot 24\text{H}_2\text{O}$ were investigated by single-crystal and powder diffraction methods. Mordenite usually crystallizes in fibrous aggregates (Passaglia et al., 1995) with needles elongated parallel *c* in the orthorhombic space group *Cmcm*, and often shows a lamellar intergrowth of the fibers. The latter effect aggravates single-crystal investigations, and the preferred orientation of the needle-shaped crystals biases the powder diffraction refinements. Here, we report the results of our

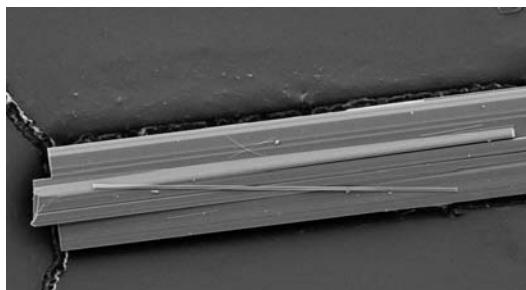


Fig 1: Mordenite needle with intergrowths

comparative studies of mordenite, using an imaging plate single-crystal diffractometer (STOE IPDS I), a standard four-circle diffractometer (STOE STADI 4), and a Bragg-Brentano powder diffractometer (Panalytical X'Pert) with Ni-filter. In addition, one sample is investigated between room temperature and 900°C to study the dehydration processes.

The chemical composition was determined by microprobe analysis and EDX spectroscopy on a scanning electron microscope also used for the photograph shown in Fig. 1. The water content was determined by thermal analysis (Netzsch 409 PC). The single-crystal structure analysis using the program SHELX (Sheldrick, 1997) confirmed the structure model for hydrated mordenite as, e.g., described by Mortier et al. (1976). The high internal residual *R*(int) of 0.1126 indicates the problems associated with the lamellar intergrowths but, finally, did not prevent a successful refinement yielding residuals of *R*₁ = 0.058. The framework structure shows a partial order of Si and Al with Al concentrated in one position. All nonframework cations could be located and their occupancies were refined without any restraints to add up within the error margins to the amount of Ca and Na determined in the chemical analysis. The same applies to the water molecules which agree well with the amount obtained by thermogravimetry. All framework atoms, except O8, could be refined with anisotropic displacement factors. The straight T2-O8-T2 angle of 180° was avoided by displacing the O8 atom from the inversion center and assuming a partial occupancy on this split position, yielding a relaxation of the angle to 160°. That way, a symmetry lowering of the space group to *Cmc*2₁, frequently described in the literature (see, e.g., Simonicic & Armbruster, 2004), was avoided.

Preliminary Rietveld refinements using the program BRASS (Birkenstock et al., 2009) resulted in rather high residuals of *R*_{Bragg} = 0.098 caused by the preferred orientation and an extreme asymmetry of the reflections in the low 2θ region.

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A new Meteorite Field in the United Arab Emirates

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Introduction: In January 2005 a ureilite [1] was found in the course of archaeological field work [2] in the Umm Az-Zamul area, southern Abu Dhabi, United Arab Emirates. Following this discovery a meteorite search was carried out in this region over 14 days in February/March 2009. The meteorite search was a cooperation between the Mineralogical Museum, University of Hamburg, The Natural History Museum, London and the Environmental Agency Abu Dhabi (EAD).

Results: During this meteorite search at the edge of the Rub' al Khali desert 26 chondrites with a combined mass of 2.78 kg were found irregularly distributed on interdunal planes which are located in between stationary megadunes. The masses of the meteorites range from 7 g to 540 g with the majority of the masses below 100 g. The interdunal surfaces consist of either bright coloured carbonatic rocks of Tertiary age, younger gypsum deposits or are covered by thin layers of carbonate-quartz sands, and stretch across up to 25 km². The meteorites found during this survey are comparatively small compared to those of other desert regions, such as Oman or Libya [3]. Furthermore, large open areas of the potential find planes did not show any meteorites. The search area, today a fenced and guarded nature and wildlife preserve, was a ground of heavy oil exploration in the past. Hence, a plausible reason for few and small meteorites is, that geologists from oil companies or other oil company workers took the oddly looking and black 'not in the area fitting' meteorites as a souvenir. This assumption is sustained by the many meteorites we found close or in between small mobile barchan dunes which occasionally cross the interdunal corridors. Here, meteorites might have been hidden at the time of extensive oil exploration and were just uncovered very recently.

All meteorites are magnetic and first macroscopic observations revealed that all are significantly weathered. Detailed classifications are currently under way and the results will be presented at the conference. The determination of terrestrial ages is in process. Further meteorite searches in the Emirates under support of the Abu Dhabi administration are in preparation.

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Spectroscopic investigations of synthetic ferrisicklerite

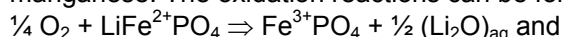
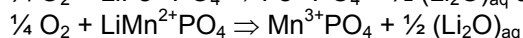
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The phosphate minerals triphylite (LiFePO_4) and lithiophilite (LiMnPO_4) often crystallise in the late stage during the evolution of granitic pegmatites. Both minerals are isotypic and crystallise in the olivine structure with the divalent ions Fe^{2+} and Mn^{2+} occupying the M2-positions and Li^+ the M1-positions (Losey, 2004). In the natural environment triphylite (LiFePO_4) and lithiophilite (LiMnPO_4) form a complete solid solution and appear as primary minerals at temperatures of around 500°C. The examination of thin sections (Quensel, 1937; Mason, 1941) showed that in later stages a redox reaction of the primary triphylite - lithiophilite solid solutions with the surrounding fluid occurs. Such reaction was found to result in a loss of lithium and in the oxidation of the divalent cations of iron and manganese. The oxidation reactions can be formulated as:



As a first step in the course of this reaction phases of the solid solution ferrisicklerite – sicklerite ($\text{Li}_{1-x}(\text{Fe}^{3+}\text{Mn}^{2+})\text{PO}_4$) appear in which the iron component is oxidised and an appropriate part of the Li has left the structure. In a second reaction step the divalent manganese is oxidised and the minerals of the heterosite – purpurite ($\text{Fe}^{3+}, \text{Mn}^{3+}$) PO_4 solid solution form. Both, the intermediate phases ferrisicklerite – sicklerite and the fully oxidised phases heterosite – purpurite are members of the so called Mason-Quensel-sequence (Fransolet et al., 1986). Since they are isostructural to the educt triphylite – lithiophilite, this process can be characterised as a topotactic replacement reaction.

The aim of our study is to investigate the temperature conditions, oxygen fugacities, and the reaction mechanism under which the formation of the phases of the Mason-Quensel-sequence form under natural conditions. The latter are characterised by the presence of a H_2O -rich pegmatitic fluid. In our experimental investigation cuboids with edge length of ~ 2.5 mm were prepared from a natural triphylite single crystal ($\text{Li}(\text{Fe}^{3+}_{0.74}\text{Mn}^{2+}_{0.21}\text{Mg}_{0.05})\text{PO}_4$) from the Palermo Mine, New Hampshire, USA. The samples were treated in 0.1N HCl_{aq} at a temperature of 120°C in externally heated, Teflon[®]-based pressure vessels. KMnO_4 served as the oxidizing agent. After 7 to 28 days a rim of 0.1mm thickness around unreacted triphylite has formed, while the overall size and shape of the cuboids are retained. This rim showed reddish brown absorption colours very similar to those known from natural ferrisicklerite ($\text{Li}_{1-x}(\text{Fe}^{3+}\text{Mn}^{2+})\text{PO}_4$). The reaction product was indeed identified as ferrisicklerite by X-ray powder diffraction, Raman, and Mössbauer spectroscopy. Electron microprobe analyses revealed no significant changes of the Fe, Mn, P, Mg, Na, K, and Ca concentrations across the reaction interface. However, whereas in the unreacted triphylite the K concentration was found below the detection limit, K was detected in the ferrisicklerite product. The K concentrations increase continuously towards the surface of the cuboid. X-ray powder investigation in combination with the Rietveld method revealed a higher rms strain in the ferrisicklerite product than in the triphylite parent phase. Polarised as well as unpolarised Raman spectra of the ferrisicklerite rim were found to be very similar to those of natural ferrisicklerites from different locations. They are characterised by relatively broad Raman bands compared to those of triphylite. Raman spectra of samples treated in an aqueous solution enriched in ^{18}O showed shifts of their Raman bands towards lower frequencies relative to spectra of samples formed in water of “normal” isotopic composition. This indicates the incorporation of ^{18}O in the ferrisicklerite lattice. Our results support the hypothesis that an interface-coupled dissolution-reprecipitation operating at an inward moving reaction front is the responsible mechanism of reaction rather than a selective, diffusion-based leaching process.

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Untersuchungen zur Verwendung von Glasmehlen als Zusatz zu zementären Systemen

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In der vorliegenden Arbeit wurde die Eignung eines Glasmehls (Mikrover, Dennert....) aufbereitetes Behälterglas als Zuschlagstoff zu einem handelsüblichen Bindemittelsystem (CEM I 42,5R) untersucht. Chemische Reaktionen zwischen unterschiedlichen Formen der Kieselsäure (SiO_2) aus den Zuschlagsmaterialien und Alkalihydroxiden (NaOH , KOH) der Porenlösung bzw von Aussen zugeführten Alkalihydroxiden (z.B. Taumittel) führt zur sogenannten Alkali-Kieselsäure-Reaktion (AKR). Das dabei entstehende Alkali-Kieselsäure-Gel kann durch Wasseraufnahme an Volumen zunehmen und damit treibend wirken. Dadurch kann es zu erheblichen Betonschäden führen [STARK & WICHT, 2001].

Das verwendete Glasmehl wurde chemisch/ mineralogisch (RFA, XRD, SEM, pH Wert bei Zumischung von Wasser, Puzzolanitätstest nach HILL & HÜNGER, 2005) charakterisiert. Des Weiteren wurden Untersuchungen am Bindemittelsystem (Zement + Glasmehl) an vorgegebenen Abmischungen durchgeführt. Der Glasmehlgehalt wurde dabei zwischen 10 Gew.% und 30 Gew.% variiert. Die durchgeführten Untersuchungen beinhalten z.B. die Bestimmung des Erstarrungsbeginns bzw. Erstarrungsende, Frischmörtelrohdichte, Untersuchungen am Glasmehl – Reaktivität als $\text{Ca}(\text{OH})_2$ Verbrauch, sowie Festigkeitsuntersuchungen. Die Festigkeitsuntersuchungen sowie damit verbundenen Schwindungs- Dehnungsmessungen wurden an Normprismen der Größe $4\text{cm} \times 4\text{cm} \times 16\text{cm}$ entsprechend DIN 196-1 nach einer Lagerungszeit von 2, 7, 28, 90, 180 sowie 360 (laufend) Tagen durchgeführt. Bis zu den entsprechenden Messungen wurden die Proben bei ca. 25°C und 95% r.F. in einer entsprechenden Klimabox feucht in Tücher eingeschlagen gelagert. Zusätzlich wurde das Hydratationsverhalten der unterschiedlichen Abmischungen mittels isoperiboler Wärmeflusskalorimetrie charakterisiert. Untersuchungen zur Mikrostruktur wurden mittels CRYO-SEM an Proben mit 10 Gew.% Glasmehlzuschlag durchgeführt. Neben drei Monate alten, bei 25°C und 95% r.F. gelagerten Proben wurden Proben untersucht die einen Monat bei 40°C und 100% r.F gelagert wurden. Zusätzlich wurde das Hydratationsverhalten bzw. die Phasenentwicklung mittels In-Situ XRD über einen Zeitraum von 72h untersucht.

Puzzolan effekt. Aktiver füllstoff, bisher keine neg erscheinungen bez. Dehnung

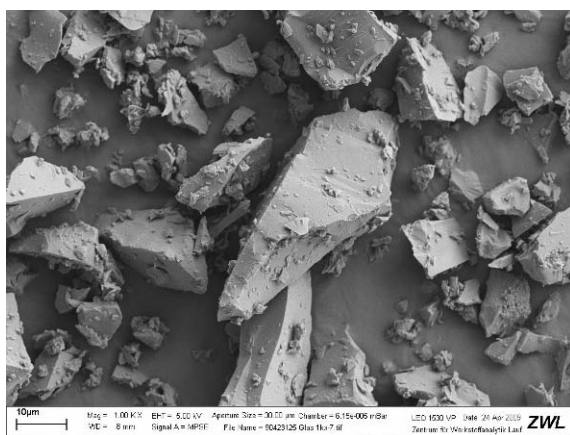


Abbildung 1: REM Aufnahme des untersuchten Glaspulvers [Dennert Poraver GmbH]

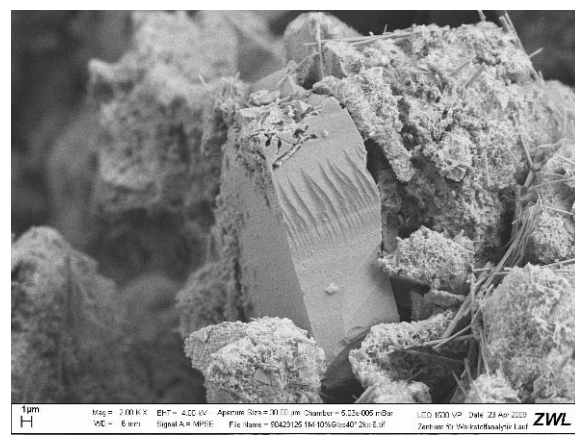


Abbildung 2: CRYO-SEM Aufnahme einer hydratisierten Zementprobe (Schwenk CEM 1 42,5R) nach 28 Tagen mit einem Zuschlagsanteil von 10% Glas Glaskorn

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In-situ U-Pb Dating of Micro-Baddeleyite

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We introduce a technique for U-Pb dating of baddeleyite using secondary ion mass spectrometry (SIMS) *in-situ* analysis of ng-crystals that cannot be efficiently extracted by conventional mineral separation techniques. Average $^{207}\text{Pb}/^{206}\text{Pb}$ ages for Precambrian baddeleyite crystals are within <0.3 % of the respective isotope dilution thermal ionization mass spectrometry (ID-TIMS) ages. $^{206}\text{Pb}/^{238}\text{U}$ ratios are corrected for instrumental fractionation calibrated through linear regression in a $^{206}\text{Pb}/^{238}\text{U}$ relative sensitivity vs. UO_2^+/U^+ calibration plot. Calibration is performed on baddeleyite separates (~100 - 200 μm in maximum dimension) mounted in random crystallographic orientation. $^{206}\text{Pb}/^{238}\text{U}$ ages for unknowns (grain mounts of FC4b and Kovdor baddeleyite, as well as FC4b *in-situ* micro-baddeleyite) are determined to within 1-2 % relative uncertainty by averaging 15 - 30 individual analysis spots with a total mass consumed during analysis of <50 ng. Comparison between silicate glass and baddeleyite, as well as replicate analysis of the same grains in different orientations relative to the direction of primary beam incidence support previous notions for bias in Pb/U sensitivity in baddeleyite due to variable crystal orientations (Wingate and Compston, 2000) By using a CAMECA ims1270 ion microprobe, however, with oxygen flooding, and a UO_2^+/U^+ -based calibration, these effects are significantly reduced compared to published SHRIMP II results.

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Application of Rietveld Analysis in the Aluminium Industry

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Aluminium is produced by electrolytic reduction from alumina. The alumina is refined from Bauxite. Aluminium production is a high-energy process since the electrolysis consumes power in the range of megawatt to smelt the alumina. Furthermore, the consumption of peat electrodes leads to substantial CO₂ production. Both power consumption and CO₂ rate strongly depend on the composition of the molten alumina bath.

Alumina is mixed with cryolite, fluorite and several other additives to lower the bath temperature and to improve the ion conductivity to save energy. Several process parameters such as the bath ratio or the excess AIF factor are calculated from the relative abundances of the phases cryolite, chiolite, Ca-cryolithe, Li-cryolithe, alumina and sodium fluorite. Depending on the used flux additives, several solid solution phases occur in bath samples.

XRD is widely used to determine the phase composition of bath samples. The peak areas of certain characteristic phase peaks are calibrated by standards to derive concentrations. This method has several drawbacks, e.g. there are several structures for Ca-cryolite with different characteristic peaks, peak overlaps and ambiguous phase identification. In these cases classical calibration methods are prone to fail. Full pattern analysis i.e. Rietveld analysis can be used to quantify the phase composition in difficult situations. Rietveld analysis is standardless and helps to describe every feature of a diffractogram. However, the setup required expert knowledge so far.

We developed a refinement strategy for the commercially available HighScorePlus package for phase quantification in potflux analysis. The refinement strategy will be set-up by PANalytical experts based on company reference samples. In a second step, an automatic quantification control file is generated. This allows for fully automated Rietveld quantification without any user input or operator knowledge. In combination with automated sample preparation lines the complete potflux analysis can be fully automated.

The Rietveld method relies on the analysis of a wide-angle diffraction pattern. Classical point-detector systems are too slow to integrate the full-pattern recording into the daily routine of a smelter. Depending on the size of the plant and of the number of electrolytic cells, several samples per hour have to be analyzed. Here the use of modern linear detector is mandatory. We use the PIXcel detector on a CubiX fast system. This semiconductor detector comes with 256 x-ray sensitive channels and can be used in several ways. For Rietveld quantification, the detector uses all channels in linear mode to record a full diffractogram in less than two minutes. For classical one-peak measurements, the detector is used in static mode. In this mode the detector records 3.5° 2θ simultaneously with a throughput time of 1 second. Single peak data can be obtained in less than 60 seconds.

The combination of modern XRD detectors with sophisticated next-level automatic Rietveld analysis improves both data quality and sample throughput. The more precise determination of bath ratios and excess AIF helps to better adjust the chemical composition of the bath to save energy and to reduce CO₂ production substantially.

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Synthese und Charakterisierung von Sorel-Bindemittel-Phasen

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Sorel-Bindemittelphasen bestehen aus basischen Metallsalz-Hydroxid-Hydraten. Grundlage bildet die Eigenschaft vieler schwer löslicher Metalloxide, mit den Lösungen ihrer Salze zu reagieren. Der so hergestellte Beton zeichnet sich durch sehr große Härte bei geringer Dichte, kurzen Abbindezeiten und Stabilität gegenüber Salzlösungen aus. Die Qualität des verwendeten Metalloxids übt dabei einen starken Einfluss auf das Abbindeverhalten, die Reaktionsprodukte und die Stabilität der Bindemittelphasen aus. Die industrielle Anwendung der Sorel-Phasen ist jedoch aufgrund ihrer Unbeständigkeit gegenüber Wasser und dem Fehlen von Grundlagenkenntnissen in vielen Systemen bislang nur beschränkt möglich und konzentriert sich vor allem auf den Bereich Dammbauwerke von salinaren Endlagern. Um das Problem der Wasserunbeständigkeit zu lösen und einen neuartigen Spezialbeton mit variablem Chemismus, guter Verarbeitbarkeit und hoher Langzeitstabilität für den Einsatz bei Reparaturen, im Salinar oder für Tiefbohrzementationen zu erzeugen, wurden in ausgewählten Systemen, wie $\text{MgO-MgCl}_2\text{-H}_2\text{O}$, $\text{MgO-MgSO}_4\text{-H}_2\text{O}$, $\text{MgO-Mg(NO}_3)_2\text{-H}_2\text{O}$ und $\text{MgO-Mg(CH}_3\text{COO)}_2\text{-H}_2\text{O}$ Sorel-Bindemittelphasen synthetisiert.

Basische Metallsalz-Hydroxid-Hydrate wurden durch Fällung aus hochkonzentrierter Lösung oder mittels Hydrothermalsynthese in einem Teflon beschichteten Autoklaven hergestellt. Die so synthetisierten, zum Teil noch unbeschriebenen Phasen wurden röntgenographisch, chemisch und thermisch charakterisiert. Zusätzlich wurden in verschiedenen Systemen Zementmischungen mit variierenden Lösungskonzentrationen, Lösungs-/ Feststoffverhältnissen, sowie MgO-Qualitäten hergestellt und mit Hilfe von Röntgendiffraktion und isoperiboler Wärmeleitungs-kalorimetrie untersucht.

Unabhängig von der chemischen Zusammensetzung bilden sich Sorel-Phasen aus einem Gel, ab einer Lösungskonzentration von 2mol/l. Geringere Konzentrationen führen zusätzlich zur Bildung von Mg(OH)_2 , wobei das Ausfällen der Sorel-Phasen mit abnehmender Löslichkeit der verwendeten Metall(II)-salze später beginnt. Es zeigt sich, dass im ternären System $\text{MgO-MgCl}_2\text{-H}_2\text{O}$, wie in der Literatur beschrieben, die $3\text{Mg(OH)}_2\text{-MgCl}_2\text{-8H}_2\text{O}$ und $5\text{Mg(OH)}_2\text{-MgCl}_2\text{-8H}_2\text{O}$ Phase auftreten, während im System der Magnesiumsulfat-Hydroxid-Hydrate lediglich die $5\text{Mg(OH)}_2\text{-MgSO}_4\text{-8H}_2\text{O}$ Phase bei Raumtemperatur stabil ist. Bei $\text{MgO-Mg(CH}_3\text{COO)}_2\text{-H}_2\text{O}$ und $\text{MgO-Mg(NO}_3)_2\text{-H}_2\text{O}$ treten dagegen zwei noch unbekannte Verbindungen auf. Die Kristallisation dieser Sorel-Phasen in einer Zementmischung erfolgt auch nach der Verfestigung. Ihr Anteil nimmt über einen Zeitraum von 90d kontinuierlich zu, während das typischerweise schlecht kristallin ausgebildete Mg(OH)_2 kaum reaktiv ist. Untersuchungen mittels Wärmeleitungs-kalorimetrie zeigen, dass das Abbinden der Sorel-Zemente unabhängig vom gewählten System im starken Maße von der Reaktivität des verwendeten Magnesiumoxids abhängt. Bei hochreaktivem MgO mit einem Blaine-Wert von 10000-40000 cm^2/g ist das Abbinden nach spätestens 24h abgeschlossen, während das Abbinden von hart gebranntem MgO mit Blaine-Werten unter 2000 cm^2/g über einen Zeitraum von 4d statt fand.

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Translokationsprozesse des Urans in der Pedosphäre von Feuchtgebieten

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Hydrogeochemische Studien natürlicher, uranakkumulierender Feuchtgebiete (Wetlands) können das Prozessverständnis bei der Urantranslokation in der Pedosphäre erweitern. Das Projekt zielt darauf, die Technologie „künstlicher Wetlands“ (Pflanzenkläranlagen i. w. S.) zur Uranrückhaltung zu optimieren, indem deren Konstruktion gezielt auf die maßgeblichen Rückhalteprozesse ausgerichtet wird. Solche Wetlands stellen eine interessante Alternative zur konventionellen Wasserbehandlung dar, insbesondere hinsichtlich Kosten- und Wartungsaufwand.

In Deutschland sind Pflanzenkläranlagen für kommunale Abwässer Stand der Technik, der Einsatz als „constructed wetlands“ bei Industrieabwässern und Bergbauwässern ist dagegen untergeordnet. Die Behandlung typischer AMD („acid mine drainage“) aus dem Bergbau wird aber weltweit seit Jahrzehnten auf hohem Niveau in Wetlands durchgeführt. Auch aus dem Uranbergbau gibt es seit einigen Jahren Erfahrungen. Erste wissenschaftliche Studien zeigen, dass Uran-Rückhaltung in solchen Wetlands mit organischen, aber auch anorganischen Substraten prinzipiell funktioniert. Der Langzeiteinsatz scheitert bisher jedoch an rasch nachlassender Reinigungswirkung oder negativen Begleiterscheinungen (z. B. Gasentwicklung). Die konkreten Mechanismen zur Uranfixierung waren, anders als bei der Behandlung typischer AMD, i. d. R. nicht offensichtlich und damit nicht gezielt steuerbar.

In dieser Studie wurden drei natürliche Wetlands im Abstrom uranhaltiger Bergbauwässer bearbeitet. Aus der Charakterisierung des jeweils vorliegenden Redoxmilieus in Kombination mit Bindungsformanalysen konnten Rückschlüsse auf den Mechanismus der Uran-Immobilisierung gezogen werden. Insbesondere rasterelektronische Untersuchungen trugen dazu bei, das Verständnis über die biogeochemischen Wechselwirkungen zu erweitern.

Auf Grundlage eines hier gefolgerten Festlegungsmodells für Uran und basierend auf Literaturdaten wurden die Prozesse, die zur Uranrückhaltung in Wetlands beitragen können, erstmalig umfangreich beschrieben und bewertet. Es wurden die Faktoren diskutiert, die die Effizienz und Langzeitstabilität dieser Prozesse beeinflussen.

Aufbauend darauf sollen weitere Studien an rezenten, uranakkumulierenden Wetlands und fossilen Pendants dem Ziel dienen, die Relevanz der neu abgeleiteten Prozesskette zu überprüfen. Parallel dazu sind Laborstudien zur Konditionierung geeigneter Substrate auf die maßgeblichen Rückhaltemechanismen angesetzt.

Phase relations in the Cu_2S – FeS – FeS_2 system

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The phase relations in the Cu_2S – FeS – FeS_2 system with special emphasis on the homogeneity region of the chalcopyrite phase were determined by X-ray powder diffraction and electron microprobe analysis.

For these investigations two types of samples of chalcopyrite, stoichiometric composition (CuFeS_2) and non-stoichiometric one with the deficiency of sulphur ($\text{CuFeS}_{1.90}$), have been prepared from the chemical elements by melting. The initial elements were 99.9998% copper, 99.99% iron, and 99.99999% sulphur. The total mass of elements of 10 g was placed into quartz ampoules which were sealed under vacuum $1 \cdot 10^{-3}$ Pa. The preparation was carried out in vertical furnaces with the heating rate of 3 K/min up to the temperature exceeding the melting point of CuFeS_2 (1148 K) on 30 – 50 K. The ampoules were kept at this temperature during 2 h and then cooled to the room temperature with the rate of 3 – 5 K/min. The equilibrium annealing was implemented (made) at 1073 K during 550 h.

The chemical composition and phase content of the samples was determined by electron microprobe analysis. It was found, that in the case of the nominal stoichiometric composition two other phases occur besides the chalcopyrite phase. These both phases are FeS_2 and bornite. The chalcopyrite phase consists of Cu-poor ($\text{Cu}_{0.9519}\text{Fe}_{1.024}\text{S}_{2.0371}$) and near-stoichiometric chalcopyrite ($\text{Cu}_{1.0074}\text{Fe}_{0.9978}\text{S}_{1.9951}$). The other sample, synthesized nominal non-stoichiometric with sulfur deficiency, consists of the chalcopyrite phase only. Here a lamellar microstructure was observed, with Cu-poor and Cu-rich compositions. Both chalcopyrites show a sulfur deficiency with values between $(\text{Cu}+\text{Fe})/\text{S} = 1.014 \dots 1.074$.

Ion tracks in apatite at high pressures. The effect of crystallographic orientation on the elastic properties of fluorapatite under hydrostatic compression

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Static elasticity measurements at high pressures were carried out on several oriented fluorapatite single crystals, of which selected crystal samples contain oriented amorphous ion tracks from experimental irradiation with relativistic heavy ions. Irradiation experiments were performed at UNILAC linear accelerator at GSI, Darmstadt, using ¹⁹⁷Au ions (11.1 MeV per nucleon energy, 1×10^{12} ions cm⁻² fluence). All high-pressure experiments on irradiated and non-irradiated crystal sections were carried out at room temperature in diamond-anvil high-pressure cells under hydrostatic conditions. In-situ single-crystal diffraction was performed to determine the high-precision lattice parameters, simultaneously monitoring the widths of XRD Bragg peaks. High-pressure Raman spectra were analyzed with respect to the frequency shift and widths of bands, which correspond to the Raman-active vibrational modes of the phosphate tetrahedra. Swift heavy ion irradiation at 1 bar ambient pressure was found to induce lattice expansion and tensile strain within the host lattice due to the apparently larger volume of the amorphous tracks. In contrast the relatively low Grüneisen parameter for the $\nu_{1b}(A_g)$ mode, which has been assigned to emerge from the volume fraction of the amorphous tracks, and accordingly the $\gamma(\nu_{1a})/\gamma(\nu_{1b})$ ratio reveals compressive strain on the ion tracks. The comparative compressibilities, as derived from lattice parameters, reveal approximately equivalent bulk moduli, but significantly different pressure derivatives ($K_T = 88.4 \pm 0.7$ GPa, $\partial K/\partial P = 6.3 \pm 0.3$ for unirradiated, $K_T = 90.0 \pm 1.7$ GPa, $\partial K/\partial P = 3.8 \pm 0.5$ for irradiated samples), which can be understood considering the tensile strain on the host lattice. The axial compressibility moduli β^{-1} reveal significant differences, which correlate with the ion-track orientation ($\beta_a^{-1} = 240 \pm 5$ GPa, $\beta_c^{-1} = 361 \pm 14$ GPa, $\partial(\beta_a^{-1})/\partial P = 11.3 \pm 1.2$, $\partial(\beta_c^{-1})/\partial P = 11.6 \pm 3.4$ for irradiation $\perp(100)$; 246 ± 9 GPa, 364 ± 57 GPa, 9.5 ± 2.9 , 14.7 ± 14.1 for irradiation $\perp(001)$, 230.7 ± 3.6 GPa, 373.5 ± 5.1 GPa, 19.2 ± 1.4 , 20.1 ± 1.8 for unirradiated material). Line widths of XRD Bragg peaks in irradiated apatites confirm the strain of the host lattice, which appears to get reduced as pressure increases. In contrast selected bandwidths of Raman signal modes increase with pressure, which was assigned to increasing strain gradients on compression, most likely to occur at the interface between the amorphous track and the surrounding host lattice.

Exploring inter-mineral Fe isotope variations in sulphide ore deposits using UV femtosecond laser ablation MC-ICP-MS

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We explore the potential of iron isotopes as a tracer for sulphide ore deposit formation processes. Samples from four different locations were investigated, all representing major nickel-copper ± platinum group mineral (PGE) ore deposits: Hartley Mine (Great Dyke, Zimbabwe), Selebi-Phikwe Complex (Botswana), Trojan Mine (Zimbabwe), Merensky Reef (Bushveld Complex, South Africa). We selected these locations because they all have a magmatic origin but different histories of secondary alteration. This offers the opportunity to study the effect of metamorphic and/or fluid alteration on Fe isotope systematics. Models for the formation of these ores suggest separation of immiscible metal-rich sulphide liquids from mafic/ultramafic magmas and subsequent settling of the former. The sulphide liquid layer crystallised as a metal sulphide solid solution and upon further cooling, pyrrhotite, pentlandite and chalcopyrite exsolved. We present the first in-situ measurements of iron isotopes in sulphide mineral assemblages consisting of pyrrhotite, chalcopyrite and pentlandite. The iron isotope compositions of sulphide minerals were measured by UV femtosecond laser ablation coupled to multi collector inductively coupled mass spectrometry (MC-ICP-MS) using a sample-standard-sample bracketing approach.

The obtained $\delta^{56}\text{Fe}$ values (given relative to IRMM-014) range from -1.10‰ to +1.73‰. Individual sulphide mineral grains are homogenous with respect to their iron isotope composition (within $\pm 0.1\%$ external reproducibility). Analyses of different $\delta^{56}\text{Fe}$ grains in each sample give consistent results, each sulphide mineral type exhibiting a distinct $\delta^{56}\text{Fe}$ value, all different from the average of bulk igneous rocks ($\delta^{56}\text{Fe} = 0.09 \pm 0.1\%$). Comparing the $\delta^{56}\text{Fe}$ values of the same sulphide mineral type in the four deposits reveals slight differences, but a remarkably consistent pattern emerges regarding the relative differences in $\delta^{56}\text{Fe}$ between sulphide minerals. Pentlandite always has the heaviest iron isotope composition ($\delta^{56}\text{Fe} = +0.81$ to $+1.73\%$) followed by chalcopyrite ($\delta^{56}\text{Fe} = +0.43$ to $+1.11\%$). Pyrrhotites always show negative $\delta^{56}\text{Fe}$ values ($\delta^{56}\text{Fe} = -0.51$ to -1.10%). Although, equilibrium inter-mineral isotope fractionation factors for pyrrhotite-pentlandite-chalcopyrite assemblages haven't been determined yet, the observed succession in $\delta^{56}\text{Fe}$ is consistent with qualitative theoretical considerations of equilibrium inter-mineral isotope fractionation based on differences in bond strength. Moreover, the relative offsets between pyrrhotite and pentlandite (average $\Delta^{56}\text{Fe}_{\text{pyrrhotite-pentlandite}} = -2.0 \pm 0.21\%$) and pyrrhotite and chalcopyrite (average $\Delta^{56}\text{Fe}_{\text{pyrrhotite-chalcopyrite}} = -1.5 \pm 0.29\%$), respectively, are remarkably similar in all four deposits. However, such large fractionations are unlikely to represent primary inter-mineral equilibrium isotope fractionation at magmatic temperatures. Therefore, the data indicate iron exchange and associated isotope fractionation between the sulphide minerals in direct contact to each other occurring at lower temperatures ($\sim 300^\circ\text{C}$). The similarity in $\Delta^{56}\text{Fe}$ values of all four deposits suggests that the observed inter-mineral iron isotope fractionation represents the closing temperature for iron diffusion in the sulphides. It has to be pointed out that despite the different alteration histories of the studied deposits the inter-mineral isotope systematics seem to have remained unaffected by subsequent metamorphism or alteration by deuteric and/or metamorphic fluids.

Our study indicates that $\delta^{56}\text{Fe}$ values of individual sulphides cannot be interpreted in terms of a source signature of the deposit or as a primary high temperature fractionation. However, in-situ analyses of multiple sulphide mineral assemblages bear the potential to obtain relative differences in iron isotope compositions ($\Delta^{56}\text{Fe}$) between different sulphide minerals, which could be used as a proxy for mobilisation (i.e., selective dissolution and/or precipitation) of sulphide minerals. In such a case a deviation from the closed system behaviour (i.e., $\delta^{56}\text{Fe}_{\text{pyrrhotite}} < \delta^{56}\text{Fe}_{\text{chalcopyrite}} < \delta^{56}\text{Fe}_{\text{pentlandite}}$) would be expected. To further develop Fe isotopes as a tool to decipher ore formation processes theoretical and experimental studies are needed to determine temperature dependent inter-mineral iron isotope fractionation factors for sulphides as well as detailed Fe isotope investigations of well characterised ore deposits.

Die Tagebauseen Mitteldeutschlands – Entstehung, Limnologie, Management

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Im mitteldeutschen Braunkohlerevier wird seit dem Ende des 17. Jahrhunderts Braunkohle gewonnen. Die ältesten Tagebauseen entstanden am Ende des 19. Jahrhunderts. Sie sind klein (≤ 10 m max. Tiefe, oft < 1 ha Wasserfläche), da die damaligen Tagebaue im Handbetrieb mit nur sehr einfachen Hilfsmitteln betrieben wurden. Mit der Entwicklung und Einführung immer größerer Tagebaugeräte wuchs auch die Größe der Tagebauseen. Derzeit entsteht im mitteldeutschen Revier mit dem Geiseltalsee der vorerst größte Tagebausee Deutschlands (ca. 80 m max. Tiefe, 18,5 km² Wasserfläche, $423 \cdot 10^6$ m³ Volumen nach vollständiger Füllung). Erst nach dem Auslaufen der sehr tiefen Tagebaue im Rheinischen Revier werden dort ab Mitte des Jahrhunderts noch größere Tagebauseen entstehen. Insgesamt gibt es derzeit ca. 140 Tagebauseen im mitteldeutschen Braunkohlerevier.

Der Wasserchemismus in den Tagebauseen ist vor allem durch die Pyritoxidation geprägt. Durch die Bergbautätigkeit kam der in der Braunkohle und in ihrem Begleitgestein lagernde Pyrit in Kontakt mit Sauerstoff und wurde oxidiert. In ca. 50% aller Tagebauseen führte das zu zumindest anfänglicher Versauerung (pH ca. 2,8, Eisenkonzentrationen ca. 150 mg/l), in allen Fällen zu erhöhten Sulfatgehalten (> 2000 mg/l in sauren Seen, bis ca. 1500 mg/l in neutralen Seen) und relativ hohen Eisengehalten der Seesedimente (bis $> 20\%$ TM). Dennoch sind nur ca. 30% der Tagebauseen, zu denen Wasserbeschaffungsdaten vorliegen, momentan sauer. Natürliche Neutralisationsmechanismen haben viele ältere, ursprünglich saure Tagebauseen inzwischen neutralisiert. Gezielte Füllung mit neutralem Flusswasser oder Sumpfungswasser aus noch aktiven Tagebauen war in den vergangenen 20 Jahren der Hauptweg, Tagebauseen in Mitteldeutschland zu neutralisieren oder ihre Versauerung von Beginn der Füllung an zu verhindern. Im Falle des Tagebausees Hain-Haubitz reichte diese Strategie nicht aus, weshalb dort zusätzlich eine Neutralisation mit Kalk stattfindet. Der Bockwitzer See wurde komplett mit Soda neutralisiert, weil dort Flusswasser oder Wasser aus aktiven Tagebauen nicht zur Verfügung stand. Die angewendeten Neutralisationsverfahren haben ebenfalls großen Einfluss auf den jetzigen Wasserchemismus ausgeübt.

Durch Subrosionsvorgänge in Salzlagern des Zechsteins und der Trias sind nicht nur Bildung und Form vieler mitteldeutscher Braunkohlelagerstätten geprägt worden sondern auch der Chemismus einiger der Tagebauseen. In diesen Fällen besteht bis heute Kontakt zu salinarem Grundwasser, was in drei Tagebauseen zu einer permanenten chemischen Schichtung (Meromixis) führte. Die Salzgehalte in den salinaren Tiefenwasserkörpern der Seen (Monimolimnia) gehen bis 70‰ und es herrschen dort anaerobe Bedingungen mit Eisenkonzentrationen von mehreren hundert mg/l. Die sehr hohen Gehalte an gelösten Stoffen im Grundwasser von Abraumkippen als Folge der Pyritoxidation und der Reaktion der freigesetzten Azidität mit den natürlich vorhandenen Mineralen haben aber auch in einigen anderen Tagebauseen zumindest zeitweilig chemische Schichtungen entstehen lassen. Auch in diesen Monimolimnia kam es zur Anreicherung von Eisen und anderen Stoffen unter anaeroben Bedingungen. Weitere Details zu den mitteldeutschen Tagebauseen finden sich bei Czegka et al. (2008a, b) und Schultze et al. (2009) sowie der dort zitierten Literatur.

Der Beitrag gibt einen Überblick über die hier nur kurz umrissene Entstehung der Tagebauseen im mitteldeutschen Revier, über ihren Chemismus und über die Management- und Sanierungsstrategien, die bisher zur Sicherung der angestrebten Seennutzung Anwendung fanden. Es soll die Vielfalt der Bedingungen aufgezeigt werden, unter denen Mineralbildungen und –auflösungen stattfinden können.

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EMP-monazite dating and thermobarometry of Variscan high-grade garnet gneiss (French Massif Central) – how can monazite provide time constraints on a *P-T* evolution?

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In the Haut-Allier region (French Massif Central), Variscan high-grade Upper Gneiss (UGU) and Lower Gneiss Units (LGU) overlie amphibolite-facies micaschists. These nappe units display different *P-T* paths with the highest maximal temperatures in the uppermost unit (Schulz et al. 1996). It was evaluated if *in-situ* monazite age dating provides time constraints and potentially may resolve a possible diachronous evolution in the units during the nappe-stacking process. Garnet crystallized with biotite, plagioclase, K-feldspar, quartz, kyanite and sillimanite in three gneiss samples from the location Agnat in the UGU. In each sample the garnets display different trends of growth zonations. In grossular-pyrope-spessartine coordinates these growth zonations partly superpose. When the garnet zonation trends in the samples labelled A1-A2-A3 are accordingly arranged, they can be combined to a general garnet evolution trend along decreasing Mn while Mg increases and Ca increases and then decreases. It was possible to evaluate a *P-T* evolution from each sample by geothermobarometry based on cation-exchange and net-transfer reactions. The *P-T* path segments from each sample also superpose and can be combined to a clockwise *P-T* evolution from 600 °C/8 kbar to 800 °C/12 kbar (A1), then to 720 °C/6 kbar (A2) and a final episode of heating/decompression to 750 °C/4 kbar (A3). A one-dimensional numerical modelling of single successive segments of this *P-T* path by variation of the geothermal gradient (20-35 °C/km) and velocity *U_z* (1-6 mm/a) was performed with METAMOD (<http://Christian.Nicollet.free.fr>) and revealed a time span of 36 Ma for the complete *P-T* evolution. Monazite with grain sizes between 20 - 100 µm is an accessory phase in the garnet gneiss. It was analysed by a JEOL JXA-8200 electron microprobe. The Th, U, Pb, Y, REE, P, Si, Ca were determined for calculation of the chemical model ages (Montel et al. 1996). After corrections of line interferences (Y on Pb; Th on U) a chemical age with a 2σ error based on the Pb counting statistics was calculated for each analysis. The single spot data was compiled in Pb vs Th* (Th*=Th+UeqTh) coordinates and define isochrons by regression. Monazite ages calculated from isochrons match the weighted mean ages and their 1σ error. Sample A1 yielded 335±17 Ma. Matrix monazites in sample A2 give 338±21 Ma. A syncrystalline rotated garnet with S-shaped inclusion trails in A2 is poorly zoned in Mg-Mn-Ca-Fe and represents a late stage of the *P-T* path at ~6 kbar. It encloses several monazite grains which give an age of 321±25 Ma. The yttrium contents in the enclosed monazite vary systematically and match the decreasing Y from core to rim in the garnet, analysed by LA-ICPMS. One can conclude that these monazites crystallized at the same time or subsequent to the garnet and thus define a minimum age for this part of the *P-T* evolution. In contrast, monazites enclosed in garnet which represents the final stage of the *P-T* path at low pressures in sample A3 give an isochron age of 356±16 Ma. Enclosed monazites with high Y are older than 340 Ma and may predate garnet growth, whereas enclosed and matrix monazite with low Y crystallized at 335±11 Ma. In consequence, enclosed monazite in garnet should not have necessarily crystallized previous to its host but may be of same age or even younger, as could be revealed by the behaviour of yttrium. At a regional scale, bulk monazite crystallization at 330 - 340 Ma appears to be related to a Late-Viséan thermal event which affected the three Haut-Allier nappe units when they were already juxtaposed in a pile. In consequence, metapelite garnet and monazite crystallization in the Haut-Allier series belong to a Late Devonian - Early Carboniferous prograde-retrograde metamorphism. Similar monazite ages and *P-T* paths were reported from the UGU in the La Sioule region to the north (Schulz 2009). This metamorphic evolution appears as an independent second metamorphic cycle subsequent to the Silurian - Early Devonian HP and HT events within the complex frame of the Variscan orogeny in the French Massif Central.

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Geochemical investigation of the three volcanoes Casablanca, Osorno, and Cabeza de Vaca, Southern Volcanic Zone, Chile

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As part of the Collaborative Research Center (SFB) 574 “Volatiles and Fluids in Subduction Zones: Climate feedback and trigger mechanisms for natural disasters”, this study is focused on magma genesis of three Chilean volcanoes. The investigation aims at a better understanding of the compositional evolution of young magmatic systems, regarding in particular the effects of subduction fluids in response to the tectonic parameters.

Casablanca, Osorno and Cabeza de Vaca Volcanoes are located between 40°45' and 41°15'S and around 72°15'W, within the Southern Volcanic Zone (SVZ) of the Chilean Andes, where arc volcanism is induced by fast convergence (70-90 mm*a⁻¹) between the subducting Nazca Plate and the overriding South American Plate. The oblique subduction of the Nazca Plate in a northeastern direction with a dip angle of 25 – 30° affects the formation of the Liquiñe-Ofqui Fault Zone (LOFZ), a major arc parallel active dextral shear zone of more than 1000 km in length. The incoming plate carries a number of fracture zones, possibly facilitating an enhanced transport of fluid-rich materials into the subduction system. Of those fracture zones, the Chiloé Fracture Zone descends towards the focal area of this study, where the subducting slab reaches a depth of 90 km beneath the active arc. Casablanca and Osorno are large, composite stratovolcanoes and lie closer to the trench than the smaller Cabeza de Vaca, which is located directly above the LOFZ.

Fresh and unaltered mafic samples were obtained during a field campaign of the SFB 574 in May, 2007 and include twenty-two tephra and nine lava samples from these volcanoes. The samples were analysed as bulk rocks for their major element geochemistry by XRF and for trace elements including rare earth elements by ICP-MS. EMP analyses have been carried out to determine the compositions of melt inclusions and their host minerals. All data are supported by petrographical studies of thin sections.

The samples comprise a series of basalts over basaltic andesites to andesites, and follow overall tholeiitic differentiation trends. The SiO₂ contents for all samples range between 50.4% and 59.9%. MgO contents lie between 7.4% and 2.1%. Variation diagrams for major and trace elements are congruent with the mineral assemblages as observed in thin section. They clearly display magma evolution trends such that MgO, Ni, Co decrease with increasing SiO₂, pointing to fractional crystallisation of olivine. A shift to dominance of plagioclase and clinopyroxene in the crystallisation sequence can be revealed from decreasing Al₂O₃ and CaO concentrations. Trace element data show a depletion of fluid-immobile elements, such as Nb and Ta, and an enrichment of fluid-mobile to highly fluid-mobile elements such as Ba, U, and Rb, typical for subduction zones. The fluid contribution to the magma, signalled e.g. by the Ba/La ratio, decreases from Osorno and Casablanca to Cabeza de Vaca. Accordingly, a higher La/Yb ratio implies a lower degree of melting at Cabeza de Vaca, likely resulting from this relatively reduced fluid influence. In contrast, melt inclusions show fractionation-independent increased Cl contents at the greater distance from the trench, which may assign importance as a pathway for transporting Cl-enriched fluids to the LOFZ.

Fachwiki „Schäden durch Salze“

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Schäden durch Salze sind eine der häufigsten Schadensursachen an historischen Gebäuden, Steinskulpturen und z. B. Wandmalereien, sind aber auch an vielen neueren Bauwerken anzutreffen. Trotz umfangreicher Forschungsarbeiten in den letzten Jahren bestehen immer noch deutliche Lücken im Kenntnisstand, so dass nicht nur Laien, sondern auch Fachleute wie Restauratoren/innen, Denkmalpfleger/innen, Bauingenieur/innen, Naturwissenschaftler/innen oder Architekt/innen in vielen Fällen ratlos vor dem durch Salz geschädigten Objekt stehen. Die Problematik am Objekt ist oft komplex. Es ist fundiertes Fachwissen notwendig, um die richtigen Maßnahmen ergreifen zu können.

Um die notwendige Forschungstätigkeit effektiver zu machen und um neue Erkenntnisse schneller in die Praxis zu überführen, ist eine verbesserte Infrastruktur der Informationsspeicherung und -verbreitung erforderlich. Deshalb wird in den kommenden zwei Jahren mit der Förderung der DFG vom Hornemann Institut der HAWK ein Fachwiki mit einem Primärdaten-Repository realisiert. Das Repository wird auch viele bislang nicht publizierte und unausgewertete Daten vereinigen, nachhaltig sichern und dadurch die Forschung fördern.

Inhaltlich gefüllt und redigiert wird das Fachwiki und das Repository von einem Forschungsverbund aus Experten aus dem In- und Ausland.

Für den Forschungsbereich „Erhaltung von Kulturgütern“ wird mit dem Fachwiki für alle Beteiligten die notwendige Basis für eine intensive Zusammenarbeit bei der Forschung geschaffen.

Mit „SalzWiki“ unterstützt die HAWK die „Open Access“ Initiative.

Literatur

J. Brase: Publication and Citation of Scientific Primary Data, 2009 CNI spring task force meeting, April 7 Minneapolis, USA

Weitere Informationen zum Fachwiki: www.SalzWiki.de

Weitere Informationen zu „Open Access“: www.open-access.net

Hydrothermale Herstellung von calciumarmen Zementen am Beispiel von Belitzement

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Die Zementhersteller sehen sich seit längerer Zeit im Fokus der Klimadiskussion - sind sie doch für ca. 5% der globalen CO₂-Emissionen verantwortlich. Zur Zeit werden verschiedene Möglichkeiten, die CO₂ Bilanz zu verbessern, diskutiert.

