*Es folgen alle Zusammenfassungen der Vorträge und Posterpräsentationen der MinPet 2019. Nach dem Abstract des Festvortrags des Becke-Medaillen-Ausgezeichneten werden alle Tagungsbeiträge in alphabetischer Reihenfolge der ErstautorInnen angeführt.*

*Informationen zu Tagung und Programm:*
*https://www.tugraz.at/events/minpet2019/home/*

# SIGNIFICANCE OF MINERAL AND FLUID INCLUSIONS IN DIAMONDS AND THEIR INDICATOR MINERALS

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Diamond mineral inclusions studies established two main types of Earth's mantle environment for diamond formation within subcratonic lithosphere: ultramafic (peridotitic) and eclogitic, i.e., U/P and E types (MEYER & BOYD, 1972; SOBOLEV et al., 1969a; SOBOLEV et al., 1971). These types were confirmed by the study of chemical compositions of garnet found in xenoliths of diamondiferous serpentinite (SOBOLEV et al., 1969b) and eclogite (SOBOLEV et al., 1972) in Siberian kimberlites. For diamonds of any size, from micro- (< 1 mm) up to large crystals (> 10.8 cts and up to 200 cts), and quality, including gems, the U/P type dominates in Siberian kimberlites (more than 90 %), and is considerably lower in northern Siberia and Ural placers (< 30 %). Key minerals for the U/P type are represented by coexisting subcalcic Cr-pyrope and chromespinel (Cr# > 80) as members of clinopyroxene-free peridotite and dunite-harzburgite (SOBOLEV, 1971; SOBOLEV et al., 1969a). Evidence of deep hydrocarbons and $CO_2$ sources for diamond formation was suggested by SOBOLEV (1960). Volatile components in diamonds and associated minerals were analysed by GC-MS using a Focus GC/DSQ II MS (Thermo Scientific, USA). It is concluded that saturated hydrocarbons (pentane to hexadecane) and their derivatives are the dominant species in fluid inclusions in diamonds and associated minerals from kimberlites and diamond placers. It is suggested that such hydrocarbons are among the major species in some mantle fluids (e.g., SOBOLEV et al., 2019; SOKOL et al., 2017, 2019). Microdiamonds from the Kokchetav Massif (Kazakhstan) occur in a wide variety of ultrahigh pressure metamorphic rocks (SOBOLEV & SHATSKY, 1990; SCHERTL & SOBOLEV, 2013). All morphological types specific for diamonds from kimberlites are found. Their average size is about 12 μm by counting in thin sections and the maximal size reaches up to 300 μm. The significance of zircon as a perfect mineral container was confirmed by the identification of coesite, garnet, diopside and magnesite inclusions and polymineralic (touching) coesite-diamond and diopside-diamond inclusions, probably suggesting ultrahigh pressure conditions. Nitrogen isotope data and negative $\delta^{13}C$ values of diamonds indicate a metasedimentary origin.

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# LAPIS LAZULI – PETROLOGICAL AND GEOCHEMICAL CHARACTERIZATION OF RAW MATERIAL AND ARCHAEOLOGICAL ARTEFACTS

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The magic ocean-deep blue of lapis lazuli gemstones beguiles humankind for over 6000 years. Lapis lazuli was used for artefacts, interior and exterior design, sometimes almost monumental objects and even today for all kinds of jewelry like necklaces or earrings (TOSI & VIDALE, 1990).

This study attempts to reveal the origin of Archaeological lapis lazuli artefacts and objects, and to reconstruct prehistoric and trade relations. Other studies involving mediterranean and eurasian lapis lazuli artefacts show mostly Afghan provenience (HERMANN, 1968). Furthermore, slightly over a dozen other modern occurrences (e.g. in Tajikistan, Russia, Myanmar, Chile) are known worldwide so far, which makes an unambiguous allocation easier in theory. A leading study on this topic is by GIUDICE et al. (2017) providing a guideline for modern lapis lazuli provenance analyses in general. The multi-technique analytical approach introduced to Archaeological provenance questions by BRANDL et al. (2018) will be applied here to our lapis lazuli artefacts and objects which includes state of the art archaeological, petrographic, mineralogical, geochemical and geological methods.

Besides a significantly larger amount of samples compared to previous undertakings (target value 30-50), this study provides a better in-depth analysis for both, non-destructive and destructive methods with FEG-EPMA and LA-ICP-MS, respectively. Egyptian lapis lazuli objects (e.g. Scarabs) will be investigated and compared to reference material from Afghanistan, Tajikistan, Lake Baikal and Myanmar. The famous lapis lazuli occurrences from Chile will additionally be studied for comparison.