- Optimierung der Verfahrenstechnik,
- verstärkter Einsatz von Sekundärbrennstoffen (biogen/ fossil),
- Ersatz von CEM I durch die Zementarten CEM III bis CEM V, welche sich durch einen deutlich reduzierten Anteil an Portlandzementklinker auszeichnen,
- Verwendung von calciumarmen Bindemitteln wie z.B. Belitzement oder Calciumsulfoaluminat-basierte Zemente, die sich durch ein, im Vergleich zum Portlandzement, reduziertes C/S-Verhältnis auszeichnen [2].

Üblicherweise wird Belit-Zement durch Umwandlung von Calciumcarbonat CaCO₃ in CaO und anschließendes, gemeinsames Sintern von Calciumoxid und SiO₂ bei über 1300°C hergestellt.

Aus [1], ist bekannt, dass α -Dicalcium-Silikat-Hydrat (α -C₂SH) bei 200 °C durch eine zweistündige hydrothermale Behandlung von gebranntem Kalk CaO und Kieselsäure für Laborsynthesen (Reinheitsgrad p.a.) entsteht. Dieses α -C₂SH wandelt sich dann im Temperaturbereich von 390-490°C in die γ -C₂S-Modifikation um, welche bei weiterem Aufheizen auf 920-960 °C in die β -C₂S-Modifikation übergeht und beim Abkühlen β -C₂S bildet. β -C₂S ist der Hauptbestandteil des Belitzements. Von Nachteil ist hierbei, dass sehr teure Ausgangsprodukte Verwendung finden.

Ziel dieser Arbeit ist es zu zeigen, dass es durch eine alkalischen Alkaliaktivierung welche der Auflösung der Siliziumquelle wie Quarz, Kieselsäure, Gläser, Schlacken, Altbeton usw. dient und durch die Zugabe von α -C₂SH-Kristallisationskeimen gelingt, einen Precursor hydrothermal bei 200°C zu synthetisieren, aus dem sich beim Aufheizen Belit bildet. Zu diesem Zweck, wurde am Forschungszentrum Karlsruhe eine Laboranlage in Betrieb genommen, die die Möglichkeit bietet, das Herstellen von Belitzement zu optimieren. Es handelt sich hierbei im Wesentlichen um einen Hydrothermalreaktor, der ein getrenntes Aufheizen von Material und Prozessflüssigkeit ermöglicht. Die Phasenanalyse des Syntheseproduktes mittels Röntgendiffraktometrie, ergab die fast vollständige Umsetzung der Ausgangssubstanzen in α -C₂SH. Die thermische Behandlung dieses Precursors bei Temperaturen zwischen 400 und 1000°C gab Aufschluss über die Stabilität der entstandenen Produkte. Diese Reaktivität dieser wurde mittels Wärmeleitungskalorimetrie ermittelt.

Die Umwandlung von α -C₂SH zu β -C₂S wurde auch mittels in situ XRD verfolgt. Dabei zeigte sich dass es sich hierbei um einen mehrstufigen Prozess handelt. Beim Aufheizen von α -C₂SH auf Temperaturen zwischen 400 und 500°C findet eine partielle Polymerisation der Silikateinheiten statt [3]. Diese wurde mittel IR- Spektroskopie und Trimethylsilylation nachgewiesen. Wasserfreie Produkte entstehen ab 600°C. Bis ca. 700°C bildet sich beim Abkühlen sowohl β -C₂S als auch γ -C₂S. Bei höheren Temperaturen kristallisiert beim Abkühlen ausschließlich β -C₂S.

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Stress Conditions in Salinar Cap Rocks of the North German Basin as an Important Aspect of CCS Risk Assessment.

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Provisions of state of stress in salinar cap rocks of the North German Basin need to be assessed as possible changes in the tectonics could redistribute stress magnitudes and orientations in the caprocks. While the horizontal stress is more uniformly oriented in the subsalinar formations, its distribution above Zechstein is heterogeneous due to possible 'decoupling effect' caused by the Late Permian salt horizon. Furthermore, salt domes and faults are found to play remarkable roles to the overall trend of stress in the suprasalt.

While available data can provide handful of information about stress magnitudes and its orientation (Figure 1), but advanced developments to measure small-and large scale in-situ stress is in priority for the safety of geological formations to be considered as storage medium for anthropogenic refuge. In addition, extensive study of salt structures is essential to understand the dynamic geotectonic processes in the North German Basin that can provide substantial information for the caprocks as safe sealing for any refuge to be stored in the salinar and subsalinar horizon.

Measurements of in-situ stress can be done by establishing appropriate 'measuring device' in geological formations. Currently laboratory experiments are being carried out to simulate in-situ stress conditions in the suprasalt. In addition, data obtained from borehole study and in-situ stress will be incorporated to develop a geomechanical model for future risk assessment concerning the stability of subsalinar formations as repository.

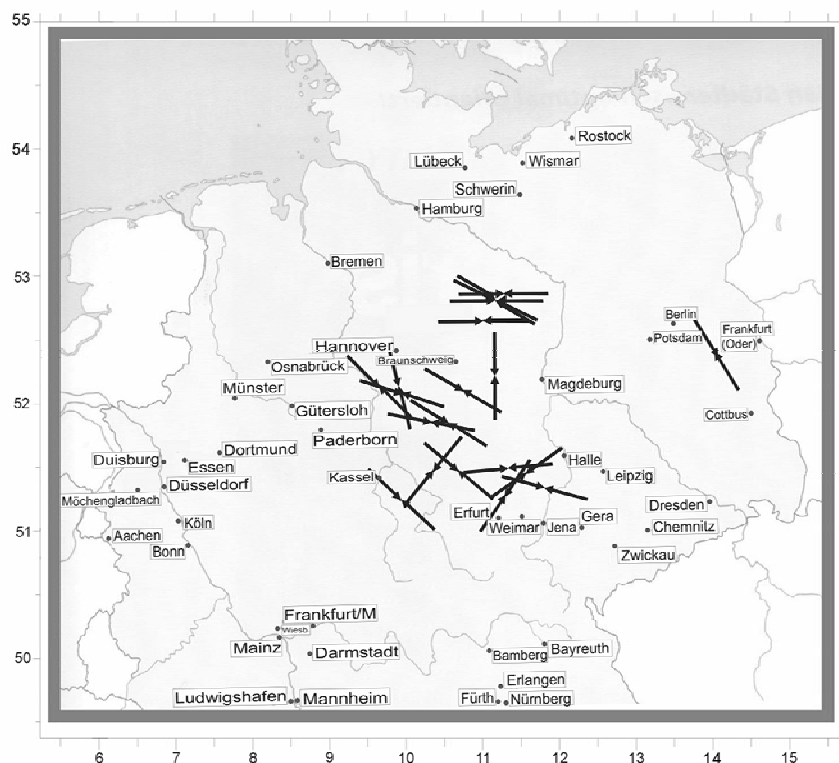


Figure 1: Orientation of the Maximum Horizontal Stress component in the Suprasalinar (Röckel and Lempp, 2003).

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The solubility of H₂O and CO₂ in basaltic melt at pressures up to 500 MPa

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Volatiles influence the properties of magmas such as density and viscosity, melting and crystallization reactions as well as dynamics of magma ascent and eruption. Water and carbon dioxide are the most abundant volatiles in the magmatic systems, hence they play a major role in volcanic processes and H₂O-CO₂ system can be used as a first approach to understand water-undersaturated magmatic systems. Therefore data on concentrations of H₂O and CO₂ in natural melts (glass inclusions in minerals, glassy rinds in pillow lavas) can provide useful information on depths and dynamics of magma crystallization, ascent and degassing in magma chambers and conduits beneath volcanoes. This information can only be gained if experimental data on H₂O and CO₂ solubility in the melts are available.

Although basalts are the most abundant magmatic rocks emplaced at crustal levels, experimental datasets on the solubility of C-O-H-bearing fluids in basaltic melts are limited (Dixon, 1995) and there are no data at pressures above 200 MPa. We present new experimental data on H₂O and CO₂ solubility in basaltic melt. The starting composition for the experiments was a glass produced by air-melting of natural low-K high Al tholeiitic island-arc basalt (sample N72) from Mutnovsky volcano (provided by M.Portnyagin). Experiments were conducted in internally-heated pressure vessel (IHPV) at 1250 °C at 50, 100, 200, 300, 400, 500 MPa. Five Au₈₀Pd₂₀-capsules, containing 50 mg of basaltic glass and H₂O and CO₂ in different proportions (the mole fraction of H₂O in the fluid phase, X_{H₂O} from 0 to 1) were run simultaneously at isobaric and isothermal conditions. The duration of each run was about 24 hours. Afterwards samples were quenched isobarically using a rapid-quench method.

The run products are bubble- and crystal-free glasses coexisting with a H₂O-CO₂-fluid phase. They were analyzed using different methods: gravimetry, KFT, FTIR, CS, Microprobe (EPMA), wet chemical colorimetric method. IR microspectroscopy demonstrates the homogeneous distribution of H₂O and CO₂ in the samples, indicating that the run duration was long enough to reach equilibrium between fluid and melt at given T and P. Concentrations of H₂O and CO₂ in the glasses considerably increase with increasing pressure and H₂O/CO₂ and CO₂/H₂O proportions, respectively, in the coexisting fluid. The solubility of H₂O in equilibrium with pure H₂O fluid increases from about 2.2 wt.% at 50 MPa to about 8.8 wt.% at 500 MPa. The concentration of CO₂ increases from about 200 to 3680 ppm in glasses which were in equilibrium with the most CO₂-rich fluids (X_{CO₂} from 0.7 to 0.8). In general, the solubilities of both H₂O and CO₂ in the basaltic melt show a non-linear dependence on the mole fraction of H₂O and CO₂ in the equilibrium fluid. Strong deviation from linearity is observed especially at higher pressures (300 - 500 MPa). The new experimental data are in good agreement with previous experimental data on H₂O-CO₂ solubility for basaltic melts at low pressures (50 – 98 MPa, Dixon, 1995). However, the comparison with existing numerical models predicting the H₂O-CO₂ solubility in basalt (Newman&Lowenstern, 2002; Papale, 2006) shows significant differences, especially at high pressure (more than 300 MPa) and for melts coexisting with CO₂-rich fluids. At 500 MPa, the model of Newman&Lowenstern (2002) underestimates the CO₂ solubility in basalts coexisting with CO₂-rich fluids by ~ 1000 ppm (underestimation of 25% relative). At the same pressure, the model of Papale (2006) overestimated the CO₂ concentrations by a factor of 2 or more.

Our dataset can be used to predict the partitioning of H₂O and CO₂ between fluids and melts. Knowing the partitioning values, the H₂O and CO₂ concentrations of natural melt inclusions from tholeiitic island-arc volcanoes can be used to estimate the depth(s) at which magmas start to degas and can provide quantitative estimations of storage conditions and dynamic processes in these volcanoes. Depending on the geodynamic settings, systematic variations for the depth at which magmas are saturated with respect to fluids can be observed.

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Die neue Internetseite des Arbeitskreises Mineralogische Museen und Sammlungen der Deutschen Mineralogischen Gesellschaft

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Der Arbeitskreis „Mineralogische Museen und Sammlungen“ ist eine Interessensvertretung öffentlich-rechtlicher mineralogischer Museen innerhalb der Deutschen Mineralogischen Gesellschaft e.V. (DMG). Regelmäßige AK-Treffen, ein E-Mail-Verbund, das gemeinsame Poster „Mineralogische Museen und Sammlungen in Deutschland“, der Typmineral-Katalog und ein vereinter Internetauftritt sind gemeinschaftliche Projekte, die in jüngerer Zeit umgesetzt wurden.

Der Internetauftritt richtet sich sowohl an die fachliche Wissenschaftsgemeinschaft wie auch an die allgemeine Öffentlichkeit. Auf der Startseite der Internetseite werden dem Besucher Ziele und Aktivitäten des Arbeitskreises vorgestellt. Unter der Rubrik „Aktuelles“ können laufende Sonderausstellungen, Termine zu Treffen und Tagungen sowie Berichte eingesehen werden. Das Menü „E-Mail-Verbund“ erlaubt dem Besucher eine vereinfachte Recherche nach und den Zugang zu mineralogischem Sammlungsmaterial durch Versenden einer E-Mail, die gleichzeitig alle Sammlungen des Verbundes erreicht. Durch Auswahl der Rubrik „Museen & Sammlungen“ können sich Interessierte über eine interaktive Karte Kontaktdaten, Ansprechpartner, Öffnungszeiten und Schwerpunkte des entsprechenden Museums bzw. der Sammlung über ein Pop-Up-Fenster abrufen. Der Analysenticker veröffentlicht kurze Abstracts aktueller Untersuchungsergebnisse aus den beteiligten Museen und Sammlungen. Der Typmineralkatalog liefert Informationen über die in deutschen Sammlungen hinterlegten Referenzproben (Holotypen, u.a.). Eine Informationsseite über die DMG sowie eine Linksammlung geowissenschaftlicher Museen bzw. Sammlungen im In- und Ausland ergänzen das Angebot der Internetseite.

Die Adresse der neuen Internetseite des Arbeitskreises „Mineralogische Museen und Sammlungen“ lautet: www.mineralogische-sammlungen-dmg.de/.

Metamorphic conditions and age of Proterozoic shearing at the eastern margin of the East European Craton

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Metagranitoid rocks in a shear zone of the Taratash complex (Middle Urals) show the syntectonic assemblage K-feldspar, plagioclase (An₃₇), biotite, muscovite, quartz, garnet (rim) and monazite. Garnet (Alm₇₂₋₈₁ – Sps₆₋₂₂ – Prp₄₋₁₃ – Grs₁₋₅) records decreasing almandine as well as increasing spessartine component from core to rim and predates shearing. Compositional zoning within garnet does not correlate with the present anhedral grain shape, pointing to fragmentation during shearing. Shear zone formation in the Taratash Complex thus clearly is an event of the retrograde path. In addition, a posttectonic retrograde mineral assemblage is characterized by plagioclase (An₅), chlorite, epidote, muscovite, quartz, apatite and allanite. The latter two minerals are formed in reaction rims around monazite. Xenotime has only rarely been found as a reaction product of monazite. Preliminary pressure-temperature estimation using garnet rims, biotite and associated dynamically recrystallized plagioclase (garnet-biotite-geothermometry and garnet-biotite-plagioclase-quartz-geobarometry) points to temperatures of 600 – 670 °C and c. 3.5 kbar.

Metasedimentary rocks exposed in the shear zone are composed of the syntectonic assemblage K-feldspar, plagioclase, biotite, muscovite, quartz, apatite and monazite. Relics of garnet (Alm₆₉₋₇₀ – Sps₂ – Prp₂₀₋₂₁ – Grs₄₋₅) are present which reacted post-tectonically and are replaced by biotite and muscovite. Within metagranitoid rocks monazite mainly occurs in anhedral crystals, partly resorbed during posttectonic greenschist facies retrogression. Three kinds of monazite domains can be distinguished: (A) euhedral, oscillatory zoned, monazite – huttonite solid solution; (B) anhedral, patchy zoned, monazite – huttonite – brabantite solid solution; (C) euhedral, Y-rich rims. The latter, so far undated type, has only been found close to garnet and may be formed in equilibrium with garnet. Type B is characterized by increased Ca-concentration and in line with the patchy appearance in BSE images shows variable element concentrations, e.g. Y varies between maximum values also encountered in type c rims and lower values. It is concluded that these patchy type b domains are formed by recrystallization of older domains in a stage characterized by the presence of additional Ca but not of additional Y. Growth of type b domains may therefore be linked to dynamic recrystallization of plagioclase during shearing. LA-ICP-SFMS U-Pb analyses yield ages between 2058 ± 22 and 2073 ± 47 Ma (±2σ). The age of type B domains can thus be related to the shear zone formation. Type A domains are interpreted to represent a magmatic formation in the s-type granitoid precursor rock. Their U-Pb age was determined at 2238 ± 36 Ma. During greenschist facies retrogression the Th-U-Pb system of some monazite domains was disturbed leading to discordance. It is so far unknown if this is caused by lead loss from the lattice or by formation of domains which are too small for the spatial resolution (16 µm) of the laser.

Monazite in metasedimentary rocks is chemically different from monazite in metagranitoid rocks due to lower concentrations of the huttonite- and brabantite components. It shows a patchy zonation and consists of domains with an age of either c. 2250 Ma or 2052 ± 16 Ma. The older age is interpreted to indicate a peak metamorphic event which caused melting in the metagranitoid unit whereas the monazite domains with the lower ages recrystallized during shear zone formation. These age data are in line with previous data obtained from other metamorphic and magmatic units of the Taratash Complex (Ronkin et al. 2007, Sindern et al. 2005)

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Lu-Hf and Sm-Nd dating of zoned garnet in eclogites from the southernmost Scandinavian Caledonides

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The Scandinavian Caledonides, an over 2500-km-long collision belt in northern Europe, experienced its main orogenic stage in Scandian time (430-395 Ma). Several of the eclogite-bearing terranes in the thrust stack of this orogen record peak metamorphism during different stages before the Scandian (e.g., Brueckner & van Roermund, 2004). Petrological and geochronological data from these terranes have provided crucial information on the geodynamic history of the Caledonian orogenic cycle. However, the overall picture is still patchy. To further refine geodynamic models, we have dated the eclogites of the Jæren nappe (Garborg locality), SW Norway, by Lu-Hf and Sm-Nd geochronology. This eclogite occurrence has not been dated so far and may, considering its geographical position, yield important information on the evolution of the southern limb of the Caledonides and uncover possible links to Caledonian tectono-metamorphic processes to the south and west of the Scandinavian Peninsula.

Five out of the six dated samples were eclogitized during the Middle Ordovician, providing a weighted mean Lu-Hf age of 469.9 ± 1.2 ($\pm 2\sigma$). The additional sample gave a significantly younger age of 457.9 ± 2.4 Ma. Major element mapping and trace element analysis showed that garnet from the younger sample comprised one concentrically-zoned growth zone (grt-1), whereas garnet in all other samples comprise a core, compositionally similar to grt-1, and a neo- or re-crystallized rim having a relatively homogeneous REE- and Ca-depleted composition. Bulk-garnet Lu-Hf ages may be systematically weighted according to Lu-distribution and may therefore not be representative for individual zones (Lapen et al., 2003). Age calculations that take Lu-contributions by individual zones into account provide an age of 471.0 ± 0.9 Ma for the cores and indicate a ca. 455 Ma age for the rims, the latter being identical to the age of monogenetic garnet of the younger sample.

Different grain size fractions of garnet from individual samples, both whole-grain and fragments, were used to construct isochrons. All Lu-Hf isochrons are characterized by reasonable MSWD values (0.21-1.7). The age heterogeneity between these is accounted for by age-mixing and is not related to the highly variable average grain size of the separates that were analyzed (0.1-3.0 mm). These aspects indicate that—in spite of a thermal overprint at $T > 750$ °C—the Lu-Hf systematics of garnet were not reset. In contrast to Sm-Nd ages, which are imprecise and reflect isotopic disturbance, the Lu-Hf ages date the growth of garnet crystals or zones. As such, they show that the studied rocks underwent Middle Ordovician HP metamorphism, which lasted for at least 16 Myr and involved two stages of garnet growth. The Lu-Hf ages define a new HP age population for the Scandinavian Caledonides, which allows more detailed insight into the subduction history that affected the margin of Baltoscandia before the Scandian continental collision. Besides this geological aspect, our study highlights the potential complexities involved in garnet geochronology and shows the strength of Lu-Hf dating for uncovering the geochronologic record of (U)HP rocks.

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Einfluss der aktuellen Prozessbedingungen beim Zementbrand auf das Feuerfestmaterial

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Die Zementherstellung ist ein energieintensiver Prozess mit entsprechenden großen technischen Herausforderungen. Um eine dauerhafte Wettbewerbsfähigkeit und Nachhaltigkeit der Zementanlage aufrecht erhalten zu können, ist es notwendig vor allem die Energiekosten, die bis zu 40 % der Klinkerherstellungskosten betragen, soweit wie möglich zu reduzieren. Die Modernisierung oder der Bau einer Neuanlage sind wesentliche Kriterien, um eine hohe Effizienz hinsichtlich Kapazität und Wirkungsgrad sowie Minimierung von Energie und Emission erfüllen können. Die Nutzung alternativer Brennstoffe (Alternative Fuels = AF) und alternativer Roh- und Zuschlagstoffe (Alternative Raw Material = AR) können weitere Einsparungspotenziale des spezifischen Energiebedarfs ermöglichen. Auf Grund steigender Preise für Primärenergien wird daher die Nutzung von AF-Brennstoffen zur Produktion von Zement weltweit weiter ansteigen, um den Anforderungen der Zementindustrie im Bezug auf Nachhaltigkeit zu entsprechen und auch der Umwelt gegenüber gerecht zu werden.

Mit dem Einbringen von Ersatzbrennstoffen und -rohstoffen haben sich die Prozessbedingungen in der Zementanlage deutlich verändert, aus denen thermische und thermochemische Prozesse mit signifikantem Einfluss auf den Verschleiß der Feuerfestauskleidungen resultieren. Nicht optimale Brennbedingungen, z. B. falsche Dosierung oder häufig wechselnde Ersatzbrennstoffe und -rohstoffe, können schnell zu lokalen Überhitzungen der feuerfesten Auskleidung führen. Weitere chemische bzw. thermochemische Verschleißeinflüsse auf die Feuerfestzustellung sind auf den Eintrag volatiler Komponenten (Alkali-, Schwefel-, Chloridverbindungen) sowie Spurenelemente ins System zurückzuführen. Ein deutlicher Anstieg dieser Komponenten und insbesondere von Schwermetallen im System ist durch die ansteigende Nutzung von AFR-Materialien und den damit verbundenen Prozessschwierigkeiten mittlerweile wohl bekannt. Aber, diese Komponenten verweilen nicht nur im Drehrohr, sondern werden auch in den davor und dahinter geschalteten Aggregaten mit hohen Konzentrationen nachgewiesen und können dadurch vermehrt Betriebsprobleme hervorrufen. Die ins System eingetragenen flüchtigen Bestandteile und Schwermetalle haben die Affinität, verschiedene Salzverbindungen zu bilden. Waren früher vorwiegend einzelne Salze wie Sylvin, Arkanit und Anhydrit im Gefüge der Auskleidung nachweisbar, so wird gegenwärtig vermehrt die Kondensation von Mischsalzen im Gefüge festgestellt (Kalziumlangbeinit, Syngenit, Aphthitalit, Langbeinit, etc.). Sofern Wegsamkeiten und entsprechende Temperaturen vorliegen, gelangen die Salze auch bis zum Stahlmantel der Anlage, um dort verschiedenste Korrosionsmechanismen wie Heißgas- und Nasskorrosion sowie Rosteffekte bei Ofenstillständen am Ofenstahl und der Stahlverankerung feuerfester Massezustellungen hervorzurufen. Eine weitere Beeinträchtigung des Feuerfestfutters ist durch ein Überangebot an SO_2/SO_3 im System in den letzten Jahren festzustellen. Der Einsatz schwefelhaltiger Brennstoffe (Petrolkoks, etc.), begünstigt dies. Freies SO_2/SO_3 , das nicht über Alkalien abgebunden werden kann, steht daher im hohen Maße für thermochemische Reaktionen mit der feuerfesten Auskleidung zur Verfügung. Durch den wechselnden Einsatz verschiedener AF-Brennstoffe sowie die gesetzlichen Auflagen, die NO_x -Emission zu senken, können auch lokale Redox-Brennbedingungen auftreten. Derartige Bedingungen führen in Gegenwart von Salzen nicht allein zur Auskristallisation von Alkalisulfaten im Gefüge, sondern auch von Alkalisulfit und -sulfiden. Bei Ofenstopps und speziell beim Ausbruch der feuerfesten Auskleidung wird schließlich H_2S -Gas freigesetzt. Stark reduzierende Brennbedingungen begünstigen darüber hinaus ein Auftreten der Boudouard-Reaktion, die zu Kohlenstoffabscheidungen in der Feuerfestauskleidung und am Ofenmantel führen.

Obwohl sich in den letzten Jahren ein Markt speziell für Ersatzbrennstoffe mit einer gleichbleibenden Qualität bezüglich Fraktion und Brennwert an die Bedürfnisse der Zementindustrie entwickelt hat, wird die Prozessführung einer Zementanlage auch zukünftig auf Grund wechselnder Verfügbarkeit dieser Brennstoffe und den damit verbundenen alternierenden Brennstoffeinsätzen wenig definiert bleiben.

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Quicklime Reactivity as a Function of Limestone Microstructure and Firing Conditions

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The quicklime reactivity is the most important feature of quicklime used in the different industries, especially the iron and steel. The main objective of this work is to optimize the quicklime reactivity as a function of both the limestone microstructure. and the firing conditions.

Ten technological samples representing Egyptian limestones of different ages and microstructure (petro-fabrics) were fired at 900 and 950 °C firing conditions. Both the proportions and reactivity (T_{60}) of the liberated free lime were measured after each firing process. They were related to the detailed microstructural parameters of the limestones (compositional and textural attributes). The data sets were treated in a statistical regime in order to optimize the conditions at which the different limestone types produce optimum reactive lime.

It was found that the smaller the size of the limestone allochems, the higher is the reactivity of the liberated quicklime under the conditions of shorter soaking times. The type and amount of the non-carbonate contents play a significant role in the optimization process.

Einfluss von Weinsäure auf Phasenentwicklung und Rheologie während der Portlandzementhydratation

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Fruchtsäuren finden in vielen bauchemischen Formulierungen Einsatz als verzögerndes und gleichzeitig verflüssigendes Additiv. Die Beschreibung der verzögernden Wirkung auf die Hydratation erfolgt bisher größtenteils auf rein qualitativer Ebene [1, 2, 3]. Vor allem in bauchemischen Spezialprodukten findet ein kombinierter Einsatz verschiedener auf die Hydratation verzögernd wirkender Fruchtsäuren mit beschleunigend wirkenden Additiven statt, um die rheologischen Eigenschaften des Zementleims punktgenau zu steuern. Sowohl zur sinnvollen Optimierung, als auch um eine ggf. negative Beeinflussung der Additive untereinander ausschließen zu können, ist ein genaues Verständnis der Auswirkungen jedes einzelnen Additivs auf die Kinetik der Hydratation notwendig.

Es wurde der Einfluss von Weinsäurezugabe (0,23 Ma.-%) auf die quantitative Phasenentwicklung, die Wärmeflussentwicklung und das rheologische Verhalten der abbindenden Zementpaste ($W/F = 0,28$) während der frühen Hydratation eines CEM I 42,5R untersucht. Die zugegebene Weinsäure wurde im Anmachwasser gelöst. Als Vergleichssystem dienten Zementpasten, die mit deionisiertem H_2O angemacht wurden. Die Präparation der Pasten erfolgte mit Hilfe eines standardisierten Anrührwerkzeugs. In-situ-XRD Untersuchungen der ersten 22 h der Hydratation wurden an einem Siemens D5000 mit SolX-Festkörperdetektor (Bruker AXS) bei 23 °C durchgeführt. Hierzu wurden die frisch präparierten Pasten in einen temperierbaren Probenhalter gebracht und mit Kapton-Folie als Schutz gegen Austrocknung abgedeckt. Die Auswertung erfolgte mit dem Programm TOPAS 3.0, unter Verwendung des Fundamentalparameteransatzes. Zur Auswertung wurden die Skalierungsfaktoren von Phasen ohne bzw. geringer Reaktivität während des untersuchten Zeitraums (z.B. Quarz, Calcit, C_2S) nicht zur Verfeinerung freigegeben. Die ermittelten relativen Phasengehalte der kristallinen Phasen wurden anschließend um den Gehalt an gebildetem, röntgenamorphen C-S-H korrigiert und auf den Gehalt in der Zementpaste umgerechnet. Die Wärmeflusskalorimetrie wurde an einem TAM Air Wärmeflusskalorimeter (TA Instruments) bei 23°C durchgeführt. Die rheologischen Untersuchungen zur Bestimmung des Abbindeverhaltens erfolgten mit einem imeter (automatisierter Gillmore-Nadelapparat; MSB Breitwieser Messsysteme, Augsburg) bei Raumtemperatur (25°C).

Die wärmeflusskalorimetrischen Untersuchungen zeigen, dass Weinsäurezugabe die Kinetik der Hydratation des CEM I 42,5R maßgeblich beeinflusst. Durch Zugabe von 0,23 Ma.-% Weinsäure wird das Auflösen der Phasen Anhydrit und C_3A sowie die Bildung von Ettringit während der ersten 45 Minuten der Hydratation stark verzögert und nach 45 Minuten stark beschleunigt. Zudem zeigt sich eine deutliche Verzögerung der Silikatreaktion. Die Unterdrückung der Ettringitbildung bis 45 Minuten mit anschließender Beschleunigung ist verantwortlich für den signifikant veränderten Härteaufbau der Zementpasten mit Weinsäure im Vergleich zu den Pasten ohne Weinsäure.

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Fluid mixing and Sr-source recorded by radiogenic Sr isotopes of barite from the Wittichen mining area, Schwarzwald, SW Germany

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Barite is a perfect monitor of fluid and element sources of hydrothermal deposits as it is widespread and usually contains high concentrations of Sr, of which the isotopic ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ can be determined. The Sr content can reach up to 10 wt.% but that of Rb is usually less than 1 ppm. Therefore, there is no significant additional radiogenic Sr incorporation after barite formation.

In this study, 3 different associations and different stages of Barite were investigated from the Wittichen mining area, SW Germany. There, granite-hosted veins with (1) an Ag-Co-As-Bi-U assemblage, (2) a Cu mineralization with fluorite and quartz, and (3) a Cu-Bi assemblage occur. The Sr content in barite varies independent of the stage and assemblage between 1 and 3 wt. % but can reach up to 4 wt.% (Fig. 1). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are also independent of the vein type and stage, and vary between 0.710 and 0.718, with a peak around 0.717. Some of the analyzed barite shows a correlation between the Sr content and the isotopic ratio: high Sr contents in barite go along with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and vice versa. Barite with ratios around 0.717 differs from this trend and can have both low and high Sr contents.

There are two possible sources of Sr in the Wittichen mining area: the Variscan crystalline basement and the Triassic sedimentary cover. The surrounding Triberg Granite Complex has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.727 and 0.985 with $^{87}\text{Rb}/^{86}\text{Sr}$ ratios between 3.5 and 62 (Schleicher 1993). The recalculated Sr isotopic composition of the granite during the vein formation age (Jurassic and Miocene) is higher than 0.72 and 0.725, respectively. The Sr isotope ratios of the sedimentary cover are significant lower and range from 0.7102 to 0.7166 in the Lower Triassic Buntsandstein and between 0.7078 and 0.7105 in the Middle Triassic Muschelkalk (Matter et al. 1987). This work also shows that recent fluids in equilibrium with the sedimentary cover have 1.4 to 9 times higher Sr contents than a fluid in equilibrium with the crystalline basement.

The relation of the Sr content in barite with its isotopic composition means that the Sr source cannot be the Granite alone. We interpret the high Sr barite with the low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a barite that has been formed from a fluid dominated by Sr from a sedimentary cover aquifer, whereas barite with a low Sr content and a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio has been formed from a mixed fluid of a deep-seated brine with the sedimentary cover fluid. The barite with ratios around 0.717 was probably formed from the mixed fluid, but the variation in the Sr content can be explained by temperature variations in the ascending fluid, as the Sr incorporation in barite is temperature-dependent. A temperature fluctuation of the ore-forming fluid of up to 100 °C has also been recorded in fluorite- and quartz-hosted fluid inclusions of the whole Schwarzwald ore district (Baatartsogt et al. 2007) and therefore supports the above interpretation. In contrast, barite that has been formed from the sedimentary fluid shows no variation in its Sr content. Also this observation is in agreement with the above interpretation, as the aquifer temperature is only dependent of the depth of burial and does not change much.

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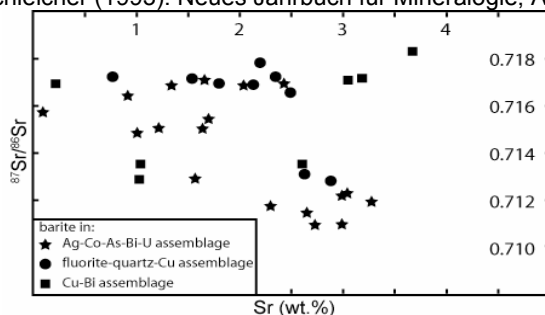


Fig. 1: $^{87}\text{Sr}/^{86}\text{Sr}$ ratio versus the Sr content of barite from the Wittichen mining area.

Untersuchung von Kohlenstoffabscheidungen bei Hochtemperaturreaktionen

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Bei einer Vielzahl von Katalysen scheidet sich unter hohen Temperaturen und entsprechendem Stoffangebot Kohlenstoff ab, der die betroffenen Technologien meist negativ beeinflusst. Intensive Forschungen sind notwendig, um den Mechanismus der Koksablagung aufzuklären und Strategien zur Vermeidung der Koksablagerungen ableiten zu können. Bei Dauerbetrieb von Abgaskatalysatoren der in der Autoindustrie und bei Abgasbehandlung von bei Verbrennungsprozessen eingesetzten Al_2O_3 -Waben wird an der Oberfläche Kohlenstoff abgeschieden, der die aktiven Zentren blockiert. Daher müssen die Koksablagerungen in periodischen Abständen entfernt werden, wenn die Aktivität des Katalysators unter ein vorgegebenes Level gesunken ist. Die Vermeidung hoher Standzeit für die Entfernung des Kohlenstoffs bzw. die Verhinderung solcher Koksablagerungen setzt eine detaillierte Kenntnis ihrer Bildung voraus. Morphologische Studien mittels 3D-Röntgencomputertomographie zeigen an der Innenwand der Al_2O_3 -Waben Ablagerungen (Abb.1), die, wie die röntgenographische Phasenanalyse zeigt, aus amorphem Kohlenstoff mit Einschlüssen von Ni- und Fe-Partikeln bestehen. Auch bei der Hochtemperaturpyrolyse aus organischen Grundchemikalien, z.B. Naphtha, werden Koksablagerungen erzeugt. Dabei werden bei Temperaturen über 800 °C die Kohlenwasserstoffe in Rohröfen gespalten, wobei sich an den Wänden der Rohrreaktoren Koks abscheidet.

Dies führt einerseits zur Einengung des Rohrquerschnitts und damit zu einer Verringerung der Durchsätze und andererseits zur Verschlechterung des Wärmeübergangs von der Brennerflamme außerhalb der Rohre, der über das Rohrmaterial in die Reaktionszone im Rohr führt. Die Koksablagerungen an der Rohrrinnenwand können durch die Wahl geeigneter Stähle oder durch Additive im Gasstrom verringert werden, wobei die Bestandteile der Rohrmaterialien katalytisch wirken und dabei (Abb. 1: Ct-Schnittbild von Al_2O_3 -Waben) zum Teil in die Koksschichten eingelagert werden. Um diese Prozesse und deren Mechanismus aufzuklären, ist eine detaillierte Untersuchung der Bildung und Struktur der Koksschichten notwendig.

Die Röntgencomputertomographie dieser Koksablagerungen (Abb.2) zeigt protuberanzähnliche Verzweigungen. Diese poröse Morphologie steht im Gegensatz zu den Ablagerungen in den Al_2O_3 -Waben der Katalysatoren, deren Mikrostruktur relativ dicht und homogen ist. Dieser Unterschied wird noch verstärkt, da der Koks aus der Hochtemperaturpyrolyse bei der XRD-Phasenanalyse signifikante Reflexe für "layered" Nanoröhren sowie untergeordnet Hämatit und Magnetit zeigt.

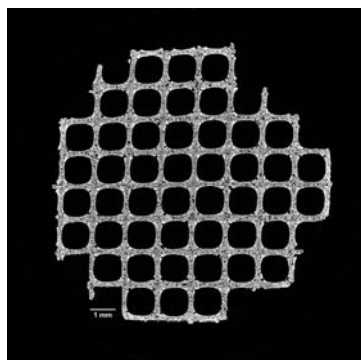


Abb. 1: Ablagerung (hell) auf Al_2O_3 -Waben (CT-Schnittbild)



Abb.2: CT-Schnittbild eines Koksrohres

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Zircon solubility and complexation of Zr in subduction zone fluids

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Igneous rocks occurring along convergent plate margins are significantly depleted in high field strength elements (HFSE). The geochemical signature of these rocks is thought to result from complex melt formation processes involving aqueous solutions, which stem from dehydration of the subducted slab. In these processes, HFSE retention may be controlled by the presence of accessory phases such as zircon and rutile, which can strongly fractionate these elements (Brenan et al. 1994). However, HFSE mobility depends on the fluid composition, e.g., the solubility of rutile increases strongly with the Na/Al ratio of Na-Al-Si bearing fluids (Manning et al. 2008). To investigate the influence of fluid composition on zircon solubility, experiments were conducted using a modified hydrothermal diamond-anvil cell (HDAC) designed for in situ SR- μ XRF experiments up to 1.5 GPa and 800°C (Bassett et al. 1993; Schmidt and Rickers, 2003). The sample chamber of the cell was loaded with a grain of synthetic crystalline zircon, distilled H₂O and a piece of NS2 (Na₂Si₂O₅) glass. Some NS2 glasses were doped with small amounts of Al. To quantify the spectra the Zr K α intensity was calibrated with a 7% HCl standard solution containing 1100 ppm Zr. SR- μ XRF spectra were taken at beamline ID24 of the ESRF, Grenoble, France and at HASYLAB beamline L in Hamburg. The observed Zr concentrations in fluids containing 23-33 wt% NS2 and varying Al contents were between 200 and 700 ppm at 600 to 650°C. These values match expected solubilities calculated from linear interpolation of the maximum solubility in pure H₂O (from the detection limit) and the solubility in the most alkaline high-silica melts reported by Ellison and Hess (1986).

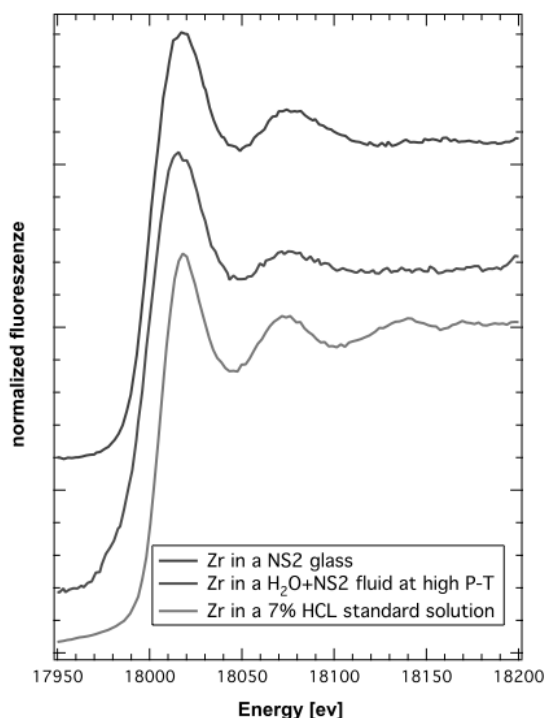


Figure 1: Zr K-edge spectra taken in different chemical environments

These high Zr concentrations found in NS2-bearing solutions signify that aqueous fluids with alkali silicates are efficient means for HFSE transport. This can be explained by complexation of HFSE with Si, Na, and perhaps also Al, via formation of polymerized solutes, as suggested by Manning (2004). To investigate this hypothesis, Zr K-edge X-ray Absorption Fine Structure (XAFS) spectra were collected on homogeneous H₂O+NS2 fluids containing Zr at and below saturation level. XAFS spectra were also collected at beamline ID24 at the ESRF. First results show clear differences between the XANES of Zr in an HCl solution at ambient pressure and those in an NS2-bearing aqueous fluid at high P-T conditions. The latter spectra display similarities to spectra of Zr in NS2 glass. This may indicate a similar structural environment for the two examined states, and thus point to Zr in silica-based polymeric units in NS2-bearing aqueous solutions.

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Anwendung von Synchrotronstrahlung in der Zementindustrie

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In der Grundstoffindustrie, z.B. bei der Herstellung und Verarbeitung von Zement, Kalk oder Gips werden Synchrotron- (SR)-basierte Messmethoden bisher kaum eingesetzt. Dies liegt zum einen an der geringen Verfügbarkeit von Synchrotronquellen und zum anderen an der fehlenden Anlaufstelle für potentielle industrielle Nutzer. Am Beispiel zementärer Bindemittel werden aktuelle Forschungsergebnisse zusammengefasst. Zukünftige Möglichkeiten für eine anwendungsorientierte Forschung mit Synchrotronstrahlung werden dargestellt.

Beton und Kalksandstein, Porenbeton und viele Spezialbindemittel – alle enthalten als „Klebstoff“ Calciumsilikathydrate. Tatsächlich gibt es keine Stoffgruppe, die industriell in größeren Mengen hergestellt wird. Dennoch sind viele Strukturen und wesentliche Aspekte der Bildung und Korrosion von Calciumsilikathydraten immer noch unbekannt. Dies betrifft sowohl einzelne Reaktionsschritte als auch die Reaktionskinetik. Eine genaue Kenntnis der Reaktionen würde die gezielte Neuentwicklung hydraulischer Bindemittel und die Verbesserung existierender Systeme erlauben.

Ein wesentlicher Grund für das bisher lückenhafte Wissen sind analytische Schwierigkeiten, die sich aus der oft geringen Partikelgröße und der geringen kristallographischen Ordnung vieler Calciumsilikathydrate ergeben. Außerdem sind die Phasen hoch empfindlich. Jede Veränderung der Luftfeuchtigkeit, Kontakt mit CO₂ und jede Form von Energieeintrag können zu massiven, oft irreversiblen Änderungen führen. SR-basierte Untersuchungen können einige dieser Probleme lösen. So sind Messungen an kleinsten Partikeln mit hoher Ortsauflösung möglich. Die zur Verfügung stehende Intensität erlaubt komplizierte experimentelle Aufbauten, so dass Messungen unter kontrollierten Bedingungen erfolgen können. So sind z.B. in situ Untersuchungen hydrothormaler Reaktionen publiziert. Ein zentraler Gegenstand der Forschung ist die Struktur von gering geordneten C-S-H Phasen, die in der Literatur oft auch als C-S-H-Gel bezeichnet werden. Mit Hilfe der SR-basierten XRD wurde ein Strukturmodell verfeinert. Aktuell werden alkalireiche C-S-H Phasen, auch mit XAS und SR-basierter IR-Spektroskopie charakterisiert. Ziel dieser Arbeit ist es, strukturelle Aspekte der Alkali-Silica-Reaktion und von Wasserglas-basierten Bindern zu beleuchten.

Kristalline Calciumsilikathydrate bilden die Basis von hydrothermal hergestellten Baustoffen wie Porenbeton und Kalksandstein. Eine weitere wichtige Anwendung sind Ölbohrzemente. Die Strukturen kristalliner Calciumsilikathydrate dienen außerdem als Modellstrukturen für gering geordnete C-S-H Phasen. Publierte ex-situ Untersuchungen mit XRD dienen meist der Strukturaufklärung. Pulvermethoden sind häufig, da genügend große Einkristalle selten zur Verfügung stehen. Mit in-situ Messungen sind insbesondere kinetische Aussagen möglich. Auch die quantitative Phasenanalyse mit der Rietveld-Methode, die mit konventioneller Strahlung längst Industriestandard ist, bietet mit SR-XRD neue Möglichkeiten. Insbesondere gelingt es, die Nachweisgrenzen zu reduzieren und strukturell sehr ähnliche Phasen zu diskriminieren. Daneben sind XAS, XRF und IR-Untersuchungen aus der Literatur bekannt. SR-Infrarotmessungen an Einkristallen ermöglichen z.B. die mikroskopische Abbildung von Phasenübergängen als Funktion der Temperatur. Dies wurde am Beispiel der Phasenumwandlung α -C₂SH → Deltait → α' -Ca₂SiO₄ gezeigt. Eine neue Meßmethode ist die hochauflösende Röntgen-Mikrotomographie. Damit wird die Untersuchung von porösen Mikrostrukturen in Beton in Echtzeit und in-situ möglich.

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Complementary observations of the Ga-rich region in the Cu_2S - Ga_2S_3 pseudobinary phase diagram

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Phase relations and structural changes in the Ga-rich region of the pseudobinary Cu_2S - Ga_2S_3 system have been studied. The focus of these study lies on the Ga-rich region close to the homogeneity region of the CuGaS_2 phase, crystallizing in the chalcopyrite crystal structure. The aim of these study is to compare the $(\text{Cu}_2\text{S})_y(\text{Ga}_2\text{S}_3)_{1-y}$ system with other well known systems of ternary $\text{CuB}^{\text{III}}\text{C}^{\text{VI}}_2$ compounds (with $\text{B}^{\text{III}}=\text{Ga, In}$; $\text{C}^{\text{VI}}=\text{Se, S}$). Powder samples have been prepared with different Cu/Ga ratios by solid state reaction of the pure elements in sealed, evacuated silica tubes at $T = 850\text{ }^\circ\text{C}$. Structural and phase analysis has been done by means of neutron powder and X-ray powder diffraction measurements, the latter with Bragg-Brentano geometry. Chemical composition and microstructural analysis have been observed by WDX microprobe analysis. The analyzed samples exhibit different phase relations as in the better known Cu_2Se - Ga_2Se_3 system. The results show different phases for the Ga_2S_3 -rich region close to the homogeneity region of the CuGaS_2 phase than proposed by other authors before [1]. Samples with a Ga_2S_3 -content higher than 52 mol-% show a secondary GaS phase. Furthermore the possible existence of other secondary phases like CuGa_5S_8 will be discussed in detail.

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Eigenschaften von Perovskiten $\text{Ca(Fe,Mn,Ti)O}_{3-d}$

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Bei der Produktion von eisenreichen Mn - Tonerdezementen kristallisieren während des Abkühlungsprozesses aus der Schmelze die Hauptphasen Calciumaluminatferrat $\text{Ca(Al,Fe)}_2\text{O}_4$ und diverse Perovskite $\text{A}_n\text{M}_n\text{O}_{3n-1}$. Aufgrund der sehr variablen Sauerstoffugazität während des Abkühlungsprozesses, tritt insbesondere Mangan in unterschiedlichen Oxidationsstufen auf, wodurch bestimmte sauerstoffdefizitäre Perovskitderivate stabilisiert werden.

Der strukturelle Aufbau dieser Verbindungen basiert auf der Wechsellagerung von Tetraeder - Oktaeder (TO), Tetraeder - Oktaeder - Oktaeder (TOO) und Oktaeder-Oktaeder (OO), welche sich von der klassischen Perovskitstruktur z.B. CaTiO_3 mit der Raumgruppe Pm-3m ableiten lassen. Zur Untersuchung der Phasenbreite und Kristallchemie der Perovskitstrukturtypen mit ABO_{3-d} : $\text{Ca(Fe,Mn,Ti)O}_{3-d}$ wurden Mischkristalle im System $\text{CaO} - \text{MnO}_2 - \text{Fe}_2\text{O}_3 - \text{TiO}_2$ aus den Oxiden und mittels Sol-Gel - Methode synthetisiert. Die Oxidationsstufen von Mn und Fe wurden mittels iodometrischer Titration bestimmt. Der Chemismus wurde am Institut für Mineralogie, Kristallographie und Materialwissenschaften mittels Mikrosonde bestimmt. Neutronenbeugungsexperimente wurden zur Strukturverfeinerung einzelner Mischkristalle am BENSC Gerät E6 des Helmholtz-Zentrum Berlin für Materialien und Energie durchgeführt. Verbindungen $\text{Ca(Fe,Mn,Ti)O}_{3-d}$ mit ABO_{3-d} - Struktur kristallisieren bevorzugt in der Raumgruppe Pnma. Mit zunehmender Fe_2O_3 - Konzentration wechselt die Symmetrie zu Pm-3m. Zunehmende Fe_2O_3 - Konzentrationen führen zur Stabilisierung einer Perovskitstruktur mit TOO und final eine Sequenz TO, typisch für eine Brownmilleritstruktur.

Temperaturbedingte Phasenübergänge in $\text{Ca(Fe,Mn,Ti)O}_{3-d}$ Mischkristallen, wurden untersucht, wobei mit zunehmendem Fe - Gehalt der Übergang Pnma - I4/mcm - Pm3m bei niedrigeren Temperaturen stattfindet [1], [2], [3].