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# PLAGIOCLASE-HOSTED Fe-Ti-OXIDE MICRO-INCLUSIONS AND BULK-ROCK MAGNETISM OF OCEANIC GABBRO

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We present mineralogical and magnetic data of 11 oceanic gabbro samples dredged from the Mid-Atlantic ridge at 13° to 17° N. Their natural remanent magnetization (NRM) is primarily controlled by two microstructural types of Fe-Ti-oxides. A first type is represented by several millimeters sized, isometric cumulus/intercumulus grains. The second type is represented by micro-inclusions hosted by pyroxenes and plagioclases. During post-magmatic evolution, the two Fe-Ti-oxide types behaved differently, affecting the bulk-rock NRM in different ways. Understanding the primary NRM and its transformation in the dynamic environment of the Mid-Atlantic ridge is important for interpreting paleo-magnetic data and for assessing information from marine magnetic anomalies.

For all studied gabbros, the Curie temperature (Tc) is in the range of 570-575 ºC, indicating that magnetite is the dominant carrier of the NRM. In some samples, additional magnetic phases with $T_C$ ~330-340 ºC corresponding to either titano-magnetite or monoclinic pyrrhotite and with $T_C$ ~700 ºC corresponding to hematite are distinguished. The intensity of the bulk rock NRM is 0.3 to 7 A/m and shows a correlation with the quantity of cumulus/intercumulus Fe-Ti-oxide grains and with the abundance of the Fe-Ti-oxide micro-inclusions in the rock-forming silicates. Based on the presence of the different microstructural Fe-Ti-oxide types, two groups of gabbro are distinguished: The first group has both cumulus/intercumulus grains and silicate-hosted Fe-Ti-oxide micro-inclusions. The second group shows silicate-hosted (mostly plagioclase) Fe-Ti-oxide micro-inclusions at low and intermediate concentrations. In the Day diagram (Mrs/Ms vs. Bcr/Bc) both groups fall into the field of pseudo-single domain (PSD) grains, but the first group plots closer to the multi-domain (MD) field and the second group plots closer to the single-domain (SD) field. The NRM in the second group amounts to 0.4 to 0.8 A/m, indicating that the micro-inclusions play a key role for the bulk-rock NRM. In the second group, the bulk coercivity ($B_C$) is 15-28 mT and the saturation magnetization ratio (Mrs/Ms) is 0.15-0.25, which is much higher than in the first group. This gives evidence of hard magnetization in the second group, which is due to the dominance of micro-inclusions. Moreover, with k = 100-160 the samples of the second group have a higher Fisher statistics parameter of the NRM vectors than the first group (k = 3-46). Importantly, in the second group almost all pyroxene grains have been replaced by late amphibole in the course of low-temperature hydrothermal alteration, which also destroyed the cumulus/intercumulus Fe-Ti-oxides. Plagioclase remained largely unaltered during the hydrothermal overprint and the plagioclase-hosted micro-inclusions preserved the primary NRM. Although the Fe-Ti-oxide micro-inclusions may be present at low concentrations, they are robust carriers of the primary NRM. When cumulus/intercumulus Fe-Ti-oxide grains and inclusion-bearing pyroxene are missing, the record of remanence is only provided by plagioclase-hosted micro-inclusions. In this case, the rocks yield accurate information on the direction of the primary NRM.