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Kristallchemie der Brownmillerite im System $\text{Ca}_2\text{Al}_{2-x}(\text{Fe}_{x/2}\text{Mn}_{x/2})\text{O}_{5\pm d}$

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„Mischkristalle“ mit der Zusammensetzung $\text{Ca}_2(\text{Al}, \text{Fe}, \text{Mn})_2\text{O}_{5+d}$ basieren auf der Brownmilleritstruktur ($\text{Ca}_2\text{AlFeO}_5$). Technische Anwendung finden Brownmillerite in zementären Produkten. Sie kristallisieren in Portland - und Tonerdezementklinkern und hydratisieren beim Anmachen des Zementes mit Wasser. Mit zunehmendem Einsatz von Sekundärrohstoffen in der Zementproduktion, werden durch die Zumahlung von manganhaltigen Reststoffen die Eigenschaften von Tonerdezementen hinsichtlich des Hydratationsverhaltens optimiert [1]. Die Brownmilleritstruktur „ $\text{A}_2\text{B}_2\text{O}_5$ “ stellt eine sauerstoffdefizitäre Perovskitstruktur „ $\text{ABO}_{2.5}$ “ da. Senkrecht zu [010] liegen abwechselnd Tetraeder und Oktaederschichten. In den Kanälen der eckenverknüpften Oktaeder und Tetraeder liegen Ca^{2+} -Ionen. Al^{3+} Ionen und Fe^{3+} Ionen besetzen Oktaeder – und Tetraederlücken, wobei eine Besetzungspräferenz von Fe^{3+} Ionen auf Oktaederplätze und Al^{3+} auf Tetraederplätze vorherrscht. Durch die Fixierung von dreiwertigem Mn^{3+} auf der Oktaederposition wird das Koordinationspolyeder stark verzerrt, da Mn^{3+} Jahn - Teller aktiv ist. Darüber hinaus bewirkt die Mn_2O_3 - Fixierung eine Stabilisierung der Pnma - Modifikation, welche in der Mischkristallreihe $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ ab ca. $x = 0.56$ in I2mb übergeht. Ziel der Untersuchungen ist, den strukturellen Aufbau in $\text{Ca}_2(\text{Al}, \text{Fe}, \text{Mn})_2\text{O}_{5+d}$ Verbindungen zu untersuchen. Verbindungen mit der chemischen Zusammensetzung $\text{Ca}_2(\text{Al}, \text{Fe}, \text{Mn})_2\text{O}_{5+d}$ wurden mittels Sol-Gel Methode (Pecchini - Prozess) [3] synthetisiert. Als Gelbildner wurde Citronensäure verwendet. Der Chemismus der Brownmillerite wurde mittels Mikrosonde in Kombination mit der quantitativen Bestimmung der Mn-Oxidationsstufen (Iodometrisch) ermittelt. Strukturverfeinerungen an Neutronenbeugungsdaten mittels Rietveldmethode (Topas 3.0) durchgeführt.

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Linking basalt to mantle source signatures

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The chemical and isotopic composition of oceanic basalts documents ubiquitous heterogeneity in the Earth's mantle. Despite about four decades of research, however, key questions remain. For example, how are heterogeneous materials manifest and distributed in the Earth's mantle, what is their origin, and what are the processes leading to mantle heterogeneity? Simple models of mantle melting and melt extraction show that care must be taken to directly equate basalt and mantle isotopic composition, because partial melting, and melt mixing during melt extraction lead to a biased representation and subdued compositional variability in the basalts relative to their mantle sources. The properties of the isotope-trace element relationships in oceanic basalts, however, serve to assess to what extent the basalts represent source signatures. The degree of correlation between the isotope and trace element ratios, for example, is influenced by the extent of melt mixing during melt extraction. Different trace element - isotope pairs therefore allow assessing how well basalt correspond to source signatures. A large amount of trace element and isotope data in oceanic basalts, shows that enriched signatures in ocean island basalts (OIB), generally correspond closely to those of their average enriched mantle components. In both ridge and ocean island settings, however, the most depleted lavas are unlikely to faithfully reflect mantle depletion. Hence the depleted part of the Earth's mantle is expected to be compositionally more extreme than even the most depleted mid ocean ridge basalts (MORB). Inferring the true composition, origin and distribution of heterogeneous components in the Earth's mantle consequently requires detailed knowledge about the mechanisms of melting and melt mixing during the melt extraction process. Only if these processes and their influence on the isotope-trace element relationship are understood, can the composition and origin of the different source components, and thus mantle heterogeneity, be accurately constrained.

Mineralogy and human well-being: changing insights into nature

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The ubiquity of minerals in practically all niches of the environment is hardly fully perceived, although more than ever in the recent times stands good the saying “All man uses had been either grown or mined”. The role of minerals and of the sciences studying them is in many aspects central to the quality of life. Among the many branches of mineralogy, environmental and applied mineralogy are gaining a still firmer position in human life.

Environmental mineralogy as a newly developing science is still seeking directions for its progress, what makes its scope very wide. Anyway, there are in principle two main specializations developing in it. The first – like in the infancy of all natural sciences – is descriptive. With the sophisticated tools at hand, this descriptions goes much deeper than it was possible earlier, and enables to deduce the nature and mechanism of mineral formation and interaction with the abiotic as well as biotic components of the environment. The other principal direction, stemming to a great degree from the first one, is the utilization of our knowledge of the properties of minerals and minerogenetic processes in protection of the environment against contamination, or amending the quality of the environment.

The descriptive environmental mineralogy is not a novelty; perhaps the first written testimony about the negative impact of mineral extraction on human health dates 2000 years back in Plinius the Younger report about ill health of slaves working in asbestos mines. While in the ancient times the areas heavily impacted by mining and processing of minerals were relatively localized, nowadays the pollution of the environment knows no frontiers. In this aspect, environmental mineralogy has a big task in distinguishing the human contribution to the overall pollution (e.g. of the atmosphere) from the contribution of natural processes. The task of serious scientists is also to point out on exaggeration or overestimation of some impacts of mineral extraction and processing by eco-activists or lobbyistic companies. One example for all is the fuss over asbestos-containing materials.

The view of environmental mineralogy is recently refocusing to nanoscale, what gives surprisingly new insights on the nature of geochemical and minerogenetic processes, different from that describing them on meso- or macroscale.

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The berlinite substitution in clinkers; environmental aspects

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The constant production of meat and bone meal (MBM) from cattle cadavers presents due to the regulations evoked BSE a problem for many countries. Combustion is an attractive option of MBM disposal. An environmentally safe way of its disposal is as alternative fuel in rotary cement kilns, as the high temperature inside these kilns (close to 2000 °C) guarantees 100% prion destruction. Fuel combustion in a cement kiln is a no-waste process, as the unburnt component – mostly Ca phosphate – gets incorporated in the clinker. The addition of P to the raw materials for clinker production presents certain problem, as it influences the properties of the melt, the clinker's phase composition, the structure of clinker minerals and their chemical composition. The experiments with MBM addition have shown that P₂O₅ contents above 0,7 wt. % P₂O₅ in clinker increase the Ca₂SiO₄ (belite) and CaO (free lime) proportions on the expense of Ca₃SiO₅ (alite). As belite is less reactive than alite, and free lime proportion above 5% is not acceptable for cement preparation, a series of experiments was performed to optimize the raw meal mix with respect to resulting clinker phase composition. The amounts of MBM ash addition ranged between 0,25 and 7,5 wt. % of P₂O₅. The distribution of P among individual clinker phases was studied using the electron microprobe. It was found that in equilibrium-burned clinkers all P incorporates in the common clinker minerals and does not form any high-P phase. The content of P₂O₅ in belite and alite distinctly grows with its bulk content in the clinker. The interstitial phases (Ca aluminate and Ca ferrite) contain much less P₂O₅, mostly below 0,8 %. P preferentially enters the structure of belite; already from the total content of 0,5 wt. % P₂O₅ in clinker is the content of P₂O₅ in belite more than twofold than in alite. PO₄ substitutes in the structure of clinker silicates SiO₄ groups and Ca₃(PO₄)₂ forms solid solutions with Ca₂SiO₄ and Ca₃SiO₅. Besides this substitution, certain portion of P appears to enter the belite as well as alite structure via the berlinite substitution ($2\text{Si}^{4+} \Leftrightarrow \text{Al}^{3+} + \text{P}^{5+}$), known e.g. from feldspars. The relationship between P₂O₅ and Al₂O₃ contents in belite and alite appears to be linear in the whole studied range of P₂O₅ contents (0.25 – 7 wt.%). The regression equation calculated from the results of spot analyses, $\text{Al} = 0.214\text{P} + 0.053$ (in a.p.f.u.) shows that the “initial” Al contents in belite is around 0.05 a.p.f.u. This finding led to experiments with raw meals jointly enriched in P and Al, which enabled the formation of alite even from mixes with more than 3% P₂O₅, not occurring in clinkers from raw meals containing both Al₂O₃ and Fe₂O₃ (patent pending).

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Das „Silberne Kreuz“, eine außergewöhnliche Silberstufe aus dem Nachlass von Kurfürstin Sophie von Sachsen (1568-1622)

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Die mineralogische Sammlung des Museums für Mineralogie und Geologie Dresden enthält neben zahlreichen historischen Silberstufen aus dem erzgebirgischen Bergbau eine besonders eigentümlich geformte Stufe, das „Silberne Kreuz“. Es stammt aus dem Besitz von Kurfürstin Sophie (1568-1622). Dieses natürlich gewachsene Silber hat wahrscheinlich in seiner christlichen Symbolik zu Lebzeiten der Kurfürstin in ihren Gemächern auf einem Hausaltar gestanden. In diesem „Eckstuben“ genannten Zimmer im Dresdner Schloss verwahrte sie in einem Schränkchen auch mehrere Handsteine aus Silbererzen auf, welche sie von ihrem Gemahl Christian I. im Jahr 1587 als Geschenk erhalten hatte. Einer dieser Handsteine zeigt die Szene „Christus am Ölberg“ und ist mit dem Monogramm „CV“ versehen. Er wurde wahrscheinlich von Caspar Ulich aus Argentit geschnitten und gehört heute zum Bestand des „Grünen Gewölbes“ in Dresden.

Das „Silberne Kreuz“ wurde auf Befehl von Kurfürst Johann Georg I. (reg. 1611-1656) im Jahr 1623 aus dem Nachlass seiner Mutter zusammen mit anderen Silberstufen an die Kunstkammer überwiesen, wie aus einem zeitgenössischen Verzeichnis hervorgeht. Seit dieser Zeit gehört es zu den viel bewunderten Stücken der Dresdner Sammlung.

Die erste Beschreibung des „Silbernen Kreuzes“ stammt vom Augsburger Patrizier Philipp Hainhofer, welcher im Jahr 1629 die Kunstkammer besuchte. Um 1640 findet es sich mit anderen wertvollen Stücken, vorwiegend gediegen Gold und Silber, zum Schutz vor Diebstahl und Staub unter Glas. 1683 erwähnt der Kunstkammerer Tobias Beutel das Stück als „ein silbern Creutz von Natur also formirt“. Als Fundort verzeichnet Christian Ernst Birkhan im Silberstufenkatlog von 1763 „von der Bergkappe-Fundgrube am Widdersberge“. Das Jahr des Fundes ist leider nicht überliefert. Die Grube Bergkappe, eine der berühmten Schneeberger Silber- und Kobaltgruben, wurde im Jahr 1513 das erste Mal erwähnt.

Drahtförmiges Silber entsteht bei der schnellen Kristallisation aus hydrothermalen Lösungen. Dabei lagern sich die Silberatome bei dieser Art der Kristallisation bevorzugt an den Ecken und Kanten eines Kristalls an. Dadurch werden keine vollständigen Kristalle ausgebildet, sondern unvollständige Kristallskelette in Form von Drähten. Diese Art des Kristallwachstums wird als dendritisches oder skelettförmiges Wachstum bezeichnet. Die Silberdrähte sind stets parallel der Längsrichtung fein gestreift und weisen oft ein spiralförmiges Wachstum auf, was zur Ausbildung des typischen Lockensilbers führt.

Das „Silberne Kreuz“ ist insgesamt 16,5 cm hoch. Es besteht aus einer 7 cm breiten Basis miteinander verwachsener Silberdrähte von 0,1 bis 0,8 cm Dicke. Die bis zu 0,5 cm dicken Drähte, die das Kreuz bilden, sind bis zur Knickstelle 15 cm lang. Im vorliegenden Fall sind diese Knickstellen spiralförmig, was auf eine natürliche Bildung schließen lässt. Insgesamt ergibt sich eine Länge von 22 cm für diese Drähte und damit eine außergewöhnliche Länge. Der spiralförmige Draht in Form einer Schlange ist 14 cm lang und wächst aus dem Silberlockengeflecht der Basis heraus.

Die Befunde lassen auf eine natürliche Bildung aus einer hydrothermalen Lösung im Drusenraum eines Ganges schließen. Auf der Bergkappe Fundgrube war der NNW-streichende Bergkappe Flache Gang aufgeschlossen, der mit BiCoNiAg- sowie Karbonat-Sulfid-Arsenid-Paragenesen mineralisiert war. Letztere als „Edle Geschicke“ bezeichnete Mineralisation enthielt auch Akanthit und gediegen Silber.

Ob nach der Bergung der Stufe bei der Kreuzesform etwas nachgeholfen wurde, kann diskutiert werden. Auf alle Fälle ist das „Silberne Kreuz“ ein außergewöhnliches Schauobjekt aus der Frühzeit des Silberbergbaus in Sachsen.

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Verwertung eines Rotschlammes aus der griechischen Alumina-Produktion in der Baukeramik

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Bei der Produktion von Aluminiumhydroxyd aus Bauxit nach dem Bayer-Verfahren, entstehen in Agios Nikolaos, Boiotien, Griechenland, jährlich ca 700.000t von Rotschlamm, welcher bis heute ins Meer versenkt wird. Probe dieses Rotschlammes wurde stofflich charakterisiert und in Hinblick auf seine Verwertbarkeit in der Produktion von Baukeramik-Artikeln untersucht.

Aus dem Rotschlamm und aus Mischungen vom Rotschlamm mit zwei verschiedenen lehmigen Ton-Typen, einen CaO-armen und Al_2O_3 -reichen und einen CaO(+MgO)-reichen, sowie aus einer Mischung vom Rotschlamm mit CaO- und Na_2O -haltigem sehr SiO_2 -reichem Flaschenglas-Pulver, wurden plastische Massen hergestellt. Der Rotschlamm war sehr reich an Fe_2O_3 und relativ reich an Al_2O_3 , CaO und H_2O , während er kleine Mengen von TiO_2 , Na_2O , MgO und geringe Mengen von K_2O , MnO und P_2O_5 enthielt. Seine Hauptbestandteile waren Hämatit und Katoit, während er noch beträchtliche Anteile von Diaspor und Goethit, kleine Gehalte von Röntgenamorphen, Ilmenit, Gibbsite, Titanit, Calcit, Cancrinit und Periklas sowie Spuren von Böhmit enthielt. Die Korngrößen der Rotschlammteilchen lagen zwischen 0,2 und $150\mu\text{m}$ ($d_{50}=10\mu\text{m}$). Der CaO-arme und Al_2O_3 -reiche Ton bestand vorwiegend aus Muscovit/Illit(+Paragonit) und Quarz, während er relativ kleine Gehalte von Calcit und Röntgenamorphen sowie geringe Mengen von Rutil, Pyrophyllit und Klinochlor enthielt. Die Korngrößen seiner Partikel lagen zwischen 0,2 und $90\mu\text{m}$ ($d_{50}=10\mu\text{m}$). Der CaO(+MgO)-reiche Ton bestand vorwiegend aus Klinochlor und Quarz, sowie aus erheblichen Mengen von Calcit und Muscovit/Illit und kleine Mengen von Paragonit, Talk, Dolomit und Chloritoid, während die Korngrößen seiner Partikel zwischen 0,2 und $100\mu\text{m}$ ($d_{50}=15\mu\text{m}$) lagen.

Durch Pressen von Proben aus diesen Mischungen, wurden Prüflinge geformt, welche in der Folge bei 950, 1.000, 1.050, 1.100, 1.150 und 1.200°C in oxidierender Atmosphäre, in mehreren Versuchsreihen unterschiedlicher Brenndauer, gebrannt wurden, sodass sie keramische Massen bildeten. Bei den so entstandenen keramischen Massen wurden die Schwindung, die Wasseraufnahme, die Porosität, die Dichte und die Biegefestigkeit bestimmt.

Es wurde festgestellt, dass die keramischen Massen, die aus den Mischungen mit den Tonen entstanden sind, nach dem Brennen bei 1150°C eine schwarzbraune Farbe bekamen, während sie bei 1200°C bereits nach einer Brenndauer von einer Stunde deutliche Schmelzblasen zeigten. Die Brenndauer-Unterschiede von einer bis zu acht Stunden, in den verschiedenen Versuchsreihen, hatten keinen wesentlichen Einfluss auf die Eigenschaften der keramischen Massen. Der Zusatz der Tone zum Rotschlamm hatte, im Vergleich zu den Massen vom reinen Rotschlamm, zu keiner wesentlichen Verbesserung der Eigenschaften der keramischen Massen geführt.

Nach dem Brennen bei 1.100°C, ergaben sich aus den Mischungen Rotschlamm/Ton rotfarbige keramische Massen, die für die Verwendung in der Produktion von Fliesen oder Bodenplatten gute Festigkeiten aber eine zu hohe Wasseraufnahmefähigkeit hatten. Bei der Mischung von 80% Rotschlamm mit 20% Flaschenglas dagegen, wurden nach dem Brennen bei 1.100°C, Wasseraufnahmewerte von 3,5% erreicht. Es ist zu vermuten, dass durch leicht abgeänderte Mischungsverhältnisse vom Rotschlamm zum Flaschenglas oder wenig höhere Brenntemperaturen eine noch niedrigere, für die Produktion von Bodenplatten akzeptable, Wasseraufnahme erreichbar sein muss.

Sowohl aus dem reinen Rotschlamm als auch aus seinen Mischungen mit den Tonen und mit dem Flaschenglas entstanden durch Brennen bei 950°C rotfarbige keramische Massen, deren Eigenschaften den Anforderungen für die Produktion von Ziegelsteinen genügten, wobei das Wasseraufnahmevermögen der Masse, die aus der Rotschlamm/Flaschenglas-Mischung resultierte wesentlich niedriger war.

Aufwältigung der Fluss- und Schwerspatlagerstätte Niederschlag

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Die Lagerstätte Niederschlag bei Bärenstein befindet sich in der Kammfläche des Mittleren Erzgebirges, 8 km nordöstlich des Fichtelberges. Das Bergbaurevier blickt auf eine über 400 Jahre alte Bergbaugeschichte zurück, lag aber immer im Schatten der großen Bergstädte Jachymov und Annaberg. Zinn, Kupfer, Silber und Kobalt standen im Mittelpunkt des Interesses früher Bergbauunternehmungen. Bereits zu Beginn des 20. Jahrhunderts wurden mehrere Bergbauversuche auf Uran unternommen.

Seinen Höhepunkt erlebte der Bergbau durch die SAG Wismut zwischen 1947 und 1954 [1]. In diesem Zusammenhang erfolgte die Entdeckung der Fluss- und Schwerspatlagerstätte Niederschlag. Sie befindet sich im Liegenden der Uranmineralisationen und markierte den Teufenhorizont für das Ende der Urangewinnung in diesem Revier.

Im Anschluss an den Uranbergbau wurde eine bergmännische Erkundung der Spatlagerstätte vorgenommen. Sie endete 1959 mit dem Nachweis einer Vorratsbasis von 0,9 Mio t Flussspat und 0,6 Mio t Schwerspat. Zu diesem Zeitpunkt war das Bergwerk bereits geflutet. Der Vorratskörper liegt im Teufenbereich zwischen 554 und 674 m NHN, ca. 60 m unter dem Standwasserspiegel des auflässigen Grubengebäudes.

Zwischen 1974 und 1977 erfolgte eine weitere Erkundungskampagne mit Hilfe von Tiefbohrungen. Sie führte zur Entdeckung weiterer Vorräte im Teufenbereich zwischen 0 und 420 m NHN und zur Erhöhung der Vorratsbasis auf 1,4 Mio t Flussspat. Im Jahr 1988 war absehbar, dass der Flussspatbedarf der DDR-Volkswirtschaft ab 2015 nur durch den Aufschluss einer neuen Lagerstätte gedeckt werden kann. Mit dieser Veranlassung begann der Geologische Betrieb der DDR Recherchearbeiten zur Lagerstätte Niederschlag. Die Resultate dieser Kenntnisstandsanalyse wurden durch KUSCHKA [2] zusammengefasst und einer kritischen Neubewertung unterzogen.

Die Erzgebirgische Fluss- und Schwerspatcompagnie GEos GmbH erhielt 2008 die bergrechtliche Bewilligung zum Abbau von Fluss- und Schwerspat auf dieser Lagerstätte. Die Aufnahme der Aus- und Vorrichtungsarbeiten für die untertägige Gewinnung ist für 2010 vorgesehen. Gegenwärtig wird an der Erstellung des Rahmenbetriebsplanes gearbeitet.

Der Vortrag beginnt mit einer Einführung zur Lagerstätte und ihrem Umfeld. Weiterhin wird die aktuelle Situation auf dem Flussspatmarkt betrachtet. Der Schwerpunkt liegt auf einem Bericht über den erreichten Sachstand und die ersten Erfahrungen bei der Realisierung dieses Vorhabens innerhalb des Naturparks Erzgebirge / Vogtland. Der Tenor unseres Beitrages gibt Anlass für Optimismus.

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Formation of highly-refractory mantle peridotites by melt-peridotite interaction, Orhaneli (Bursa), NW-Turkey

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The mantle section of the Orhaneli ophiolite (NW-Turkey), composed of highly depleted harzburgite and dunite cut by numerous dyke of pyroxenite, represent the remnant of the Cretaceous Neotethys Ocean and records magmatic processes typical of supra-subduction zones. Mantle peridotites have extremely low concentrations of Al_2O_3 (0.11-0.72 wt%) and heavy rare earth elements (HREE), and show light REE enrichment compared to the middle REE on chondrite-normalized diagram, indicating an interaction between LREE-enriched melt and LREE-depleted mantle residues. Consistent with whole-rock geochemical data, composition of chromian spinel (Cr# 43-82; average 70) and coexisting olivine (Fo = 89-94; average 91.6) indicate that they are residual after extensive partial melting (20-40%). Although the composition of olivine-spinel coexisting phases in most of the samples plotted within olivine-spinel mantle array, few samples plot right hand side of this field with lower Fo content of olivine for corresponding Cr#. These samples are characterized with higher Fe, Mn, Zn, and Rb contents, and are more enriched in LREE, although HREE concentrations are highly depleted when compared to other samples. Calculated equilibrium temperatures and oxygen fugacities (Ballhaus et al., 1991) are 703-763 °C, and 0.17-1.67 ($\Delta\log \text{FMQ}$), respectively. Calculated oxygen fugacities are well correlated with Cr# of spinel and plot within the oceanic arc peridotite field of Pearce et al. (2000). The high $f\text{O}_2$ seems to be associated with aqueous-fluid related metasomatism in peridotite samples. Cr# of spinel in mantle peridotites is expected to increase with increasing degree of partial melting. However, TiO_2 concentration of spinel grains are positively correlated with Cr#, indicating residual peridotites are the product of intense interaction between peridotite and melt under high oxygen fugacity condition.

Because the most fertile peridotite sample (harzburgite) in the Orhaneli ophiolite is found to be depleted ($\text{Cr\#}_{\text{spl}} = 43.1$, $\text{Mg\#}_{\text{spl}} = 63.1$), it would be much difficult to form highly depleted dunite by simple partial melting of this depleted harzburgite under anhydrous environment. However, it is well known that the degree of melting increased by the addition of water. Low equilibration temperature, high $f\text{O}_2$ calculated values and highly depleted character of the peridotite samples, as well as LREE-enriched chondrite-normalized REE patterns, suggest the occurrence by injection of hydrous melt into the host harzburgite. The presence of water would have been necessary to lower the solidus of the peridotite and melting of orthopyroxene. Therefore, the mantle wedge above the subduction zone is the most likely tectonic setting where hydrous melt can be formed and percolate. Reaction of the Orhaneli peridotites with such a melt could easily explain the observed LREE enrichment in the peridotite samples.

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Thermal treatment of clay minerals

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The long term response of physicochemical properties of clay minerals on different influencing effects is an important research topic in different applications of clays, e.g. as barrier material in waste disposal. There are physical effects like temperature, pressure or ionizing radiation as well as chemical reactions. The presented work focuses on temperature induced changes in properties of different clays. Influences are especially expected on layer charge and cation exchange capacity as well as on connected changes in properties like swelling behaviour.

Different clays and clay minerals were investigated: Na-bentonite MX80, Ca-bentonite Calcigel, kaolinite, Na-smectite Cloisite, vermiculite and illite). The clays were stored at various temperatures (50°C – 200°C) for more than two years (still running). While one suite of samples is stored in an open system, the second is kept in a closed system with different water content. In certain time intervals samples are taken and analyzed. The analysis includes XRD and TG-MS for changes in the mineralogy and crystal chemistry. The cation exchange capacity (CEC) and exchangeable cations of the clays and the layer charge (MLC) of the smectites were measured (Cu-complex method and $\text{NH}_4\text{C12}$ intercalation, resp.). As physical parameters the surface area, the water uptake under free swelling conditions (Enslin-Neff procedure) as well as the swelling behaviour (pressure, displacement) were analyzed.

First results show different responses on thermal treatment for MX80, Calcigel, and Cloisite. In case of Calcigel there is a significant influence, the CEC decreases with time and temperature (till now approximately 10%). The CEC of MX80 drops slightly within a short time of heating (less than one month) but then remains constant regardless of the time and temperature of treatment. On the other hand, the CEC of Cloisite changes even after more than one year of heating only insignificantly. The response of the MLC on increasing temperature is fast in all cases. In less than one month a slight decrease in MLC could be measured; later the values remain constant. The different behaviour in CEC development has to be explained by other processes than changes in MLC, e.g. by a stronger binding of cations in the interlayer/ditrigonal cavities in the tetrahedral sheet preventing their exchange. A further possible process is the formation of interlayers, which are not longer accessible for the exchanging Cu-complex solution, e.g. due to occurring cementations or clay mineral transformations. XRD-investigations and the study of water uptake and swelling behaviour will give further insight to explain this phenomenon.

Arsenite Adsorption on Goethite at Elevated Temperatures

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Experimental closed-system ΔT acid-base titrations between 10 °C and 75 °C were used to constrain a temperature-dependent 1-pK basic Stern model of the goethite surface complexation reactions. Experimental data for the temperature dependence of pH_{PZC} determined by the one-term Van't Hoff extrapolation yield in a value for goethite surface protonation enthalpy of $-49.6 \text{ kJ mol}^{-1}$ in good agreement with literature data (Figure 1a). Batch titration data between 10 °C and 75 °C with arsenite concentrations between 10 μM and 100 μM yield in adsorption curves, which increase with pH, peak at a pH of 9, and decrease at higher pH values. The slope of this bend is becoming steeper with increasing temperature. A 1-pK charge distribution model in combination with a basic Stern layer option could be established for the pH-dependent arsenite adsorption. Formation of two inner-sphere bidentate surface complexes best matched the experimental data in agreement with published EXAFS spectroscopic information. The temperature behaviour of the derived intrinsic equilibrium constants can be well represented by the linear Van't Hoff $\log K_T^{\text{int}}$ vs. $1/T$ plot. Adsorption of arsenite on the goethite surface is exothermic (negative $\Delta_r H_{298}$ values) and becomes therefore weaker with increasing temperature. The same behaviour was found recently also with the silicate oxoanion (Kersten & Vlasova, 2009). Application of the new constants with the aqueous speciation code VMINTEQ predicts that the As(III) concentration in presence of goethite sorbent is decreasing by 10 times once the hydrothermal solution is cooled down from 99 °C to 1 °C. The model curve matches data from a natural thermal water spring system (Figure 1b). The change of adsorption efficiency for arsenic along the temperature gradient may well serve as an additional process to mitigate ecosystem contamination by arsenic-rich water seepage from geothermal energy generation facilities.

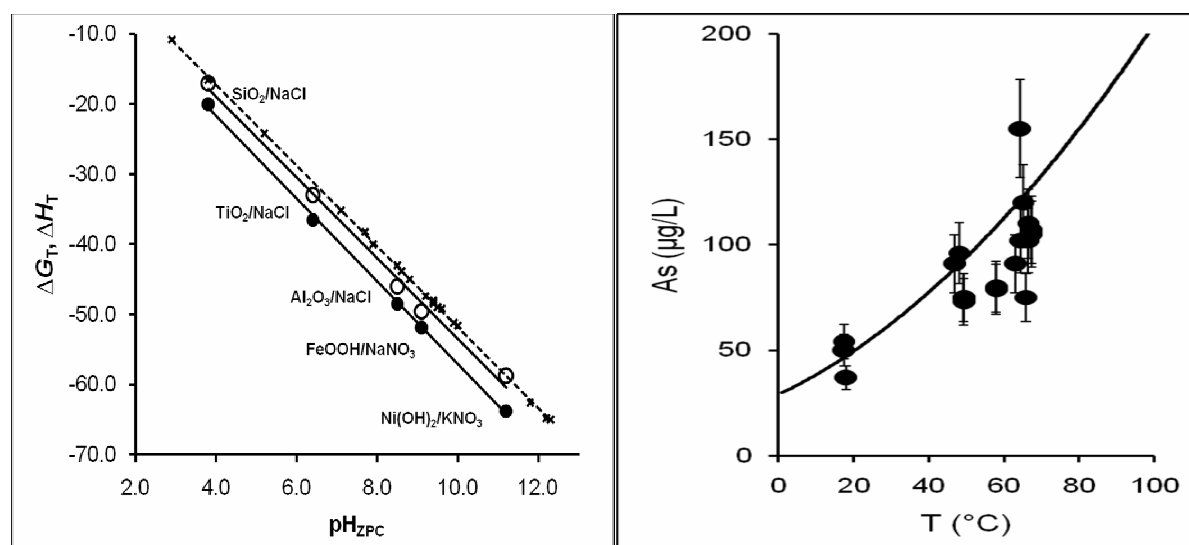


Figure 1: (a, left) linear regression of goethite protonation energies (black dots) and enthalpies (open dots) vs. their pH_{PZC} values at 25 °C for the 1-pK BSM adsorption model. The data pair for $\text{FeOOH}/\text{NaNO}_3$ is from this study, the other data pairs from literature; (b, right) experimental data points (black dots) of thermal water from three different thermal springs in the Wiesbaden spa area (Schwenzer et al., 2001), together with the model curve from this study.

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Sorelphasen als Reaktionsprodukte von Natronwasserglas mit MgCl_2 -reichen Salzlösungen bzw. Mineralen.

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Wassergläser sind wässrige Lösungen von Alkalisilikaten, d.h. chemische Systeme, die neben Wasser Na_2O (Natronwasserglas) bzw. K_2O (Kaliwasserglas) und Anionen der Kieselsäure enthalten. Charakteristisch für Wassergläser ist ihr alkalischer pH-Wert, der bei einem Anstieg des SiO_2 - $\text{Na}_2\text{O}(\text{K}_2\text{O})$ -Verhältnisses, auch als Modul bezeichnet, geringfügig sinkt. Mit einer Zunahme des Moduls ist eine Abnahme der Wasserlöslichkeit von Alkalisilikaten gekoppelt.

Natronwasserglaslösungen erhärten beim Kontakt mit salinaren Lösungen sowie festen Chloriden und Sulfaten, wie Halit, Bischofit oder Kieserit. Diese Lösungen und Salze können demnach als Härter der Wassergläser bezeichnet werden. Bei der Reaktion entstehen spontan aufgrund der äußerst geringen Löslichkeit von Si in Salzsäurelösungen amorphe Silikatphasen (vgl. Marshall & Warakowski, 1980). Die Silikate wachsen unter Bildung eines dreidimensionalen Netzwerkes aus angrenzenden kolloidalen Teilchen zusammen (Henisch, 1996). Die Bildung weiterer Reaktionsprodukte ist abhängig von der Art und Menge der vorhandenen Salze, wobei umfangreiche Mineralneubildungen in MgCl_2 -Systemen auftreten. Die Reaktionsprozesse wurden bei Verwendung von Bischofit sowie technischen und natürlichen MgCl_2 -Lösungen untersucht. Zum Einsatz kamen u.a. Gleichgewichtslösungen des quinären und hexären Systems, wie die Lösungen Q bzw. IP21.

Bei der Reaktion von getrocknetem Natronwasserglas und von Silikatgel, das durch Kontakt mit Halit erhärtete, bildeten sich vor allem Magnesiumoxichloride. Röntgendiffraktometrische Aufnahmen zeigten, dass sich nach relativ kurzer Zeit die chemisch stabile Magnesiumoxichlorid-Phase 3-1-8 bzw. das Mineral Korshunovskit $[\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}]$ bildet. Nach lichtmikroskopischen und elektronenoptischen Untersuchungen mittels Elektronenstrahlmikrosonde liegen in den Lösungen zunächst einzelne Nadeln vor, die mit der Zeit in eine dichte verfilzte Masse übergehen. Beim Kontakt zwischen Bischofit-Körnern und Natronwasserglas bildet sich ein festes poröses Gerüst bestehend aus Korshunovskit.

Nach D'Ans et al (1955) ist die 3-1-8-Sorelphase ($3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$) in konzentrierten salinaren Magnesiumchlorid-Lösungen als stabil zu bewerten. Andere Sorelphasen wie z.B. die 5-1-8-Phase sind als Zwischenphasen zu betrachten, die bei weiterem Lösungskontakt in die stabile 3-1-8-Phase übergehen. Reagieren Sorelphasen mit Kohlendioxid entstehen Carbonatverbindungen wie z.B. Chlorartinit, welcher im Vergleich zu den Sorelphasen eine noch geringere Löslichkeit aufweist (Anthony et al, 2003).

Wir danken Prof. K. Mengel, Institut für Endlagerforschung der TU Clausthal, für die Durchführung der in diesem Rahmen notwendigen mineralogischen Untersuchungen.

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Impact of bound water on the dielectric relaxation behaviour of partially saturated porous media

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High frequency electromagnetic determination of moisture in porous media, e.g. soil, is based on the strong relationship between volumetric water content θ and relative dielectric permittivity ϵ_r . In particular, in fine-grained soils the movement of water is influenced by different surface bonding forces due to interface processes [1]. The interface effects lead to a number of dielectric relaxation processes (free and physically bound water phase, Maxwell-Wagner-effect, counterion relaxation effects) [2-4]. These relaxation processes are the reason for the strong frequency dependence of the dielectric material properties of soil below 1 GHz [5-8]. The matric potential is a measure of the bonding forces on water in the soil. Hilhorst et al. 2001 [9] suggested a thermodynamic approach for the relationship between soil matric potential and dielectric relaxation behavior of water in different binding states. Based on this approach a dielectric relaxation model was developed which considers low frequency dispersion to 1 MHz as well as losses due to a direct current conductivity of the aqueous pore solution. The sensitivity of the model on the Soil Water Characteristic Curve (SWCC) was systematically analyzed based on a pedotransfer function (PDF) by Carsel and Parrish 1988 [10] for soil textures ranging from pure sand to pure clay. In addition, a well-graded clay free sand of a dike model [11] as well as a silty clay loam from a flood protection dike of the river Unstrut in Thuringia/Germany [8] with known SWCC is studied. The numerical results are compared with known empirical or semiempirical functions and theoretical mixing models, e.g. complex refractive index model (CRIM). With the Hilhorst approach, the impact of the physically bound water phase on the $\theta - \epsilon_r$ relationship for fine grained soils is quantified, and the resulting differences to the frequently used theoretical and empirical models are demonstrated. As expected the contribution of the bound water phase to the dielectric relaxation behaviour of the sandy soils in the frequency range above 1 MHz can be neglected. The $\theta - \epsilon_r$ relationship is determined according to the appropriate mixing model. However, the Hilhorst approach fails for fine grained soils with marked electrical losses, (e.g. with strong dispersion and absorption of the electromagnetic properties (MWE or CRE)), but the consideration of these effects in applications in the frequency range < 1 GHz is highly important [4, 5, 7, 8]. The use of CRIM in combination with the Hilhorst approach improves the model markedly.

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Precious metals in some parts of the historical mining districts of the German Kupferschiefer

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The sediment-hosted copper mineralisation within the Kupferschiefer sensu stricto, as well as in its hanging and footwall has been the subject of episodic exploration and scientific research (e.g. Kulick et al. 1984, Rentzsch et al. 1997, Wedepohl & Rentzsch 2006). Here the main focus was on the metallogenesis and mineralisation of copper, lead and zinc, but only sparse work has been done on the content of precious metals (e.g. Hammer et al. 1988, Borg et al 2005). Several German historical mining districts (Sangerhausen/Mansfeld and Richelsdorf), as well as substantial copper exploration prospects (Spremborg/Weisswasser and Spessart/Rhoen) occur along the southern margin of the Southern Permian Basin and were the subject of industrial and scientific interest.

During this study the content of precious metals in some parts of the historical mining districts of the German Kupferschiefer and its adjacent strata will be examined. An initial investigation on the content of Au and PGE in the Kupferschiefer south of the Harz Mountains has been carried out by Borg et al. (2005) and identified two local occurrences with elevated amounts of gold and PGE. Here the elevated precious metal values occurred in a narrow fringe between the copper zone and the zone of epigenetic oxidation, the Rote Fäule (Borg et al. 2005). The current study is focused on several drill cores from boreholes of the Sangerhausen and Richelsdorf mining district, which intersect the Kupferschiefer and its adjacent strata. These drill cores have been examined on their content and distribution of gold and PGE (Fig. 1).

In both historical mining areas, the Sangerhausen as well as the Richelsdorf mining district, elevated gold contents have been identified. The highest gold content (borehole Ldo 6/62 in the Sangerhausen district) of 12 ppm gold occurs spatially immediately below the zone with the highest copper content within the borehole and is closely associated with the oxidized facies (Rote Fäule) (Fig. 1). Therefore a spatial and probably also metallogenetic association of the precious metals with the base metal (copper) mineralisation and thus an association with the epigenetic redox event (Rote Fäule) exists in all areas investigated so far. The lateral distribution of precious-metal-bearing and barren areas within the copper mineralised districts is still under investigation but a structural and lithological (basement) control appears most likely.

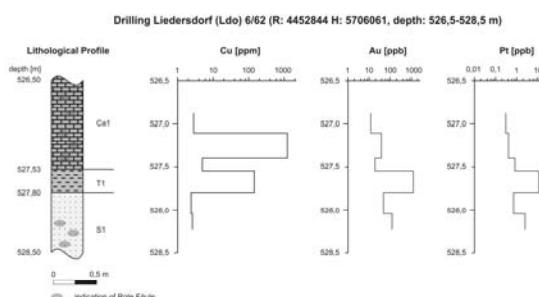


Figure 1: Metal zonation in borehole Ldo 6/62, Sangerhausen mining district

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Petrological investigations and Electron microprobe analysis (EPMA) of rocks from the Palghat-Cauvery lineament, southern India

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Southern India exposes one of the major parts of east Gondwana, and comprises an accumulation of different tectonic blocks that assembled during different times of the Earth's history. The oldest unit of these cratonic blocks is the Dharwar Craton (DC) that underwent initial growth during the Early Archean and was last consolidated at the end of the Archean c. 2,5 Ga ago. The terrains of the DC have not preserved any significant younger event. In contrast to this, Proterozoic blocks of the Southern Granulite Terrain (SGT) show strong imprints of the Pan-African (550-500 Ma) and, to the same extent, of Grenvillian high-grade metamorphism. In this study 23 samples were taken from a c. 400 km large area in the eastern part of the transition zone between the DC in the north and the SGT in the south, the so called Palghat-Cauvery lineament, which interpreted as a Proterozoic shear zone. The studied area lies west to the town of Erode, and mainly consists of highly deformed gneisses with intercalations of metabasites, BIF and other rock types. The common stable assemblage in the metabasites comprises quartz, hornblende, garnet, orthopyroxene, clinopyroxene and plagioclase and reflects granulite-facies metamorphism. The P-T evolution of these mafic granulites has been constrained with TWQ (version 2.02) and, yielded peak conditions of ~ 900°C and 10 +/- 1 kbar. These results correspond well with other P-T data from the literature (Srikantappa et al., 2003). Microtextures of BIF show spectacular pyroxene-plagioclase symplectites around garnet, which indicate a stage of decompression. The application of TWQ to these rocks gave P-T data of 600 – 800 °C and 6 - 8 kbar. Electron-microprobe (EPMA) dating of monazite has been applied to two gneiss samples. The monazite grains vary strongly in shape and size and only some of them show zonation. Determined monazite ages range between 706-331 Ma with a strong predominance of Pan-African ages between 550 – 500 Ma. These data support the available geochronological data that the last major tectonic-thermal event in the SGT took place during the Pan-African orogeny (Meissner et al., 2002). Because of their different lithology it is not possible to link the monazite ages of with the P-T data from the metabasites. It therefore remains unclear if the P-T path recorded in the metabasites already formed during an archean event and were not subsequently overprinted during the Pan-African orogeny or if they can be correlated with the age data from the gneisses and thus reflect a Pan-African stage of high-grade metamorphism and decompression. We assume the textures inside the metabasites form during the archean and were preserved during the Pan-African event.

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Complex aluminum hydrides as potential solid-state hydrogen storage materials

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Hydrogen is considered as one of the most promising energy carriers for a future energy economy. Several technical approaches for storing hydrogen, e.g., in a high pressure tanks, are currently under evaluation. For technical reasons, the chemical storage in solids is one of the most promising strategies. In the past, intensive efforts have been invested in the investigation of alkali metal aluminum hydrides (e.g. NaAlH_4) and alkaline-earth aluminum hydrides (e.g. $\text{Mg}(\text{AlH}_4)_2$) as solid-state hydrogen storage materials. The crystal structures of the different complex aluminium hydrides as well as the specific dehydrogenation pathways, reversibility of hydrogen uptake and release, and thermodynamic properties have been intensively investigated.¹⁻⁴ The crystal structures of the aluminum hydrides are mostly built up by $[\text{AlH}_4]^-$ or $[\text{AlH}_6]^{3-}$ units. However, the variation of the connectivity of tetrahedra or octahedra by differently coordinated cations results in a broad diversity of crystal structures. X-ray powder diffraction investigations performed in situ during hydrogen release and hydrogen uptake have shown that complex decomposition processes associated with structural phase transformations take place.^{5,6} Monitoring the processes proceeding during hydrogen release by means of in situ diffraction shades light on the question why storage in a certain system is successful or not. Because of physical limitations, most of the conventional complex aluminum hydrides do not fulfil the requirements for reversible hydrogen storage. Research has been directed towards alternative complex hydrides, such as transition metal aluminum hydrides. Recently, novel types of complex rare-earth aluminum hydrides have been synthesized. The materials were characterized by refinement of structures predicted theoretically, investigation of structural details by solid state NMR techniques, and determination of the physicochemical properties.⁷ Calculation of thermodynamic data have indicated that these materials might be suitable for reversible hydrogen uptake under specific physical conditions.

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Timing and mineral evolution during low-temperature fluid-rock interaction on upper crustal level: an approach of $^{40}\text{Ar}/^{39}\text{Ar}$ apophyllite-(KF) dating, apatite fission track analysis and thermodynamic modeling on Alpine fissures

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The mineral assemblage quartz, laumontite and apophyllite-(KF) occur as museum quality specimen in a fissure within the Southern Aar granite, located in the south-eastern Aar Massif in the Central Swiss Alps. The fissure assemblages were found during excavation of the new Gotthard rail base tunnel (Gotthard NEAT) 2 km below the surface. The zeolites and apophyllite form as a result of water-rock interaction at relatively low temperatures (< 250°C) in the upper continental crust. The zeolites typically overgrow earlier formed minerals of the fissure assemblages in granite and gneiss. They were formed during the exhumation of the Alpine orogen and laumontite and apophyllite marks the latest fissure minerals in the Central Alps. A combined study of $^{40}\text{Ar}/^{39}\text{Ar}$ apophyllite-(KF) age dating, apatite fission track analysis of tunnel and surface samples of the Southern Aar granite and chemical characterization of the fissure sample are presented to carry out the position of low-temperature water-rock interaction in respect to the Alpine history.

The apatite fission track analysis yields an exhumation rate of 0.45 mm a^{-1} , whereas a cooling rate of $13 \text{ }^{\circ}\text{C Ma}^{-1}$ and a geothermal gradient of $28 \text{ }^{\circ}\text{C km}^{-1}$ can be calculated. Combining these with the $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age for apophyllite of 2 Ma, a minimum formation temperature and depth of 70 °C and 2800 m for apophyllite-(KF), respectively can be assumed. Temperature-time evolution of fissures in the Aar Massif and thermodynamic mineral evolution indicate that laumontite were formed between 7 and 2 Ma before present at temperatures between 150 and 70 °C.

Elements for laumontite formation were derived during dissolution of primary minerals (clinozoisite/epidote, albite and quartz). During laumontite growth, calcium decreases, whereas the contents of the sodium, potassium and barium increase as well as the Si/Al ratio from core to rim. Changes of laumontite chemistry could be an effect of temperature drop or a change in fluid chemistry that would be supported by later apophyllite formation. The formation of apophyllite-(KF) require a source for fluorine, which may be derived from biotite breakdown or during leaching of fissure fluorite.

Welchen Beitrag können die Staatlichen Geologischen Dienste zur Rohstofferkundung in Deutschland leisten?

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Die Gründung der Staatlichen Geologischen Dienste Deutschlands (SGD) im späten 19. und frühen 20. Jahrhundert geht im Kern auf die Einsicht zurück, dass nur durch die geologische Erforschung des Untergrundes die Rohstoffversorgung langfristig gesichert werden kann. Nach und nach sind aufgrund weiterer gesellschaftlicher und wirtschaftlicher Anforderungen viele andere Aufgaben hinzugekommen. Nach vielen Jahren des Personalabbaus und bei gleichzeitigem weiterem Aufgabenzuwachs können Mitarbeiter vieler Geologischer Dienste meist nur noch termingebundene Routinearbeiten z. B. als Träger öffentlicher Belange wahrnehmen. Können die Geologischen Dienste angesichts dieser Veränderungen heute überhaupt noch die Rohstofferkundung in Deutschland unterstützen, ihr vielleicht sogar wesentliche Impulse geben?

Die SGD haben Ende 2008 dem Bund-Länder-Ausschuss GEO eine Bestandsaufnahme zur Situation der fachlichen Rohstoffsicherung in Deutschland vorgelegt (Bericht publiziert unter: www.infogeo.de). Über die in dieser Bestandsaufnahme als erforderlich genannten Maßnahmen hinaus, die ohne Personal- und Sachmittelerhöhung nicht umzusetzen sind, gibt es Möglichkeiten, wertvolle Impulse und Hinweise für die industrielle Lagerstättenerkundung zu geben. Die möglichen Beiträge zur Rohstofferkundung in Deutschland seitens der SGD sind grundsätzlich drei Handlungsfeldern zuzuordnen:

- (1) Bereitstellung von umfangreichen Geodaten in analoger oder digitaler Form aus über 100 Jahren Landesaufnahme und gutachterlichen Tätigkeiten sowie fachliche Hilfestellungen bei der Vernetzung und Interpretation vorhandener Daten und Forschungsergebnisse.
- (2) Eigene Erkundungsmaßnahmen, Spezialkartierungen und Analytik im Vorfeld der Industrie.
- (3) Unterstützung bei der Ausbildung von Studenten in den angewandten Geowissenschaften. In allen Bereichen kann es zu vielfältigen Synergien zwischen SGD, Industrie und Hochschulen kommen.