# THE EPITHERMAL CHAH-MESI Cu-Pb-Zn-(Ag-Au) DEPOSIT, SE IRAN: ORE MINERALOGY AND FLUID INCLUSIONS

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In the southeastern part of the Cenozoic Urumieh-Dokhtar Magmatic Belt of Iran the NW-trending Kerman porphyry copper belt hosts major porphyry Cu-(Mo-Au) deposits (PCD) of Miocene age; e.g. the diorite-type Cu-Au Meiduk and granodiorite-type Cu-Mo Sar Cheshmeh deposits. The polymetallic vein type deposit Chah-Mesi is located ~1.5 km south of the Meiduk porphyry (Cu-Au) deposit. This study aims to clarify its genetic relation to the porphyry system. At Chah-Mesi, Paleocene to Eocene calc-alkaline volcanic and pyroclastic rocks of mainly basaltic-andesitic composition were intruded by Miocene microdioritic dykes. The host rocks were affected by intense hydrothermal alteration exhibiting a central zone of strong silicification that grades into sericitization and propylitic alteration towards the peripheral parts. Argillic alteration is restricted to superficial areas and in direction to the Meiduk PCD propylitic alteration changes into potassic alteration. Six different vein types are distinguished: including two porphyry-related vein types, three alteration-related types of veinlets as well as mineralized veins showing massive, banded, crustiform and brecciated textures. Mineralization occurs as open space fillings and minor replacement and breccia bodies. The paragenetic sequence encompasses four mineralization stages starting with the early high sulfidation assemblage pyrite + chalcopyrite + enargite + luzonite-famatinite ± bornite with a continuous transition into intermediate sulfidation state assemblages comprising pyrite + chalcopyrite + tennantite-tetrahedrite ± electrum ± Ag-bearing sulfosalts. The late paragenetic stage with sphalerite + galena + pyrite ± electrum overprints the earlier ones. Supergene mineralization with chalcocite + covellite + Fe-oxyhydroxides + Cu-hydrocarbonates is restricted to the shallow weathered part of the deposit. A regional zoning of ore minerals is apparent; central parts of the deposit are dominated by Cu-Fe-rich sulfides showing a transition to Pb-Zn-dominated zones mainly in the deeper and distal sections. Variations in the chemical composition of fahlores range from Fe-rich tennantite to Zn-rich tetrahedrite with a strong positive correlation between Sb and Ag contents. The fahlores are complexly zoned and display a progressive increase of Sb concentration with increasing distance to the nearby Meiduk deposit. Primary fluid inclusions in mineralized veins are low saline aqueous $H_2O$-salt inclusions. They yield homogenization temperatures ($T_{h\ LV\rightarrow L}$) between 115 to 295 °C for sphalerite and 145 to 397 °C for quartz. Salinity values range between 1.2 to 9.9 and 2.1 to 9.2 wt% NaCl equiv., respectively. Raman spectroscopy confirms low $CO_2$ concentrations of the vapor phase of the fluid inclusions. The fluids are interpreted to be of magmatic origin as indicated by stable isotope studies. We propose that ascending cooling magmatic fluids were responsible for the transport of metals and mineral precipitation occurred in the epithermal regime upon dilution of magmatic fluids with circulating meteoric water. Similar low-salinity, $CO_2$-bearing fluids were reported from the nearby Meiduk porphyry stock suggesting a genetic link between these two deposits.

# RARE METAL MOBILITY IN A METAMORPHOSED BASE METAL DEPOSIT: THE SCHNEEBERG / MONTE NEVE Zn-Pb-(Cu-Ag) SHMS

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Sphalerite, (Zn,Fe)S, is an important ore mineral in many types of base metal sulphide deposits. A number of elements can substitute for Zn and Fe in sphalerite, thus this sulphide is an economically important carrier of rare metal by-products Ga, Ge, In, Co, (also Sn, Sb, Ag, Cd). Metamorphism, deformation, and metasomatic remobilisation as partitioning processes for trace metals in sphalerite are not thoroughly investigated, even though a good understanding of mobility and partitioning of rare metals in ore will advance our knowledge on metal cycling in nature, on ore genesis and metallurgy, as well.

We present evidence for rare metal (Ga, In, Co, Ag) mobility at the sample and mineralogical scale in the metamorphosed, sedimentary massive sulphide (SHMS) deposit Schneeberg, the largest metal deposit in the Ötztal-Stubai crystalline block (VAVTAR, 1988). Stratiform, massive Zn-Pb±Cu±Ag sulphide ore bodies are interbedded with biotite ± muscovite ± garnet gneisses and in places ore is hosted in biotite-garnet-amphibole-siderite schists (the so-called "Filone Facies" *sensu stricto)*. While gneisses represent the unmineralised sedimentary strata above and below ore, the Filone Facies is a distinct, Mn-Mg-Fe-richer and partly mineralised rock type. Textures in the Filone Facies suggest a remobilised nature: garnets are mostly one-phases in contrast to two-phase garnets in regional gneisses, fibrous amphiboles crosscut metamorphic fabrics, and sulphides lack coarse granoblastic textures that are commonly associated with peak-metamorphic overprint.

Minor elements that are predominantly in solid solution within sphalerite are Fe, Cd, Mn, Cu, Hg, Co, In, Ga. Other detected metals (Pb, Ag, As, Sb, Sn, Bi) are predominantly controlled by sulphosalt inclusions (ANGERER et al., 2017). Sphalerite in the remobilised Filone Facies ore shows distinct depletion of Cu, Co, In, Ga, Ge, Sn, Bi and enrichment of Cd, Mn, Hg, Pb, Ag, As, Sb compared with primary massive ore. Associated biotite is a secondary host for Ga, Co, and Sn, which suggests a metamorphic fractionation between sphalerite and biotite. Amphiboles and garnet, on the other hand, are no significant hosts in the Filone Facies.

Sphalerite deformation textures include three types: coarse granoblastic, medium retrograde static annealed, and fine retrograde dynamic recrystallised. Metal partitioning associated with these deformation textures, based on EMPA and Nano-SIMS mapping, will be presented.

The evidence for complex mobility of rare metals impacts on genetic studies of sphalerite-rich ore and also may improve technical beneficiation of trace metals from sulphide concentrates.

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# SIEVE STRUCTURE AND SECONDARY COMPOSITIONAL ZONING IN GARNET FROM MAFIC GRANULITES OF THE GFÖHL UNIT, MOLDANIBIAN ZONE, LOWER AUSTRIA

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We report on peculiar sieve structures and associated secondary compositional zoning of garnet from mafic granulites at the contact zone towards felsic granulites found in the Gföhl unit of the Dunkelsteiner Wald. The garnets are up to a few millimetres in size and are partially replaced by plagioclase and subordinate clinopyroxene. Micro-CT revealed that in 3D the plagioclase forms several 10s of micrometres wide and several 100 of micrometres long finger-like corrosion tubes, which produce the sieve-like microstructure in 2D sections. Around the corrosion tubes a concentric compositional zoning developed in the relic garnet with a decrease of $X_{gro}$ from 0.4 to 0.18 and a concomitant increase of $X_{pyr}$ from 0.40 to 0.52 and of $X_{alm}$ from 0.20 to 0.30 along traverses from the original garnet to the interface with the corrosion tubes.

This secondary zoning is ascribed to intracrystalline diffusion in the course of partial replacement and re-equilibration of the garnet. The enrichment halo of Fe extends substantially deeper into the garnet than the depletion halo of Ca, which is compatible with the notion that $D^*_{Fe} > D^*_{Ca}$, where $D^*$ means tracer (self) diffusion coefficient. This leads to a local minimum in Mg-concentrations at the position, where Fe has already arrived and Ca has not yet left. Within the framework of vacancy mediated multicomponent interdiffusion in an ionic crystal, the observed compositional patterns allow to constrain the proportions of $D^*_{Fe}$ / $D^*_{Mg}$ / $D^*_{Ca}$ . Linking these ratios to experimentally determined tracer self diffusion coefficients yields durations on the order of $10^2$ to $10^4$ years , depending on the choice of the experimental calibration, for the corrosion/re-equilibration event. In any case, this is extremely short as compared to what is expected for the duration of thermally controlled processes in the lower crust. We infer that the corrosion and re-equilibration of the garnet is linked to the juxtaposition of relatively hot mafic and comparatively cool felsic units in a supra-subduction zone setting. On its way to shallower crustal levels, previously subducted and now buoyant felsic material sampled fragments of the mantel during its passage through the mantle wedge. Corrosion and re-equilibration of the garnets from the mafic granulites was driven by chemical interaction of the mafic rocks with the surrounding felsic lithologies, whereby the mafic rocks hosting the garnet started to loose heat into the felsic lithology and cooled immediately after juxtaposition. The secondary zoning of garnet thus testifies to a relatively short lived thermal perturbation at generally high temperatures caused by the buoyancy driven ascent of felsic lithologies in a supra-subduction setting.

# GROWTH OF BRUCITE ON PORTLANDITE CRYSTALS

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The present work is framed within the context of self-protective layer formation on concrete. In the course of exposure to the environment, various layers of different nature may form on the concrete surface. For example, concrete exposure to $CO_2$ is known to lead to calcite formation, which partially inhibits further chemical reactions (GALAN et al., 2015). The potential protective effect of brucite formation on concrete has been less explored (BUENFELD & NEWMAN, 1986). In the present study portlandite crystals, as a main mineral in common concrete, were synthesized (Fig.1a) and subsequently coated with nail polish, leaving only one of the hexagonal surfaces free. The partially coated crystals were immersed in magnesium containing solutions for the brucite layer to grow (Fig.1b). Three magnesium salt solutions were chosen: sulfate, nitrate and chloride. To identify and characterize the brucite grown on the surface of the crystals XRD, FTIR and optical microscopy were used. The concentration of $Ca^{2+}$ and $Mg^{2+}$ in the solution was followed with time by means of Ionic Chromatography. Thermodynamic calculations were performed with PHREEQC to analyze the effect of the variables on the precipitation of brucite in the presence of portlandite. The growth of brucite is affected by the nature of the anion accompanying magnesium: in the magnesium sulfate solution, additionally gypsum forms, whereas in the case of nitrate and chloride only brucite precipitates. The ratio of the exposed surface of the crystal to the volume of water and that of the exposed surface to the concentration of magnesium in the solution control the growth and the final quality of the surface layer. Preliminary results on the effect of various parameters on brucite layer formation on portlandite will be presented and discussed.