Zu (1): Die von den Marktverhältnissen und wechselnden Strategien internationaler Konzerne abhängigen, meist kleinen Explorationseinheiten der Rohstoffkonzerne sind nicht in der Lage, die erforderlichen Geodaten in der zur Verfügung stehenden kurzen Zeit zu sammeln und auszuwerten. Sie benötigen hierfür die Unterstützung durch das Fachpersonal der SGD. Andererseits können die Erfahrungen aus anderen Gebieten der Erde und neue Techniken und Modelle der Rohstofffirmen bei der (Neu)Bewertung der vorhandenen Daten über die Landesgeologie helfen. Als Synergie können Lagerstättenmodelle leichter unter Nutzung der Datenauswertung aus verschiedenen Projekten der SGD heraus erstellt werden. Meist sind die Grundlagendaten dazu nicht oder nur teilweise veröffentlicht.

Zu (2): Die Geologischen Dienste können auch konkrete Hinweise auf lagerstättenhoffige Bereiche geben, da sie im Rahmen der Landesforschung oft neue Erkenntnisse zu Rohstoffvorkommen gewinnen und für ihre Geländearbeiten inkl. Bohrungen und Geophysik keine bergrechtlichen Konzessionen erforderlich sind. Angesichts knapper Landesmittel können Forschungsvereinbarungen und Drittmittelprojekte mit der Industrie bei der Realisierung von Bohrprogrammen helfen. Als Beispiel wird auf Erkundungsarbeiten im Schwarzwald eingegangen, die schon mehrfach – zuletzt im Jahr 2008 – wirtschaftlich interessante Mineralanreicherungen nachgewiesen haben (LGRB-Nachricht 7/2008).

Zu (3): In den vergangenen zwei Jahrzehnten ging der Anteil der Lagerstättenlehre an den deutschen Universitäten deutlich zurück, lagerstättenrelevante Diplom- und Doktorarbeiten wurden immer seltener. Durch die Bachelor- und Master-Studiengänge wird auch die Tiefe der Ausbildung eingeschränkt. Die engere Zusammenarbeit der Angewandten Geowissenschaften mit Firmen und SGD ist bei der Verbesserung der Kenntnisse der Studierenden sehr nützlich. Beispiele aus dem Bereich der Rohstoffsicherung auf Landesebene zeigen, dass bei einer häufigeren Einbindung von studentischen Arbeiten in aktuelle Untersuchungen der SGD beide Seiten profitieren können (Beispiele in: LGRB-Nachricht 8/2005). Gute angewandte Kenntnisse der Absolventen sind für Industrie und Landesdienste von großem Interesse. Den Studenten helfen derartige Kooperationen ganz wesentlich bei ihrer beruflichen Orientierung und bei der Verbesserung ihrer Chancen am Arbeitsmarkt.

X-ray spectroscopic techniques using synchrotron radiation for studying geomaterials

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In the last two decades, synchrotron radiation (SR) has become an indispensable tool for studying geomaterials using X-ray spectroscopic techniques. The continuous spectrum and the high brilliance produced by a SR source not only enable the acquisition of high quality spectral data in short time, but also provide the possibility to focus the SR beam into a small spot with a very high photon flux. Particularly the latter feature is a prerequisite for many applications in Earth sciences. In this contribution a sequence of examples using X-ray spectroscopic techniques is discussed, which highlight the versatile applicability to several fields in geological sciences.

One very important application in many studies is the determination of the oxidation state of Fe using the fine structure observed at the absorption edge (XANES). Particularly the pre-edge region provides an almost direct way of quantifying the oxidation state in many crystalline and non-crystalline compounds (Wilke et al. 2001), even with a spatial resolution that is similar to the chemical analysis with the electron micro-probe (e.g. Schmid et al. 2003, Kanngießer et al. 2004). XANES at the S K-edge may be used to study S-redox equilibria in melts (e.g. Wilke et al. 2008) or to characterize S phases in various types of samples (e.g. Fleet 2005). Time-resolved XANES may even be used to determine the progress and mechanism of redox reactions, e.g., in the case of oxidation of Mn(II) by bacteria (Bargar et al. 2000). Due to the rather low absorption of hard X-rays, SR opens up the possibility to perform measurements in high-pressure or reaction cells. For example Schmidt & Rickers (2003) and Schmidt et al. (2007) showed the great potential of SR micro-XRF for obtaining trace element concentrations in aqueous fluids in-situ at high P and T using an XRF-optimized diamond anvil cell, with detection limits in the lower ppm range. Such low detection limits may even be achieved for a low Z element such as Ti if an undulator SR source is used (Manning et al. 2008). A particular advantage over any quench technique is the possibility to study directly the kinetics of equilibration (Borchert et al. 2009). Furthermore, the high-pressure setup was used to investigate changes in the element complexation in aqueous fluids by acquiring X-ray absorption spectra at conditions of the Earth's crust as shown for the structural environment of REE in model fluid compositions (e.g., Mayanovic et al. 2009). XANES measurements on Fe in hydrous melt provide evidence for structural re-organizations in the Fe environment during the quench to a hydrous glass (Wilke et al. 2006), pointing out that differences in the coordination of Fe found for dry and hydrous glasses are likely to be related to the thermal history of the samples. Such data cannot be achieved on quenched samples at all and show the importance of these studies particularly for the understanding of processes at high P and T.

The soon dedication of PETRA III, the new German 3rd generation SR source for hard X-rays, will make sure that the conditions for such studies will improve and will certainly open up possibilities for new experiments to provide access to parameters not accessible so far.

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Untersuchung der Gefügeentwicklung bei β -stabilisierten γ -TiAl-Basislegierungen mittels Rasterelektronenmikroskopie (REM/EDX) und Hochtemperatur Röntgendiffraktometrie (HT XRD)

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Ziel dieser Untersuchungen war es, die für Leit- und Laufschaufeln in Hochdruckverdichtern und Niederdruckturbinen eingesetzten β -stabilisierten γ -TiAl-Basislegierungen mittels REM (elektronenoptisch) und XRD (phasenanalytisch) zu charakterisieren. Dabei standen verschiedene β -stabilisierte γ -TiAl-Basislegierungen, die sich in ihren Legierungselementen leicht unterscheiden, im *as cast* Zustand und im *wärmebehandelten* Zustand zur Verfügung.

Allgemeine Bemerkungen zu Hochtemperaturwerkstoffen

Basismetalle für Hochtemperaturwerkstoffe müssen einen Schmelzpunkt von mindestens 1400°C aufweisen, damit eine ausreichend hohe Langzeitkriechfestigkeit erreicht werden kann. Als Hochtemperaturlegierungen werden meist Nickelbasislegierungen eingesetzt, weil diese sehr hohen Temperaturen standhalten und über gute mechanische Eigenschaften verfügen. Nachteil dieser Legierungen ist aber, dass sie relativ schwer sind. Daher wird nach Hochtemperaturlegierungen gesucht, die leicht und temperaturstabil sind und außerdem noch über gute mechanische Eigenschaften verfügen. Üblicherweise werden die Titanlegierungen nicht zu den Hochtemperaturlegierungen gezählt, weil diese besonders aus Oxidationsgründen nur knapp die Temperatureinsatzgrenze von etwa 500°C überschreiten. Intermetallische Phasen auf der Basis von γ -TiAl und α_2 -Ti₃Al wären für höhere Temperaturen geeignet, stehen jedoch erst an der Schwelle zum großtechnischen Einsatz und müssen noch optimiert werden. Der Vorteil der β -stabilisierten γ -TiAl-Basislegierung liegt darin, dass diese ein sehr homogenes feinkörniges Gefüge besitzt, welches durch Wärmebehandlung gut eingestellt werden kann. Die β -Phase in den γ -TiAl-Basislegierungen führt dazu, dass diese Legierungen sich gut schmieden lassen. Außerdem besitzen diese Legierungen eine hohe Kriechfestigkeit. Der Herstellungsprozess dieser Legierungen folgt über die β -Phase.

Ergebnisse der Untersuchungen von β -stabilisierten γ -TiAl-Basislegierungen

Die Auflösung der β -Phase konnte anhand der durchgeführten Versuche bestätigt werden. Die β -Phase ist im *as cast* Zustand erwünscht, weil diese eine bessere Schmiedbarkeit der Bauteile zulässt. Diese Phase ist erst bei hohen Temperaturen unerwünscht, weil diese die Kriechbeständigkeit negativ beeinflusst. Die Untersuchungen der verschiedenen Legierungen im *as cast* Zustand und nach der Wärmebehandlung zeigten, dass die β -Phase durch eine optimierte Wärmebehandlung fast vollständig aufgelöst werden kann. Wie gut sich die β -Phase dadurch auflösen lässt, hängt von dem Mengenanteil an Molybdän ab, der in der Legierungszusammensetzung vorhanden ist. Je geringer dieser Anteil ist, desto leichter lässt sich die β -Phase auflösen. Mittels Hochtemperatur-XRD konnte bei den wärmebehandelten Proben geklärt werden, dass bei 800°C noch keine merkliche Phasenänderung stattfindet sondern erst bei 1200°C. Die wärmebehandelten Proben sind also bis 800°C thermisch stabil. Bei 800°C, die der maximalen Einsatztemperatur entspricht, sind Phasenneubildungen unerwünscht. Zwischen 800°C (= maximale Einsatztemperatur) und 1200°C (= Schmiedetemperatur) gibt es eine Umwandlungstemperatur, bei der die Phasenneubildung beginnt. Bei welcher Temperatur diese Umwandlung beginnt konnte mit diesen Versuchen nicht beantwortet werden. Dazu sind weitere Versuche notwendig. Die Umwandlungstemperatur bei der die Phasenneubildung beginnt kann beispielsweise mittels kontinuierlichem Aufheizen geklärt werden. Es konnte aber nicht festgestellt werden, wie diese neuen Phasen chemisch und kristallographisch aufgebaut sind. Es kann nur gesagt werden, dass die Kristallsysteme kubisch, tetragonal und hexagonal auch bei hohen Temperaturen bestehen bleiben und es sich auch um Ti-Mischkristalle handelt.

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Untersuchungen zum Einsatz von LDH's der Hydrotalcit-Gruppe als Zwischenspeicher für Nitrat im Boden

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Nitratauswaschung, insbesondere während des Winterhalbjahres ist eine Hauptursache für den Verlust von Stickstoff in der Pflanzenproduktion. Zur Vermeidung dieser Problematik ist die Eignung von Layered Double Hydroxides (LDH) vom Hydrotalcit-Typ, die als Anionenaustauscher bekannt sind, untersucht worden. Ziel ist die Entwicklung eines möglichst nitratspezifischen LDHs. Das Material muss eine hohe Speicherkapazität für Nitrat besitzen, über mehrere Wachstumsperioden im Boden wiederholt Nitrat einbauen und abgeben können und darf sich möglichst nicht zersetzen. Die Untersuchungen wurden mit Mg-Al-Nitrat- und -Chlorid-LDHs der allgemeinen Zusammensetzung $[Mg_{1-x}Al_x(OH)_2][A_x(H_2O)_n]$ ($A = NO_3, Cl$) mit verschiedenen Mg-Al-Verhältnissen durchgeführt.

Im Gegensatz zu anderen LDHs weisen Nitrat-Verbindungen mit wachsendem Al-Gehalt einen stark ansteigenden Basisabstand c' auf: von 8,07 Å bei Mg : Al = 6 ($x = 0,14$) bis 9,03 Å bei Mg : Al = 2 ($x = 0,33$) mit einem sehr steilen Anstieg um Mg : Al = 3 (s. Abb.). Dies hat erhebliche Auswirkungen auf den Anionenaustausch. In Austauschversuchen mit Einzel- und Multianionenlösungen höherer bis niedriger Konzentration und simulierten Bodenlösungen wurde der Einfluss von Carbonat (Hydrogencarbonat), Nitrat, Chlorid, Sulfat und Phosphat untersucht. Der für LDHs bekannte leichte Carbonateinbau zeigte sich auch hier, jedoch gibt es eine starke Abhängigkeit vom Basisabstand. LDH mit Mg : Al = 5 : 1 erwies sich als überraschend hoch nitratspezifisch. Unter Bodenverhältnissen kann ein Teil des Carbonats wiederholt gegen Nitrat ausgetauscht werden. Chlorid wird leicht durch Nitrat oder Carbonat verdrängt. Sulfat und Phosphat werden nicht in die Zwischenschicht eingebaut. LDH mit Mg : Al = 2 : 1 weist zwar eine niedrige Selektivität für Carbonat auf, jedoch wird Sulfat bevorzugt eingebaut und unter Bodenverhältnissen nicht mehr gegen Nitrat ausgetauscht. Ebenfalls ungeeignet wegen niedriger Nitratspezifität sind LDHs mit Mg : Al-Verhältnissen um 4 : 1 bis 3 : 1.

Bei den für den Einsatz im Boden geeigneten LDHs mit Mg : Al = 5 : 1 ($x = 0,17$) sind lediglich die Anionen Nitrat und Carbonat relevant. Durch den Ersatz von Nitrat durch Carbonat verringert sich hier der Basisabstand von etwa 8,15 Å für Nitrat-LDHs auf etwa 7,6 Å für Carbonat-LDHs, jedoch nicht linear. Selbst bis zu sehr hohen Carbonatgehalten von 0,99 $CO_3/(CO_3+NO_3)$ sinkt der Basisabstand nur langsam ab auf Werte um 8,03 Å. Die vereinzelt in der Zwischenschicht verbliebenen Nitrat-Anionen verhindern ein Absinken des Basisabstandes auf etwa 7,6 Å. Der für Carbonat-LDHs um etwa 0,4 Å zu hohe Wert erlaubt so unter Bodenverhältnissen einen wiederholten Austausch von Carbonat gegen Nitrat, wenn auch nicht in vollem Umfang. Solange der Basisabstand über etwa 8,0 Å liegt, ist das LDH im Boden als Nitratspeicher wirksam. Mit längerer Verweildauer im Boden sinkt jedoch der Anteil austauschbaren Carbonats. Der Basisabstand für die Carbonat-Nitrat-Mischkristalle ist bei den jeweiligen $CO_3/(CO_3+NO_3)$ -Verhältnissen pfadabhängig. Beim Anionenaustausch Carbonat / Nitrat ergeben sich ausgehend von einem Carbonat-LDH bzw. fast reinem Carbonat-LDH andere Werte als ausgehend von einem Nitrat-LDH. Dies hat erhebliche Auswirkungen auf die Austausch-Eigenschaften des LDHs im Boden, da auch bei starkem Nitratinbau der Basisabstand nicht mehr auf den ursprünglichen Wert ansteigt, sondern sich auf einem niedrigeren Wert einpendelt.

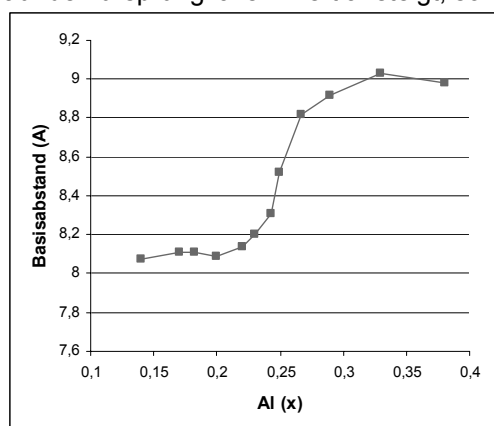


Abb. 1. Basisabstand c' in Mg-Al-Nitrat-LDHs in Abhängigkeit vom Al-Gehalt

Korrelation der saalezeitlichen Kiessande im südlichen Sachsen-Anhalt anhand von Schwermineraluntersuchungen

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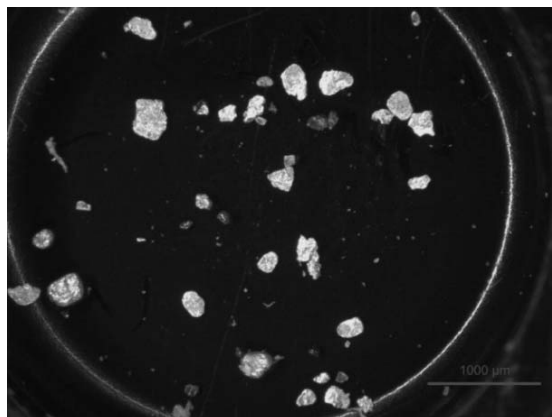
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Als Thema einer im Mai 2009 begonnenen Diplomarbeit werden die saalezeitlichen Kiessande der Hauptterrasse der Saale zwischen Merseburg, Weißenfels und Naumburg auf ihren kompletten Schwermineralinhalt hin untersucht. Die Schwermineralanalysen werden im Wesentlichen für die Fragestellung eingesetzt, die die Unterscheidung und Zuordnung fluviatiler Komplexe im südlichen Sachsen-Anhalt ermöglichen soll, mit dem Ziel für die Hauptterrasse der Saale eine Verfeinerung der Stratigraphie zu erzielen und Stoffeinträge, Umlagerungen sowie Sedimentationspfade der Schwerminerale zu rekonstruieren. Ebenso werden wirtschaftlich potenziell relevante Schwerminerale erstmals komplett für dieses Gebiet erfasst, hier vor allem das über die Saale und ihre Nebenflüsse transportierte Gold aus dem Thüringer Schiefergebirge.

Zur Lösung dieser Aufgabenstellung wurden bzw. werden Kiesgruben mit Nass- sowie Trockenabbau beprobt. In diesen Kiesgruben werden, belegt durch stratigraphische Profile und Geröllanalysen, mit einer relativen Sicherheit die Kiessande der Saale-Hauptterrasse abgebaut. Die Schwermineraluntersuchungen werden an bisher 20 Proben vorgenommen, deren Ausgangsmaterial direkt aus den Abbauwänden stammt bzw. von Abscheidungsmaterial das bei der Aufbereitung an den Kieswäschen oder Schöpfrädern anfällt. Die Aufkonzentration der Schwerminerale erfolgt durch waschen des Ausgangsmaterials in der Waschrinne und Pfanne, gefolgt von einer Schwereretrennung mit Bromoform (2,89 g/cm³). Die zu untersuchende Fraktion liegt im Bereich zwischen 0,063µm – 0,5µm.

Die Analyse des Schwermineralkonzentrates erfolgt durch optische Auswertung mittels Durchlichtmikroskopie. Für die weitergehenden Untersuchungen der Schwerminerale erfolgen Messungen mittels REM sowie der Auswertungssoftware MLA (Mineral Liberation Analysis). Zur Untersuchung mit der MLA, erfolgt eine Abtrennung der magnetischen Fraktion (überwiegend Magnetit) aus dem Konzentrat. Für diese abgetrennte Fraktion wird eine Untersuchung mit der XRD angestrebt. Durch makroskopische Untersuchungen im Feld und ersten Ergebnissen der Durchlichtmikroskopie (6 Proben) können erste vorsichtige Aussagen getroffen werden: Das Schwermineralspektrum wird mengenmäßig dominiert von Ilmenit, Zirkon und stellenweise Magnetit. Die von Müller et al. (1988) beschriebene Epidotvornacht in den Sedimenten der Saale-Hauptterrasse bestätigen sich bis zum jetzigen Zeitpunkt der Analysen nicht. Darüber hinaus tritt das ganze Spektrum von instabilen und stabilen Schwermineralen auf. Gold ist als Wertmineral an allen Probepunkten gefunden worden, die Konzentrationen sind allerdings minimal.



Separierte Goldflitter/-staub (Wallendorf)

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Kinetics of Solution of Yttria Stabilized Zirconia (YSZ) in Molten Chloride Salts at Medium Temperatures

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Thin layers of yttria stabilized zirconia (YSZ) with the high hot corrosion resistance have been widely used for protection of the steel of the vessel tubes in municipal solid waste incinerators (MSWI) (Spiegel, 2002). Usually YSZ is not directly coated on the vessel tubes but on an interlayer of a Ni-Cr-alloy-coating due to the big differences of the thermal expansion coefficient between the steel and the ceramic.

In order to in situ investigate the kinetics of solution of YSZ in molten chlorides system KCl-ZnCl₂-CrCl₂/CrCl₃ at 400-700 °C and different nitrogen-hydrogen chloride atmospheres a thin ceramic layer (30-50 µm) of YSZ was coated on the inside of quartz glass with the atmosphere plasma spraying (APS) method. Furthermore, a special apparatus with a corrosive gas system was created (Ishitsuka et al., 2000), with which the concentrations of HCl can be controlled.

The influence of the hydrogen chloride concentrations in the gas system and the concentrations of CrCl₂/CrCl₃ in molten salts on the solubility of the ceramic was investigated. The data of the solubility are very important for the recrystallization of YSZ. The first data indicated that Cr²⁺ species is a very strong reductive agent and in the case of oxygen existence the O²⁻ ions will be introduced in the molten salts, which results in the ceramic precipitation and recrystallization. The concentrations of the concerned elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) and flame atomic absorption spectrometry (FAAS).

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Detailed P-T-t Paths - new methods – new challenges

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Over the last ten years progress in theoretical petrology and the development of new techniques for geochronology and textural analyses have opened a wide door, enabling modern geoscientists to infer more and more detailed information about the evolution of metamorphic rocks through time – known as P-T-t paths – and in the end, to set more and more tight constraints on geotectonic processes which affected Earth's crust during the past. The first big step forward was the development of methods for the construction of quantitative phase diagrams – known as P-T pseudosections - for very complex compositional systems. These methods now enable geoscientists to constrain (very) detailed P-T paths for nearly all kinds of metamorphic rocks by comparison between observed (thin section) and calculated (P-T pseudosection) parameters comprising: (1) mineral assemblages, (2) mineral modes, and (3) mineral compositions. Nevertheless, applying the “phase diagram method” to natural rocks has important limits, which can result from effects like fractionation, diversification, and kinetics. A second important step forward was the development of new techniques for *in-situ* isotope analyses (e.g., SHRIMP or LA-ICP-MS), which help geoscientists to constrain the timing of their inferred P-T evolutions more and more precisely, but also to understand the dynamics in the formation and alteration of accessory minerals used for geochronology. Examples for this will be provided and some problems related to the interpretation of combined petrological and geochronological data sets from polymetamorphic gneiss terranes will be discussed. The detailed analysis of rock textures, e.g. by micro-CT (or some other techniques), provides another important tool. Even though not widely used by geoscientists at the moment, it has the potential to provide important information about the process and timing of mineral nucleation and growth, about ripening and reaction processes. Examples which illustrate the power of the different techniques will be provided for rocks from the Limpopo Belt, the Moine Supergroup, and the Ruhla Crystalline Complex.

Electronic and magnetic structure of pyroxenes II. Orthoferrosilite

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The electronic and magnetic structure of the chain silicate orthoferrosilite $\text{Fe}^{2+}_2\text{Si}_2\text{O}_6$ has been investigated by electronic structure calculations in the local spin density approximation. All calculations are based on experimentally determined geometrical data at room temperature. The calculated spin-allowed $d-d$ excitation energies and hyperfine parameters are in quantitative agreement with the respective experimental data from optical absorption and Mössbauer spectroscopy. Inside one ribbon that is parallel to the crystallographic c -axis and contains two non-equivalent M1 and M2 sites, all iron spins are ferromagnetically coupled with coupling constants of about $+16 \text{ cm}^{-1}$. Between these ribbons within the (b,c) -plane a weak ferromagnetic coupling of about $+2 \text{ cm}^{-1}$ is obtained. Neighbouring (b,c) -planes are coupled antiferromagnetically via chains of Si^B -tetrahedra but ferromagnetically via chains of Si^A -tetrahedra. This theoretically determined "double-plane antiferromagnetic" spin structure is at variance with an experimentally derived magnetic structure. This discrepancy is attributed to differences between the room temperature structure and the currently not available geometry at temperatures below the Néel temperature.

Exkursionen / Excursions

Kupferschiefer zwischen Halle und Harz – Mineralogie, Geologie, Geschichte

GERHARD H. BACHMANN, KLAUS STEDINGK, MARTIN TREU & THOMAS WITZKE
mit Beiträgen von RALPH BRAUMANN

Mit 10 Abbildungen

Fahrtroute: Halle (Saale) – Eisleben – Ahlsdorf – Helbra – Mansfeld – Hettstedt – Halle (Saale).
Top. Karten/Geol. Karten: Geol. Übersichtskarte 200: CC 4734 Leipzig; TK 100: C 4734 Halle (Saale),
C 4334 Bernburg (Saale); TK 25 /GK 25: 4334 Leimbach, 4335 Hettstedt, 4434 Mansfeld, 4435
Eisleben

Vorwort

Das Mansfelder Land zwischen Halle und Harz ist das Typusgebiet des mitteleuropäischen Perms, das aus den beiden Gruppen Rotliegend und Zechstein besteht. Beide Begriffe wurden von Bergleuten im Mansfelder Land geprägt, welche hier etwa ab dem Jahr 1200 das Kupferschieferflöz abgebaut haben. Jahrhundertlang war die Region eines der bedeutendsten Bergbau- und Hüttengebiete Deutschlands. 1969 wurde die Förderung in der Mansfelder Mulde eingestellt, 1990 im Sangerhäuser Revier. Zusammenfassende Beschreibungen der Stratigraphie, der Regionalgeologie und des Bergbaus findet sich in der „Geologie von Sachsen-Anhalt“ (BACHMANN et al. 2008).

Diese Exkursion hat das Ziel geologische, mineralogische, historische und kulturgeschichtliche Fakten und Ereignisse um den historischen Kupferschieferbergbau und MARTIN LUTHER aufzuzeigen und interdisziplinär zu verbinden.

Schichtenfolge

Rotliegend

Der Begriff „Rotliegend“ (früher: „Rotliegendes“) entstand aus dem alten Mansfelder Bergmannsausdruck „Roths Todtes Liegendes“ für das rotgefärbte erzfreie Liegende des Kupferschieferflözes. Das Oberrotliegend wird im Raum Halle in Halle-, Hornburg- und Eisleben-Formation gegliedert (EHLING 2009). Lithologisch dominieren in der Eisleben-Formation Rotsedimente, die südlich der Linie Eisleben-Halle im Wesentlichen aus Konglomeraten („**Porphyrkonglomerat**“) bestehen. Nördlich davon gehen basale konglomeratischen Schüttungen nach oben in sandig-tonige Gesteine über („**Sandsteinschiefer**“). Die Mächtigkeit der Eisleben-Formation ist stärkeren Schwankungen unterworfen der Linie Wettin–Arten zieht sich am Nordrand des Saale-Beckens eine Schwelle hin, auf der sich die Mächtigkeit der Eisleben-Formation auf weniger als 5 m reduziert. Südlich dieser Schwelle werden im Raum Querfurt wieder bis 100 m erreicht. Nördlich der Schwelle greift die Sedimentation auf das Grundgebirge bis in die Subherzyne Mulde über, wo der Übergang in die Hannover-Formation erfolgt (CHR. SCHUBERT 2003), welche im Norddeutschen Becken bis 700 m mächtig werden kann (PLEIN 1995). Das Exkursionsgebiet liegt am Nordrand dieser Schwelle; die Eisleben-Formation ist hier nur etwa 20 m mächtig.

Über den Sandsteinschiefern folgt hier das „**Weissliegend**“, das früher zum Zechstein gestellt wurde (RADZINSKI 2009). Bei einer Auflagerung auf Rotliegend, wird dessen gelegentlich gebleichter oberster Teil auch als „**Grauliegend**“ bezeichnet. Das Weissliegend besteht aus fein- bis mittelkörnigen Sandsteinen, die teils als äolisches und anschließend z. T. aquatisch umgelagertes, teils als marines Sediment (Sandbarren) gedeutet werden. Besonders am Ostrand der Mansfeld-Mulde schwillt das Weissliegend gelegentlich zu langgestreckten, bis zu mehrere Meter mächtigen sog. „Flözbergen“ an, über denen der Kupferschiefer ausdünn (MEINECKE 1910). Nach Übereinkunft werden Weissliegend bzw. das grobkörnige Zechstein-Konglomerat lithostratigraphisch ins höchste Oberrotliegend eingeordnet, denn in den Logs von Bohrungen lässt sich zwar der Kupferschiefer als Gammastrahlen-Spitze leicht identifizieren, Weissliegend und Zechstein-Konglomerat dagegen nicht.

Lithostratigraphisch haben die Fazieskörper des Porphyrkonglomerats, Sandsteinschiefers und Weissliegend bzw. Zechsteinkonglomerat den Rang von Subformationen (Member) der Eisleben-Formation. Es ist jedoch auch möglich, die hochauflösende Gliederung der Hannover-Formation in mehrere zyklisch definierte Member (PLEIN 1995) auf diese Formation zu übertragen. Dabei stellt sich heraus, dass am südlichen Beckenrand die Eisleben-Formation nur die obersten Member der Hannover-Formation vertreten (ELLENBERG et al. 1976, CHR. SCHUBERT 2003).

Zechstein

Der Begriff „Zechstein“ wurde ebenfalls von den Mansfelder Bergleuten übernommen. Er bezog sich ursprünglich auf den obersten Teil des Zechsteinkalks, in dem die Kupferschiefer-Bergwerke (Zechen) angelegt waren, nach einer anderen Version auf das zähe Gestein des Zechsteinkalks (mundartlich: „zach“). Heute gilt die Bezeichnung Zechstein im lithostratigraphischen Sinne für die Schichten vom Kupferschiefer bis zur Untergrenze des Buntsandsteins (RADZINSKI 2009).

Der **Kupferschiefer** ist der erste durchgehend marine Horizont über dem Rotliegend an der Basis des Zechsteins. Es handelt sich um einen 0,3–0,6 m dicken feingeschichteten kohlig-bituminösen Mergelstein, der in etwa 200–300 m Wassertiefe unter euxinischen Bedingungen abgelagert wurde. Das Bodenwasser war weitgehend ohne O₂, mit H₂S verseucht, fast frei von Benthos, und vom überstehenden, durchlüfteten Wasser durch eine Sprungschicht (Chemokline) getrennt (ZIEGLER 1990). Das Oberflächenwasser bot z. B. Fischen günstige Lebensbedingungen. POMPECKJ (1914, 1920) postulierte als Erster dieses „Stagnationsmodell“ und verglich die Ablagerungsbedingungen mit dem heutigen Schwarzen Meer (lat.: *pontus euxinos*). Einen umfassenden Überblick gibt PAUL (2006).

Der Kupferschiefer wird nach alter Überlieferung vom Liegenden zum Hangenden in „Feine Lette“, „Grobe Lette“, „Kammschale“, „Schieferkopf“ und „Schwarze Berge“ gegliedert. Die einzelnen Lagen unterscheiden sich nach Aussehen, Erz- und Kohlenstoffgehalt, Härte und Gefüge. Wegen der Verwitterung sind Übertage-Aufschlüsse im Kupferschiefer relativ selten.

Der Kupferschiefer ist eine bedeutende Fossilagerstätte, mit zum Teil zusammenhängenden Fischskeletten sowie Pflanzen- und Saurierresten. Bisher wurden 4 Arten Wirbellose, 17 Fisch- und 18 Pflanzenarten sicher bestimmt (BRANDT 1997, 1999). In großer Zahl treten Fische auf, vor allem im unteren Teil, und oft in vererzter Erhaltung. Typisch, und mit etwa 90 % am häufigsten, ist der meist 10–20 cm große ganoidschuppige Knochenfisch *Palaeoniscus freieslebeni* (früher *Palaeoniscus f.*), im Volksmund auch „Kupferschieferhering“ genannt. Eine umfangreiche Fossiliensammlung befindet sich in den Geowissenschaftlichen Sammlungen der Universität Halle. Nähere Ausführungen und weitere Literatur finden sich bei WEIGELT (1928), HAUBOLD & SCHAUMBERG (1985) und BRANDT (1997, 1999). Der Kupferschiefer ist auch wissenschaftsgeschichtlich bedeutsam, weil seine Fischreste erstmals von LUTHER in seiner Genesis-Vorlesung von 1535–1545 und AGRICOLA (1546: 371) als Reste früherer Lebewesen erkannt wurden (FREYDANK 1939, BRANDT 1999). Ein Kupferschieferfisch in MÜNSTERS „Cosmographie“ von 1550 gilt als die älteste gedruckte Abbildung eines Fossils.

Kupferschiefer-Bergbau und -Genese wurden von STEDINGK (2008) ausführlich beschrieben, dem nachstehender Text folgt. Der Bergbau nahm von Hettstedt aus seinen Anfang, wo der Überlieferung nach zwei Bergleute aus Goslar namens Nappian und Neucke um 1200 das Flöz entdeckt haben (NEUSS 2001). Bis in die Mitte des 19. Jh. blieb die erzeugte Metallmenge vergleichsweise gering. Erst die Einführung moderner Technik, insbesondere von Dampfmaschinen (seit 1785) und Elektrifizierung (seit 1905), ermöglichte die vollständige Nutzung des Lagerstättenpotenzials und brachte den Revieren Mansfeld und Sangerhausen die Spitzenstellung in der Silber- und Kupferproduktion Mitteleuropas. Von erheblicher wirtschaftlicher Bedeutung war ebenfalls die Erzeugung von Zink, Blei und untergeordnet Molybdän, Kobalt, Gold, Selen und anderen Elementen. Erst spät wurden lokal auch interessante Gehalte an Platingruppen-Elementen festgestellt (KUCHA 1990). 1969 wurde die Förderung in der Mansfelder Mulde eingestellt, 1990 im Sangerhäuser Revier. Über die Geschichte des Berg- und Hüttenwesens in beiden Revieren berichten ausführlich JANKOWSKI (1987, 1988, 1996), HARTWIG et al. (1999), ROLOFF (1999) und ROMMEL (1999). Einen guten Überblick gibt die „Geologisch-montanhistorische Karte der Reviere Mansfeld und Sangerhausen 1 : 50 000“ (STEDINGK & RAPPSILBER 2000). PAUL (2006) behandelt die Entstehung des Kupferschiefers.

Die regionale strukturelle Kontrolle der Kupfererzführung im Grenzbereich Saxothuringikum / Rhenoharzynikum (Mitteleuropäische Kristallzone – Variszische Sutur – Nördliche Phyllitzone) ist seit langem bekannt (JUNG et al. 1971, RENTZSCH & FRANZKE 1997). Die Anreicherungen und Lagerstätten erstrecken sich von Richelsdorf in Hessen (MESSER 1955), über das südöstliche Harzvorland, nach Südbrandenburg, die Niederlausitz und Niederschlesien und werden als „Mitteleuropäischer Kupfergürtel“ bezeichnet.

Die Bildung der Mineralisation vom Typ Kupferschiefer ist an die Hauptabsenkung des Mitteleuropäischen Beckens zwischen dem höheren Oberrotliegend und Buntsandstein gebunden. Die Sulfidmineralisation an der Zechsteinbasis erfolgte polystadial und lässt sich in die Stadien (a) Syngeneese, (b) Frühdiagenese, (c) Spätdiagenese und (d) Epigenese untergliedern.

(a) Nach der Ingression des Zechsteinmeeres wurden im Zusammenhang mit der Ablagerung des sapropelitischen Kupferschiefers in der H₂S-Zone Pyrit und Spuren von Buntmetallsulfiden gebildet (Syngeneese).

(b) Im Zusammenhang mit der schnellen Absenkung des Zechsteinbeckens kam es dann zum strukturell kontrollierten Aufstieg von Formationswässern aus den unterlagernden permiosilesischen vulkano-sedimentären Einheiten und von Fluiden des Grundgebirges (sog. „Basement-Brines“; BORG 1991). Die mineralisierenden Lösungen waren schwach sauer und reduzierend. Kontrolliert wurde dieses Hydrothermalsystem durch tiefreichende NNE-SSW und NNW-SSE streichende Störungssysteme und mehrfache Wechsel der hydraulischen Regime (sog. „seismisches Pumpen“). Die Lösungen waren Zn-dominiert und enthielten vermutlich ähnliche Metallkonzentrationen, wie sie aus rezenten Thermalwässern bekannt sind (WEDEPOHL & RENTZSCH 2006). Es ist davon auszugehen, dass komplexe Lösungs-Mischungsvorgänge und die Generierung von Sulfidschwefel durch thermochemische Sulfatreduktion (durch Kohlenwasserstoffe) zur fraktionierten Ausfällung der Sulfide führten. An der H₂S-Barriere der frisch abgelagerten Tonmergelsteine („Proto-Kupferschiefer“) wurden um die Lösungsaufstiegszentren herum zonal Cu-Fe-, Pb-, Zn- und weitere Fe-Sulfide gefällt. Die weiträumige regionale Zonalität dieses wichtigsten Mineralisationsstadiums ist nur bei frühdiagenetischer lateraler Lösungsmigration im Kupferschiefer mit noch hohem Porenwassergehalt möglich (Frühdiagenese).

(c) In einzelnen Regionen, die seit dem höheren Oberrotliegend relative Hebungsgebiete darstellen und wo in den Sedimenten an der Zechsteinbasis (Kupferschiefer, Weißliegend) eine erhöhte Sedimentationsenergie und Fossilreichtum nachweisbar sind, stiegen strukturell kontrolliert O₂-haltige Na-Ca-Cl-Fluide mit unterschiedlichen Buntmetallkonzentrationen auf. Im Zuge ihrer lateralen Ausbreitung an der Zechsteinbasis oxidierten sie den in der Umgebung der o. g. Gebiete mit Flachwasserfazies (z. B. Sandbarren) den frühdiagenetisch mineralisierten Kupferschiefer unter Bildung der Roten Fäule. Diese laterale diagenetische Ausdehnung der Roten Fäule führte zum diskordanten Auftreten der „Kupfer-Silber-Reicherzkörper“ in der erzführenden Zone (Spätdiagenese; RENTZSCH & THIERGÄRTNER 1972).

(d) Die an postvariszische Störungen gebundenen Gangmineralisationen („Mansfelder Rücken“) und mit Kupfer angereicherte Metasomatose-Zonen im Bereich der Zechsteinbasis gehören dem mesozoischen Mineralisationszyklus an. Diese epigenetischen Mineralisationen führten zu lokalen Umlagerungen und Anreicherungen in der erzführenden Zone, die jedoch das regionale Bild der Mineralisation an der Zechsteinbasis nicht beeinflussten (Epigenese).

Nachdem alle Befunde eine Syngenese der Hauptmineralisation ausschließen und eine mehrphasige Stoffzufuhr bzw. massive Mobilisation und Wiederausfällung der Wertmetalle nachgewiesen sind, stellt sich die Frage nach dem Alter dieser Stoffumsetzungen. Paläomagnetische Altersbestimmungen am Hämatit der Roten Fäule ergaben 250–220 Ma (JOWETT et al. 1987). K-Ar-Altersbestimmungen an den diagenetisch gebildeten Illiten des Kupferschiefers der polnischen Lagerstätten führten zu Modellaltern von 256–239 Ma (BECHTEL et al. 1996). Re/Os-Datierungen an Mineralseparaten der Bohrung Lengefeld 17/61 erbrachten Alter von 225±5 Ma (BRAUNS et al. 2003). Diese Ergebnisse untermauern das vorgelegte Genesemodell. Gleiche Alter ergeben neuere Datierungen für die Quarz-Sulfid Hauptphase im Unterharz (SCHNEIDER et al. 2005). Die Übereinstimmung deutet auf die Existenz eines überregional wirksamen Fluidsystems hin, dem ein erheblicher Teil der mitteleuropäischen Buntmetallagerstätten seine Herkunft verdankt (STEDINGK 2002).

Kupferschiefer-Mineralie der Mansfeld- und Sangerhausen-Mulde

Kupferschiefer-Mineralie im engeren Sinne

Die Erzmineralisation des Kupferschiefers liegt überwiegend in sehr fein verteilter Form vor mit Korngrößen von 0,01–0,1 mm; nur sporadisch treten Aggregate bis über 1 mm auf. Daneben finden sich schichtparallele Erzlineale, größere bohnenförmige Anreicherungen (sog. „Erzhielen“), dünne Bleche und massivere Imprägnationen (speziell im unmittelbaren Liegenden des Kupferschiefers).

Die Entstehung der Erzlineale untersuchte JOWETT (1987) an polnischen Kupferschiefer-Lagerstätten. Danach sind im Tertiär zunächst kleine Spalten durch hydrostatischen Druck unter zusätzlicher Mitwirkung von aus dem Kupferschiefer freigesetzten Gasen aufgerissen. Aus zirkulierenden metallführenden Lösungen und der Reduktion von Sulfat-Ionen zu Sulfid durch organische Substanzen kam es zur Ausfällung der Metallsulfide in den Spalten.

Gelegentlich finden sich auch durch Chalcopyrit oder Silber mineralisierte fossile Fischreste.

Die wichtigsten und häufigsten Sulfidminerale im Kupferschiefer sind Bornit (Cu₅FeS₄), Chalcopyrit (CuFeS₂), Chalcosin (Cu₂S), Galenit (PbS), Sphalerit (ZnS), Pyrit und Markasit (FeS₂). Wo rotfarbene Basissedimente des Zechsteins vorhanden sind (Rote Fäule), fehlen Buntmetallsulfide weitgehend und es tritt Hämatit auf (FREESE & JUNG 1965, RENTZSCH & KNITZSCHKE 1968). Weiterhin in

der Literatur erwähnt werden (KNITZSCHKE 1965) Covellin (CuS), Digenit (Cu_9S_5), Enargit (Cu_3AsS_4), Idait (Cu_3FeS_4), Magnetit (Fe_3O_4), Silber, Stromeyerit (AgCuS) und Tennantit ($\text{Cu}_3\text{AsS}_{3,25}$). Für einen Teil dieser Minerale fehlen jedoch sichere analytische Belege. Neuere Untersuchungen hierzu liegen nicht vor. An welche Phasen die Platinmetalle gebunden sind, ist nicht bekannt.

Minerale der Rückenvererzungen

Bei den Rückenvererzungen („Mansfelder Rücken“) handelt es sich um Gangmineralisationen, die an postvariszische Störungen gebunden sind und meist nur zwischen den versetzten Kupferschiefer-Flözteilen erzführend sind. Nur selten setzt sich die Erzmineralisation bis in das Liegende (Rotliegend) oder Hangende (Zechsteinkalk, Werraanhydrit) fort. GERLACH (1995) unterscheidet vier Abfolgen. Die Mineralisation beginnt mit Ankerit/Calcit, Hämatit und Spuren von Pyrit. Es schließt sich eine Calcit-Anhydrit-Sulfid-Abfolge mit Chalcosin, Bornit, Chalcopyrit, Galenit, Sphalerit und Matrkasit an. In der dritten Abfolge werden Baryt, Calcit und Arsenide (Maucherit, Nickel, Rammelsbergit) abgeschieden sowie Molybdänit und Uraninit. Die jüngste Abfolge enthält Calcit und silberführenden Chalcosin.

Die Rückenvererzungen hatten eine gewisse wirtschaftliche Bedeutung; auf Grund des sporadischen Auftretens und der geringen Reichweite war jedoch kein kontinuierlicher Bergbau darauf möglich. Ab 1775 wurden Co-Erze aus den Rückenvererzungen zur Produktion von Smalte zur Verwendung in der schlesischen Leinenindustrie und für blaue Farben in der Porzellanindustrie gewonnen, ab Mitte des 19. Jahrhunderts auch Ni-Erze zur Herstellung von Neusilber (Cu-Ni-Zn -Legierung). Von 1949–1952 erfolgte im Auftrag der SAG Wismut eine Prospektion auf Uranerze auf den Rückenvererzungen. Die Arbeiten wurden jedoch eingestellt, da sich die Uraninit-Vorkommen als nicht bauwürdig erwiesen.

Eine Neuuntersuchung von „Kupferglanz“- (Chalcosin) Proben zeigte (SIEMROTH & WITZKE 1999), dass der eigentliche Chalcosin (Cu_2S) nicht so häufig wie angenommen unter den Kupfersulfiden der Rücken vorkommt, während Digenit (Cu_9S_5), Djurleit ($\text{Cu}_{31}\text{S}_{16}$) und Anilit (Cu_7S_4) recht verbreitet sind. Später ließ sich auch noch der weltweit nur von sehr wenigen Fundorten bekannte Roxbyit (Cu_9S_5) nachweisen.

Acanthit	Coelestin	Markasit	Silber
Anhydrit	Coffinit	Maucherit	Sphalerit
Anilit	Covellin	Millerit	Stromeyerit
Baryt	Digenit	Molybdänit	Uraninit
Betekhtinit	Djurleit	Nickelin	Wismut
Bornit	Dolomit	Pyrit	Spionkopit ?
Calcit	Fluorit	Quarz	Yarrowit ?
Chalcosin	Galenit	Rammelsbergit	
Chalcopyrit	Hämatit	Roxbyit	
Cobaltit	Jalpait	Safflorit	

Tab. 1: Minerale der Rückenvererzungen

Sekundärminerale aus dem Kupferschiefer

Die in vielen anderen Lagerstätten erfolgte Anreicherung von Metallen in der Oxidations- und Zementationszone ist aus den Mansfelder und Sangerhäuser Revieren kaum bekannt. Eine Zementationszone hat sich nicht ausgebildet und am Ausstreichen des Kupferschieferflözes ist der Schiefer gegenüber frischem Material noch an Kupfer verarmt. Lediglich auf sog. Lettenlagern hat überwiegend im 18. Jh. ein lokaler Bergbau stattgefunden. Hier konnten Azurit-Malachit-Konkretionen, z.T. mit sulfidischen Relikten im Kern, durch Waschen angereichert werden (SIEMROTH & WITZKE 1999).

Die Verwitterung des Kupferschiefers auf den Halden und Untertage führt zur Neubildung zahlreicher Minerale. Sehr verbreitet ist Gips, der sich in kleinen Kristallen auf der Oberfläche und Rissen von Schieferstücken findet. Bekannt sind die Reviere jedoch besonders für die bis dezimetergroßen, dickprismatischen Gipskristalle, die sich in wassergefüllten Schlotten im Werra-Anhydrit bilden. Dringen mit Gips gesättigte Wässer aus dem Hangenden in gut bewetterte Grubenbaue ein, kommt es auch hier zu Bildung von langprismatischen Gipskristallen. Untertage an

den Stößen kommt, neben Gips, auch sehr häufig Calcit vor. Durch Kupfer- und Cobaltgehalte sind die Calcitkrusten oft grün bis hellblau bzw. rosa bis violett gefärbt.

Verbreitete sekundäre Kupferminerale sind Brochantit und Malachit. Andere Minerale wie Langit, Devillin, Connellit, Cuprit, Chalcantit u.a. sind seltener. Trotz des hohen Zinkgehaltes im Kupferschiefer sind sekundäre Zinkminerale außerordentlich selten. Bekannt ist ein Einzelfund von Cu-haltigem Gordait (JAHN & WITZKE 1999). Erst vor kurzem konnte das Zink-Uranyl-Carbonat Znuclit nachgewiesen werden.

Mit Anglesit und Linarit sind zwei sekundäre Bleiminerale bekannt. Recht verbreitet in kleinen Ausblühungen auf Kupferschiefer ist das Cobaltmineral Erythrin. Bemerkenswert ist, dass mit Bromargyrit ein sekundäres Silbermineral vorkommt. Auch Uranminerale konnten als Verwitterungsbildungen beobachtet werden. Neben dem bereits erwähnten Znuclit sind Natriumzippeit und Schröckingerit nachgewiesen, Liebigit ist nicht sicher belegt.

Anglesit	Chalcantit	Halit	Smithsonit
Annabergit	Connellit	Kupfer	Tenorit
Azurit	Cuprit	Langit	Znuclit
Botallackit	Devillin	Linarit	Aragonit ?
Brochantit	Erythrin	Malachit	Atacamit ?
Bromargyrit	Gips	Natriumzippeit	Liebigit ?
Calcit	Gordait	Schröckingerit	

Tab. 2: Sekundärminerale aus dem Kupferschiefer

Minerale aus Schlacken

Die Verhüttung des Kupferschiefers ist entsprechend der Anzahl der gewonnenen Metalle sehr komplex. Im Hauptprozess der Kupfergewinnung wurde der Kupferschiefer zunächst in Schachtöfen auf sulfidischen Kupferstein verschmolzen, der 35–45 % Cu enthielt. Bei diesem Prozess fielen pro eingesetzter Tonne Kupferschiefer etwa 720 kg Schlacken an. Weiterhin entstand metallisches Eisen, die sog. „Eisensau“, mit Gehalten von weniger als 0,1 % an Mo, Ni, Co und anderen Metallen. Der anfallende Flugstaub wurde nass abgeschieden (Theisenschlamm), eingedickt und zum Teil auf Blei und Zink weiter verarbeitet. Der Kupferstein aus dem Schachtöfen wurde in der Bessemerie wieder eingeschmolzen und in Konvertern oxydierend auf Schwarzkupfer mit 98 % Cu verblasen. Die hier entstehenden Schlacken gingen im Wesentlichen als Zuschlag in die Rohschmelze zurück. Das Schwarzkupfer wurde erneut eingeschmolzen, zu Anoden gegossen und gelangte in die Elektrolyse, wo Elektrolytkupfer mit mindestens 99,95 % Cu erzeugt wurde. Der Anodenschlamm wurde auf Ag, Au, Pd, Pt und Se verarbeitet (WITZKE & PÖLLMANN 1996, EISENHUTH & KAUTZSCH 1954).