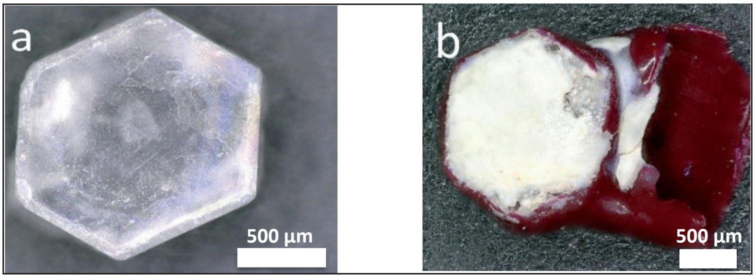

Figure 1. a) portlandite crystal. b) brucite coated crystal.

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BUENFELD, N.R., NEWMAN, J.B. (1986): Cem. Concr. Res. 16, 721-732.

# A NEW SEDIMENT-HOSTED CU-CO DEPOSIT IN THE KUNENE REGION, NORTHWESTERN NAMIBIA

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The Cu-Co deposits of the Central African Copperbelt are world-famous and well-known. In recent years a sediment-hosted Cu-Co deposit, referred to as the Dolostone Ore Formation (DOF), has been found and explored in the Ombombo Subgroup of the Otavi Group in the Kunene region, northwestern Namibia. The Ombombo Subgroup represents a transgressional sequence from the active rift clastic sediments of the Nosib Group into a passive margin platform environment (MILLER, 2008). The over 40 km mineralized DOF horizon is hosted within the upper part of an about 6 km thick sequence of interbedded layers of carbonates, marly sediments, carbonaceous shales, and siltstones.

Current exploration resulted in a maiden resource containing 126100 tons Co at a cut-off grade of 600 ppm (CELSIUS RESOURCES, 2018). The deposit has the potential of becoming Namibia's first Co mine. The DOF mineralization is defined by an enrichment in Cu, Co, Zn, Ni, Fe and Mn. The ore horizon has a sharp contact to the footwall, but fades upwards into the hanging wall. This upper, gradual contact is referred to as the Wider DOF and is enriched in the same metal assemblage as the main DOF horizon.

The predominant sulfides of the DOF ore horizon are pyrite, pyrrhotite, chalcopyrite, and sphalerite. Several Co phases have been observed within the Co-Ni-As-S system. The ore horizon comprises several different mineralization types: disseminations, nodules**,** veins, breccias, and syn-sedimentary slump-like structures. Various superimposed deformational textures can be seen throughout the succession reflecting the effect of the Damaran Orogeny.

The ultimate aim of this study is to establish an appropriate genetic model for the DOF, which can be applied to exploration. First results already point out that the DOF does not share several of the key features of possibly similar Cu-Co deposits in the Central African Copperbelt and the Kupferschiefer. No evaporites have been identified in the stratigraphic sequence during extensive exploration, which is believed to have played a crucial role in the formation of the Kupferschiefer (BORG et al., 2012). Many deposits of the Central African Copperbelt can be related to first reductants in the sedimentary succession (MILLER, 2013), however, the DOF represents neither the first nor a specifically strong reductant.

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# PETROLOGIE UND PHASENBEZIEHUNGEN IN CHARNOCKITEN AUS INDIEN UND SRI LANKA

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Erstmalig wurden Anfang des 20. Jahrhunderts orthopyroxenführende Granitoide in Pallavaram, Chennai, Indien als Charnockite beschrieben. Im petrologischen Kontext bezieht sich der Prozess der Charnockitisierung auf die Neubildung von Orthopyroxen unter Einwirkung von Fluiden in der Unterkruste hochgradiger Terrains. Primär unabhängig von ihrem Ausgangschemismus werden sie als Gesteine aufgefasst, in welchen unter amphibolit- bis granulitfaziellen Bedingungen durch Infiltration von Fluiden mit geringer $aH_2O$ wasserhaltige Minerale (Amphibol, Biotit) im Festzustand dehydrieren. Dabei ist die Bildung von Orthopyroxen für den Prozess der Charnockitisierung charakteristisch. Im Zuge dieser Untersuchungen wurden zwei Charnockitgesteinsproben aus Kabbal, Indien und Udadigana, Sri Lanka analysiert. Probe Kabbal (3-9) stammt aus der Nähe des gleichnamigen Ortes Kabbal im sündindischen Bundesstaat Karnataka, ca. 70 km südwestlich von Bangalore. Die Probenentnahme von Udadigana D4-K7 erfolgte in Udadigana, Distrikt Kurunegala, Sri Lanka, unweit der Stadt Kandy innerhalb des zentralen Hochlands.

Die Fluid-Gesteins-Wechselwirkung innerhalb dieser Proben wurde mittels Durchlicht-mikroskopie, Mikrosondenanalytik und thermodynamische Modellierungen unter der Anwendung von THERMOCALC v. 3.33 beschrieben. Die mineralogisch unveränderte Zone in den Probe aus beiden Lokalitäten besteht aus folgender Mineralparagenese: Bt + Hbl + Kfs + Pl + Qtz ± Zrn ± Ap ± Mag ± Ilm. Im charnockitisierten Bereich sind nun eindeutige Mineralreaktionen zu beobachten und die Mineralparagenese lautet: Opx + Cpx + Bt + Amp + Kfs + Pl + Qtz ± Zrn ± Ap ± Mag ± Ilm. Ausgangspunkt für die thermodynamische Modellierung ist die Hypothese, dass die Charnockitisierung während der P-T Bedingungen des Metamorphosehöhepunkts (Kabbal: 700-800 °C und 0.5-0.6 GPa; Udadigana: 700-750 °C und 0.65 GPa) stattfand. Um die möglich abgelaufenen Mineralreaktionen und Stabilitätsfelder der beteiligten Phasen im Zusammenhang mit der Temperatur und dem Druck zu bringen wird die Schreinemakers-Methode angewandt. Semiquantitative Abschätzungen mittels invarianter Punkte geben eine grobe Einschätzung der damals vorherrschenden P-T-Bedingungen wieder. Der Zusammenbruch von Amphibol zu Orthopyroxen ± Klinopyroxen läuft z.B. nach folgender Modellreaktionen ab: Ts + Qtz = En + An + $H_2O$ und Tr = En + Di + Qtz + $H_2O$.

Es konnte gezeigt werden, dass in den untersuchten Proben vor allem der Amphibolzusammenbruch für die Umwandlung in Orthopyroxen verantwortlich ist. Damit die berechneten Mineralreaktionen abliefen, musste ungefähr eine stark verminderte Wasseraktivität von $\leq 0.3$ geherrscht haben.

Prof. Robert C. Newton wird für die Bereitstellung der beiden Proben herzlich gedankt.

# PROVENANCE ANALYSES OF CHIPPED STONE TOOLS FROM NEOLIHIC PLATIA MAGOULA ZARKOU, THESSALY (GREECE)

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For prehistoric archaeologists, provenance studies of lithic raw materials for stone tool production are one of the keys for reconstructing prehistoric economic behaviour. However, traditional approaches were not able to cover the full scope of analytical techniques required for a secure "fingerprinting" of geological sources and the assignment of archaeological artefacts to specific source areas. This is especially true for silicites, such as chert, flint and radiolarite. The main problems concern the oftentimes high visual similarities and relatively pure nature of $SiO_2$ materials (e.g., HUGHES, 2010; BRANDL et al., 2018).

Here we show that the *Multi Layered Chert Sourcing Approach* (MLA) achieves a clear differentiation of radiolarites from Thessaly combining visual grouping, stereomicroscopic analyses of microfossil inclusions, geochemical trace element analyses applying Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and statistical analyses employing Compositional Data Analysis (CODA) (e.g. BRANDL et al., 2018). LA-ICP-MS allows for the detection of trace element concentrations down to 0.1 ppm, which is essential for the analysis of silicites.