Die Schlacken der Kupferschieferverhüttung bestehen im Wesentlichen aus Glas und Eisen-, Mangan-, Zink- und Calciumsilikaten. Unter den Silikaten dominieren Pyroxene (Diopsid), daneben sind Fayalit, Willemite, Hardystonit und Äkermanit anzutreffen. Die Schlacke weist eine durchschnittliche Zusammensetzung von 46–49 % SiO₂, 17–21 % CaO, 16–19 % Al₂O₃, 5–9 % MgO, 3–5 % K₂O + Na₂O und 3–5 % FeO auf (EISENHUTH & KAUTZSCH 1954). Aus der flüssigen Schlacke wurden zahlreiche Produkte hergestellt, darunter die bekannten „Mansfelder Schlackensteine“, welche weithin als Straßenpflaster Verwendung fanden und bis Holland zum Deichbau exportiert wurden (EISENÄCHER 2002).

Die Kupfer- und Zinkgehalte liegen bei 0,2 %, die Blei-gehalte bei 0,02 %. In der dichten bis porösen Grundmasse finden sich eine Reihe von Sulfiden und Elementen, die zum Teil Relikte ursprünglich vorhandener Erzminerale, überwiegend aber Bildungen aus der Schmelze darstellen. Es handelt sich hier hauptsächlich um Chalcopyrit, Bornit, Sphalerit und Kupfer. Häufiger anzutreffen sind auch Djurleit, Galenit und Blei. Nur selten wurden bisher Digenit, Messing und eine nicht mit Bronze identische Kupfer-Zinn-Legierung nachgewiesen (SIEMROTH & WITZKE 1999).

In einer frühen Phase nach der Erstarrung der Schlacken können sich in Hohlräumen feine Drähte von Kupfer und Silber bilden. Auch die Neubildung von Blei in kleinen Kristallen ist sehr selten beobachtet worden, während es in Tröpfchen in der Schlacke öfter vorkommt. Als sehr frühe Verwitterungsbildung unter niedrigen Eh-Werten sind der Grüne Rost (Fougerit), Nantokit und Cotunnit anzusehen.

Bei fortschreitender Verwitterung mit steigendem Eh-Wert bilden sich vorrangig Sulfate, Oxichloride und Oxide wie Atacamit, Clinoatacamit, Boleit, Lithargit, Spangolit, Anglesit, Antlerit, Lanarkit, Brianyoungit, Elyit, Ludlockit und andere. Zuerst gebildete Verwitterungsminerale wie das Cu^+ -Chlorid Nantokit werden oxidiert und in das Cu^{2+} -Hydroxid-Chlorid Clinoatacamit umgewandelt, der Grüne Rost oxidiert zu röntgenamorphen Eisenhydroxid, Cotunnit wird z. T. durch Anglesit oder Cerussit verdrängt. Ungewöhnlich ist das Auftreten des Kupfer-Selenits Chalcomenit in den Schlacken. Der Selengehalt im Kupferschiefer liegt nach HAMMER et al. (1990) zwischen 11,4 und 163 ppm. In der Schlacke könnte das Selen an Kupfersulfide wie Digenit gebunden sein und bei dessen Verwitterung mobil werden (WITZKE & PÖLLMANN 1996). In stark verwitterter Schlacke finden sich schließlich Carbonate wie Malachit, Aragonit und Monohydrocalcit.

Äkermanit	Digenit	Galenit	Sphalerit
Blei	Diopsid	Hardystonit	Willemit
Bornit	Djurleit	Kupfer	Cu-Sn-Phase
Chalcopyrit	Fayalit	Messing	

Tab. 3: Primären Phasen in Schlacken

Acanthit	Clinoatacamit	Ktenasit	Posnjakit
Anglesit	Connellit	Kupfer	Schwefel
Antlerit	Cotunnit	Lanarkit	Serpierit
Aragonit	Covellin	Langit	Silber
Atacamit	Cuprit	Linarit	Spangolit
Blei	Diaboleit	Lithargit	Tenorit
Boleit	Elyit	Ludlockit	Vivianit
Brianyoungit	Gips	Malachit	Zincit
Brochantit	Gordait	Massicotit	$\text{Pb}_4\text{O}_3(\text{SO}_4) \cdot \text{H}_2\text{O}$
Calcit	"Grüner Rost"	Monohydrocalcit	
Cerussit	Hydrocerussit	Namuwit	
Chalcomenit	Jarosit	Palmierit	

Tab. 4: Sekundärminerale aus Schlacken

Erstbeschreibungen von Mineralen

Die Mansfeld- und Sangerhausen-Mulde sind die Typusgebiete der Minerale Covellin, Digenit, Maucherit und Betekhtinit.

Covellin wurde erstmals von FREIESLEBEN (1815) als „Blaues Kupferglas“ von Sangerhausen beschrieben. Nach der indigoblauen Farbe nannte BREITHAUP (1818) das Mineral „Kupferindig“. 1832 wurde schließlich der Name Covellin eingeführt.

1844 beschrieb BREITHAUP (1815) das Mineral **Digenit** von Sangerhausen. Das Material stammt offenbar aus einer Rückenvererzung und fand sich zusammen mit „Kupferglanz“. Eine Lötrohranalyse wurde von PLATTNER durchgeführt, der feststellte, dass die Zusammensetzung zwischen der von „Kupferindig“ und „Kupferglanz“ liegt. Die von BREITHAUP aufgestellte Formel liegt dicht an der heute gültigen für Digenit (Cu_9S_5). Nach röntgenografischen und erzmikroskopischen Analysen tritt Digenit recht verbreitet in den Rückenvererzungen des Mansfelder und Sangerhäuser Kupferschiefers auf (SIEMROTH & WITZKE 1999).

Aus Co- und Ni-führenden Rückenvererzungen von Eisleben beschrieb GRÜNLING 1913 das neue Mineral **Maucherit**, ein Nickel-Arsenid mit der Zusammensetzung $\text{Ni}_{11}\text{As}_8$. Es fand sich hier in rötlich-silberweißen, an der Luft dunkler werdenden Massen und kleinen, tafeligen Kristallen zusammen mit Baryt, Nickelin, Wismut und anderen. GRÜNLING benannte das Mineral nach Wilhelm MAUCHER (1879–1930), dem Inhaber der Süddeutschen Mineralienzentrale, der es zuerst bemerkt und nach Lötrohruntersuchungen ein neues Mineral vermutet hatte.

Auf Material aus einer Rückenvererzung vom Vitzthumschacht von Volkstedt bei Mansfeld konnte ein im Auflicht unter dem Erzmikroskop weißgelbes bis cremegelbes Mineral in enger Verwachsung mit Bornit, Galenit und Silber entdeckt werden, das zunächst für Wittichenit, Emplektit oder Bornit gehalten wurde. Die Röntgenpulverdaten zeigten jedoch keine Ähnlichkeiten zu den Daten dieser Minerale. Der Fund weiterer Proben im Fortschrittschacht erlaubte umfangreichere Untersuchungen. Das Mineral bildete hier nadelige Kristalle bis maximal 2 cm Länge. Die chemische Analyse zeigte, dass es sich bei den Nadeln um ein neues Blei-Kupfer-Sulfid handelt (SCHÜLLER & WOHLMANN 1955). Es weist die Zusammensetzung $\text{Pb}_2(\text{Cu,Fe})_{21}\text{S}_{15}$ auf. Das neue Mineral wurde nach dem bekannten sowjetischen Mineralogen Anatoli Georgievich BETECHTIN (1897–1962) benannt. International hat sich die Schreibweise **Betekhtinit** durchgesetzt.

Martin Luther

„So bin ich zu Eisleben geboren, zu Mansfeld erzogen, ..., und nun Doktor zu Wittenberg“.

MARTIN LUTHER (1520)

Das Mansfelder Land gehört zum mitteldeutschen Ursprungsgebiet der Reformation, wo MARTIN LUTHER (*1483–1546) gelebt und gewirkt hat. In der Kleinstadt Eisleben wurde er geboren als der erste Sohn von HANS LUDER und dessen Frau MARGARETE und dort starb er auch. Aufgewachsen ist er in Mansfeld selbst, wo sich der tüchtige Vater zielstrebig zum wohlhabenden Bergwerks- und Hüttenbesitzer empor gearbeitet hat.

MARTIN LUTHERS charismatische Persönlichkeit, sein Lebenswerk, seine Sprachgewalt, seine schroffe Derbheit, sind ohne das Wissen um den familiären Hintergrund im Mansfelder Bergbau kaum zu verstehen. Der Vater wollte ihm ein Jura-Studium in Erfurt ermöglichen. Er aber fühlte sich zum Mönch berufen und studierte Theologie. Die neu gegründete Universität zu Wittenberg berief den vielversprechenden jungen Augustinermönch zum Professor für Theologie. Von Wittenberg ging seine Reformation des christlichen Glaubens aus, ein Ereignis welches wie wenige andere die Geschichte Deutschlands, Europas und der Welt bis zum heutigen Tage beeinflusst hat.

Exkursion

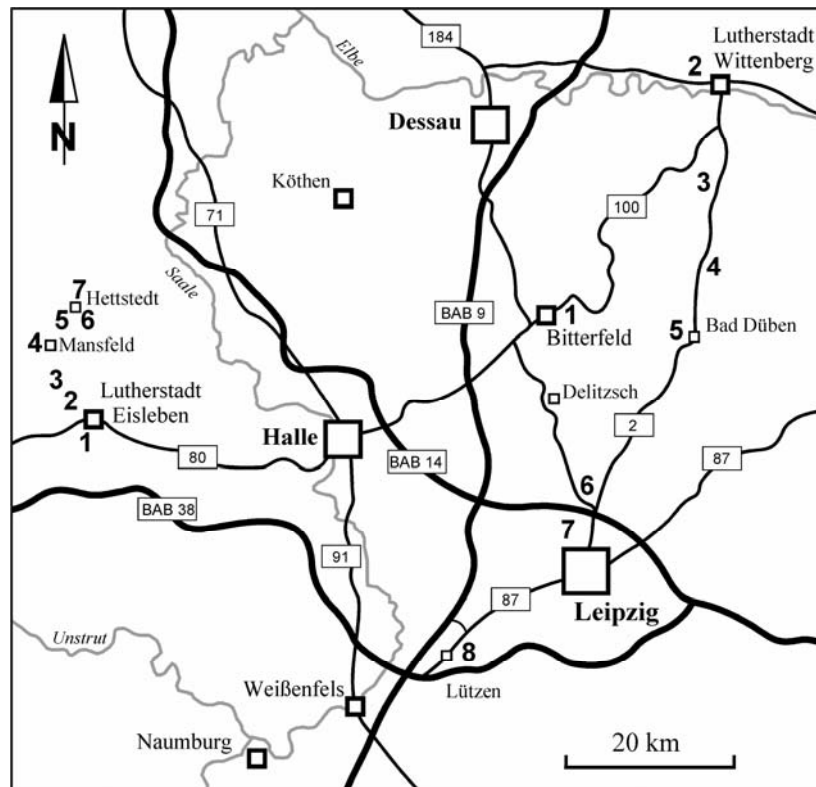


Abb. 1: Routenskizze mit Haltepunkten. Exkursion „Kupferschiefer“ westlich von Halle, Exkursion „Luther“ östlich von Halle.

Fahrt Halle – Eisleben

Die Exkursion führt von Halle aus in westlicher Richtung auf der Bundesstraße B 80 zur 30 km entfernten Lutherstadt Eisleben (Abb. 1). Geologisch gehört das Exkursionsgebiet zur Mansfeld-Mulde (Abb. 5), deren Kern hier vom Buntsandstein und Muschelkalk eingenommen wird. Darüber können noch mehr oder weniger mächtiges Tertiär und Quartär folgen. Zwischen Halle-Neustadt und Bennstedt gibt es mehrere alte Steinbrüche im Unteren Muschelkalk, der hier in der Nietlebener Spezialmulde erhalten geblieben ist. Weiter nach Westen heben sich Oberer, Mittlerer und schließlich Unterer Buntsandstein heraus.

Weithin sichtbar ist die 80 m hohe Abraumhalde des ehemaligen *Kalibergwerks Krügershall* bei Teutschenthal. Im Bereich des Teutschenthaler Salzkissens (Teutschenthal-Sattel) wurde hier 1905–1962 das Kaliflöz Staßfurt abgebaut (Exk. Halde Teuschenthal). Weitere Kalischächte befanden sich in der Umgebung. Zwischen der Halde und der B 80 hat sich die sogenannte *Binnensalzstelle Teutschenthal* (NSG) entwickelt, eine Art Sabkha mit Ausscheidung von Gips, Mirabilit (Glaubersalz) und Steinsalz sowie einer reichen Halophyten-Flora. Daneben stehen in einer Tongrube Rupeltone an, die teilweise kaolonitisiert sind. Nach der Kreuzung Wansleben verläuft die B 80 auf dem Boden des ehemaligen *Salzigen Sees*, der eine lange, Ost-West gestreckte Subrosionssenke einnahm. Der See musste 1894 trocken gelegt werden, weil sein Wasser über Karstverbindungen in die Kupferschieferbergwerke bei Eisleben eindrang. Südlich des Salzigen Sees befindet sich in der Randmulde des Teutschenthaler Salzkissens das Tertiärbecken von Oberröblingen mit dem *Tagelbau Amsdorf*. Dort wird bitumenreiche mitteleozäne Braunkohle gewonnen und weiter zu „Montanwachs“ verarbeitet.

Der *Süße See*, das „Blaue Auge der Grafschaft Mansfeld“, befindet sich ebenfalls in einer langgestreckten Subrosionssenke. Auf einer Halbinsel am Ostende befindet sich *Burg Seeburg*, eine der größten Befestigungen Mitteldeutschlands mit Bauten der Romanik, Gotik und Renaissance. Diese Anlage war 1300 Jahre lang das politische Zentrum des historischen Hosgaus zwischen Saale und Harz.

Das Gebiet um den Süßen See liegt im Regenschatten des Harzes und ist mit rund 450 mm Niederschlag eines der trockensten in Deutschland. Das ausgeglichene Klima begünstigt Obst- und Weinbau. Bei *Höhnstedt* befindet sich das nördlichste geschlossene Anbaugebiet von Qualitätsweinen der Saale-Unstrut-Region.

H e l f t a liegt in einer weiten, noch aktiven Subrosionssenke in nordwestlicher Verlängerung des Salzigen Sees. Das Zisterzienserinnen-Kloster Helfta wurde bekannt für seine Beiträge zur mittelalterlichen Frauenbildung und religiösen Mystik. Wie fast alle Klöster des Mansfelder Landes wurde es im Bauernkrieg geplündert, zerstört und später aufgelöst. Seit 1990 wird das Kloster wieder aufgebaut und von Ordensfrauen genutzt.

Südlich von Helfta und Eisleben trennt der NNW-SSE verlaufende H o r n b u r g - S a t t e l die Mansfeld-Mulde von der Sangerhausen-Mulde (Abb. 5). An seinen Flanken hebt subrodierter Zechstein mit dem Kupferschiefer heraus. Der Sattelnkern wird von der Hornburg- und Eisleben-Formation des Rotliegend gebildet.

Literatur: EISOLD & LAUTSCH (1992), FRIEDRICH & FRÜHAUF (2002), HEROLD & STROBEL (19999, JANKOWSKI (1988), MENNE & BERGER (2002), OELKE (2002), RICHTER (2001), ULE (1891), WÖHLBIER (2000)



Abb. 2: Eisleben. Markt, Lutherdenkmal, Rathaus, St. Andreaskirche. Foto: BACHMANN 1995.

Lutherstadt Eisleben

Eisleben war bis ins 20. Jh. ein wichtiges Zentrum von Kupferschieferbergbau und -verhüttung. Das Abbaugelände „Eisleber Berg“ erstreckte sich südlich und westlich der Stadt von Neckendorf bis Ziegelrode. Die Stadt stand unter der Hoheit der Grafen von Mansfeld, bevor sie nach dem Westfälischen Frieden 1648 zu Preussen kam. Von Anfang des 13. Jh. bis 1676 hatte Eisleben eine Münzstätte (Haus Münzgasse 10). Im Stadtschloss Hinterort, Markt 58, war von 1571 bis 1861 der Sitz des Bergamtes. Seit 1852 war hier der zentrale Verwaltungssitz der „Kupferschiefer bauenden Gewerkschaft Mansfeld“, dann der Mansfeld AG, und nach 1945 des Mansfeld-Kombinats. Die traditionsreiche Eisleber Bergschule bestand von 1798 bis 1993.

Eisleben steht auf subrosionsgefährdetem Untergrund. Ab 1892 kam es vor allem am Südwestrand der Altstadt zu bedrohlichen Senkungen bis zu mehreren Metern, welche zu schweren Gebäudeverlusten führten. Auch der Ostteil der Stadt steht in einer weiten Subrosionssenke in streichender Fortsetzung des Süßen Sees. Dort befand sich der im 12./13. Jh. trockengelegte Faulige See. Die Absenkungen im Stadtgebiet halten in geringem Umfang bis heute an.

Besonders berühmt ist Eisleben als Geburts- und Sterbeort von MARTIN LUTHER (*1483–1546). Der Name „Lutherstadt“ wurde 1946 zum 400. Todestag des Reformators verliehen.

Literatur: EISOLD & LAUTSCH (1992), HEROLD & STROBEL (1999), MELLER (2008), SLOTTA & RIEDEL in ROLOFF (1999), SCHLENKER et al. (1998), STEDINGK & RAPPSILBER (2000), STEFFENS (2002)

Halt 1a: Eisleben, Luthers Geburtshaus (UNESCO-Weltkulturerbe)

Im Sommer 1483 wohnte das junge Ehepaar HANS und MARGARETHE LUTHER einige Wochen in Eisleben in dem Haus in der heutigen Lutherstraße 16. HANS LUDER, wie er sich nannte, war der nicht erberechtigte Sohn eines wohlhabenden Bauern in Möhra/Thüringen. Im aufblühenden Kupferschieferbergbau wollte er für sich und seine Familie eine Existenz aufbauen. Ihr erster Sohn wurde am 10. November 1483 hier geboren und am nächsten Tag in nahen **Pfarrkirche St. Peter und Paul** auf den Namen des Tagesheiligen „Martin“ getauft. Wahrscheinlich hatten seine Eltern das Haus nur zum Teil gemietet. Traditionell gilt die kleine Kammer hinter der Stube als Geburtszimmer des Reformators. Kurz nach der Geburt zog die junge Familie weiter nach Mansfeld, wo sie festen Wohnsitz fanden und HANS LUTHER eine bessere Anstellung als Bergmann erhielt. Das originale Geburtshaus blieb beim Stadtbrand von 1601 unversehrt, brannte allerdings 1689 bei einem weiteren großen Stadtbrand nieder. MATTHES in MELLER (2008) berichtet ausführlich über archäologische Befunde. Nach dem Brand eignete sich die Stadt Eisleben das Grundstück an und ließ 1693 das heutige „Geburtshaus“ errichten, in dem traditionell die kleine Kammer hinter der Stube als Geburtszimmer des Reformators gilt. Heute dienen Haus und Nebengebäude als Gedenkstätte und Museum. Die umfangreiche Ausstellung zeigt unter anderem die um 1290 entstandenen Original-Konsolfiguren der beiden legendären Entdecker des Kupferschieferflözes Nappian und Neucke (Abb. 6).

Halt 1b: Eisleben, Markt

Der Markt bildet ein geschlossenes architektonisches Ensemble. Durch die Hanglage ergibt sich eine eindrucksvolle Staffelung von Lutherdenkmal, Rathaus und der alles überragenden St. Andreaskirche (Abb. 2).

Der Sockel des 1883 eingeweihten **Lutherdenkmals** ist aus schwedischem Granit. LUTHERS überlebensgroßes Standbild ist in Bronze aus Mansfelder Kupfer gegossen. Im linken Arm hält der Reformator die Heilige Schrift, mit der rechten Hand zerknüllt er die Bannbulle von Papst Leo X.

Das **Rathaus** stammt aus dem 16. Jh. und wurde 1910 umgebaut. Die ehemaligen **Stadtschlösser** der gräflichen Familien Mansfeld-Vorderort und Mansfeld-Hinterort stehen links vom Rathaus (Markt 56 und 58). Der ehemalige Stadtsitz der Familie Mansfeld-Mittelort befindet sich unterhalb des Marktes (Markt 34).

Halt 1c: Eisleben, Stadtkirche St. Andreas, Museum „Luthers Sterbehaus“

Die den Marktplatz Eislebens architektonisch beherrschende **St. Andreaskirche** wurde 1276 erstmals urkundlich erwähnt. In der ersten Hälfte des 15. Jh. wurde sie zu einer das Stadtbild prägenden dreischiffigen gotischen Hallenkirche umgebaut. Das Patronat lag beim Bischof von Halberstadt, während der Reformationszeit also bei LUTHERS Gegner Erzbischof Albrecht von Magdeburg, welcher gleichzeitig Administrator von Halberstadt und Erzbischof von Mainz war.

Nach der Reformierung Eislebens wurde die Kirche sowohl von den beiden evangelischen Linien der gräflich-mansfeldischen Familie, als auch von der katholisch gebliebenen Linie gemeinsam genutzt. Graf Hoyer von Mansfeld-Vorderort veranlasste, dass sein Hofprediger Georg Witzel die traditionelle Messe las, sehr zum Missfallen LUTHERS und auch der meisten Bürger der Stadt. Das Grabmahl Hoyers befindet sich noch heute in der Kirche. Auf der Kanzel hielt Luther kurz vor seinem Tod im Februar 1546 seine letzte Predigt. Gleichzeitig ordinierte er zum letzten Mal Geistliche für die Mansfelder Kirche.

LUTHER weilte Anfang 1546 in Eisleben, um eine Erbstreitigkeit in der gräflichen Familie zu schlichten. Er starb am 18. Februar in des „4. Graven Brunen Haus“, wo heute das Hotel „Graf von Mansfeld“ steht (Markt 56). Das Haus gehörte Luthers Freund Dr. Drachstedt, dessen Familie ein weiteres Haus neben der St. Andreaskirche besaß. Im 17. Jh. kam es zur Verwechslung beider Häuser. Der preussische Fiskus übernahm irrtümlich das Haus neben der St. Andreaskirche als künftige Gedenkstätte, das heutige **Museum „Luthers Sterbehaus“** (UNESCO-Weltkulturerbe).

In der Sangerhäuser Straße, oberhalb der Andreaskirche, steht der figurenreiche **Knappe Brunen**, dahinter befindet sich das ehemalige Katharinenstift, das 1817–44 als **Bergschule** diente. Die sogenannte **Eislebener Neustadt** im Westen der Altstadt wurde 1511 von Graf Albrecht VII. von Mansfeld-Hinterort als Bergmannssiedlung gegründet. „**Kamern Martin**“, eine farbige kniende Bergmannsfigur mit geschulterter Keilhau und dem Wappen von Mansfeld-

Hinterort, wurde um 1590 aufgestellt und ist das Symbol der Bergstadt und des Mansfelder Bergbaus überhaupt. Dieses älteste profane Denkmal eines Bergmanns in Deutschland steht gegenüber dem ehemaligen Neustädter Rathaus am Breiten Weg.

Fahrt Eisleben – Wimmelburg – Hergisdorf – Ahlsdorf

Die Weiterfahrt in westlicher Richtung folgt dem Tal des Flüsschens „Böse Sieben“, zunächst auf der B 80 nach Wimmelburg. Ab Wimmelburg verläuft das Tal ungefähr an der Grenze vom Unteren Buntsandstein zum Zechstein, der hier nach Westen gegen den Harz zu heraushebt (Abb. 5). Das schmale Tal mit den sog. „Grunddörfern“ und seine Umgebung ist durch eine Vielzahl von Kupferschiefer- und Schlackenhalden gekennzeichnet, darunter die gewaltige Schlackenhalde der ehemaligen Karl-Liebnecht-Hütte (Krughütte).

Literatur: JANKOWSKI (1987), ROLOFF (1999, 2004)

Halt 2a: Eisleben, Schlackenhalde der ehem. Karl-Liebnecht-Hütte (Krughütte)

(TK/GK25 4434 Mansfeld, R: 44 66 700, H: 57 10 150)

Zufahrt: Von der B 80, kurz vor dem östlichen Ortsende von Eisleben an der Gaststätte „An der Krughütte“ rechts (N) bergauf zum Gelände der großen Schlackenhalde. Dieses ist eingezäunt, Zutrittsgenehmigung ist erforderlich.

EISENÄCHER (2002) beschreibt ausführlich die Entwicklung dieser ersten Großhütte. Sie war 1870–1972 in Betrieb und verhüttete zunächst vor allem das Erz der nahen Großförderanlagen Ottoschächte, Martinschächte und Segengottesschächte (Otto-Helm-Schächte). Benannt wurde sie nach Oberberghauptmann Krug v. Nidda (1810–1885), welcher seit 1860 Leiter des preußischen Berg- und Hüttenwesens war; umbenannt wurde sie 1950. Die charakteristische und oft fotografierte Silhouette der Hütte mit der (wegen hoher Baukosten) so genannten „Millionenbrücke“ stand und steht symbolhaft für das Mansfelder Hüttenwesen. 1976 entstand auf dem Betriebsgelände durch Subrosion ein großer Senkungskessel von 150 m Durchmesser und 15 m Tiefe.

Von der Hütte geblieben sind, außer einigen wenigen Gebäuderesten, mehrere gewaltige Schlackehalden, die im Laufe der langen Betriebszeit nach und nach entstanden sind. An den Schlackehalden sind, besonders an steilen Hängen, deutlich die Fließstrukturen zu erkennen, die durch das Abkippen der flüssigen Schlacke aus Loren entstanden sind. Dieses Material zeigt nach dem Erstarren bizarre, zum Teil an Stricklava erinnernde Oberflächenstrukturen. Es weist einen hohen Glasanteil und zahlreiche Poren auf. Dauerte es durch Verzögerungen im Betriebsablauf zu lange bis zum Abkippen der Schlacke, so begann sie schon in den Loren von außen nach innen zu erstarren. In diesem Fällen mussten die Lorenfüllungen als große Blöcke abgekippt werden, welche ebenfalls auf der Halde zu sehen sind. Durch die langsame Abkühlung weisen sie im Inneren größere Hohlräume mit Fayalit- und Pyroxen-Kristallen auf.

Bedingt durch die niedrigen Metallgehalte in den Schlacken der jüngeren Betriebsperiode, sind Sekundärminerale hier nicht sehr verbreitet. Bevorzugt sind sie in sehr porösem Material anzutreffen, während sie in der dichten, glasreichen Schlacke fast völlig fehlen.

Literatur: ROLOFF (1999, 2004), <http://kupferspuren.artwork-agentur.de>

Halt 2b: Wimmelburg, Lutherhalde „vorm Beerbaum“ (optional)

(TK/GK25 4434 Mansfeld, R: 44 64 410, H: 57 10 685)

Zufahrt: Von der Hauptstraße am nördlichen Ortsende Wimmelburg links (westlich) ab in die Straße Oberdorf – Max-Lademann-Straße – Goldgrund, vorbei an der Ruine der „Neuen Hütte“, auf einem Fahrweg bis zum letzten Einzelhaus. Hinter diesem liegt die Halde rechts des Wegs.

Die kleine Schlackenhalde der Hütte „vorm Beerbaum“ liegt im Goldgrund nordwestlich von Wimmelburg. Sie stammt aus den Jahren 1495–1509 und ist eines der letzten Sachzeugnisse von HANS LUTHERS Tätigkeit als Hüttenmeister. Die Schmelzhütte auf der linken Seite des Goldbachs hatte ein bis zwei „Feuer“ (Schmelzöfen) und lag wie alle Hütten an einem Wasserlauf. Mit Mühlrädern wurden Blasebälge angetrieben, die den zur Verhüttung nötigen Wind lieferten. Die Schlacken selbst bestehen aus glasartigem Schmelzfluss mit schlierigen dunkelblauen, blaugrauen und grünlichgrauen Farben.

100 m weiter, rechts des Goldbachs, sind die Reste einer weiteren Lutherhalde zu finden, welche von der Hütte „zum Rodichen“ mit ihren zwei Feuern stammen.

Der Historiker FREYDANK (1939) konnte HANS LUTHER bei Mansfeld und Großörner weitere Halden der Hütten „vorm Raben“, „auf der Wiesen“ und „bei der Mühle“ zuweisen, die aber inzwischen

abgegangen sind. Darüber hinaus benennt er zahlreiche Schächte zwischen Wimmelburg und Mansfeld, an denen HANS LUTHER beteiligt war.

Für die bergrechtliche Verfassung des Mansfelder Landes war bezeichnend, dass nicht die Inhaber der Bergwerke maßgebend waren, sondern die Hüttenmeister (FREYDANK 1939). „*Wer die Zumessung von Teilen auf dem Berge verlangte, mußte in der Lage sein, die gewonnenen Minern selber zu verhütten ...*“. HANS LUTHER dürfte schon um 1501 mehrere Hütten gepachtet haben. Mit dem Ertrag von zwei Feuern hat er seinen Sohn MARTIN an der Universität zu Erfurt studieren lassen.

Die eigentliche Wertschöpfung, d. h. die Erzeugung von marktfähigem Kupfer und Silber, geschah ausschließlich durch die Verhüttung der Erze (Minern). Montanarchäologische Befunde zeigen, dass es erst an der Wende vom 12. zum 13. Jh. gelang, wirtschaftlich Kupfer und Silber aus dem dispers mineralisierten und schwer schmelzbaren Kupferschiefer zu gewinnen (EISENÄCHER 2002). Noch bis in die jüngste Vergangenheit stellte die Verhüttung von Kupferschiefer die Ingenieure vor erhebliche Probleme (EISENÄCHER et al. 1999, HEBESTEDT 2002). Der entscheidende Schritt, die Trennung des Silbers vom Kupfer, erfolgte im sog. Seigerverfahren, das technisch in dieser Form vom frühen 15. Jh. bis weit in das 19. Jh. zur Anwendung kam (Abb. 3). Dieser komplexe Hüttenprozess, welcher die Phasenübergänge zur Gewinnung eines silberreichen Werkbleis nutzte, setzte schon damals erhebliche technische Kenntnisse voraus und war wegen seines hohen Aufwands, besonders dem Verbrauch großer Mengen von Holzkohle, Blei und anderen Materialien, recht kostenintensiv (EISENÄCHER 1998). Im Vergleich zu den zuvor im Mittelalter angewandten Verfahren war die Seigerung dennoch ein bedeutender technologischer Fortschritt, der die wirtschaftliche Verarbeitung auch ärmerer Erze zuließ und zu Beginn der frühen Neuzeit einen starken Aufschwung des Montanwesens nach sich zog.



Der Ofen zum Verschmelzen der Schlacken A. Der Ofen zum Legieren von Kupfer mit Blei B. Tür C. Der in die Erde eingelassene Spurtiegel D. Kupferne Form E. Das Streichholz F. Der Haken G. Das gesplattene Holz H. Der Ausleger des Kranes I; sein Kettenhaken K.

Abb. 3: Inneres einer Seigerhütte (AGRICOLA 1556) mit den beiden Schachtöfen (A, B) und Vortiegeln (D). Im linken Ofen erfolgte das Verbleien und dadurch die Entsilberung des Kupfers.

Halt 3a: Ahlsdorf, ehem. Steinbruch am „Schafberg“, Kupferschiefer
(TK/GK25 4434 Mansfeld, R: 44 62 570, H: 57 12 080)

Zufahrt: Von der Hauptstraße in Ahlsdorf nach Westen in die Grundstraße, Bärenstraße, dann an den letzten Häusern halbrechts auf einem Fußweg zum Waldrand bis kurz vor die Bahnlinie.

In einem ehemaligen Steinbruch am westlichen Ortsrand (aufgelassen 1857), eines der besten Kupferschieferprofile im Gebiet aufgeschlossen (vgl. Abb. 9).

- Werra-Sulfat (Residuen, „Untere Aschen“), oberhalb des Steinbruchs im Wäldchen	
> 4 m Zechsteinkalk, plattig	
0,3 m Kupferschiefer	Zechstein (Werra-Formation)
<hr/>	
0,35 m Weißliegend-Sandstein	Rotliegend (Eisleben-Formation)
> 1 m (Sandsteinschiefer)	

Am Hang unterhalb des ehem. Steinbruchs treten Bänke der tieferen Eisleben-Formation (Porphyrokonglomerat) aus.

Literatur: KAISER (2001: 26), KARPE (1995: Nr. 59, 1999), SCHRÖDER et al. (1933)

Unausgelaugt ist der Werra-Anhydrit hier ca. 50 m mächtig, das Werra-Steinsalz ca. 10 m. Die Residuen („Untere Aschen“) erreichen ca. 25 m.

Der Zechsteinkalk wird bis 8 m mächtig und kann (von oben) in a) bankigen bis plattigen „Zechstein“, b) dünnplattige bis schieferige „Fäule“ und c) „Dachklotz“ gegliedert werden.

Der Kupferschiefer lässt sich im Raum Mansfeld in mehrere Lagen gliedern, welche sich gesamten Ablagerungsgebiet zu drei weiträumig parallelisierbaren Ton-Mergel-Kleinzyklen zusammenfassen lassen, von oben nach unten:

3. Zyklus: „Dachklotz“ des Zechsteinkalks (ca. 20 cm)
„Schwarze Berge“ (13–15 cm)
2. Zyklus: „Grauer und Schwarzer Kopf“ (10–12 cm)
„Kammschale“ (3–4 cm)
1. Zyklus: „Grobe Lette“ (5–6 cm)
„Feine Lette“ (3–4 cm)

Nur in den drei untersten Lagen ist ein schmelzwürdiger Erzgehalt vorhanden, auf Grund dessen er abgebaut wurde. Die Untergrenze Zechstein ist an der Basis des Kupferschiefers definiert.

Das „Weißliegend“ ist generell 0–ca. 1 m (max. 10 m) mächtig und meist aus feinem, z. T. grobem Quarzsand. In grober Ausbildung wird es auch als „Zechsteinkonglomerat“ bezeichnet.

Die Eisleben-Formation des Rotliegend wird hier etwa 20 m mächtig und besteht (von oben) aus ca. 8 m Sandsteinschiefer, einer Wechsellagerung von rotbraunen Sand- und Tonsiltsteinen, und ca. 12 m Porphyrokonglomerat aus dickbankigen Sandsteinen und Konglomeraten. Sie überlagert mit einer schwachen Winkeldiskordanz die Hornburg-Formation (Rundkörniger Sandstein, Quarzitkonglomerat). Gut aufgeschlossen ist dieser Bereich westlich von Hergisdorf im Kliebigsbachtal und im Bahneinschnitt Blankenheim (GÄRTNER 1997, KARPE 1995: Geotop 59; 1999: Geotope 4434/6, 4435/5, LÜTZNER 1988).

Fahrt Helbra – Mansfeld

Die Fahrt verläuft im Grenzbereich Zechstein/Unterer Buntsandstein. In der Stadt Helbra war bis zur Schließung 1990 ein wichtiges Zentrum der Kupferschieferverhüttung. Weithin sichtbar ist die große Schlackenhalde der ehemaligen August-Bebel-Hütte (Kochhütte) zwischen Ahlsdorf und Helbra.

Halt 3b: Helbra, Schlackenhalde der ehem. August-Bebel-Hütte (Kochhütte, optional) (TK/GK25 4434 Mansfeld)

Zufahrt: Von der Str. Helbra–Wimmelburg am Ortsende von Helbra rechts (W) am Schmidtschacht bergauf zum Gelände der großen Schlackenhalde. Diese ist eingezäunt, Zutritts-genehmigung ist erforderlich.

Die Kochhütte wurde 1879/80 mit zunächst 5 Schachtöfen errichtet. Wie auf allen Mansfelder Rohhütten wurde der Kupferschiefer zunächst auf Brennplätzen gebrannt, weil der enthaltene Kohlenstoff beim Schmelzprozess erhebliche Schwierigkeiten bereitet hätte. Das Brennen erforderte aber mehr Arbeiter als der Schmelzbetrieb selbst. Zudem verursachten die entweichenden Rauchgase erhebliche Gesundheitsprobleme und Umweltschäden. Erst nach dem 1. Weltkrieg wurde ungebranntes Roherz verschmolzen. Rohschlacke war ein wichtiges Nebenprodukt des Schmelzprozesses. Die Produktion von Schlackensteinen wurde auf der Kochhütte schon 1881 aufgenommen; sie erfuhr nach 1920 einen enormen Aufschwung und übertraf schließlich bei weitem den Geldwert der Silberproduktion. Nach dem 2. Weltkrieg waren auf der August-Bebel-Hütte, wie sie nun genannt wurde, 9–10 Öfen in Betrieb. Die unzureichende Ausrüstung dieser Anlagen verursachte

jedoch über die Abgase enorme Umweltbelastungen und auch hohe Kupferverluste. Am 10. September 1990 wurden die beiden letzten noch verbliebenen Öfen ausgeblasen und der Hüttenbetrieb eingestellt. Derzeit erinnert nur noch die gewaltige Schlackenhalde daran, dass hier einmal ein metallurgischer Großbetrieb stand.

Auf der Schlackehalde der Rohhütte Helbra wurden große Mengen von stark Zink-haltigem Theisenschlamm abgelagert. Regenwässer haben das Material in der Halde verteilt und Zink freigesetzt. Aus der Halde entspringt eine Quelle, der sogenannte Stadtborn, mit Mischwasser aus einer überbauten Quelle und Regenwasser. Das Stadtborn-Wasser enthielt bis 3500 ppm Zn (Schreck, 1996), durch die Beräumung der Deponie sank die Zinkbelastung. Am Stadtborn fällt aus dem Wasser das Zink-Aluminium-Hydroxid-Sulfat-Hydrat Glaucozerinit aus, eine LDH-Struktur. Die Aluminiumkomponente dürfte durch Auslaugung aus den Schlacken freigesetzt werden. Bei Trockenheit entwässert das Material zu Zincoewoodwardit. Durch die Glaucozerinit-Fällung erfolgt eine Reduzierung der Zn-, Cu- und Al-Gehalte im Haldenwasser um 5 – 15 % auf einer Fließstrecke von 50 Metern (WITZKE 1997). Fällungsexperimente haben gezeigt, dass durch weitere Zugabe von Al in Lösung und leichter Erhöhung des pH-Wertes eine effektive und praktisch vollständige Entfernung von Zn und anderen Metallen aus dem Wasser erreicht werden kann (SCHRECK et al. 2000).

Literatur: EISENÄCHER (2002), ROLOFF (1999, 2004)

Halt 4: Mansfeld (optional)

„Danach ... ist mein Vater gen Mansfeld gezogen, und daselbst ein Berghauer geworden; daher bin ich.“

MARTIN LUTHER

Die Stadt Mansfeld liegt zwischen zwei Tälern auf tieferer Hornburg-Formation. Unter dem Rotliegend hebt nach Westen die Grillenberg-Formation (Stefan C) heraus, welche ihrerseits im Ostharz der Wippra-Zone des variszischen Grundgebirges aufliegt (Abb. 5). Östlich der Stadt erhebt sich der steile Schloßberg aus Hornburg- und Eisleben Formation. Gleich jenseits des Schlosses streicht der Kupferschiefer aus. Die Hochfläche selbst wird vom Zechstein und Unteren Buntsandstein eingenommen. Das Revier „Mansfelder Berg“ erstreckte sich von Ziegelrode bis Burgörner.

Schloß Mansfeld war der Stammsitz der Mansfelder Grafen. Nach der Erbteilung von 1501 in die Linien Vorder-, Mittel- und Hinterort errichtete jeder Graf einen repräsentativen Wohnbau. Ab 1517 wurde das Schloß zu einer der mächtigsten Festungen in Deutschland ausgebaut, die auch im Dreißigjährigen Krieg nie eingenommen wurde. In den Jahren 1674/75 wurde sie auf Drängen der Städte und Stände weitgehend geschleift. Erhalten sind Schloß Vorderort und die reich ausgestattete gotische Schloßkirche, die zu den schönsten ihrer Art zählt. LUTHER hat hier wahrscheinlich mehrmals gepredigt. Albrecht VII. von Mansfeld-Hinterort und Gebhard VII. von Mansfeld-Mittelort gehörten zu den ersten Adeligen, die für die Reformation eintraten und sich später dem Schmalkaldischen Bund anschlossen (Exk. G, dieser Bd.). Nur die Linie Mansfeld-Vorderort blieb katholisch.

Die spätgotische **Stadtkirche St. Georg** enthält wertvolle Schnitzaltäre von Anfang des 16. Jh. und die Grablege der Mansfelder Grafen. Neben der Kirche steht das **Schulhaus**, in der das Kind MARTIN bis zum 14. Lebensjahr Unterricht erhielt. An die drakonische Erziehung denkt LUTHER später noch mit Schrecken: sie sei „unendlich elend“, eine „Teufelsschule“, eine „Hölle und ein Fegefeuer“ mit „ungeschickten Tyrannen und Stockmeistern“ gewesen. Hinter der Kirche im **SPANGENBERG-Haus**, wohnte CYRIAKUS SPANGENBERG (*1528–1604), der bekannte Verfasser der „Mansfeldischen Chronica“ (1572), in den Jahren 1553–74 als Generaldekan und Historiker. **Luthers Elternhaus** in der heutigen Lutherstraße 26 ist als kleines Museum eingerichtet. Der **Lutherbrunnen** in der Stadtmitte zeigt Szenen aus LUTHERS Leben: „Hinaus in die Welt“, „Hinein in den Kampf“, „Hindurch zum Sieg“. SCHLENKER et al. (2007) und STAHL & SCHLENKER (in Meller 2008) berichten über archäologische Ausgrabungen und Bauforschungen an Luthers Elternhaus.

Die Übersiedlung der Familie HANS LUTHERS im Frühjahr 1484 von Eisleben nach Mansfeld hatte wohl wirtschaftliche Gründe. Hier lebten wohlhabende Verwandte seiner Frau, welche seinen beruflichen Aufstieg gerade in den Anfangsjahren unterstützten. Bereits 1491 wird er als „Vierherr“ genannt, d. h. als einer der vier Vertreter der Gemeinde gegenüber dem Magistrat. Offensichtlich gelang es ihm schon früh, Anteile an Schmelzhütten pachtweise zu erwerben. Leider wissen wir nicht, wann HANS LUTHER sein Wohnhaus erwarb. Bei der ersten Nennung im Jahr 1507 lag noch eine Schuld von 100 Gulden darauf.

Der wirtschaftliche Erfolg Hans Luthers lässt sich deutlich am Berufsweg seines Sohnes ablesen. Offensichtlich investierte er einen erheblichen Teil seiner Gewinne in dessen Schulbildung,

die zunächst in Mansfeld, dann in Magdeburg und Eisenach erfolgte. Ganz ungewöhnlich für einen Mann seines Standes war die Finanzierung des Jurastudiums, das sein Sohn ab 1502 an der Universität Erfurt auf Wunsch seines Vaters aufnahm. An der Wende vom 15. zum 16. Jh. fand im Deutschen Reich eine Umstellung vom traditionellen auf das Römische Recht statt und professionelle, verschriftlichte Verwaltungen wurden eingerichtet. Dies bot auch Söhnen aus bürgerlichen Familien gute Aussichten auf eine erfolgreiche Karriere. Die Enttäuschung des Vaters über den Klostereintritt des Sohnes und ihr zeitweiliges Zerwürfnis erklären sich also vor allem aus ökonomischen Gründen.

Literatur: MELLER (2008), DIEWALD (2003), ECKE (2005), EISOLD & LAUTSCH (1992), SPANGENBERG (1572), EISENÄCHER (1998), EISENÄCHER et al. (1999), REITZIG & MÜLLER (2000)

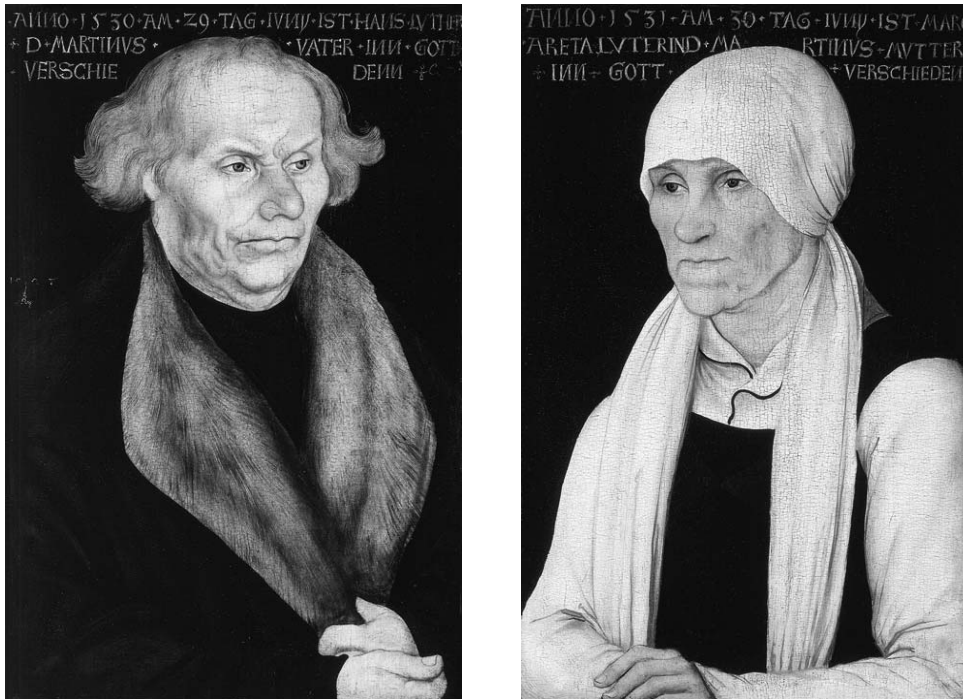


Abb. 4: HANS und MARGARETHE LUTHER, die Eltern von MARTIN LUTHER. Ölgemälde auf Holz von LUKAS CRANACH d. Ä., um 1527. Wartburg-Stiftung Eisenach.

Die Weiterfahrt über Leimbach, Großörner nach Hettstedt folgt dem Tal der Wipper mit dem ausstreichenden Zechstein und Rotliegend

Hettstedt

„Es hat aber dieser Ort – nämlich Kupferberg – den Namen vom Kupfer, weil man an diesem Ort zum erstenmal nach dem 1190. Jahr das Kupferertz gefunden. ... Dazumal sind zween Bergverstandige zu Heckstedt gewesen, deren einer mit Zunamen Neuke, der ander Napian geheießen. Die haben den Schiefen zum ersten funden ... “

CYRIAKUS SPANGENBERG (1572): Mansfeldische Chronica

Hettstedt besitzt noch Reste der mittelalterlichen Stadtmauer mit Toren und Türmen.

Den Marktplatz umgibt ein schönes Ensemble mit der Stadtkirche St. Jacob und dem Rathaus aus dem 16. Jh. Ein Denkmal von 1950 erinnert an den damals 750-jährigen Kupferschieferbergbau.

Der Beginn des Kupferschieferbergbaus liegt am „Kupferberg“ im Osten der Altstadt von Hettstedt. Dort, im Ausgehenden des Kupferschiefers, haben der Überlieferung nach zwei Bergleute aus Goslar namens NAPPIAN und NEUCKE um 1199 das Flöz entdeckt (Abb. 5, 6). Die sagenhaften Oberharzer, deren Namen und Darstellungen an erzschürfende Zwerge erinnern, waren aber wohl historische Personen, deren Nachkommen noch lange in Hettstedt gelebt haben (NEUSS 2001). Der Ortsteil Kupferberg, bis 1886 eine eigenständige Gemeinde, gilt als die charakteristischste

Bergmannssiedlung des Mansfelder Landes mit steilen, schmalen Gassen und Reihen kleiner Bergmannshäuser.

Literatur: NEUSS (2001: 316 ff., 307 ff.), ROMMEL (1999)

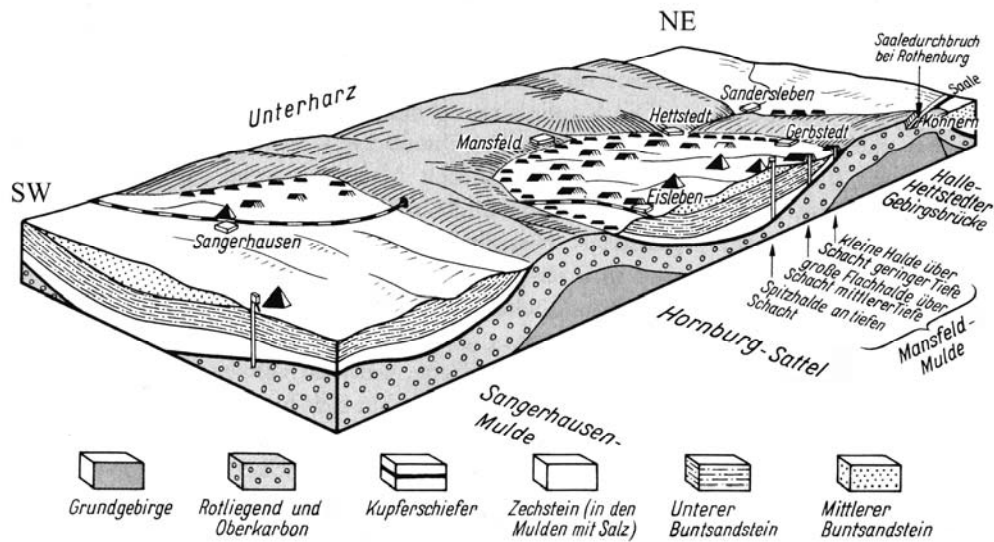


Abb. 5: Mansfeld- und Sangerhausen-Mulde mit verschiedenen Generationen von Kupferschieferhalden, deren Größe und Form von der Tiefenlage des Kupferschiefers abhängen (WAGENBRETH & STEINER 1989).

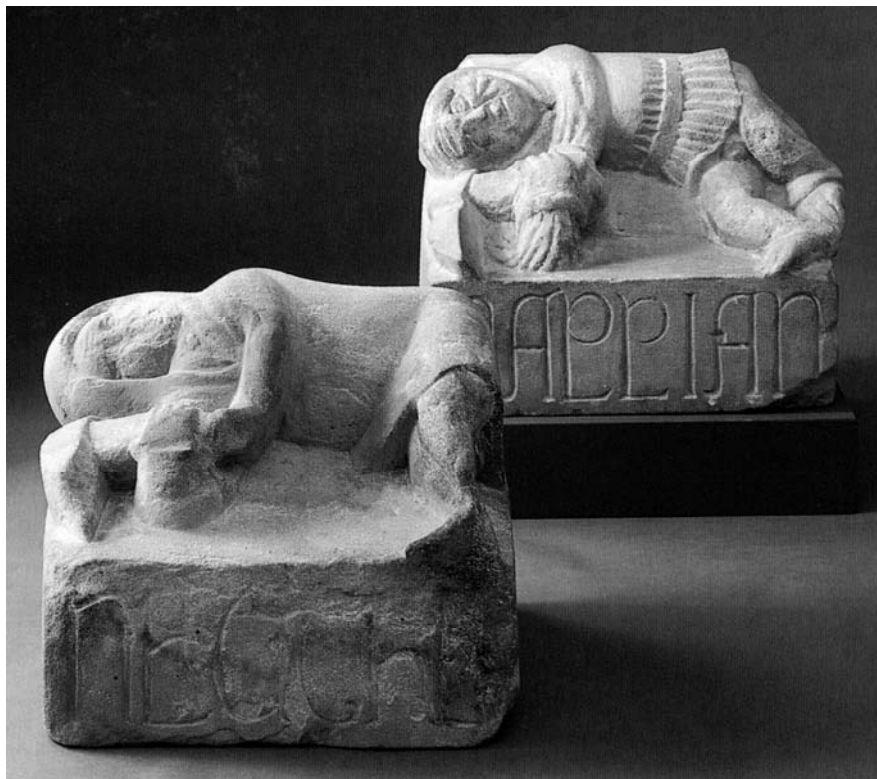


Abb. 6: NAPPIAN und NEUCKE, die beiden legendären Entdecker des Kupferschieferflözes in Bergmannskleidung und typisch liegender Haltung beim Abbau des Flözes mit der Keilhaue. Konsolfiguren aus Stein von der Kapelle am Welfesholz, um 1290. Höhe ca. 35 cm, Originale im Museum Luthers Geburtshaus in Eisleben (TREU 2000).

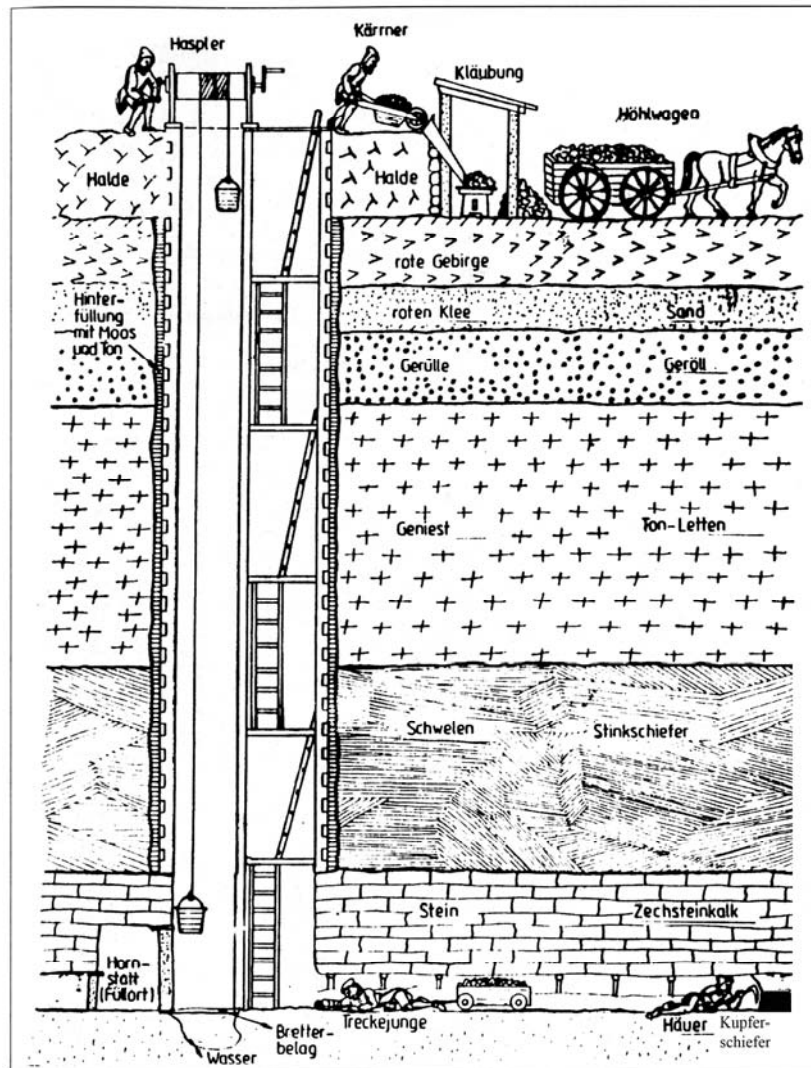


Abb. 7: Kupferschieferschacht mit Haspelförderung im 16. Jh., etwa 15–20 m tief (JANKOWSKI 2001)

Halt 5: Hettstedt, Mansfeld-Museum mit erster deutscher Dampfmaschine

Das Mansfeld-Museum (in Hettstedt ausgeschildert) befindet sich in unmittelbarer Nähe der hier im 19. und 20. Jh. auf- und ausgebauten traditionellen Hüttenstandorte, z. B. der Gottesbelohnungshütte. Die meisten Betriebe wurden nach 1990 geschlossen, nur mit der Firma MKM ist noch ein Produzent von Buntmetall-Halbzeug vorhanden.

Das Mansfeld-Museum ist im sog. Humboldt-Schlösschen aus dem Jahr 1721 untergebracht, das ehemals als Herrenhaus des Ritterguts Burgörner diente (ROMMEL 2003). Im 18. Jh. war es in den Besitz der Familie Dacheröden gelangt. Wilhelm von Humboldt (*1767–1835) hatte hier Caroline von Dacheröden kennengelernt und 1791 geheiratet. Damit ist das barocke Hauptgebäude des Museums zugleich eine Erinnerungsstätte an den grossen preussischen Staatsmann, Reformator und Gelehrten. Anlass für die Gründung des Museums war das 200jährige Jubiläum der sog. „Hettstedter Feuermaschine“ im Jahr 1985. Auf Initiative der Leitung des damaligen Mansfeld-Kombinats erfolgte die Sanierung und der Umbau des bis dahin als Wohnhaus genutzten Hauptgebäudes. Etwa zeitgleich wurde ein Neubau für die Unterbringung des in dreijähriger Bauzeit rekonstruierten Modells der ersten deutschen Dampfmaschine errichtet. Weiterhin gestaltete man den früheren Schlosspark in ein großzügiges Freigelände um.

Schwerpunkte des Museums sind Dauerausstellungen zur Lagerstättengeologie, Mineralogie und Gewinnung des Kupferschiefers. Breiten Raum nimmt die Darstellung des Hüttenwesens und der Halbzeugherstellung ein. Starke Berücksichtigung finden auch die sozialen und kulturellen Aspekte des Mansfelder Montanwesens, die Arbeitswelt der Berg- und Hüttenleute sowie das Brauchtum und Münzwesen. Ein beträchtlicher Teil des heutigen Bestandes stammt noch aus den Sammlungen der 1852 gegründeten „Mansfelder Kupferschiefer bauenden Gewerkschaft“ und der Mansfeld AG (bis 1945).

Im Freigelände sind beeindruckende Großexponate ausgestellt, von denen einige noch bis zur Produktionseinstellung im Jahr 1990 in Nutzung standen. Hierzu gehören z. B. Rohsteinkonverter, Schachtofenriegel, Theisenwäscher oder Walzwerke und Verseilmaschinen. Eine kleine untertägige Strecke mit Revierstube und Hapelschacht, eine Zimmerei, Bergschmiede und ein Kläubestall räumen auch dem Bergbau, der Förderung und Aufbereitung hinreichenden Raum ein. Nicht zuletzt wird auch die Schlackenverwertung mit einer Anlage zum Guß von Schlackensteinen anschaulich vermittelt.

Im sogenannten Humboldt-Hain des Museumsgeländes befindet sich ein Gebäude mit dem „Lichtloch 24“ des „**Schlüsselstollens**“. Dieser ist der längste von zahlreichen Stollen (Stolln), die im Laufe der Jahrhunderte zur Entwässerung der Grubenfelder aufgefahen wurden. Er verläuft am Nord- und Westrand der Mansfeld-Mulde von Friedeburg bis Wimmelburg, ist 31 km lang und noch heute aktiv und befahrbar. Die Auffahrung dauerte von 1809–1879. Am Lichtloch 24 liegt der Kupferschiefer 93 m tief.

Die Hauptattraktion des Museums ist der originalgetreue Nachbau der „**Hettstedter Feuermaschine**“, der ersten deutschen Dampfmaschine Watt'scher Bauart, die in ihrer Funktion und allen technischen Einzelheiten vorgeführt werden kann. Diese Maschine wurde in drei Jahren Bauzeit mit Hilfe der alten Unterlagen rekonstruiert und 1985 in Betrieb gesetzt (Abb. 8; HEBESTEDT & SIEMROTH 1996).

Der Grund für den Einsatz einer Dampfmaschine war der verstärkte Wasserandrang in den Hettstedter Revieren, welcher mit konventionellen Mitteln, wie Pferdegöpel, nicht mehr zu beherrschen war. König Friedrich II. höchstselbst befahl am 1780, den Einsatz der in England mit großem Erfolg arbeitenden Maschinen zu prüfen. Preussische Bergbeamte wurden nach England geschickt, darunter Bergassessor C. F. Bückling, der nach seiner Rückkehr den Bau dieser ersten deutschen Dampfmaschine nach dem Watt'schen Prinzip leitete. Sie war von 1785 bis 1793 auf dem „König-Friedrich-Schacht“ südöstlich von Hettstedt im Einsatz (s. u.) und wurde dann zum Hoffnungsschacht im Löbejüner Steinkohlenrevier überführt, wo sie bis 1849 Dienst tat.

Die Maschine von 1785 war allerdings nicht die allererste Dampfmaschine in der Region. Schon einige Jahre zuvor hatte man auf dem Braunkohlenschacht Altenweddingen bei Magdeburg eine atmosphärische Dampfmaschine nach Thomas Newcomen aus England eingesetzt, die sich aber nicht bewährte. Auch auf dem Steinkohlenschacht bei Oppenrode nahe Ballenstedt soll damals schon eine atmosphärische Dampfmaschine gestanden haben.

Die Konstruktion und der erfolgreiche Einsatz der ersten Dampfmaschine 1785 im Hettstedter Revier markieren einen Wendepunkt in der deutschen Industriegeschichte, da hiervon ein wesentlicher Impuls für die nachfolgende stürmische Industrialisierung Mitteleuropas ausging.

Literatur: JANKOWSKI 1987, ROLOFF (1999), ROMMEL (2003), HEBESTEDT & SIEMROTH (1996)

Die Weiterfahrt erfolgt ansteigend entlang dem so genannten „Lichtlöcherberg“ zur B 180.

Halt 6a: Burgörner, Halde des Eduard-Schachts, Haldenlandschaft (optional)

(TK/GK25 4335 Hettstedt, R: 44 67 000, H: 57 21 000)

Zwischen den Orten Burgörner und Welfesholz befindet sich die wohl schönste und eindrucksvollste Haldenlandschaft des Mansfelder Landes mit Kupferschiefer-Halden vom Mittelalter bis ins 19. Jh.. Hier grenzte das einstige Revier „Preussische Hohheit“ an das „Sächsische Revier“. Strukturell befindet sich das Gebiet an der Südflanke des Rothenburg-Sattels (= Halle-Hettstedter Gebirgsbrücke, Abb. 5), wo die Schichten generell flach nach Süden einfallen. Eine besonders gute Übersicht hat man von der großen Halde von Schacht Eduard, ca. 1 km nach dem Ortsende von Hettstedt-Burgörner. Deutlich zeigt sich, wie vom Ausgehenden des Kupferschiefers bei Welfesholz der Abstand der Schächte (Halden) von Norden nach Süden zunimmt und die Halden mit der Schachttiefe immer größer werden (Abb. 5, 7). Auf diese Weise lassen sich hier und anderorts am Rand der Mansfeld-Mulde mehrere Generationen von unterschiedlich großen Halden unterscheiden.

Das hier etwa 0,4 m mächtige Kupferschieferflöz besteht aus feingeschichteten, kohlig-bituminösen, sulfidführenden Tonmergel- bis Mergelsteinen (Abb. 9). In seinen früher bauwürdigen Bereichen enthält es als wichtigste Sulfidminerale Bornit (Cu_5FeS_4), Kupferkies (CuFeS_2), Kupferglanz (Cu_2S), Covellin (CuS), Tennantit ($\text{Cu}_3\text{AsS}_{3,25}$), Bleiglanz (PbS), Zinkblende (ZnS), Pyrit und Markasit (FeS_2).

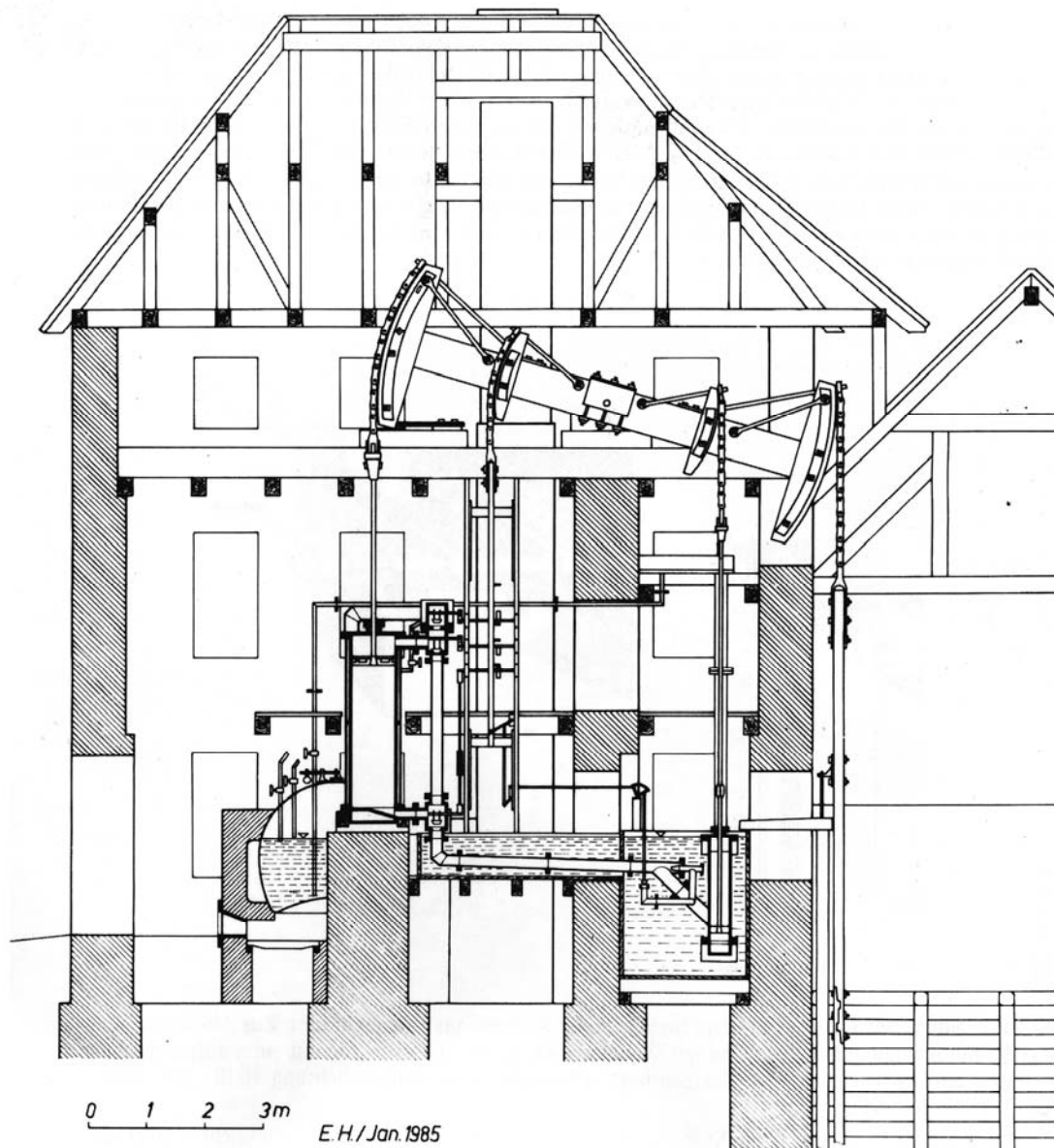


Abb. 8: Rekonstruktion von Dampfmaschine und Maschinengebäude auf dem König-Friedrich-Schacht 1785 (HEBESTEDT & SIMROTH 1996)

In den ehemaligen Baufeldern bei Hettstedt/Burgörner wies der Kupferschiefer mit 3,1 % Cu im Fördererz überdurchschnittlich gute Metallgehalte auf, bei zugleich hohen Silber- und Zinkgehalten. Die Unterlagen lassen auf einen Gewinn bringenden Bergbau durch den preußischen Staat seit 1768 schließen (LANGELÜTTICH 2003). Der Abbau entwickelte sich daher schnell zu Teufe. Hierdurch wurden umfangreiche Maßnahmen zur Wasserhaltung, wie Stollenauffahrungen und letztlich der Einsatz von Dampfmaschinen unumgänglich.

Am gegenüberliegenden Hang befindet sich die von Bäumen umgebene Halde des „**König-Friedrich-Schachts**“ mit dem „**Maschinendenkmal**“ im Revier „Preussische Hoheit“. Das Denkmal besteht aus einem Granitwürfel, der auf einen gemauerten Porphyrsockel steht. Eine Bronzetafel erinnert an die technische Revolution im Mansfelder Bergbau: „Am 25. August 1785 / kam an dieser Stelle, dem / König Friedrichschachte, / zum ersten Male eine aus / deutschem Material und von / deutschen Arbeitern hergestellte / FEUERMASCHINE / in Betrieb, zu / dauernder gewerblicher Benutzung.“ „Errichtet vom / Verein Deutscher Ingenieure / im Jahre 1890 / erneuert 1985 durch die / Bürger der Stadt Hettstedt.“ Die andere Seite zeigt eine Tafel mit dem Reliefbild der Feuermaschine. Ein Nachbau der gewaltigen Maschine steht im Mansfeld-Museum in Hettstedt (Halt 5). Von 1774 bis 1815 war auf dem Friedrich-Schacht eine zweite Dampfmaschine in Betrieb.

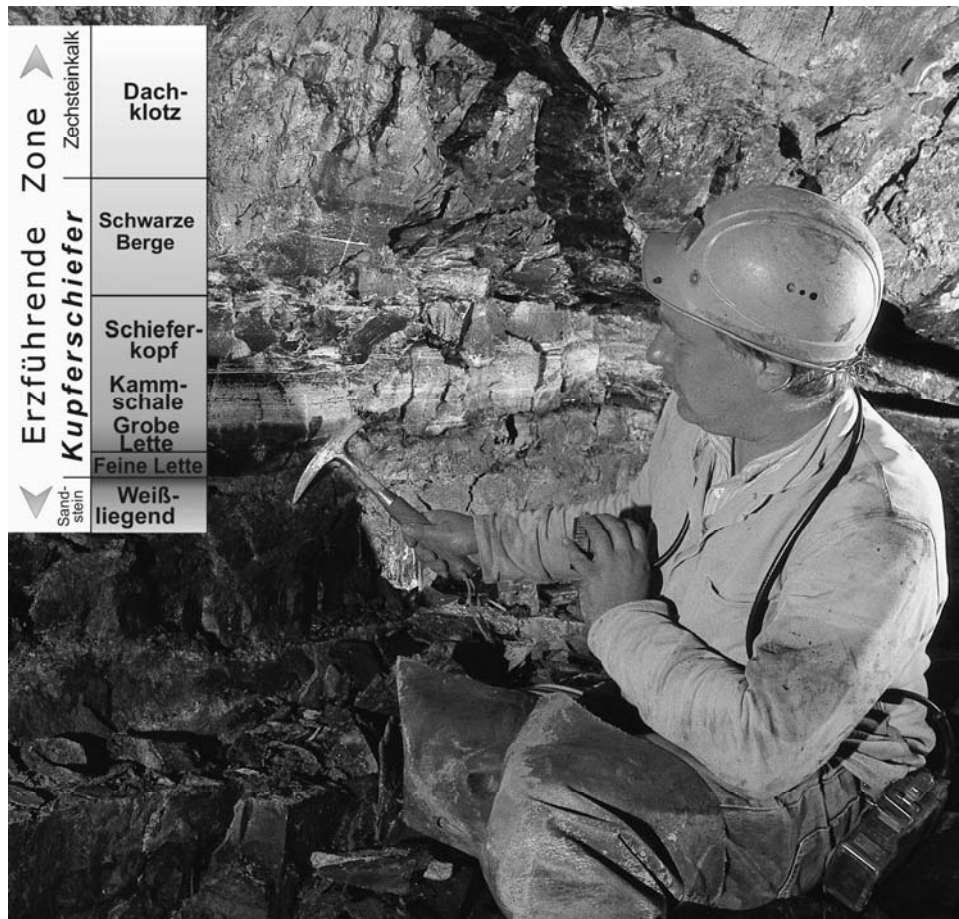


Abb. 9: Kupferschieferflöz mit an Zink und Kupfer reicher Vererzung im Freieslebener Flözgraben unterhalb des Zabenstedter Stollens bei Burgörner in 100 m Teufe. Hammer markiert Grenze Weißliegend/Feine und Grobe Lette. Herr B. FRIEDRICH, Hettstedt. Foto: STEDINGK 2002.

Der Friedrich-Schacht selbst setzte in der Calvörde-Formation an und wurde 1780 – 1783 mit einem Durchmesser von 3 x 3 m bis auf 115 m abgeteuft. Der Kupferschiefer wurde in 101 m angetroffen und in Produktion genommen. Schon während des Abteufens machen sich starke Wasserzutritte bemerkbar. Zur Erleichterung wurde in 50 m Tiefe eine Verbindung zum 500 m weiter nördlich verlaufenden Burgörner Stollen hergestellt. Dem Friedrich-Schacht kam als damals tiefstem Schacht im Revier besondere Bedeutung zu.

Zufahrt zum Maschinendenkmal (Ausschilderung): Durch eine Bahnunterführung ca. 0,5 km nach dem Ortsausgang von Hettstedt auf einem Fahrweg nach Osten.

Die **Eduard-Schächte I und II** (benannt nach Bergrat Eduard Schrader, *1823–1891) selbst hatten Teufen von 252 m bzw. 328 m und standen 1868–1910 in Förderung. Sie gehörten zu den ersten Anlagen des Mansfelder Kupferschieferbergbaus, auf denen nach 1905 elektrische Fördermaschinen und Seilfahrten eingeführt wurden.

Das Haldenmaterial der Eduard-Schächte und anderer Schächte bestehen im Allgemeinen aus den metallärmeren Hangendschichten des Kupferschiefers, die abbautechnisch mitgewonnen werden mussten und unter Tage nicht als Versatz eingebracht werden konnten. Unter Beachtung der Sicherheit gibt es auf den Halden noch bescheidene Fundmöglichkeiten für Fossilien und Mineralien (Rückenvererzungen).

Nordöstlich der Halde der Eduard-Schächte befindet sich das Wäldchen **W e i ß e s h o l z**. Nach diesem ist die bedeutende und sagenumwobene Schlacht vom 11. Februar 1115 benannt, welche Kaiser Heinrich V. und sein Feldherr Graf Hoyer von Mansfeld gegen den Sachsenherzog Lothar von Supplinburg verlor (NEUSS (2001)). Dieses Ereignis schwächte die kaiserliche Zentralgewalt unwideruflich.

Literatur: BRANDT (1997), HAUBOLD & SCHAUMBERG (1985), HEBESTEDT & SIMROTH (1996), NEUSS (2001: 298 ff.), JANKOWSKI (1987: 20)

Halt 6b: Siersleben, Halde der Niewandt-Schächte I und II, Haldenlandschaft (optional)
(TK/GK25 4335 Hettstedt)

Zufahrt: Vom Bahnübergang der B 80 und der Mansfelder Bergwerksbahn. Die ehemalige Schachanlage ist in einem umzäunten Betriebsgelände, die Halde selbst ist ebenfalls umzäunt; Genehmigung ist erforderlich.

Die **Niewandt-Schächte** (benannt nach dem Hauptaktionär) wurden 1869–1894 abgeteuft. Der Schacht I war 459 m, der Schacht II 447 m tief. Mit der Aufnahme der Produktion und einer Belegschaft von bis zu 2.000 Mann (1892) entwickelten sie sich zu einem stabilen Faktor der Kupferschieferproduktion im Nordteil der Mansfelder Mulde. Ab 1913 dienten sie dann als Flucht- und Wasserhaltungsschächte. Vorhanden sind heute noch ein Schachtgebäude und die riesige Halde mit eingeschlossenen ehemaligen Industriedeponien für Zinkoxidflugstäube und Neutrasschlamm (1982–1995). Bereiche der Halde sind durch spontane Selbstentzündung des sulfid- und kohlenstoffreichen Kupferschiefers in Brand geraten (VOLKMANN et al. 2000). Dadurch ist ein sehr poröses, aufgeblähtes bis geschmolzenes, Mullit- und Spinell-haltiges, durch Hämatit-Neubildung rötlich gefärbtes Material entstanden. Am SW-Fuß der Halde ist eine etwa 1 m dicke, offenbar deponierte Schicht des Brandmaterials angeschnitten. Von der Halde selbst hat man einen guten Rundumblick auf die eindrucksvolle Landschaft mit Kupferschiefer-Halden vom Mittelalter bis ins 20. Jahrhundert.

Unmittelbar nördlich der Halde liegt das „Lerchenfeld“, auf welchem im Jahr 1115 die Schlacht am Welfesholz geschlagen wurde (s. Halt 6a).

Literatur: JANKOWSKI (1987)

Halt 7: Hettstedt, ehem. Steinbruch im „Tal der heiligen Reiser“, Siebigerode-Formation (Stefan C), Eisleben-Formation (Rotliegend)
(TK/GK25 4335 Hettstedt, R: 44 66 550, H: 57 23 920)

Zufahrt: Auf der Hauptstraße (B 180) in Richtung Aschersleben, an der Kaufhalle rechts ab in die Straße „Am Plattenberg“, dann links in die Straße „Promenade“, nach ca. 300 m rechts durch eine Bahnunterführung. Links vom ersten Haus der Talstraße führt ein Fußweg bergauf, von dem nach 30 m ein Pfad hangauf zum Steinbruch abzweigt.

Der ehem. Steinbruch im „Tal der heiligen Reiser“ ist einer der bekanntesten und sehenswertesten Aufschlüsse im Exkursionsgebiet. Der vordere Teil zeigt eine eindrucksvolle ca. 200 m lange Felswand, an der die Eisleben-Formation (Oberes Oberrotliegend II) mit schwacher Winkeldiskordanz die Siebigerode-Formation (Mansfeld-Subgruppe, Stefan C) überlagert (Abb. 10). Die Siebigerode-Formation besteht aus fluviatilen violettroten Feinsandsteinen mit hohem Glimmergehalt und Schiefertönen und fällt mit wenigen Grad in östliche Richtung ein. Die Eisleben-Formation besteht unten aus 6 m dickbankigen Konglomeraten mit Geröllen von Quarzen und Vulkaniten (Porphyrkonglomerat), die in Alluvialfächern abgelagert wurden. Es folgen 6 m wenig verfestigte Feinkonglomerate und Sandsteine, z. T. als rinnenförmige Kleinzyklen mit erosiver Basis (Sandsteinschiefer). Schrägschichtung und Geröllorientierung zeigen eine nordöstliche Transportrichtung der fluviatilen Systeme an. Bis zum Zechstein fehlen noch ca. 7 m. Von diesem ist hier nur noch der untere Teil vorhanden, weil sich der Aufschluss strukturell wenig südlich des Scheitels des Rotenburg-Sattels (= Halle-Hettstedter Gebirgsbrücke) befindet, und die Schichten generell mit ca. 5° nach Süden einfallen.

Die Eisleben-Formation ist hier insgesamt nur etwa 20 m mächtig. Die Korrelation mit Bohrungen im Beckeninneren zeigt, dass dieses Profil dem oberen Teil der bis 700 m mächtigen Hannover-Formation entspricht und deren Niendorf-, Munster- und Hedberg-Subformationen vertritt (SCHUBERT 2002).

Ein Pfad führt bis zum linken Ende des Bruchs, wo die Schichtenfolge besser zugänglich und die Sedimentstrukturen stärker herausgewittert sind als an der Steilwand. Von der Siebigerode-Subformation steht hier ein sandigerer Abschnitt an als im vorderen Teil. Dieser wurde untertägig zur Herstellung von Mühlsteinen abgebaut.

Die Schichtlücke zwischen Siebigerode- und Eisleben-Formation umfaßt hier das Unterrotliegend und Oberrotliegend I – eine Zeitspanne von etwa 30 Ma. Der Aufschluss wird oft als Typuslokalität der „Saalesschen Diskordanz“ genannt. Diese ist jedoch zwischen Unterrotliegend und Oberrotliegend bei Halle und Wettin definiert (STILLE 1924).

Ein weiterer, gut zugänglicher Aufschluss in der Eisleben-Formation im Grenzbereich Porphyrokonglomerat / Sandsteinschiefer befindet sich am Hang der „Promenade“, gegenüber Haus 39. Die Schrägschichtung weist hier generell nach Norden.

Die Bahnlinie durch Hettstedt neben dem Steinbruch und der Promenade war die sog. „Kanonenbahn“, eine nach der Reichsgründung gebaute strategische Direktverbindung von Berlin nach Elsaß-Lothringen.

Literatur: KARPE (1995: Nr. 609, 1999: 55, Geotop 4335/2, Abb. 10), SCHRÖDER (1935)
Profile: KUNERT (1970) mit älterer Literatur, LÜTZNER (1987), CHR. SCHUBERT (2003)

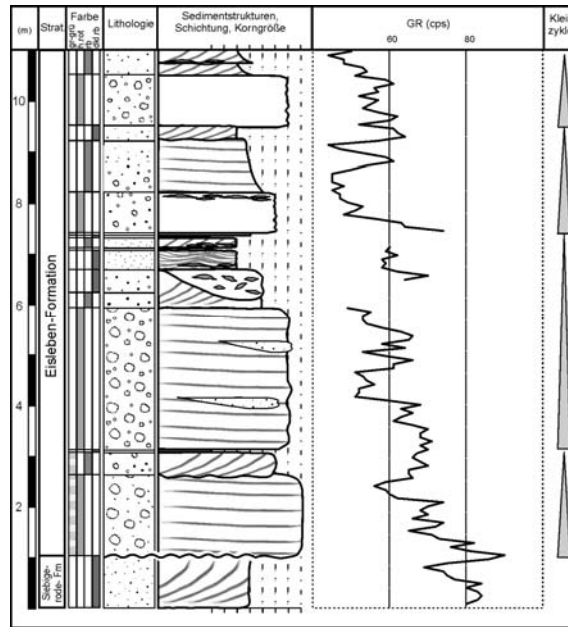


Abb. 10: Hettstedt, ehem. Steinbruch im „Tal der heiligen Reiser“. Siebigerode-Formation (Mansfeld-Subgruppe, Stefan C) und Eisleben-Formation (Oberrotliegend) mit Kurve der natürlichen Gamma-Strahlung (CHR. SCHUBERT 2003, verändert).

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Literatur

(am Ende der **Exkursion „Martin Luther“**, dieser Band)

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Martin Luther, Stätten der Reformation, Schlachtfelder der Glaubenskriege im geologischen Umfeld

Wittenberg, Dübener Heide, Schlachtfelder von Breitenfeld (1631), Lützen (1632)

Von GERHARD H. BACHMANN, MAIK REICHEL, MARTIN TREU, PETER TROPP, STEFAN WANSA,
REINHARD WILKE & ROLAND WIMMER

Mit 8 Abbildungen

Fahrtroute: Halle (Saale)– Bitterfeld – Gräfenhainichen – Wittenberg – Bad Dübener Heide – Leipzig – Lützen – Halle (Saale)

Top. Karten/Geol. Karten: Geol. Übersichtskarte 200: CC 4734 Leipzig, CC 5534 Zwickau; TK 100: C 4734 Halle (Saale), C 4338 Dessau, C 4738 Leipzig; TK 25 /GK 25: 4141 Wittenberg, 4240 Gräfenhainichen, 4241 Kemberg, 4339 Bitterfeld-West, 4340 Bitterfeld-Ost, 4341 Söllichau, 4441 Dübener Heide, 4540 Zschortau, 4738 Lützen

Vorwort

„So bin ich zu Eisleben geboren, zu Mansfeld erzogen, ..., und nun Doktor zu Wittenberg“.
MARTIN LUTHER (1520)

MARTIN LUTHER (*1483–1546) wurde in der Kleinstadt Eisleben westlich von Halle geboren als der erste Sohn von HANS LUTHER und dessen Frau MARGARETE und dort starb er auch. Aufgewachsen ist er in Mansfeld, wo sich der tüchtige Vater zielstrebig zum wohlhabenden Bergwerks- und Hüttenbesitzer empor gearbeitet hat.

MARTIN LUTHERS charismatische Persönlichkeit, sein Lebenswerk, seine Sprachgewalt, seine oft schroffe Direktheit, sind ohne das Wissen um den familiären Hintergrund im Mansfelder Bergbau kaum zu verstehen (Exkursion Kupferschiefer, dieser Band). Der Vater wollte ihm ein Jura-Studium in Erfurt ermöglichen. Er aber fühlte sich zum Mönch berufen und studierte Theologie. Die neu gegründete Universität zu Wittenberg berief den viel versprechenden jungen Augustinermönch zum Professor für Theologie. Von Wittenberg ging seine Reformation des christlichen Glaubens aus, welche ihn zu einer Person der Weltgeschichte werden ließ. Die Reformation hat wie wenige andere Ereignisse die Geschichte Deutschlands, Europas und der Welt bis zum heutigen Tage beeinflusst. In der Spaltung und Erneuerung des christlichen Glaubens aber lag der Keim für spätere politische Auseinandersetzungen und Kriege. Mehrere große Schlachten der so genannten Glaubenskriege wurden hier, im Kernland der Reformation, geschlagen.

Diese Exkursion hat das Ziel, historische und kulturgeschichtliche Ereignisse um MARTIN LUTHER und die Reformation aufzuzeigen und mit ihrem geologischen Hintergrund interdisziplinär zu verbinden. Die vorangehende Exkursion „Kupferschiefer“ (dieser Band) führt ins Mansfelder Land zum historischen Kupferschieferbergbau und in die Lutherstadt Eisleben. Diese Exkursion besucht nunmehr die Lutherstadt Wittenberg mit ihren berühmten Stätten der Reformation und schließlich, nahe Leipzig, zwei große Schlachtfelder des Dreißigjährigen Krieges bei Breitenfeld (1631) und Lützen (1632).

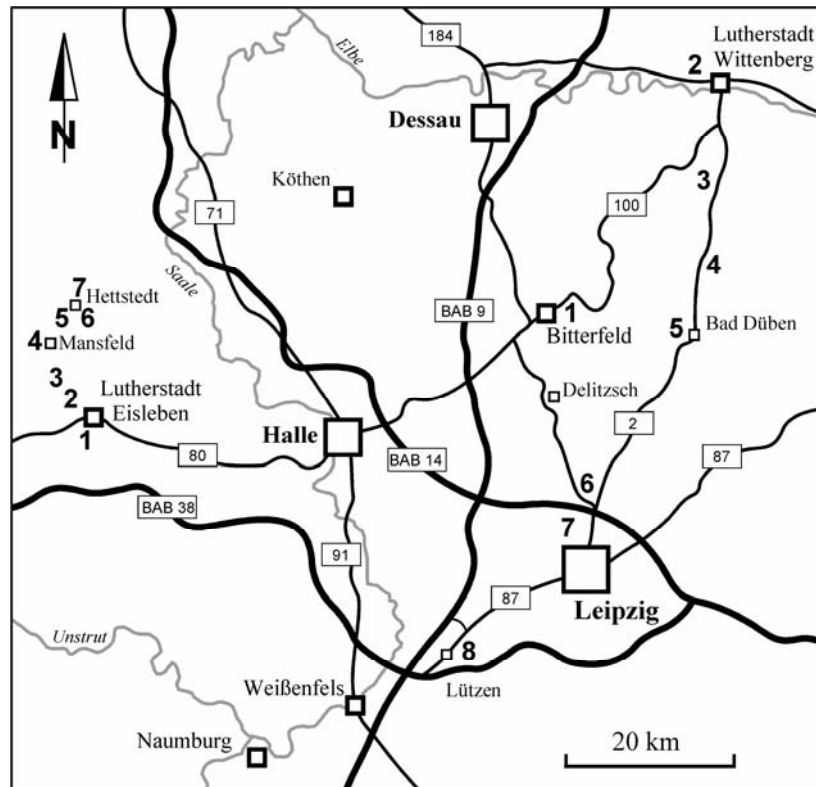


Abb. 1: Routenskizze mit Haltepunkten. Exkursion „Kupferschiefer“ westlich von Halle, Exkursion „Luther“ östlich von Halle.

Fahrt Halle – Bitterfeld

Die Exkursion verläßt Halle in nordöstlicher Richtung auf der B 100. Die überwiegend flache Landschaft um 100 m über NN ist kennzeichnend für den Übergang zur *Leipziger Tieflandsbucht*, welche seit SIEGERT & WEISSERMEL (1911) zu den klassischen Gebieten quartärgeologischer Forschung gehört. Die Oberfläche wird entlang der Fahrtstrecke hauptsächlich von Grundmoräne und Schmelzwasserablagerungen der Saale-Vergletscherung eingenommen. Das Pleistozän ist von etwa 60–90 m mächtigem Tertiär unterlagert, welches aus marinem, littoralem und fluviatil-estuarinem Eozän bis Untermiozän besteht und Braunkohlenflöze enthält. Von wirtschaftlicher Bedeutung war der untermiozäne Bitterfelder Flözkomplex. In den vergangenen Jahrzehnten wurde in den Braunkohlentagebauen wichtige Erkenntnisse über den Aufbau des mitteldeutschen Quartärs und Tertiärs gewonnen.

Der tiefere Untergrund wird vom Paläozoikum der *Halle-Wittenberg-Scholle* gebildet. Es handelt sich um einen SE-NW streichenden Horst von etwa 60 km Breite, welcher durch die Halle-Störung im Südwesten und die Wittenberg-Störung im Nordosten gegen das Mesozoikum versetzt ist und durch oberkretazische Inversionsbewegungen entstand. Unter dem Tertiär sind hier vor allem Sedimente des Rotliegend und Stefans sowie Rotliegend-Porphyre vorhanden (Exk. K, dieser Bd.). Bis zur A 9 ragen häufig Kuppen von grobkristallinen Porphyren des Landsberg-Lakkoliths aus der quartären Bedeckung. Bei *Landsberg* trägt eine solche Kuppe (148 m NN) die berühmte romanische Doppelkapelle St. Crucis aus dem 12. Jh.. 2 km nördlich der B 100 werden Schwerzer Porphyre abgebaut, die sich in Chemismus und Struktur unterscheiden. 12 km nordwestlich von hier erhebt sich der weithin sichtbare *Petersberg* (250 m NN), welcher aus feinkristallinen Porphyren des Petersberg-Lakkoliths besteht. Unterlagert wird das Permokarbon von Gesteinen der Mitteldeutschen Kristallinzone des Variszikums.

Südöstlich von Bitterfeld, im Bereich der Nordwestsächsischen Scholle, sind unter dem Tertiär jungproterozoische (riphäische) Grauwacken und Wechselagerungen von kambrischen Ton- und Sandsteinen vorhanden, in die Intrusivgesteine, insbesondere oberkarbonische Granitoide, eingedrungen sind. Diese Gesteine gehören zum Nordrand der Saxothuringischen Zone des Variszikums.

Die Gesteine unter dem Tertiär sind im ganzen Bereich 20–30 m tief kaolinitisiert, an Störungszonen bis 150 m.

Literatur: EISSMANN (1970), EISSMANN & LITT (1994), KNOTH & SCHWAB (1972), RÖLLIG et al. (1995), SCHLENKER et al. (1998)

Halt 1: Bitterfeld, Parkplatz an der Biermannschen Villa, Sanierungsgebiet Goitzsche

GK 25 4339 Bitterfeld-West, R: 45 24 500, H: 57 22 000

Der Name „Goitzsche“ oder „Goitsche“ ist slawischen Ursprungs und bezeichnete einen rund 760 ha großen Auenwald östlich der Stadt Bitterfeld. Der Begriff wurde auf einen 1949–1990 in Abbau befindlichen Braunkohlentagebau übertragen, in welchem das etwa 10–14 m mächtige untermiozäne Flöz Bitterfeld gewonnen wurde.

Um 1800 begann die Kleinstgewinnung von Braunkohle in sogenannten „Bauerngruben“. Bauern aus Wolfen belieferten mit ihren mit Kohle beladenen Pferdefuhrwerke die Salzsieder in Halle. Nach mehreren erfolglosen Versuchen nahm die Grube Auguste 1839 am südwestlichen Stadtrand von Bitterfeld die Kohleförderung auf. Infolge der nicht zu beherrschenden Wasserverhältnisse konnte zunächst nur der obere Teil des Bitterfelder Flözes abgebaut werden. Bis 1850 wurden sechs weitere Gruben aufgeschlossen, welche vor allem die im Umland entstehende Industrie, wie Ziegeleien, Zuckerfabriken und Brennereien, mit Feuerkohle versorgten. Die Einführung der bergtechnischen Grubenwasserhaltungen und der 1857 beginnende Bau der Eisenbahnstrecken von Bitterfeld nach Dessau und von Halle nach Berlin führten zu einer ständig steigenden Förderleistung im Bitterfelder Grubenrevier. Durch das Aufblühen der Tonwarenindustrie und die Ansiedlung von chemischer Industrie entwickelte sich der Bitterfelder Braunkohlenbergbau rasch zu einem wichtigen Industriezweig. Im Jahr 1872 wurde die erste Brikettfabrik auf der „Deutschen Grube“ errichtet. Um 1900 waren neun Braunkohlenwerke im Revier Bitterfeld tätig. In den 1920er Jahren jedoch setzte im Raum um Bitterfeld und Wolfen ein Konzentrationsprozess der Braunkohlengruben und der chemischen Industrie ein. Auch die Weltwirtschaftskrise (1928–1933) und die beiden Weltkriege beeinflussten den Bergbau nachteilig. Nach 1945 wurde die Kohleförderung im Revier unter der neuen Struktur der Braunkohlenwerke (BKW) fortgesetzt. Der Wiederaufbau der industriellen Basis, der chemischen Industrie und der Energiegewinnung bedingte eine enorme Steigerung der Förderung aus den bestehenden Gruben. Da diese den Bedarf bald nicht mehr decken konnten, folgte eine intensive Erkundung und der Aufschluss weiterer Braunkohlenfelder mit den Tagebauen Freiheit I bis IV, Holzweißig, Muldenstein und Goitzsche. 1991 wurde die Kohleförderung eingestellt. In der über 40-jährigen Betriebszeit wurden rund 317 Mio. t Rohbraunkohle (Brikettier- und Kesselkohlen) gefördert und etwa 850 Mio. m³ Abraum bewegt und wieder verstürzt (VEREIN DER BITTERFELDER BERGLEUTE E. V. 1998).

Zusätzlich zur Braunkohle wurde ab 1975 Bernstein im Bereich der beiden Tagebaue Niemegk und Mühlbeck als „geheimer“ sog. Begleitrohstoff „01“ abgebaut, bis zu 50 t pro Jahr, die vor allem der Schmuckindustrie zugeführt wurden.

Seit der Stilllegung im Jahr 1991 wird das Bitterfelder Revier saniert. Das Flutungsbauwerk und der **Pegelturm** für die rund 20–30 m tiefe Goitzsche befinden sich im nördlichen Randbereich und wurden 1998 fertiggestellt. Die reguläre Flutung begann im Mai 1999. Während der Flutung repräsentierte der Pegelturm die aktuelle Höhe des Wasserstandes, jetzt zeigt seine Höhe die Tiefe des Tagebausees an. Zugleich ermöglicht der Turm einen Überblick über die Bergbaufolgelandschaft.

Die Flutung des Mitteldeutschen Braunkohlenreviers wird begünstigt durch die wasserreichen Flüsse Mulde, Saale und Weiße Elster. Dieser Vorzug kann sich auch schnell zum Negativen wenden, wie die Flutkatastrophe des Jahres 2002 zeigte. Der Tagebau Goitzsche war bereits bis 71,5 m NN geflutet. Das Endziel waren 75,00 m NN. Am 14. 08. 2002, während des Hochwassers, brachen rund 11 km oberhalb der Goitzsche die Deiche der Mulde und die Wasser ergossen sich im alten natürlichen Tal in Richtung Tagebau, strömten in diesen ein und verursachten in kürzester Zeit einen Anstieg des Stausees um 7 m, rund 3 m über den geplanten Endwasserstand. Die ungefähr 100 Mio. m³ Wasser bedrohten die Stadt Bitterfeld, brachten aber gleichzeitig eine dringend notwendige Entlastung für die Unterlieger an der Mulde. Der Grund für das Hochwasser waren großflächige hohe Niederschläge im Erzgebirge, die schnelle Abflüsse zur Folge hatten.