We demonstrate the potential of the MLA chert sourcing method in a case study from a Neolithic and Bronze Age tell site in western Thessaly, Platia Magoula Zarkou[1] (GALLIS, 1996), where chert and radiolarite were extensively used for chipped stone tool production. Although Platia Magoula Zarkou represents a key site for the study of the Neolithic in Greece covering a time span from 5800 to 5100 BC, systematic provenance studies of the chipped stone industry have never before been undertaken. Our pilot project was able to reveal the origin of selected stone tools from the site, identify primary and secondary sources of the enigmatic "Pindos radiolarite", and establish the Koziakas mountain range with its adjacent rivers as a potential source area for early farming communities in the entire Thessalian plain.

BRANDL, M., MARTINEZ, M.M., HAUZENBERGER, C., FILZMOSER, P., NYMOEN, P., MEHLER, N. (2018): PLoS ONE, 13(8): e0200647. https://doi.org/10.1371/journal.pone.0200647

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[1] The archaeological site was investigated in the course of the FWF project P 27159 *Platia Magoula Zarkou in Thessaly*.

# MULTI-ISOTOPES APPROACH ($\delta^{44/40}$CA, $\delta^{88/86}$SR AND $^{87}$SR/$^{86}$SR) OF RHIZOLITHS FORMATION MECHANISMS IN TERRESTRIAL SEDIMENTS OF NUSSLOCH (GERMANY)

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Carbonates in loess-paleosol sequences are considered as a good paleo-environmental proxy for climate change during the Quaternary period. In this study, we present a new dataset of $\delta^{44/40}$Ca, $\delta^{88/86}$Sr and $^{87}$Sr/$^{86}$Sr to understand the formation of rhizoliths (roots encrusted with $CaCO_3$) within these kinds of sequences from Nussloch region (Germany). Our results indicate that the leached fractions of rhizoliths (sampled at 3.2 m, 6.6 m, and 8.4 m depths and leached with HCl) have lower $\delta^{44/40}$Ca and $\delta^{88/86}$Sr, and higher $^{87}$Sr/$^{86}$Sr isotopic values than the leached fractions of rhizosphere and loess of the same stratigraphic levels. Rhizoliths $CaCO_3$ reflect a mixture between loessic $CaCO_3$ from the stratigraphic level in which rhizoliths are found and $CaCO_3$ precipitated within the root itself, whose isotopic signatures are representative of a Holocene near-surface soil level (0.65 m depth).

A new scheme of the rhizolith formation mechanisms has been proposed involving: (1) deepest roots encrustation until the only roots available to uptake water and nutrients were located in the near-surface level, (2) a massive removal of Sr and Ca from the soil at 0.65 m depth, which represents the last available reservoir, (3) a translocation of Sr and Ca through the phloem in the lignin parts of the encrusted roots not yet decomposed, and (4) a $CaCO_3$ precipitation within the cells of the roots, whose isotopic signatures will be identical to the last level from which nutrients were collected.

# INFLUENCING CARBONATE SCALING BY TAILORED DRAINAGE MATERIALS IN TUNNELS - AN EXPERIMENTAL APPROACH

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Unwanted calcium carbonate mineral deposits (scaling) in technical drainage systems result in high costs for cleaning and maintenance works for operators, in particular for large underground infrastructures like motor- and railway tunnels. Appropriate pre- and postdepositional measures for scaling reduction require a detailed knowledge on individual types and physicochemical reaction mechanisms of their formation at the precipitate–drainage substrate material interface. Therefore, the applied research project *PolyDrain (with contributions of the OeBB Infrastruktur AG, ASFINAG and BMVIT)* envisages an experimental approach developed to critically assess the crystal nucleation, growth behavior and textures of different $CaCO_3$ polymorphs and crystal shapes of precipitates on distinct plastic pipe surfaces, i.e. PVC, PE, PP and PE + various additives, designed as draining materials. The overall aim of the project is to evaluate and develop site-specific and tailored materials in terms of scaling reduction on surfaces exposed to tunnel waters (heterogeneous crystallization) and/or within the bulk solution (homogeneous crystallization in suspension), as well as to trigger precipitate textures with relatively soft consistency to ease cleaning.
The experimental laboratory setup allows to simulate scaling progress based on case-specifically adapted aqueous solution compositions interacting with the different surface materials at different temperatures, flow rates, etc.. The aqueous reaction solution – continuously generated by mixing of two stock solutions – is flowing (laminar) through a 2 m long pipe, where the hydrochemical evolution of the solution and related carbonate precipitates are monitored in-situ and by time-resolved sampling, various fluid- and solid-phase analytical techniques and modeling approaches.