Nach Bitterfeld führt die B 100 im Norden um die Goitzsche herum und quert hinter Pouch die Mulde am Einlaufbauwerk zum **Muldestausee**. Der Bitterfelder Muldestausee entstand 1975 durch die Flutung von zwei Teilbecken des ehemaligen Tagebaus Muldenstein. Die ursprünglich westlich der Orte Pouch, Mühlbeck und Friedersdorf fließende Mulde wurde dabei im Zuge der Neuerschließung des Tagebaus Goitzsche durch das Restloch des ehemaligen Tagebaus Muldenstein geleitet. Mit dem Bau einer rund 5 m hohen Staumauer entstand ein Stausee, der die beiden Teilbecken (Friedersdorfer Becken und Hauptbecken) miteinander verbindet. Der Muldestausee ist knapp 6 km lang und maximal 1,9 km breit, hat eine Fläche von rund 6 km² und enthält ein Wasservolumen von

ca. 118 Mio m³. Sein vorderes Hauptbecken ist über 30 m tief. Der Wasserspiegel liegt je nach Stauhöhe bei ca. 79 m NN.

Die Weiterfahrt verläuft hauptsächlich auf drenthezeitlicher Grundmoräne. Gräfenhainichen ist der Geburtsort von PAUL GERHARDT (*1607–1676), dem größten evangelischen Liederdichter nach LUTHER.

Unmittelbar am nördlichen Stadtrand von Gräfenhainichen befindet sich der aufgelassene Braunkohlen-Tagebau G o l p a - N o r d. Der südliche Stadtrand grenzt an die bergmännische Hohlform des ehemaligen Tagebaus G r ö b e r n. Dieser wurde 1984 als Nachfolge für den bis dahin weitgehend ausgekohnten Tagebau G o l p a - N o r d aufgeschlossen und 1993 als letzter Tagebau im Bitterfelder Revier stillgelegt. In beiden Tagebauen wurde das untermiozäne Bitterfelder Flöz abgebaut. Heute befinden sich beide Tagebaue im Endstadium der bergtechnischen Sanierung und werden über ein Rohrleitungssystem mit Muldewasser geflutet.

Hinter Uthhausen wird der Westrand der warthezeitlichen „Schmiedeberger Stauchendmoräne“ gequert (s. u.). Die Landschaft zeigt sich kuppig und mit Kiefern bestanden.

Wittenberg und die Reformation

Die Elbaue ist bei Wittenberg 8–10 km breit und folgt einem weichselzeitlichen Urstomtal. Zahlreiche Altwasser zeugen vom einst viel windungsreicheren Lauf der Elbe vor ihrer Begradigung. Die Aue wird auf beiden Seiten von mehr oder weniger breiter weichselzeitlicher Niederterrasse begleitet. 1180 wurde Wittenberg erstmals als Burg erwähnt, welche im Zuge der Ostexpansion angelegt wurde, um eine Furt durch die Elbe zu schützen. Wie fast alle derartigen Befestigungen liegt sie auf der jenseitigen, nordöstlichen Seite der Elbe. Die weißen Sande der Niederterrasse gaben wohl Burg und Siedlung den Namen.

Durch Wittenberg führte eine alte Handelsstraße von Magdeburg in die Lausitz, deren Verlauf mit der Schloss- und Collegienstraße noch heute die Hauptachse der Stadt bildet. Nach der Teilung des wettinischen Territorialstaats im Jahr 1485 in eine albertinische und ernestinische Fürstenlinie wurde Wittenberg zur Residenz der Ernestiner erhoben und erlebte seine glanzvollste Epoche. Kurfürst Friedrich III. der Weise (*1463–1525) ließ eine Elbrücke errichten, das Schloß ausbauen und gründete 1502 in Konkurrenz zu Leipzig die „Leucorea“, die erste landesfürstliche Universität in Deutschland. 15 Jahre später wurde diese Universität Ausgangspunkt und Zentrum der Reformation. Der Beiname „Lutherstadt“ wurde Wittenberg 1927 verliehen.

In der zweiten Hälfte des 15. Jh. spielten Glaube und Frömmigkeit eine immer größere Rolle im täglichen Leben der Deutschen. In einem krassen Gegensatz dazu stand das Verhalten der meisten großen und kleinen kirchlichen Würdenträger. Weite Teile der Bevölkerung wurden dadurch beunruhigt und bekamen das Gefühl, dass die traditionelle Kirche ihrer Rolle nicht mehr gerecht würde. Was man einige Generationen zuvor noch klaglos und demütig hingenommen hatte, wie ungelehrte Priester und die Umgehung des Zölibats, erregte nun immer stärker Anstoß und Ärgernis. Die Forderungen nach einer Reformation der Kirche „an Haupt und Gliedern“ wurden immer lauter, und bald kamen auch Wünsche nach einer politischen Reform des Reichs dazu.

MARTIN LUTHER war 1512 als Theologieprofessor nach Wittenberg berufen worden. Ob er sich schon damals mit diesen Bewegungen konfrontiert sah, ist nicht bekannt, aber anzunehmen. Ihn beschäftigte vor allem die Frage der persönlichen Heilsgewissheit – wie der Mensch „Gottes Zorn“ (Römer 1,18) entgehen könne. Um darauf eine Antwort zu finden, vertiefte er sich immer mehr in das Studium der Bibel. Dabei kam er zur Erkenntnis, dass nicht die Taten und Werke, sondern allein der Glaube an die Gnade Gottes und die Erlösung durch Christus den sündigen Menschen vor Gott rechtfertigen und vor der Verdammnis erretten (Römer 3,28): *„Der Gerechte wird aus Glauben leben“* (Römer 1,17).

Seit 1514 begegnete LUTHER in seinem Nebenamt als Stadtprediger Wittenbergs auch der religiösen Alltagswelt außerhalb von Kloster und Universität. Besonders erschreckte und empörte ihn die um sich greifende Vorstellung der Gläubigen, dass nicht Reue und Buße, sondern der Kauf von Ablässen das Seelenheil garantieren könne. *„Wenn das Geld im Kasten klingt, die Seele aus dem Fegefeuer springt!“* Zwar lehrte die Römische Kirche offiziell solche Behauptungen nicht, duldeten und unterstützten aber den Verkauf von Ablässen. So zog im Jahr 1517 der Dominikaner Tetzl marktschreierisch mit Ablasszetteln durch das Land, deren Erlös angeblich dem Bau der Peterskirche in Rom dienen sollte. LUTHERS Kritik am Ablasshandel hatte vor allem seelsorgerliche Gründe. Sein erster Vorstoß am 31. Oktober 1517 durch den Anschlag von 95 Thesen in lateinischer Sprache blieb folgenlos (Halt 2a). Erst als er sich im März 1518 mit einer deutschen Zusammenfassung an eine

breitere Öffentlichkeit wandte, verbreiteten sich die Thesen in ganz Deutschland und wurden vom Volk begeistert aufgenommen. Papst Leo X. sah sich zum Eingreifen genötigt. In seinem Auftrag versuchte Kardinal Cajetan vergeblich LUTHER zum Widerruf zu bewegen. In einer Disputation in Leipzig mit Johannes Eck, seinem schärfsten Gegner, bestritt LUTHER zum ersten Mal die Vorrangstellung des Papstes und die Unfehlbarkeit der Kozilien (Halt 4). Als gesicherte Wahrheit ließ er nur gelten, was in der Bibel begründet war, sie allein war ihm die Richtschnur des Glaubens. In der Folgezeit wurde Luther einer der produktivsten und populärsten Schriftsteller im deutschen Raum. Seine Schrift „*An den christlichen Adel deutscher Nation*“ rief die Deutschen zu Mitstreitern auf. „*Von der babylonischen Gefangenschaft der Kirche*“ richtete sich gegen die kirchliche Sakramentslehre. „*Von der Freiheit eines Christenmenschen*“ verkündete die durch den Glauben gewonnene Freiheit und christliche Nächstenliebe.

Papst Leo drohte mit dem Bann, doch LUTHER verbrannte die Bulle öffentlich (Halt 2c). Schließlich wurde LUTHER 1521 vor den Reichstag in Worms geladen, wo er in Gegenwart von Kaiser Karl V. den geforderten Widerruf verweigerte. Der Kaiser verhängte daraufhin die Reichsacht über ihn, aber LUTHERS Landesfürst Friedrich III. (der Weise) ließ ihn auf der Wartburg bei Eisenach in Sicherheit bringen. Dort begann er sein bedeutendstes Werk: die Übersetzung der Bibel ins Deutsche. Mit dieser historischen Tat ermöglichte LUTHER nicht nur jedem lesekundigen Christen das Wort Gottes zu studieren und sein eigener Priester zu sein, sondern begründete damit auch die deutsche Nationalsprache. 1522 kehrte LUTHER nach Wittenberg zurück. Seine Lehre hatte inzwischen eine große Popularität in allen gesellschaftlichen Schichten erreicht. Bürger, Bauern und Adelige bekannten sich zum reformierten Glauben – allerdings waren ihre politischen Ziele und Wünsche meist verschieden. Eine Zäsur brachte der sogenannte Bauernkrieg im Jahr 1525, in dem LUTHER eine klare Stellung gegen die Aufständischen und für die Obrigkeit bezog.

Unter LUTHERS Einfluss entwickelten sich eine grundlegende Umgestaltungen des kirchlichen Kultus, welcher den Laien erstmals ein Mitwirkungsrecht ermöglichte. Die neue Interpretation der christlichen Nächstenliebe führte zu einer neuen Form der Armenversorgung. Schließlich gingen von LUTHER weitreichende Anstöße für die Errichtung eines flächendeckenden Elementarschulsystems in den protestantischen Gebieten aus. Mit dem Versuch einer Reform des Wirtschafts- und Finanzwesens im christlichen Sinne scheiterte er jedoch. Um dem Reformwerk Luthers dauerhaften Bestand zu geben, wurden auf der Grundlage der territorialen Verfassung des Reiches evangelische Landeskirchen gegründet. Damit gewannen die Landesfürsten auch politischen Einfluss auf ihre jeweiligen Kirchen, den sie bis 1918 behielten.

LUTHER selbst hat sich nicht als Reformator verstanden, sondern als Werkzeug Gottes. Der Urheber der Bewegung blieb für ihn Gott, der in seinem Wort wirkt.

Literatur: BAINTON (1950), DIWALD (2003), EISOLD & LAUTSCH (1992), JUNGHANS (1996), LEVEBRE (1996), MELLER (2008), PARKER (2003), SCHLENKER et al. (1998)

Halt 2a: Schlosskirche (UNESCO-Weltkulturerbe)

27. These: „*Menschliche Gedanken predigen diejenigen, die sagen: Sobald die eingeworfene Münze im Kasten klingt, fliegt die Seele aus dem Fegefeuer in den Himmel!*“.

MARTIN LUTHER (1517)

1496 ließ Kurfürst Friedrich III. der Weise die ehemalige askanische Stiftskapelle aufwändig im Stil der obersächsischen Hallenkirchen umbauen, auch um die repräsentative Ausstellung seiner umfangreichen und kostbaren Reliquiensammlung, das „Wittenberger Heilthum“, zu ermöglichen.

Der Überlieferung nach schlug MARTIN LUTHER am 31. Oktober 1517 seine 95 Thesen gegen den Ablasshandel an der nordöstlichen Kirchentür an, welche als „Schwarzes Brett“ der Wittenberger Universität diente (Abb. 2). Historiker datieren diesen Tag als den Beginn der Reformation, die evangelischen Kirchen feiern den 31. Oktober als Reformationstag.

Im Oktober 1760, während des Siebenjährigen Krieges, wurde die Kirche bis auf die Grundmauern zerstört, lediglich die Gräber LUTHERS und MELANCHTHONS blieben erhalten. Zunächst wurde sie provisorisch wieder aufgebaut. 1858 ließ König Friedrich IV. die Thesentür in Bronze neu gestalten (Abb. 2). 1883, unter persönlicher Leitung des Kronprinzen Friedrich Wilhelms, dem späteren Kaiser Friedrich III., begannen Planungen für eine Wiederherstellung der Kirche im neugotischen Stil als Monument der Reformation. Fertiggestellt und neu geweiht wurde die Kirche erst 1892 unter Kaiser Wilhelm II.



Abb. 2: Wittenberg, Thesentür an der Schlosskirche, 1858 in Bronze erneuert (www.landesbildarchiv.bildungs-lsa.de).

Der 88 m hohe Kirchturm ist mit einer reich verzierten neogotischen Haube versehen, und trägt die Umschrift: „*Ein feste Burg ist unser Gott*“. Bedeutende Kunstwerke im Chor der Kirche sind die beiden bronzenen Epitaphe für Kurfürst Friedrich den Weisen (*1463–1575) und dessen Nachfolger Johann den Beständigen (*1468–1532), gefertigt von PETER VISCHER D. J. (1527) und HANS VISCHER (1532). Die beiden Förderer und Beschützer der Reformation sind auch als kniende Ganzfiguren zu beiden Seiten des Altars dargestellt.

Vor dem Chor befinden sich die schlichten Gräber von MARTIN LUTHER und PHILLIPP MELANCHTHON. LUTHERS Grabplatte trägt auf Latein die Inschrift: „*Hier ist begraben der Leib des Doktors der heiligen Theologie Martin Luther, der im Jahre Christi 1546, am 18. Februar in seiner Heimatstadt Eisleben starb, nachdem er 63 Jahre, 2 Monate, 10 Tage gelebt hatte*“.

Literatur: EISOLD & LAUTSCH (1992), ROESGEN (1980)



Abb. 3: Wittenberg, Markt mit Rathaus, Luther- und Melanchthondenkmal, Stadtkirche St. Marien (www.landesbildarchiv.bildung-lsa.de).

Halt 2b: Markt

Der Markt, eigentlich nur eine Ausweitung der zentralen Ost-West-Achse, bildet seit der Gründung der Stadt das Zentrum Wittenbergs (Abb. 3). Hier wohnten die wohlhabendsten Bürger in repräsentativen Stadthäusern, umgeben von besonders großen Grundstücken. In der Schloßstraße 1 und am Markt 4 sind die beiden Häuser der Malerfamilie CRANACH mit dem sogenannten „**Cranachhof**“ erhalten. LUKAS CRANACH d. Ä. war 1504 als Hofmaler von Kurfürst Friedrich III. berufen worden. Das stattliche **Rathaus** mit seinem reich verzierten Altan wurde um das Jahr 1570 gebaut. Bis heute zeugt der Platz von der Macht und dem Reichtum der Bürgerschaft im letzten Drittel des 16. Jh., welches auch die höchste Blüte der Wittenberger Universität mit sich brachte. Die Unterbringung der vielen Studenten verlangte neue Bauten, welche vor allem zwischen Markt und **Stadtkirche (UNESCO-Weltkulturerbe)** sowie zwischen der Collegien- und Mittelstraße entstanden.

Nachdem Wittenberg 1815 preußisch geworden war, sorgte König Friedrich Wilhelm III. dafür, dass das ursprünglich für das Mansfelder Land vorgesehene **Lutherdenkmal** von FRIEDRICH SCHADOW hier auf dem Markt aufgestellt wurde. Es ist das erste Denkmal für einen Bürgerlichen im öffentlichen Raum in Deutschland. 1860 kam dann das Denkmal für PHILIPP MELANCHTHON als Gegenstück hinzu.

Halt 2c: Lutherhaus (UNESCO-Weltkulturerbe)

1504 begann der Orden der Augustinereremiten mit finanzieller Unterstützung des Kurfürsten mit dem Bau eines Klosters im äußersten Osten der Stadt. Der Plan für eine aufwändige Vierflügel-Anlage wurde jedoch aufgegeben. Ausserdem verhinderte die Reformation den vorgesehenen Ausbau der Klosterkirche. Die Größe des Hauses erklärt sich aus seiner ursprünglichen Bestimmung zum „Studium Generale“ der thüringischen Ordensprovinz.

MARTIN LUTHER kam 1512 endgültig als Professor an die Leucorea. Ob er in den Anfangsjahren auch Vorlesungen im Kloster gehalten hat, lässt sich nicht mit Sicherheit sagen. Unter dem Einfluss der Reformation löste sich nach 1522 die Ordensgemeinschaft der Augustinereremiten auf. LUTHER blieb mit seinem Famulus in den verwaisten Räumen zurück. Dies änderte sich erst 1525 nach seiner Heirat mit KATHARINA VON BORA. Die rührige und äußerst geschäftstüchtige Frau führte im Haus ihren großen Familienhaushalt sowie ein Studentenheim und ließ dafür den Innenausbau fertigstellen. Aus dieser Zeit stammt auch das Sitznischenportal an der Nordseite.

Nach dem Tod MARTIN LUTHERS erwarb 1563 der sächsische Kurfürst AUGUST das Haus. Zusammen mit dem Neubau an der Nord- und Westseite wurde die Anlage eine der größten Studentenstiftungen einer Universität in den protestantischen Ländern.

Mit der Schließung der Universität im Jahre 1817 erhielt zwar der Straßenflügel durch das Königliche Predigerseminar „**Collegium Augusteum**“ eine neue Nutzung, der Südflügel mit der berühmten Lutherstube stand aber leer. Auf königliche Initiative hin baute der Architekt FRIEDRICH AUGUST STÜLER in einer Jahrzehnte währenden Arbeit das gesamte Haus innen und außen völlig um. 1883 konnte schließlich das Museum „Lutherhalle“ eröffnet werden. Die letzte Umgestaltung mit der Errichtung eines neuen Eingangsgebäudes erfuhr das Museum 2002 (Architekturpreis des Landes Sachsen-Anhalt 2004). SCHMITT & GUTJAHR (in MELLER 2008) berichten über archäologische Ausgrabungen und Bauforschungen an Luthers Wohnhaus.

Wenige Meter neben dem Augusteum steht das 1536 errichtete **Melanchthonhaus (UNESCO-Weltkulturerbe)** von LUTHERS Kollegen und Weggefährten PHILIPP MELANCHTHON (*1497–1560), heute ein Museum für das Leben und Werk des „Praeceptor Germaniae“. Anschließend folgen mit dem „**Fredericianum**“ die ehemaligen Hauptgebäude der Wittenberger Universität, in denen jetzt die Universitätsstiftung „Leucorea“, das Zentrum für Reformationsgeschichte und Lutherische Orthodoxie und andere Universitätseinrichtungen ihren Sitz haben. Gedenktafeln erinnern hier und andernorts an die zahlreichen bedeutenden Persönlichkeiten, die an der Leucorea gelehrt und studiert haben oder in der Stadt als Besucher weilten (STRAUCHENBRUCH 2008). „... *willst du studieren, so geh nach Wittenberg*“ lautete ein alter Studentenspruch. Auch SHAKESPEARES (fiktiver) Dänenprinz Hamlet und seine Begleiter konnten seinerzeit nur in Wittenberg studiert haben. *Hamlet: „Im Ernst, was führt Euch weg von Wittenberg?“. Horatio: Ein müßiggängerischer Hang, mein Prinz“.* (W. SHAKESPEARE, 1623: Hamlet Prinz von Dänemark, 1. Akt, 2. Szene).

Östlich der Altstadt, vor dem ehemaligen Elstertor, steht die „**Luthereiche**“. Diese ersetzt seit 1830 einen Baum, der an der Stelle stand, wo MARTIN LUTHER am 10. Dezember 1520 die Bannandrohungsbulle von Papst Leo X. verbrannt hat.

Literatur: EISOLD & LAUTSCH (1992), JUNGHANS (1996), STRAUCHENBRUCH 2008, TREU (1995, 1999, 2003), TREU et al. (2000)

Südlich von Wittenberg ist die Elbaue etwa 8–10 km breit. Der Schutzdeich verläuft jedoch schon nach knapp 2 km bei Pratau und schränkt die Überflutungsfläche auf etwa ein Fünftel ein.

K e m b e r g, das „Nordtor zur Dübener Heide“, liegt etwas erhöht auf schmaler weichselzeitlicher Niederterrasse. Im September 1631 hatte König GUSTAV ADOLF von Schweden in einem Haus am Marktplatz sein Hauptquartier, bevor er sich in Düben mit der sächsischen Armee vereinigte (Halt 5). „*Hier kommt der sündige Schwede!*“, scherzte er bei seiner Ankunft. Neben der B 2 befindet sich eine große vorgeschichtliche Ringwallanlage, die seit dem 16. Jh. als Friedhof dient (WALDENBURGER 2003). Die „Dübener Heide“ ist heute großteils bewaldet. Ihr Untergrund wird bis hinter den Lutherstein von der warthezeitlichen „Schmiedeberger Stauchendmoräne“ gebildet (s. u.). Die Landschaft ist kuppig und weithin mit Kiefern bestanden.

Halt 3: Kiessandtagebau Köplitz/Ateritz

(Mitteldeutschen Baustoffe GmbH; TK/GK25 4241 Kemberg, R: 45 42 300, H: 57 32 600).

Der Kiessandtagebau liegt 0,5 km nordwestlich vom Forsthaus Oppin, unmittelbar neben der B 2. Geologisch befindet er sich im nordwestlichen Randbereich der **Schmiedeberger Stauchendmoräne** (Abb. 4; KNOTH 1978). Die Lagerungsverhältnisse im Tagebau sind gekennzeichnet durch starke glazitektonische Stauchungen. Bei guten Aufschlussverhältnissen sind steil aufgerichtete Schollenpakete zu sehen, bestehend aus oberligozänen Bitterfelder Glimmersanden, der untermiozänen Bitterfelder Flöz- und Decktonfolge, frühpleistozänen Schottern, Dehlitz-Leipziger Bänderton, Erster Elster-Grundmoräne und glazifluvialen elster- bis saalezeitlichen Schmelzwassersanden und -kiesen. Durch die starke Schrägstellung treten alle Schichten nahezu bis an die heutige Geländeoberfläche und streichen dort aus. Sie werden meist nur von geringmächtigen saalezeitlichen Schmelzwassersanden bedeckt, die von einer losen Steinsohle mit zum Teil windbeschleunigten Geschieben abgeschlossen werden. Abgebaut werden vorwiegend Kiese und Sande für die Baustoffindustrie, aber auch bindige Rohstoffe wie Geschiebemergel und siltige Tone für den Deichbau.

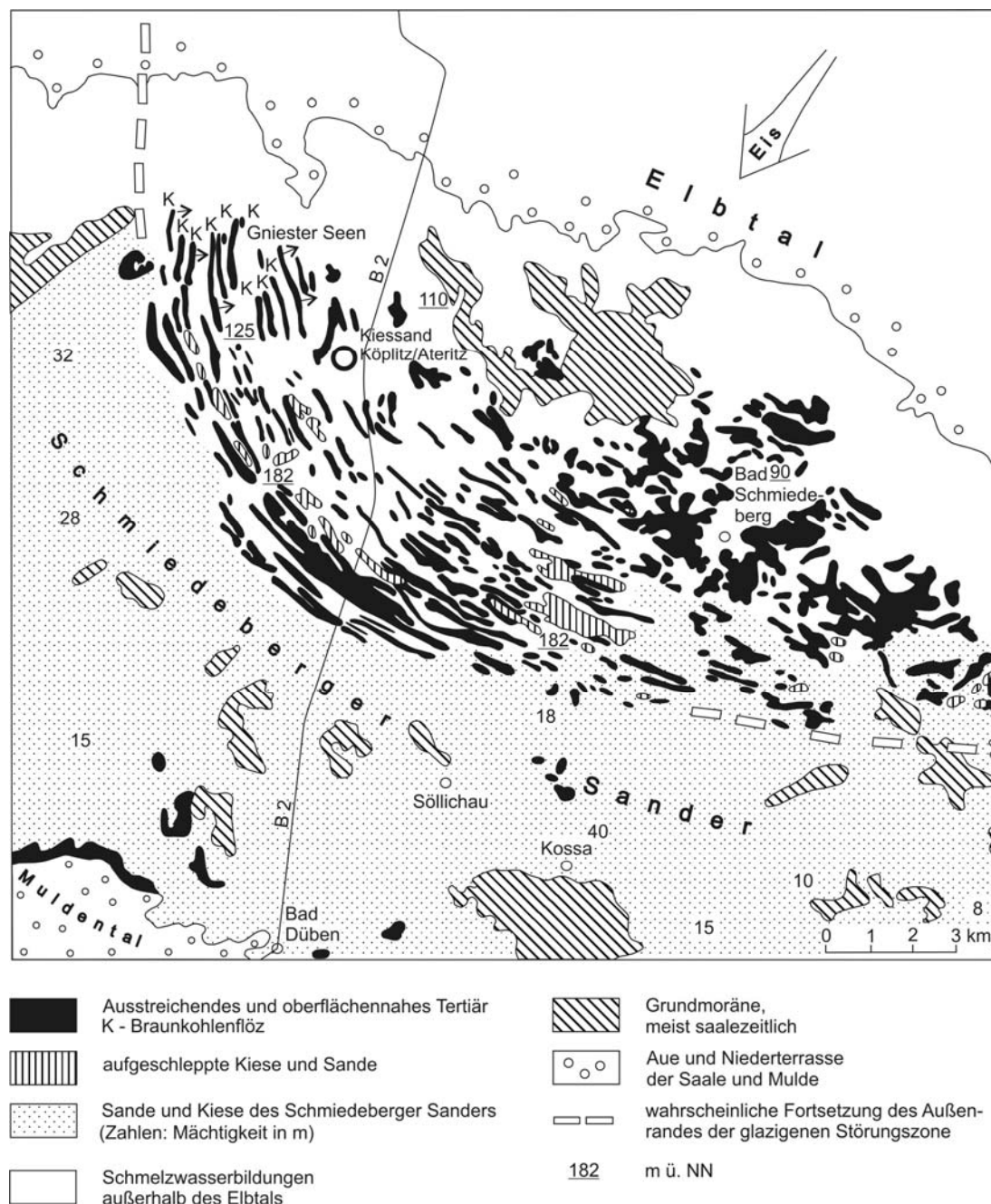


Abb. 4: Schmiedeberger Stauchendmoräne (EISSMANN 1975, 1987), Lage des Kiessandtagebaus Köpplitz/Ateritz (Halt 3)

Morphologisch ist das Stauchmoränengebiet durch eine sehr unruhige und wellige Geländeoberfläche gekennzeichnet. Aufgrund der Morphologie und dem Waldreichtum wurde der Name „Gniester Schweiz“ geprägt. Die Schmiedeberger Stauchendmoräne, welche dem bekannten Muskauer Faltenbogen in der Lausitz ähnelt, zeigt typische vom Gletscher geschaffene injektive „Fließfalten-Schuppen“. Ein aus nordöstlicher Richtung vorgedrungener, mindestens 20 km breiter Lobus von Inlandeis stauchte und quetschte den Untergrund bis in eine Tiefe von 50–175 m. Auf 3–5 km Breite entstanden so 12 bis 15 Fließfalten, die zu injektiven Falten und schließlich zu injektiven Faltenschuppen modifiziert wurden, indem der ursprünglich zuunterst liegende Bitterfelder Glimmersand die Sättel durchbrach und zum Teil sogar die Oberfläche erreichte. Die im Streichen über 3–5 km verfolgbaren „Schuppen“ erweisen sich jedoch als rotierte Schollen, welche nur aufwärts verschoben, aber kaum horizontal transportiert worden sind. Dies ist im Rückland der Schuppen belegt, wo keine Schichtlücken vorhanden sind, die der Summe des vermeintlichen, tatsächlich aber dehnungsbedingten Überschiebungsbetrages entsprechen. Statt dessen ist die erste „Faltenschuppe“ nur eine Schichtaufbiegung, welche die Flanke eines mit dem ungestörten Schichtverband noch verbundenen Sattels bildet (EISSMANN 1987, BÜCHNER 1999).

Der nahezu lehrbuchhafte Stauchungswall überragt das Zungenbecken des Gletschers stellenweise über 100 m. Heute ist er in geschlossener Form nur noch im Westen und Süden erhalten. Im Osten fällt er ins Elbtal ab, wo die größte glaziäre Destruktionsstruktur im mitteldeutschen Raum, die elsterzeitliche Elbtalglazialwanne ausgebildet ist (MÜLLER 1973, 1988). Der Stauchungswall verläuft bogenförmig von Reuden–Uthausen (westlich von Kemberg) bis zum Forsthaus Tornau–Lutherstein in Richtung Nord-Süd bis NNW-SSE, biegt dann nach SE bis ESE um und lässt sich bis an das Elbtal verfolgen. Er entstand er in der Fläming-Phase (Warthe) des Saaleglazials.

250 m westlich des Kiessandtagebaus beginnt das Braunkohlen-Altbergbauggebiet von Gniest, mit seinen „ertrunkenen Gruben“, den sog. Gniester Seen. Im Gebiet von Gniest streichen auf ca. 4 km Breite bis zu 14-mal miozäne Kohleflöze in strenger Nord-Süd-Richtung aus. Der rasche Wechsel und die ständige Wiederholung von Ton, Braunkohle, Sand, Ton sind das Resultat der glazitektonischen Verfaltung und Verschuppung, die durch steile Außenränder mit maximal 70° und flache Innenränder mit bis 15° Schichtneigung geprägt sind. An der Oberfläche ausstreichenden Braunkohlenflöze waren von 1850–1913 Gegenstand des Bergbaus, z. B. in den Gruben Marie, Roberts Hoffnung, Friederike, Theodora, Gustav II und Friedrich IV. Diese wurden anfänglich nicht selten wegen Durchbrüchen von Liegendwasser auflässig. Im Südosten des Stauchungsgebietes wurde Braunkohle seit 1864 in der Grube Nr. 462 bei Kemberg und in der Grube Wilhelm bei Hohenlubast abgebaut.

Während des Bergbaus fand sich Bernstein in den Bitterfelder Glimmersanden, welcher bereits 1756 in den Braunkohlengruben um Bad Schmiedeberg vom Sächsischen Bergrat J. F. HENKEL als „Sächsischer Bernstein“ beschrieben und als autochthon erkannt wurde (KRUMBIEGEL & KOSMOWSKA-CERANOWICZ 1989).

Südlich an den Schmiedeberger Endmoränenbogen schließt ein weitflächiger Sander an, der bei Kossa bis zu 40 m Mächtigkeit erreicht.

Glaziale Geschiebe und Findlinge

Während den Elster- und im Saale-Kaltzeiten war das Exkursionsgebiet mehrmals von mächtigem Inlandeis bedeckt. Davon zeugen glaziäre Sedimentfolgen aus Grundmoränen und Schmelzwasserablagerungen, die im Deckgebirge der Braunkohlentagebaue und in zahlreichen Kiessandgruben aufgeschlossen waren oder sind. Die Grundmoränen sind aufgrund ihrer weiten Verbreitung und guten Unterscheidbarkeit wichtige lithostratigraphische Leithorizonte. Sie enthalten ein reiches Inventar an Geschieben verschiedenster Größe und petrographischer Zusammensetzung, das die beste Quelle für die Rekonstruktion der Bewegungsrichtungen des Eises bildet und als wesentliches Kriterium für die Zuordnung der Grundmoränen zu den verschiedenen Vergletscherungsphasen gilt. Die stratigraphische Interpretation der Geschiebeanalysen muss stets unter Berücksichtigung des Grundmoränengefüges, der Lagerungsverhältnisse und der Kenntnis regionaler Besonderheiten erfolgen.

In Mitteldeutschland wird vor allem die **Kleingeschiebezählung** erfolgreich angewendet. Bei dieser Methode wird der Gesamtbestand einer festgelegten Kornfraktion in Geschiebegruppen eingeteilt, z. B. Nordisches Kristallin, paläozoischer Kalkstein, Feuerstein, Sandstein/Quarzit, Quarz usw. In großem Umfang liegen Analysen der Fraktion 4–10 mm vor, die nach einer in der DDR standardisierten Methode durchgeführt wurden und daher eine gute Vergleichbarkeit der Ergebnisse gewährleisten. In der Regel lassen sich durch die Verteilung der Kleingeschiebe die Saale-Grundmoränen sowohl untereinander als auch gegen die Elster-Grundmoränen gut abgrenzen. Im Raum Gräfenhainichen, wo das Elster-Glaziärstockwerk bis vor wenigen Jahren umfassend aufgeschlossen war, zeichnet sich die Obere Grundmoräne gegenüber der Unteren durch einen deutlich höheren Gehalt an tertiärem Material aus. Daraus resultiert die meist feinere Körnung und die charakteristische schwarzbraungraue Farbe (MÜLLER 1988, WANSKA 1991, 2004). Wie bei den Elster-Grundmoränen, ist auch bei den Saale-Moränen festzustellen, dass im liegenden Teil der unteren Moräne erhöhte Quarzgehalte auftreten, die aus der Eis-Überföhrung von Schotterkörpern resultieren. Im Mittel sind die Elster-Grundmoränen stärker quarzföhrend als die Saale-Grundmoränen. Die Moränen der Leipziger Phase weisen erhöhte Anteile an paläozoischen Kalksteinen auf, die Warthe-Moräne ist außerdem oft reich an Dolomit (EISSMANN 1975). Die Geschiebeföhrung altersgleicher Grundmoränen ändert sich jedoch regional.

Findlinge sind wegen ihrer Größe auffallende Geschiebe mit Durchmessern von mehreren Dezimetern bis in den Meterbereich (SPEETZEN 1998). Auch sie können Hinweise auf die Transportrichtung des Eises geben, werden aber wegen der eingeschränkten statistischen Auswertbarkeit nur selten in die Betrachtung einbezogen. Findlinge sind jedoch als auffällige Zeugen

der erdgeschichtlichen Entwicklung von besonderer Bedeutung. Deshalb sind viele als Geotop registriert und unter Schutz gestellt (KARPE 1995, 1999).

Halt 4: Lutherstein

Der Lutherstein ist ein Findling (ND) am südwestlichen Randbereich der Schmiedeberger Stauchendmoräne (Abb. 4). Er befindet sich, von vier Eichen umgeben, etwa 900 m nordöstlich von Eisenhammer, unmittelbar rechts der B 2. Der Geschiebeblock ist rund 2,5 m lang, 1 m breit, ragt 0,6 m aus dem Boden und wiegt mehr als 10 t. Petrographisch handelt es sich um einen grobkörnigen Quarzsyenit. An Mineralkomponenten besitzt er u. a. rosa Kalifeldspäte mit vielen, glänzenden Spaltflächen, bis zu 8 mm große graue Quarze und einzelne Biotitschuppen (BÜCHNER et al. 2004).

Auf seiner Oberfläche eingemeißelt sind die Buchstaben „D.M.L.“ (für Dr. MARTIN LUTHER) und die bekannte Zeile „Eine feste Burg ist unser Gott“. MARTIN LUTHER hat die Straße zwischen Wittenberg und Leipzig oft benutzt und hier Rast eingelegt. Hier an der kursächsischen Grenze soll Luther von Wittenberger Studenten und Bürgern empfangen worden sein, als er 1519 von der berühmten Disputation mit Dr. ECK in Leipzig zurückkehrte. Auf dem Stein stehend berichtete Luther von dieser Auseinandersetzung. Auch soll er im April 1521 von Wittenberger Studenten bis hierher begleitet worden sein und von diesem Stein gesprochen haben, bevor er weiter zum Reichstag nach Worms reiste.

Kulturhistorisch gehört der Lutherstein zu den sog. Näpfchensteinen. Auf seiner Oberfläche sind in regelloser Verteilung etwa 20 Näpfchen in Form von kreisförmigen Vertiefungen enthalten. Sie sind 2–4 cm tief und 3–5 cm im Durchmesser. Die von Menschenhand vor ca. 5000–3000 Jahren durch Reiben, Bohren und Einklopfen geschaffenen Vertiefungen sind Zeugnisse der „Megalithkultur“ in Mitteleuropa (FIEBER 2004).

Literatur: KARPE (1999: Geotop 4341/2), WALDENBURGER (2003), WANSKA (2004)

Nach dem Lutherstein wird der Untergrund von drenthezeitlichem Glazifluvial gebildet. Links befindet sich eine Köhlerei. Namen wie *Eisenhammer* und *Hammermühle* zeugen von Abbau, Verhüttung und Verarbeitung von Raseneisenerz in der Mitte des 18. Jh.. Südlich von Eisenhammer wird das Gelände eben und ist zum Teil beackert. Hinter Tornau überschreitet man die sächsische Landesgrenze.

Von 1557 bis 1866 wurde nordwestlich von Düben ein *Alaunwerk* betrieben, das zu den bedeutendsten in Deutschland zählte und in viele Länder Europas exportiert hat (WALDENBURGER 2003). Chemisch handelte es sich um Eisenalaun, ein wasserhaltiges Doppelsulfat $[\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}]$, das vor allem in der Gerberei Verwendung fand. Als Rohstoff dienten schwarze untermiozäne Tone, in denen das Alaun durch Oxidation von fein verteiltem Schwefeleisen (Pyrit, FeS_2) entstand. Das „Rote Ufer“ nördlich der Muldeau ist bis 15 m hoch und entstand durch die Aufhaldung von ausgelaugter schwarzer und gerösteter roter Alaunerde. Neben dem Alaun werden seit Anfang des 19. Jh. um Bad Düben und Bad Schmiedeberg auch vitriolführende Torfe für Badezwecke gewonnen, u. a. für das Kaisermoorbad bei Bad Düben.

Der jahrhundertelange Holzeinschlag für die Eisen- und Alaunindustrie ließ die „Dübener Heide“ entstehen.

Schlacht bei Mühlberg an der Elbe (1547)

Drei Jahrzehnte nach dem Beginn der Reformation bekannten sich fast ganz Norddeutschland, Mitteleuropa und große Teile Süddeutschlands zum evangelischen Glauben. Kaiser Karl V. (*1500–1558) aber war entschlossen, Deutschland mit allen Mitteln zum alten Glauben zurückzuführen. Er verhängte die Reichsacht über Kurfürst Johann Friedrich (den Großmütigen) von Sachsen und Landgraf Philipp von Hessen, den beiden führenden Männer des Schmalkaldischen Bundes, zu dem die Evangelischen sich 1531 zusammengeschlossen hatten.

Am 24. April 1547 kam es bei Mühlberg an der Elbe, 60 km südöstlich von Wittenberg, zur Entscheidungsschlacht, die für Kurfürst Johann Friedrich verloren ging. Wittenberg wurde belagert und schließlich kampflos übergeben. Im kaiserlichen Feldlager westlich der Stadt wurde der besiegte Kurfürst zunächst zum Tode verurteilt, dann begnadigt. Schließlich unterschrieb er die „Wittenberger Kapitulation“. Johann Friedrich verlor Fürstentum und Kurwürde an seinen gleichfalls evangelischen Vetter Moritz von Sachsen, der auf der Seite des Kaisers stand. Nur kleinere Teile in Thüringen verblieben den beiden Söhnen Friedrichs.

MARTIN LUTHER war ein Jahr vor der Schlacht gestorben. Kaiser Karl V. soll LUTHERS Grab in der Schloßkirche zu Wittenberg besucht haben, das er entgegen den Forderungen seiner spanischen Begleiter unversehrt ließ.

Anfang Juni zog Karl V. nach Halle an der Saale. Landgraf Philipp von Hessen, der zweite Kopf des Schmalkaldischen Bundes, gab sich ihm dort gefangen. Im großen Saal der Neuen Residenz, in welcher der Kaiser Quartier genommen hatte, musste er kniefällig dem Sieger huldigen (Exk. B, dieser Bd.).

Eine endgültige Entscheidung gegen die Protestanten war aber nicht gefallen, zumal Moritz von Sachsen bald die Seite wechselte. Erst mit dem Augsburger Religionsfrieden von 1555 wurde der Konflikt vorläufig beigelegt. Kaiser Karls V. Kampf gegen den Protestantismus war gescheitert, die Glaubensspaltung besiegelt.

Literatur: GROSS (2001), HARTMANN & SCHNITH (1996), HELD (1997), SEIBT (1997), KÖTZSCHKE & KRETZSCHMAR (1935)

Ausbruch des Dreißigjährigen Krieges (1618)

Der Augsburger Religionsfrieden, mit dem sich Katholiken und Protestanten gegenseitige Toleranz zugesichert hatten, wurde zunehmend von katholischer Seite unterlaufen, um die alte Vorherrschaft des Katholizismus wieder herzustellen. Besonders unter Kaiser Ferdinand II. (*1578–1637), verstärkte sich die Gegenreformation. Schließlich schritten 1618 die protestantischen böhmischen Stände zum gewaltsamen Widerstand. Mit dem „Prager Fenstersturz“ begann der „Dreißigjährige Krieg“, in den fast alle europäischen Mächte zumindest zeitweise verwickelt waren. Zunächst ging es um konfessionelle Gegensätze zwischen den konkurrierenden katholischen und protestantischen Parteien, später fast ausschließlich um machtpolitische Interessen, vor allem des Hauses Habsburg auf der einen Seite und Frankreichs und Schwedens auf der anderen. Anfangs gewann die katholische Liga unter Habsburgs Führung die Oberhand. Herzog Maximilian von Bayern und dessen Feldherr Johann Tserclaes Graf von Tilly (*1559–1632) siegten 1620 am Weißen Berg bei Prag über die protestantische Union und den gewählten böhmischen „Winterkönig“ Friedrich V. von der Pfalz (*1596–1632).

Literatur: HARTMANN & SCHNITH (1996), HUCH (1912/14), WILKE (2004), WEDGWOOD (1967)

Schlacht an der Dessauer Brücke (1626)

Nach dem Erfolg in Böhmen schritt die Katholische Liga auch in Norddeutschland zur gewaltsamen Rekatholisierung. 1624 trat auf evangelischer Seite König Christian IV. von Dänemark in den Krieg ein. Im Zuge der militärischen Maßnahmen ließ der zum Oberbefehlshaber der kaiserlichen Truppen ernannte Wallenstein (*1583–1634) bei Dessau das rechte Elbufer befestigen, um den einzigen bis Magdeburg vorhandenen festen Flußübergang zu sichern (Abb. 1). Im April 1626 griff eine mit 20 000 Mann weit überlegene protestantische Armee unter Graf Ernst von Mansfeld drei Wochen lang die von Oberst Aldringen kommandierten Stellungen an, wurde aber am 25. April verlustreich zurückgeschlagen. Wenige Monate später wurde König Christian IV. bei Lutter am Barenberge nahe Hildesheim von Tilly besiegt und schied aus dem Krieg aus.

Bald war fast ganz Mittel- und Norddeutschland von der katholischen Liga überrannt oder in Abhängigkeit gebracht und zahlreiche Städte und Dörfer grausam geplündert und zerstört. Kaiser Ferdinand befand sich auf der Höhe seiner Macht. Unter diesem Eindruck erließ er 1629 das „Restitutionsedikt“, welches die katholische Kirche wieder in ihre vorreformatorischen Rechte und Besitztümer einsetzte. Die protestantische Sache schien verloren. Widerstand gegen eine Besetzung leisteten nur noch die Städte Stralsund, welches sich mit dem Schwedenkönig Gustav II. Adolf verbündet hatte, und Magdeburg.

Literatur: HARTMANN & SCHNITH (1996), HÖFER (1994), MANN (1971), MIEHE in SCHLENKER et al. (1993), WEDGWOOD (1967)

König Gustav II. Adolf von Schweden greift ein (1630)

Die militärischen Erfolge der Katholischen Liga veranlassten König Gustav II. Adolf von Schweden (*1594–1632) zum Eintritt in die Auseinandersetzungen. In erster Linie ging es dem überzeugten und frommen Lutheraner wohl darum, militärischen und ideologischen Angriffen auf das eigene Land zuvorzukommen und den bedrängten Glaubensbrüdern zu helfen (SCHWEDE 1979). Im Juli 1630 landete eine schwedische Streitmacht auf der Insel Usedom und marschierte in

Norddeutschland ein, um dort die Kaiserlichen zurückzudrängen. Im Vertrag von Bärwalde in der Altmark versicherte sich der König der Unterstützung und Subsidien durch das katholische Frankreich. Die protestantischen Länder Pommern, Brandenburg und Sachsen zeigten sich zunächst noch unentschlossen, ob sie die Schweden unterstützen sollten.

Ab März 1631 zog General Tilly, der Nachfolger des in Ungrnade gefallenen Wallenstein, mit 30 000 Soldaten einen Belagerungsring um die strategisch wichtige protestantische Stadt **M a g d e - b u r g**. Das neutrale Sachsen verwehrte König Gustav Adolf den Durchmarsch und verhinderte so den rettenden Entsatz. Nach tapferer Verteidigung war die Stadt schließlich doch bereit, vor der Übermacht zu kapitulieren. Da gelang es den Angreifern unter Führung von Pappenheim am 10. Mai die Befestigungen zu überwinden und in die Stadt einzudringen. Im Chaos einer Feuersbrunst plünderten und mordeten die Sieger aufs grausamste. *„Eine Würgeszene fing jetzt an, für welche die Geschichte keine Sprache ... hat“* (F. SCHILLER 1791). Nur der Dom, in den sich viele Bürger geflüchtet hatten, und einige wenige Häuser blieben von der einst blühenden Stadt. Von den 30 000 Einwohnern verloren über 25 000 ihr Leben.

Die protestantischen Länder und das zeitgenössische Schrifttum reagierten mit Entsetzen und Abscheu. Die Zerstörung von Magdeburg und General Tillys nachfolgender widerrechtlicher Einmarsch in das neutrale Sachsen führten dazu, dass sich Kurfürst Johann Georg I. am 11. September im Vertrag von Coswig nahe Wittenberg mit Gustav Adolf verbündete und mit diesem gegen die kaiserliche Liga zog.

Literatur: GROSS (2001), HUCH (1912/14), MANN (1971), MIEHE in SCHLENKER et al. (1993), PUHLE (1998), WEDGWOOD (1967)

Halt 5: Bad Düben, Schwedenstein, Pesttor

Die Altstadt von Düben liegt erhöht auf weichselzeitlicher Niederterrasse, unmittelbar nördlich der Muldeau.

An der Gustav-Adolf-Straße steht ein **Denkstein** mit der Inschrift: *„An dieser Stelle fand am 15. September 1631 die persönliche Begegnung der verbündeten protestantischen Fürsten, des Königs Gustav Adolf von Schweden und des Kurfürsten Johann Georg I. von Sachsen, statt. Die verbündeten Armeen, etwa 38000 Mann, rückten von hier aus zu ihrem Sieg bei Breitenfeld vor.“*

Die Stelle befand sich damals außerhalb und nördlich der Stadtmauern. Im Pestjahr 1577 wurde hier ein Friedhof mit dem **„Pesttor“** angelegt. Der im Renaissance-Stil gestaltete Eingang gliedert sich in drei Bogen: der große mittlere Bogen war für besonders aufwändige Anlässe gedacht, der reich gestaltete rechte Bogen für begüterte Bürger und der linke, einfache Bogen für die Armen und Verbrecher.

Burg Düben steht unmittelbar am Muldeübergang auf einem bronzezeitlichen Wall. Sie wurde erstmals im Jahr 981 erwähnt und war Bestandteil der mittelalterlichen Grenzsicherung gegen die Slawen. Wie die meisten derartigen Burgen wurde sie als Brückenkopf auf der östlichen Flußseite angelegt. 1637, im Dreißigjährigen Krieg, wurde sie zerstört. Im Oktober 1813 war die Stadt Düben Sammelstelle des französischen Heeres vor der Völkerschlacht bei Leipzig. Kaiser Napoleon nahm in der Burg vier Tage Quartier.

Seit 1915 ist Bad Düben Moorbad. In der Burg ist heute das Landschaftsmuseum Dübener Heide eingerichtet.

Literatur: FELLMANN (1991), WALDENBURGER (2003)

Die Aue mit der windungsreichen Mulde ist bei Düben etwa 2 km breit und folgt einem weichsel-zeitlichen Urstomtal. Dorf und Schloß Schnaditz befinden sich in etwas erhöhter Lage inmitten der Aue.

Wellaune

„An den Ufern der Havel, um die Mitte des 16. Jahrhunderts, lebte ein Roßhändler, namens Michael Kohlhaas, ... einer der rechtschaffensten und entsetzlichsten Menschen seiner Zeit. ... Das Rechtsgefühl aber machte ihn zum Räuber und Mörder.“

H. v. KLEIST (1810): Michael Kohlhaas

Ein Denkstein an der historischen Gaststätte „Kohlhaasen Krug“ erinnert an die Stelle, wo im Jahr 1532 der Junker Günther von Zaschnitz vom nahen Schloss Schnaditz dem Kaufmann Hans Michael Kohlhaase aus Cölln an der Spree zwei Pferde beschlagnahmte, welche er später übel

zugerichtet zurückgab. Kohlhasens Bittschriften und Klagen auf Schadenersatz blieben fruchtlos, weil der Junker von Zaschnitz über beste Beziehungen zum kurfürstlich sächsischen Hof verfügte. Als Kohlhasen 1533 seinen Prozess auf Burg Düben verlor, erklärte er dem Junker von Zaschnitz und dem Kurfürsten von Sachsen die Fehde. Die Fehde als Rechtsmittel war jedoch bereits seit dem Reichstag zu Worms im Jahre 1495 verboten, nach welchem der „Ewige Landfriede“ galt. Kohlhasen zerstörte mit seinen Leuten Schloss Schnaditz und zog brennend und plündernd durch Nordsachsen. Der Angriff wuchs sich rasch zu einer Rebellion aus, die Land und Leute in Angst und Schrecken versetzte und vielen das Leben kostete. MARTIN LUTHER, an den sich Kohlhasen 1534 um Hilfe gewandt hatte, riet ihm in einem Brief zum Nachgeben: „... lasset euch euren Schaden von Gott zugefügt sein, und verbeißets umb seinetwillen ...“. Kohlhasen aber führte starrköpfig seine Fehde fort, wurde schließlich gefasst und 1540 in Berlin hingerichtet. HEINRICH VON KLEIST setzte „dem Charakter maßloser Tugend“ mit seiner berühmten Novelle ein literarisches Denkmal.

Literatur: DEITERS (1955), JONSCHER et al. (2007: 40), KLEIST (1810), KRÜGER in MELLER (2008), WALDENBURGER (2003)

Die Straße verläuft bis vor Lindehagen auf reliefarmem Glazifluvial, danach hauptsächlich auf Grundmoräne des Saale (Drenthe)-Glazials.

In der Nacht vom 16./17. September lagerte die schwedische Armee beim Ort Wölkau nahe Krenschitz, die sächsische Armee beim Dorf Hohenleina nahe Krostitz (WALZ 1994), jeweils 14–18 km von Düben entfernt. Am 17. September marschierten beide Armeen rund 10 km bis vor die Stellungen, welche das feindliche kaiserliche Heer nördlich von Leipzig bezogen hatte. Die Exkursionsroute folgt den vorrückenden Armeen der Schweden und Sachsen.

Krostitz

Am 17. September 1531 marschierten die Truppen des Schwedenkönigs bei großer Hitze auf der staubigen Landstraße durch das Dorf Krostitz. Der Überlieferung nach reichte der Gutsherr von Klein-Krostitz dem König eine Silberkanne mit Bier, welches für das bevorstehende Erntedankfest gebraut worden und daher besonders gut und kräftig war. Der König leerte die Kanne, lobte den Trunk und schenkte dem Gutsherrn einen mit Rubinen besetzten Goldring. Fortan nannte dieser die Quelle, aus welcher das Brauwasser stammte, den „Schwedenquell“. Aus der Gutsbrauerei entwickelte sich später die Krostitzer Brauerei, welche als Markenzeichen das Porträt des Schwedenkönigs führt.

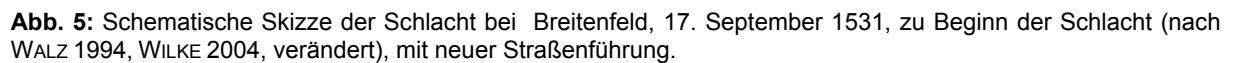
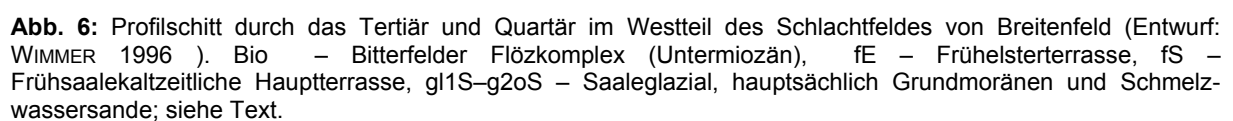
Literatur: www.ur-krostitzer.de

Halt 6: Schlachtfeld von Breitenfeld (1631) bei Podelwitz

Geologie

Das historische Schlachtfeld liegt nördlich von Leipzig zwischen den Ortschaften Breitenfeld, Seehausen, Göbschelwitz, Zschölkau und Podelwitz (Abb. 5), in einer flachwelligen, sich allmählich nach Norden senkenden Landschaft mit damals weithin abgeernteten und ausgedörrten Ackerfluren.

Geologisch handelt es sich um den zentralen Teil der Brehna-Schkeuditzer Grundmoränenplatte, die überwiegend aus saaleglaziären Ablagerungen besteht. Am südlichen Rand wird die Grundmoränenplatte von den Endmoränen bei Breitenfeld und Taucha begrenzt (Abb. 6). Beide Endmoränen entstanden am Rande eines bis Leipzig reichenden saalezeitlichen Inlandeislobus während des Eisrückzuges in der Leipzig-Phase (EISSMANN 1997). Die Breitenfelder Endmoräne findet im Nordwesten ihre Fortsetzung in der Petersberger und im Osten in der Tauchaer Endmoräne. Die Breitenfelder Endmoräne streicht West-Ost und tritt morphologisch weniger in Erscheinung als die Petersberger und Tauchaer Endmoränen. Sie hat keinen markanten, durchgehenden Höhenzug und ist nur durch einzelne Höhenrücken mit Geländehöhen um 130–148 m NN entlang der Linie Kursdorf – Freiroda – Radefeld – Breitenfeld – Göbschelwitz – Gotscheina gekennzeichnet. Ein typischer vorgelagerter Sander, wie bei der Tauchaer Endmoräne, ist nicht vorhanden, jedoch wurden durch viele Erkundungsbohrungen auf Braunkohle entlang der o. g. Höhenrücken glazifluviale Sedimente in flächiger Verbreitung nachgewiesen.



Die quartären Ablagerungen sind durchschnittlich 25–30 m mächtig, in glaziären Rinnen bis 60 m, und überdecken den untermiozänen Bitterfelder Flözkomplex. Im Raum Delitzsch - Breitenfeld beginnt das Quartär mit flintfreien Sanden und Kiesen, den frühelsterzeitlichen Schottern der Saale (Leipziger Saalearm) und Saale-Mulde (Connewitzer Muldelauf; EISSMANN 1997, GROSSE & FISCHER 1989). Darüber folgen die Ablagerungen der zweiphasigen Elster-Verletscherung mit dem bis zu 1 m mächtigen Dehlitz-Leipziger Bänderton, auf dem die Erste (Untere) Elster-Grundmoräne der Zwickau-Phase liegt. Sie wird mitunter durch glazifluviale Sande und Kiese, Beckensilte und -tone, von der Zweiten (Oberen) Elster-Grundmoräne (Markranstädt-Phase) getrennt. Während der spätesten- bis frühsaalezeitlichen fluvialen Erosionsphase wurde die Obere Elster-Grundmoräne weitflächig ausgeräumt. Die Abschmelzphase der zweiten Elstervereisung ist durch Rückzugsschottern gekennzeichnet, welche überwiegend aus einheimischen Geröllen der wieder auflebenden Flüsse bestehen, aber auch reichlich nordisches Geröllmaterial enthalten (EISSMANN 1975).

Ablagerungen aus der Holstein-Warmzeit sind in der weiteren Umgebung von Breitenfeld durch zahlreiche limnische Sedimentfolgen nachgewiesen. Sie liegen meist in glaziären Resthohlformen spätelstereiszeitlicher Rinnen oder in Toteislöchern (DASSOW 1987). Die 8,5–13 km breite und maximal 15 m mächtige frühsaalezeitliche Hauptterrasse des Fluss-Systems Weiße Elster–Pleiße–Vereinigte Mulde, trennt das elsterzeitliche vom saalezeitlichen Glaziärstockwerk. Der Terrassenkörper wurde mehrphasig von der ausgehenden Holstein-Warmzeit bis zum Vordringen des saalezeitlichen Inlandeises aufgeschüttet, d. h. vorwiegend während der Fuhne-Kälteschwankung und der Delitzsch-Phase. Der Schotterkomplex der Hauptterrasse bildet im Saale-Elbe-Gebiet einen wichtigen Leithorizont für die Gliederung des Quartärs (EISSMANN 1994).

Nahezu brettartig liegt auf der Hauptterrasse die zyklisch aufgebaute glaziäre Folge des Saale-Komplexes. Sie beginnt mit dem nur wenige Millimeter bis Zentimeter starken Böhlen-Lochauer Bänderton und der Ersten Saale-Grundmoräne (Zeitz-Phase) und wird durch Rückzugs- und Vorstoßbänderton sowie glazifluviale kiesige Sande des Bruckdorfer Horizontes von der darauf folgenden Unteren Bank der Zweiten Saale-Grundmoräne (Delitzscher Bank der Leipzig-Phase) getrennt. Eine dritte Saale-Grundmoräne, die Obere Bank der Zweiten Saale-Grundmoräne (Breitenfelder Bank der Leipzig-Phase) ist im Gebiet um Breitenfeld ausgebildet. Diese war früher in den ehemaligen Kiessandgruben nahe der Breitenfelder Kapelle aufgeschlossen. Diese Grundmoräne wird durch Schmelzwassersande und -kiese und glazilimnische Warventone, dem sog. Breitenfelder Bänderton, von der Unteren Bank der Zweiten Saale-Grundmoräne getrennt.

Im Gebiet um Breitenfeld sind die Ablagerungen des Bruckdorfer Horizonts und der obere Teil der Ersten Saale-Grundmoräne intensiv glazigen gestört. Es handelt sich um eindrucksvolle eng gestaffelte Sättel und Mulden mit nordwest-südöstlichem und west-östlichem Streichen und ausgeprägter Südvergenz. Auf einer Länge von 200 m ist der obere Moränenteil der Ersten Saale-Grundmoräne in 8–15 injektive Fließ- und Quetschfaltenschuppen gelegt. Unter der Auflast des Gletschers wanderte der obere Moränenteil ab und stieg zu schmalen und breiten Sätteln auf, wobei das Hangende im Wesentlichen passiv mitbewegt wurde (EISSMANN & WIMMER 1988, WIMMER et. al. 1988). Die Stauchungen verursachen an der Oberfläche schwache Erhebungen. Den Abschluss des Quartärs bildet ein bis 0,5 m mächtiger weichselzeitlicher Sandlöss, auf dem der rezente Boden, eine Sandlöss-Parabraunerde entwickelt ist.

Die tiefste Stelle des Gebietes ist die Niederung des Loberbachs bei Zschölkau mit knapp 120 m NN. Die höchsten Erhebungen von rund 130–140 m NN bildet der Aussenrand der Breitenfelder Endmoräne zwischen Breitenfeld und Göbschelwitz, welcher die Wasserscheide zwischen Mulde und Elster bildet. Die geringen Höhenunterschiede fallen heute kaum noch auf, da sich Autobahn und Eisenbahn durch das Gelände ziehen, welches auch sonst mit Straßen und Industrie stark verbaut ist. Nur das Gebiet südlich von Podelwitz und westlich von Göbschelwitz vermittelt noch, wie die Gegend um 1631 ausgesehen haben mag.

Vor der Schlacht

Die schwedisch-sächsischen Truppen zählten etwa 39 000 Mann. Davon waren 26 000 Fußtruppen, überwiegend Musketiere, und 13 000 Kürassiere und Dragoner, welche etwa 75 zumeist leichte Feldstücke (Kanonen) mit sich führten. Die von Norden über Zschölkau heranziehenden Verbündeten mussten zunächst den Bach Lober überqueren, welcher damals mehr Wasser führte als heute. Die Passage der sumpfigen Niederung war ein schweres Hindernis, wie zeitgenössische Berichten mehrfach betonen. Nach der Loberpassage entfaltete sich die Armee am Vormittag in Schlachtordnung südlich vor dem Dorf Podelwitz in einer Länge von etwa 4 km (Abb. 5). Dabei hatten sie Sonne und Staubwind gegen sich und außerdem gegenüber die flach ansteigende Anhöhe von 10–15 m mit der gegnerischen Artillerie. Den rechten Flügel bildete die Reiterei unter König Gustav Adolf, dem Oberbefehlshaber. Zwischen den Reitertruppen waren Einheiten von Musketieren und Pikenieren postiert. Das Zentrum mit schwedischen Fußtruppen befehligte Ake Oxenstierna. Der linke Flügel der Schweden setzte sich zusammen aus Reitern, Musketieren und Pikenieren unter

Feldmarschall Gustaf Horn. Das 2. Treffen (Reserve), bestehend aus Reiterei und Infanterie, kommandierten General Banér und Oberst Hall. Das Besondere und Neue an der schwedischen Gefechtstaktik war eine lineare, nur wenige Glieder tiefe Aufstellung und Unterteilung der Truppen in kleine, gut gedrillte und bewegliche Einheiten. Die Musketiere waren zum Teil zwischen den Reitern aufgestellt. Sie verfügten über verbesserte Gewehre mit neuartigen Radschlössern anstatt der Lunten und konnten deshalb ein anhaltendes „rollendes“ Salvenfeuer unterhalten. Die Zahl der Pikeniere, welche vor Reiterangriffen schützen sollten, war zugunsten der Musketiere reduziert. Die Artillerie war leicht beweglich und vor den Linien postiert. Die sächsische Streitmacht mit Fußtruppen, Reiterei und Artillerie unter Kurfürst Johann Georg I. und General Hans Georg von Arnim stand am äußersten linken Flügel der Aufstellung. Der Schlachtruf des Heeres war „*Gott mit uns!*“

Anfang September 1631 hatte die gegnerische kaiserliche Armee unter General Tilly die Städte Halle, Naumburg und andere befestigte Plätze ohne nennenswerten Widerstand eingenommen. Am 13. September musste auch Leipzig nach kurzer Belagerung die Tore öffnen. Um den anrückenden schwedisch-sächsischen Verbündeten den Weg nach Leipzig zu verlegen, bezog Tilly eine gut gewählte Defensivstellung quer zur Landstraße Düben–Leipzig, die ziemlich genau der heutigen B 2 folgt (Abb. 5).

Die Stellungen erstreckten sich entlang dem oben genannten etwa West–Ost verlaufenden Endmoränenrücken zwischen den Dörfern Breitenfeld und Göbschelwitz. Auf diesen Anhöhen postierte General Tilly seine Feldgeschütze, es sollen nur 23 Stück gewesen sein, in zwei Gruppen am Galgenberg und Birkholz westlich von Göbschelwitz (WALZ 1994). Seine Truppen ließ er zunächst verdeckt zwischen Wiederitzsch und Göbschelwitz hinter der Geländeerhebung in Wartestellung gehen, so dass sie für die anrückenden Verbündeten zunächst nicht sichtbar waren. Sie umfassten etwa 36 000 Mann, davon 25 000 Fußtruppen, vorwiegend Pikeniere und Musketiere sowie 11 000 Kürassiere und Dragoner. Nach traditioneller spanischer Schlachtordnung waren sie in großen Einheiten aufgestellt. Am linken Flügel befehligte General Heinrich von Pappenheim die Kavallerie, vorwiegend Kürassiere. Im Zentrum standen unter dem Befehl von Tilly die Fußtruppen in 17 tief gegliederten Schlachtenhaufen, sogenannten „Terzios“, dazu die Kavallerie. Der rechte Flügel bestand hauptsächlich aus leichten kroatischen Reitertruppen unter Fürstenberg und Isolani. Der Schlachtruf des katholischen Heeres war „*Maria hilf!*“.

Die Berichte und die spätere Literatur über die Aufstellung der Truppen und den Schlachtverlauf stimmen oft nicht überein und können deshalb nur ungefähr angegeben werden (Abb. 5). Auch die Zahlen der Soldaten und Opfer gehen auseinander.

Die Schlacht

König Gustav Adolf ging nur zögernd in die Schlacht, denn es stand viel auf dem

Spiel – „*eine Krone und zwei Kurhüte*“, wie er gesagt haben soll. Sein Gegner Tilly war zwar schon 72 Jahre alt, aber ein sehr erfahrener Feldherr, der noch keine Schlacht verloren hatte. Auch Tilly war vorsichtig und auf Defensive eingestellt, denn sein Heer war zahlenmäßig etwas, seine Artillerie sogar stark unterlegen.

Das Hauptgefecht begann um die Mittagszeit mit einer Kanonade. Schließlich gab Tilly dem Drängen Pappenheims nach und ließ diesen mit 2 000 schweren Reitern einen Flankenangriff gegen den rechten schwedischen Flügel führen. Die Angriffstaktik der Kaiserlichen war die traditionelle „Karakole“, bei der die Reiter ihre Karabiner und Pistolen abfeuerten und dann abschwanken. Wären Gustav Adolfs Truppen in der üblichen Aufstellung angeordnet gewesen, so hätte diese Situation für sie verhängnisvoll werden können. So aber konnten die schwedischen Einheiten augenblicklich Front gegen den Angriff machen, wodurch der Feind zwischen dem 1. und 2. Treffen eingeschlossen wurde (WEDGWOOD 1967). Pappenheim forderte Verstärkung und ließ weitere sechs Mal zur Attacke blasen – alle scheiterten im Dauerfeuer der Musketiere. „*Dieser Mensch wird mich noch um Ehr und Reputation und den Kaiser um Land und Leute bringen!*“, entfuhr es Tilly.

Inzwischen hatte am rechten Flügel Fürstenbergs leichte Kavallerie die Sachsen angegriffen und in wilde Flucht geschlagen, Kurfürst Johann Georg mitten unter ihnen. Im Zentrum traten nun die kaiserlichen Truppen aus ihrer Deckung und marschierten vor ihre Feldartillerie (WALZ 1994), die nicht so schnell vorgezogen werden konnte. Diese mußte jetzt die eigenen Verbände überschießen, was Unruhe und Eigenverluste mit sich brachte. Da nach der Flucht der Sachsen Tillys rechter Flügel über den linken Flügel des Gegners hinausragte, befahl er seinen Truppen links herumzuschwenken und die Schweden an der Flanke anzugreifen und zu umfassen (MONTGOMERY 1968). Aber die Schweden manövierten und schwenkten schneller, machten Front gegen den Gegner und rückten ebenfalls vor.

Mittlerweile schien den Schweden die nach Westen gewanderte Sonne nicht mehr in die Augen. Auch der Wind hatte gedreht und blies jetzt den Kaiserlichen dichten Staub entgegen. Zwischen 16 und 17 Uhr ergriff Gustav Adolf die Initiative und ließ seinen rechten Flügel, verstärkt durch die Reiterei des 2. Treffens, vorgehen und entgegen dem Uhrzeigersinn herumschwenken.

Dabei drückte er Tillys geschwächten linken Flügel ein und umfasste das kaiserliche Zentrum seitlich und im Rücken.

Nach dieser Umfassung wurden die Kaiserlichen nach und nach aufgerieben und begannen zu fliehen. Die Schweden setzten ihnen nach. Tilly, selbst schwer verwundet, floh mit Resten seiner Truppen nach Halle. Pappenheim versuchte zu retten was zu retten war und zog sich in Staub und Dämmerung mit einigen Regimentern nach Leipzig und am nächsten Tag ebenfalls nach Halle zurück. Die blutige Schlacht kostete etwa 8 000 Kaiserlichen das Leben, 6 000 Mann blieben verwundet auf den Feldern von Breitenfeld zurück. 3 000 Soldaten wurden gefangen genommen, die Artillerie und der Troß gingen verloren.

Gustav Adolf hatte einen großen Sieg errungen, doch um den Preis von 5 000 gefallenen Schweden und Sachsen. Aber das Blatt hatte sich gewendet. „Die Habsburger waren geschlagen, der letzte Kreuzzug war misslungen“ (WEDGWOOD 1967). Die Schlacht von Breitenfeld wurde zum Symbol des Sieges über die Katholische Liga und Gustav Adolf zum protestantischen Helden.

Halt 6 ist etwa 1 km südlich von Kömmlitz an der heutigen B 184 (Abb. 5). Hier ungefähr befand sich der rechte schwedische Flügel mit dem 1. und 2. Treffen. Südöstlich voraus befindet sich der allmähliche Anstieg zum Rand der Breitenfelder Endmoräne, wo sich die linken Positionen der Kaiserlichen befanden. Von dort aus muss Pappenheim seine berühmte Reiterei auf die rechte schwedische Flanke geführt haben, hier müssen sie im Abwehrfeuer zerbrochen sein. Von hier aus rückte schließlich der rechte schwedische Flügel zu seinem Umfassungsangriff vor, welcher den Sieg brachte.

Literatur: BÜCHELER (1994), FIEDLER (2002), MANN (1971), KEEGAN (1995: 483), MONTGOMERY (1968), PREIL (1996), POEKELL (1647), REICHEL & SCHUBERT, I. (2007), SCHWEDE (1979), WALZ (1994), WEDGWOOD (1967), WILKE (2004)

Die heutige B 184 und A 14 queren den flachen, ungefähr WSW-ENE verlaufenden Endmoränenrücken. Die Brücke der B 184 befindet sich etwa in dessen Scheitel. Zum Dorf Breitenfeld zweigt eine Straße nach rechts ab.

Halt 7: Gustav-Adolf-Denkmal bei Breitenfeld

„Am 17. September 1631/Rettete bei Breitenfeld/Glaubens-Freiheit für die Welt/Gustav Adolf, Christ und Held“

Etwas östlich vom Dorf Breitenfeld erinnert das „Gustav-Adolf-Denkmal“ an die Schlacht (Abb. 5). Der große Sandsteinquader mit der oben genannten Inschrift wurde 1831 zum 200. Jahrestag der Schlacht von dem Rittergutsbesitzer Ferdinand Gruner aus Breitenfeld errichtet. Das Denkmal, von vier Linden umgeben, befindet sich etwas außerhalb des eigentlichen Schlachtfeldes im Scheitel des Breitenfelder Endmoränenrandes.

Am 2. November **1642** fand bei Breitenfeld eine zweite Schlacht statt. Südlich von Podelwitz, beiderseits der Straße von Podelwitz nach Wiederitzsch, besiegte der schwedische Oberbefehlshaber Lennart Torstenson mit 18 000 Mann in 4 Stunden in einem Flankenangriff ein 22 000 Mann starkes Heer unter Erzherzog Leopold Wilhelm, dem Bruder des Kaisers. Die Schlacht forderte etwa 10 000 Tote. Das von Kaiserlichen besetzte Leipzig kapitulierte daraufhin und blieb bis 1650 von den Schweden besetzt.

Literatur: WALZ (1994), WEDGWOOD (1967), WILKE (2004), PREIL (1996)

Die Weiterfahrt auf der A 14 nach Westen führt über die fast ebene drenthezeitliche Grund- und Endmoräne der Breitenfelder Randlage zum Autobahnkreuz Schkeuditz, dann auf der A 9 nach Süden, wobei die 2 km breite Aue der Weißen Elster und der Luppe gequert wird. Der Nordrand der Elsteraue markiert im Untergrund etwa die Fortsetzung der Halle-Störung, welche die Südgrenze der Halle-Wittenberg-Scholle bildet, hier aber fast völlig ausgeklungen ist. An der Abfahrt Bad Dürrenberg in Richtung Makranstädt zur B 87 und auf dieser in Richtung Lützen zur Gustav-Adolf-Gedenkstätte.

Halt 8: Schlachtfeld von Lützen, Gustav-Adolf-Gedenkstätte

Vorgeschichte

Nach Breitenfeld begann König Gustav Adolf, der „Löwe aus Mitternacht“, seinen Siegeszug in Süddeutschland. Der Kaiser und die Katholische Liga hatten ihm militärisch nicht mehr viel entgegenzusetzen. Viele protestantische Städte öffneten den Schweden bereitwillig die Tore. Im Gegensatz zu den kaiserlichen Truppen verhielten sich die Schweden in Freundesland der Zivilbevölkerung gegenüber zumeist diszipliniert, sonst drohten harte Strafen. Hohe Kontributionen mußten freilich auch hier erbracht werden.

Bei R a i n a m L e c h verlor Tilly im April 1632 eine wichtige Abwehrschlacht und wurde selbst tödlich verwundet. In dieser Notlage berief Kaiser Ferdinand II. erneut Wallenstein zum Oberbefehlshaber. Diesem gelang es in kürzester Zeit ein Heer aufzustellen und den Schwedenkönig in einer Defensivstellung um die Reichsstadt N ü r n b e r g festzuhalten. Der Versuch der Schweden, Anfang September das kaiserliche Lager bei der „Alte Veste“ westlich von Nürnberg zu stürmen, scheiterte blutig und Gustav Adolf verlor dadurch seinen Nimbus der Unbesiegbarkeit. Wallenstein ließ das schwedische Heer vorerst unbehelligt abziehen und wandte sich nach Sachsen, um dieses zu unterwerfen und dort ein sicheres Winterquartier für das Gros seiner Truppen zu finden. Gustav Adolf mußte ihm folgen, wollte er nicht Gefahr laufen, Sachsen als Verbündeten zu verlieren und von der Ostsee abgeschnitten zu werden. Seine Verbände waren jedoch geschwächt und mußten zunehmend mit nichtschwedischen Söldnern aufgefüllt werden, was sich schlecht auf die Moral und Disziplin des Heeres auswirkte.

Am 3. November 1632 besetzte Gustav Adolf die Stadt Naumburg. Wallenstein rückte am 11. November bis Weißenfels vor und bot dem König die Schlacht an (BÜCHELER 1996). Gustav Adolf, zahlenmäßig unterlegen, zog es vorerst vor, in der Stadt verschanzt zu bleiben. Wallenstein und seine hohen Offiziere waren nun der Meinung, dass Gustav Adolf Winterquartier bezogen hätte. Deshalb beschloss Wallenstein, sich mit der Hauptmacht in und um Leipzig einzuquartieren. Pappenheim sollte zunächst die Stadt Halle mit der Festung Moritzburg einnehmen. Als König Gustav Adolf am 15. November von der unverhofften Teilung der kaiserlichen Truppen erfuhr, rückte er sofort aus, um deren Schwäche zu nutzen. Als Wallenstein vom überraschenden Anmarsch der schwedischen Truppen hörte, nahm er Quartier im Schloss der kleinen kursächsischen Stadt Lützen und schickte dringende Order an Pappenheim, umgehend wieder zu ihm zu stoßen: *„Der feindt marchirt hereinwarths, der herr lasse alles stehen undt liegen undt incaminire sich herzu mitt allem volck undt stücken auf das er morgen frue bey uns sich befünden kann. Ich aber verbleibe des herrn dienstwilliger AhzM.. Lützen den 15. November Ao 1632. Er ist schon an dem pas wo gestern der böse weg gewest ist“*. Dieser schriftliche Befehl Wallensteins wurde später blutbefleckt unter Pappenheims Brustpanzer gefunden in befindet sich heute im Heeresgeschichtliches Museum Wien.

Taktisch umsichtig hatte Wallenstein 7 km südwestlich von Lützen bei dem Dorf Poserna, *„an dem pas wo gestern der böse weg gewest ist“*, rund 1000 Mann Musketiere und Reiter zurück gelassen. Diesen gelang es, die Schweden in blutigen Gefechten an der sumpfigen Niederung und den steilen Nordhängen des Rippachtals aufzuhalten und damit Wallensteins verstreutes Heer vor der drohenden Vernichtung zu retten (PREIL 1996). Damit verloren die Schweden ihren Zeitvorteil und konnten erst am späten Nachmittag das Rippachtal überqueren und ihr Nachtquartier aufschlagen.

Geologie

„Das Terrain war so günstig, wie es im flachen Lande sein kann.“

GOLO MANN (1971): Wallenstein

Die kleine Stadt Lützen und das historische Schlachtfeld liegen auf der etwa 120 m NN hohen, schwach welligen Ebene der Lützenser Grundmoränenplatte. Die quartären Sedimente sind etwa 15 m mächtig und beginnen mit 4–8 m frühelsterkaltzeitlichen Flussschottern der Saale (Lützen-Schkeuditzer Saalelauf). Darüber folgen Ablagerungen der Zwickau-Phase der Elster-Kaltzeit mit einem bis zu 0,7 m mächtigen Warvensediment (Dehlitz-Leipziger Bänderton) und die 2–5 m mächtige Erste (Untere) Elster-Grundmoräne, welche lokal von kiesigen Schmelzwassersanden überlagert wird. Das saalezeitliche Glaziärstockwerk beginnt mit der 3–5 m mächtigen ersten Saale-Grundmoräne (Zeitz-Phase).

Im Osten und Süden wird die Grundmoränenplatte von einem 5–8 km breiten, hufeisenförmigen Höhenzug überragt, der aus bis zu 15 m mächtigen saalezeitlichen Schmelzwassersanden und -kiesen besteht, die südlich von Lützen und bei Rückmarsdorf intensiv glazitektonisch deformiert sind (EISSMANN 1975). Der Höhenzug ist die sog. Dehlitz-Rückmarsdorfer Endmoräne, deren stratigraphische Position innerhalb der saalezeitlichen Vereisungsphasen noch nicht völlig geklärt ist.

Die Gegend um die Stadt Lützen wurde im Jahr 1632 wie heute großteils landwirtschaftlich genutzt. Die alte Landstraße von Lützen nach Leipzig verlief zunächst nach Nordosten, ungefähr wie die heutige B 87, dann in einem weiten Bogen nach Osten und schließlich nach Nordosten (Abb. 7). Südöstlich und östlich der Stadt Lützen befindet sich der „Floßgraben“, ein schmaler Kanal, welcher von der Weißen Elster bei Zeitz zur Saale bei Dürrenberg führte und zum Flößen von Holz benutzt wurde.

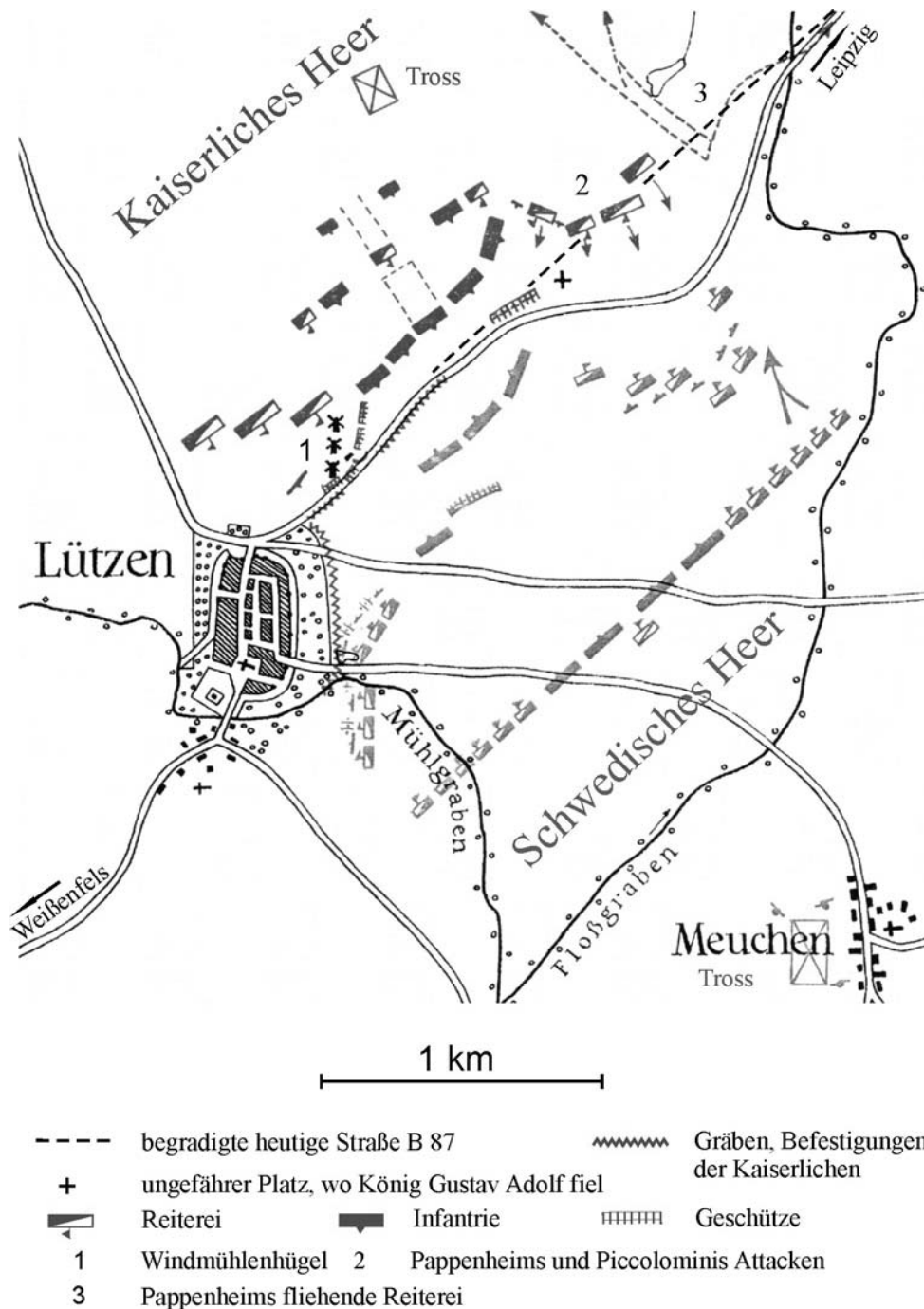


Abb. 7: Schematische Skizze der Schlacht bei Lützen, 16. November 1632, ungefähr zur Zeit als König Gustaf Adolf fiel (Gustav-Adolf-Gedenkstätte Lützen).

Vor der Schlacht

In der Nacht vom 15./16. November lagen Wallensteins Truppen unmittelbar nordöstlich der Stadt Lützen an der Straße nach Leipzig (Abb. 7). Wallenstein ließ Verteidigungsstellungen aufwerfen, die Straßengräben vertiefen, befestigen und mit Musketieren besetzen. Sein Heer hatte nun etwa 17 000 Mann, davon etwa 10 000 Infanteristen, 7 000 Reiter und 24 Geschütze. Pappenheims Truppen, die aus Halle heraneilten, bestanden aus rund 2 700 Infanteristen und 2 300 Kavalleristen. Insgesamt

war die Schlachtreihe etwa 2 km lang. Der starke rechte Flügel mit schwerer und leichter Kavallerie lehnte sich an Lützen an (Abb. 7). Davor, am sog. Windmühlenhügel, waren die Geschütze positioniert. Das Zentrum unter dem direkten Befehl Wallensteins wurde von zwei Treffen Infanterie gebildet, welche nicht mehr in schwer beweglichen Terzios angeordnet waren, sondern in kleineren Einheiten nach schwedischem Vorbild. Der linke Flügel mit Reiterei und Geschützen erstreckte sich bis fast zum Floßgraben und war zunächst zahlenmäßig unterbesetzt, denn hier sollten die herbeigerufenen Pappenheimer Truppen einrücken.

Die schwedische Armee verfügte über etwa 13 000 Mann Infanterie, 6 000 Mann Kavallerie und 60 Geschütze, war also zahlenmäßig überlegen, solange Pappenheim noch nicht eingetroffen war. Sie nahmen am Morgen des 16. November gegenüber den kaiserlichen Stellungen auf den Äckern östlich der Stadt in zwei Treffen Aufstellung, das Dorf Meuchen mit dem Troß im Rücken (Abb. 7). Der starke rechte Flügel, der vor allem aus Reiterei und Musketieren bestand, reichte bis zum Floßgraben und wurde von Gustav Adolf selbst befehligt. Das Zentrum bestand hauptsächlich aus Infanterie. Der linke Flügel, welcher wie der rechte Flügel hauptsächlich aus Kavallerie und Musketieren bestand, lehnte sich an Lützen an und wurde von Herzog Bernhard von Sachsen-Weimar kommandiert. Die Geschütze waren vor der Front aufgestellt. Das 2. Treffen (Reserve) setzte sich hauptsächlich aus deutschen Verbänden zusammen und stand etwa 500 m hinter dem 1. Treffen.

Die Schlacht und Gustav Adolfs Tod

Gegen 10 Uhr war der Aufmarsch des schwedischen Heeres beendet, doch behinderte dichter Nebel die Sicht. Dazu kamen beißende Rauchschwaden, denn auf Wallensteins Befehl war die Stadt in Brand gesteckt worden. Wie immer betete Gustav Adolf und wahrscheinlich wurde auch der Feldchoral gesungen *„Verzage nicht du Häuflein klein, obschon die Feinde willens sein, dich gänzlich zu verstören, ...“*.

Das Gefecht begann mit einem Artillerieduell, *„... mit einer solchen Furi, das niemandt ein solches gesehen oder gehört hat. ...“*, wie Wallenstein später an Aldringen schrieb. Sobald sich gegen 11 Uhr der Nebel etwas hob, befahl Gustav Adolf den Angriff: *„Gott mit uns!“*. Der rechte schwedische Flügel fand wenig Widerstand. Daraufhin warf Wallenstein schwere Reiterei an die gefährdete Flanke. Die schwedische Infanterie im Zentrum konnte die Straße und die Gräben überwinden, die nachfolgenden Reiter jedoch nicht. So kam der massive Angriff der Schweden ins Stocken, zumal gegen 12 Uhr Pappenheim mit seinen Kürassieren auf dem Schlachtfeld eintraf. Zunächst konnten diese einige schwedische Regimenter zurückschlagen, aber dann wurde Pappenheim durch eine Drahtkugel tödlich verwundet und seine Männer wandten sich zur Flucht – um weiter draußen die eigene Bagage zu plündern. *„Ist denn keiner mehr, der für den Kaiser treulich fechten will?“*, soll der sterbende Pappenheim gerufen haben.

Isolanis kroatische Reiter griffen nun den linken schwedischen Flügel gezielt von der Flanke her an. Sie drangen bis zum 2. Treffen vor und schließlich bis zum Troß bei Meuchen, und konnten erst von Kavallerie des rechten Flügels wieder vertrieben werden.

Um den festgefahrenen Angriff am linken Flügel und im Zentrum wieder in Bewegung zu bringen, eilte Gustav Adolf gegen 13 Uhr an der Spitze seiner Reiter zur Attacke. Wieder schränkte Nebel das Gesichtsfeld ein, der König war seinem Gefolge weit voraus – da traf ihn ein Musketenschuss in den linken Ellenbogen. Seine wenigen Begleiter versuchten ihn in Sicherheit zu bringen, doch die anreitenden kaiserlichen Kürassiere unter Oberstleutnant von Falkenberg – welche den König zunächst nicht erkannten – fügten ihm mehrere Stich- und Schussverletzungen zu. Gustav Adolf fiel tödlich verletzt vom Pferd. Wie alle Toten wurde auch der Leichnam des Königs von den kaiserlichen Soldaten geplündert.

Die vom Tod ihres Königs erschrockenen und demoralisierten Schweden begannen sich auf der ganzen Frontlinie zurückzuziehen. Piccolomini führte sieben heftige Kürassier-Attacken gegen den rechten Flügel der Schweden. Herzog Bernhard von Weimar erkannte die Gefahr und übernahm den Oberbefehl. Das 2. Treffen, das bisher kaum in den Kampf eingegriffen hatte, rief nach Rache und begann einen neuen entscheidenden Angriff an: *„Wer beweisen will, dass er seinen König lieb gehabt hat, der tue es jetzt!“*.

Unter dem wuchtigen Vorstoß des schwedischen Heeres zerbrach Wallensteins rechter Flügel. Auch der Windmühlenhügel mit der Artillerie wurde genommen. Die Pulvervorräte explodierten. Trotz erbitterten Widerstandes von schnell zusammengezogenen Musketieren und Pikenieren mußte Wallenstein bei Einbruch der Nacht den Befehl zum Rückzug nach Leipzig geben. Das schwedische Heer behauptete das Schlachtfeld und blieb die ganze Nacht dort. *„Keine Partei verfolgte die andere mit einem einzigen Schuss, so müde des Spieles und der Victorie ungewiss war man auf beiden Seiten ...“*, berichtete General Holk. Die kaiserliche Armee ließ etwa 6 000 Mann Tote und Verwundete bei Lützen, das schwedische Heer verlor etwa 5 000 Soldaten – es war eine der größten und verlustreichsten Schlachten des ganzen Krieges. Die Schuld für den entgangenen Sieg gab

Wallenstein den nach dem Tod ihres Kommandeurs geflohenen Pappenheimischen Reitern und strafte die Verantwortlichen 1633 beim „Prager Blutgericht“.

Der nackte, geplünderte Leichnam Gustav Adolfs und seine getöteten Begleiter wurden erst am Abend gefunden. Man brachte ihn in die kleine Kirche des Dorfes Meuchen, wo der schwedische Troß stand. Dort wurde er gewaschen, königlich bekleidet und aufgebahrt. Den langen Holztisch, auf dem er gelegen haben soll, zeigt man noch heute. Am nächsten Tag brachte man den königlichen Leichnam nach Weißenfels ins „Geleitshaus“, wo die Überführung nach Schweden vorbereitet wurde. Im Juni 1634 wurde König Gustav II. Adolf von Schweden in Stockholm in der Riddarholmkirche beigesetzt.



Abb. 8: Lützen, Gustav-Adolf-Gedächtniskapelle, Schwedenstein mit Baldachin von F. SCHINKEL (REICHEL 2003).

Gustav-Adolf-Gedenkstätte

Ein Findling, von dem die Legende berichtet, er sei vom schwedischen Reitknecht Erikson und Meuchener Bauern an die Stelle gerollt worden, wo man den toten König fand, war bis ins 19. Jh. die einzige Erinnerungsstätte. Über 200 Jahre nach der Schlacht, im Jahr 1837, wurde der 10 m hohe, aus filigranem Gußeisen gestaltete Baldachin über dem „Schwedenstein“ errichtet (Abb. 8). Entworfen hat ihn der berühmte klassizistische Baumeister FRIEDRICH VON SCHINKEL. „*Hier fiel Gustav Adolf am 6. November 1632*“ liest man in Goldschrift von der Straßenseite aus. Wahrscheinlich aber lag die wirkliche Todesstelle etwa 200 m weiter nördlich (PREIL 1996).

Zur 275. Jahrfeier wurde 1906/07 eine Kapelle hinter dem Denkmal errichtet, gespendet vom schwedischen Konsul OSCAR EKMAN (Abb. 8). Die Bausteine stammen aus den Schaumkalkbrüchen von Freyburg/Unstrut, das Kiefernholz für den Dachstuhl aus Schweden. Unter dem Turmaufsatz befindet sich ein Reiterstandbild des Königs mit hoch erhobenem Schwert. Die Turmkrone endet in einer Korngarbe (schwed.: *Wasa*), die ein hohes Kreuz trägt. Ein großes dreiteiliges Altarbild von 1908 stellt den König als Verteidiger des evangelischen Glaubens dar, die Rechte auf der Bibel, das Schwert in der Linken. Ihm gegenüber steht MARTIN LUTHER. Das Mittelbild, durch ein Kreuz geteilt, zeigt einen trauernden Engelsreigen um das Schlachtfeld von Lützen. Der Dachstuhl ist offen und erinnert an ein kieloben schwimmendes Wikingerschiff. Die Kirche bietet Platz für 200 Personen. Jeden 6. November findet hier ein Gedenkgottesdienst statt.

Neben der Kirche stehen zwei Blockhäuser, die an schwedische Bauernhäuser erinnern und als Museum dienen. Zum 400. Geburtstag Gustav II. Adolfs am 9. Dezember 1994 wurde durch das schwedische Königspaar eine neue Ausstellung eröffnet, die über den Dreißigjährigen Krieg, die Schlacht von Lützen und König Gustav Adolf informiert. Die Gedenkstätte gehört der Stadt Lützen. Nur eine Legende ist, dass die Anlage extraterritoriales schwedisches Gebiet sei.

Der erste Kilometer der heutigen B 87 von Lützen nach Leipzig folgt ungefähr dem Verlauf der alten Straße. Die alte Straße schwenkte dann vor dem Denkmal in einem weiten Bogen nach Osten (Abb. 7). Dort sind jetzt Gehölze und Kleingärten. Die ursprüngliche Straße wurde in späteren Jahren begradigt, jetzt führt die B 87 direkt an der Gedenkstätte vorbei. In Bezug auf das Schlachtgeschehen steht die Gedenkstätte zwischen dem stark umkämpften linken Flügel und dem Zentrum der Kaiserlichen.

Einen guten Eindruck vom einstigen Schlachtfeld hat man von der Stelle, wo die heutige Straße den Floßgraben quert (Abb. 7). Hier befand sich der bedrängte linke Flügel der Kaiserlichen. Hier rückten Pappenheims Eskadronen ein und flohen, nachdem ihr Kommandeurs tödlich verletzt worden war. Und hier ritt Piccolomini seine sieben vergeblichen Attacken. Voraus bis zur Stadt Lützen standen das Zentrum und der rechte Flügel der Kaiserlichen.

Links der heutigen Straße befanden sich die schwedischen Linien, zunächst die Kavallerie und die Musketiere unter Gustav Adolfs Führung. Hier begann der König seinen Todesritt, der nahe dem heutigen Schwedenstein endete. Etwa 1 km von der heutigen Straße entfernt, reihte sich das 2. Treffen.

Die kleine Stadt **Lützen** liegt an der seit dem Mittelalter wichtigen Fernstraße zwischen den Messestädten Frankfurt am Main, Erfurt und Leipzig. Am **Rathaus** befindet sich ein überlebensgroßes steinernes Standbild des Schwedenkönigs. Das Museum im **Schloß Lützen** zeigt eindrucksvolle Dioramen der Schlachten bei Lützen und Großgörschen.

Wenige Kilometer südlich von Lützen, bei **G r o ß g ö r s c h e n**, fand am 2. Mai 1813 eine der großen Schlachten der Befreiungskriege statt, welche oft auch als „Schlacht von Lützen“ bezeichnet wird. Nordöstlich von hier wurde vom 14. bis 19. Oktober 1813 die „**V ö l k e r s c h l a c h t v o n L e i p z i g**“ geschlagen. Insgesamt fanden im Laufe der Jahrhunderte in der näheren und weiteren Umgebung von Leipzig und Halle über 20 bedeutende Schlachten statt. Die Ursache für diese ungewöhnliche Konzentration von militärischen Auseinandersetzungen ist – neben politischen und strategischen Gründen – darin zu suchen dass das „Terrain“, die geologisch-geomorphologischen Verhältnisse, das Gebiet für den Marsch, Aufenthalt und Kampf mittelalterlicher und neuzeitlicher Heere besonders geeignet machten (BACHMANN et al. 2002, BACHMANN 2004).

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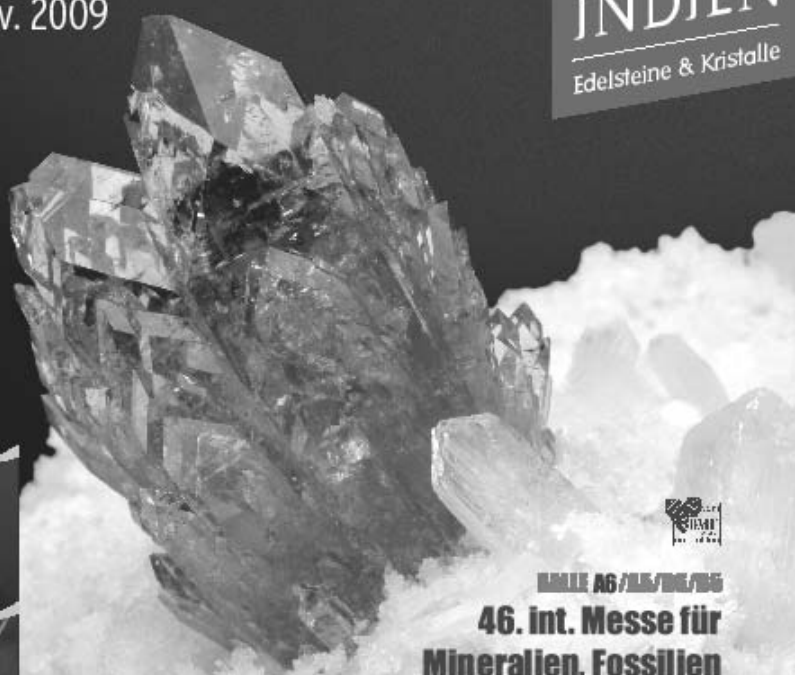
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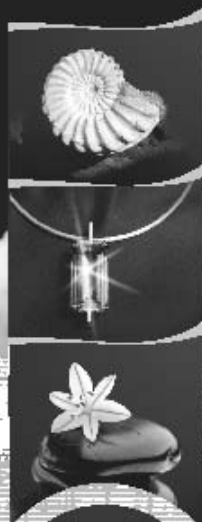
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