Preliminary results show that the mineral precipitates consist of various forms of calcite and that there are significant differences in the nucleation (crystallite abundance and size) and overall amounts and even in the crystal shapes on the different plastics. This makes it possible to provide a ranking of the tested plastic materials with respect to carbonate scaling tendency. This classification indicates that common materials used in drainage systems (mainly PVC, PE and PP) are not suited as well as previously thought, whereas tailored plastics perform much better in the dynamic laboratory tests.

# VARISCAN I-TYPE GRANITOIDS IN THE EASTERN ALPS AND THEIR GEODYNAMIC SETTING: AN UPDATED DISCUSSION BASED ON NEW GEOCHRONOLOGICAL RESULTS

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Variably deformed granitoids with Devonian, Carboniferous and Permian formation ages, commonly termed “Variscan granitoids”, are widespread in the basement units of the eastern Alps. Many of them are I-type (volcanic-arc-type) tonalites and granodiorites and were, thus, considered to be related to the Palaeotethys subduction system located along the southern Variscan fold belt flank (FINGER et al., 1997). However, the issue could be more complicated. New geochronological and geochemical research over the past twenty years has shown that the Variscan I-type granitoids in the Eastern Alps are not cogenetic but form separate plutonic provinces, that were magmatically active at different times. Single granite-forming events likely reflect different tectonic/geodynamic stages during the evolution of the Variscan orogen. An early generation of Late Devonian to Lower Carboniferous I-type granitoids (370-330 Ma) comprises the dioritic-tonalitic-granodioritic Cetic granitoids of the Helvetic unit (FRASL & FINGER, 1988; THÖNI, 1991), the mainly granodioritic Seckau-Bösenstein granitoids (MANDL et al., 2018), and distinct deformed tonalite gneisses in the eastern Tauern Window (“Altkristalline Tonalitgneise” – SCHMIDT, 2017).

A second generation of I-type granitoids with Upper Carboniferous ages (330-300 Ma) occurs in the Eastern Tauern Window (Malta Tonalite, Hochalm Granite, Kölnbrein Granite).

A third, early Permian generation of I-type granitoids (ca. 290-300 Ma) is prominent in the central and western Tauern Window (Venediger Tonalite) and in the Southern Alps.

The following questions must be asked, considering the recent tectonic models for the Variscan orogen (VON RAUMER et al., 2013): i) Which of the intra-Alpine Variscan I-type granitoids are directly subduction-related, i.e., formed above an active subduction zone? ii) Is it possible that some of the intra-Alpine Variscan I-type granitoids belong to the Rheic and not to the Palaeotethys subduction system? iii) Alternatively, is it possible that parts of the intra-Alpine Variscan granitoids have inherited their I-type characteristics from the remelting of older volcanic-arc-type crust, thus being not subduction related in the strict sense.

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# THE EVOLUTION OF THE STEINBERG VOLCANO, STYRIAN BASIN

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The Pannonian Basin is an extensional basin, which is situated between the Alpine, Carpathian and Dinaride orogenic belts. It consists mainly of two major terrains: a) the northern ALPACA (Alpine-Carpathian-Pannonian) block and b) the Southern Pannonian Eastern Carpathian ("Tisza-Dacia") block. Two sub-basins, the Vienna- and the Styrian-Basin, belong to the Pannonian Basin as well.

The formation of the Pannonian Basin is associated with the northwards motion of the Adriatic plate and its collision with the Southern Alps in the late Oligocene. The compressional forces caused the separation of the two major blocks from the Southern Alps that migrated eastward to form the Pannonian Basin (RATSCHBACHER et al., 1991). The extensional tectonics that occurred in the Early Miocene has been attributed to the retreat and roll-back of the subducting lithospheric slab along the Carpathian Arc (HUISMANS et al., 2002).

An intensive volcanic activity characterizes the Pannonian Basin. The volcanic rocks with compositions that range from intermediate subalkaline to K- and Na-alkalic have been devided into (a) Miocene (21–13 Ma) silicic pyroclastic (mostly ignimbrite) suite; (b) middle Miocene to Quaternary (16.5–2 Ma) calc-alkaline volcanic rocks; (c) Miocene to Quaternary (15–0.02 Ma) potassic and ultrapotassic rocks; and (d) late Miocene to Quaternary (11–0.2 Ma) alkalic sodic (HARANGI & LENKAY, 2007).

The Steinberg volcano with an age of 2.2 Ma, belongs to the Styrian Basin and consists mainly of nephelinites, phonolitic tephrites and basanites (ALI et al., 2013). The volcanic activity is complex and reveals multiple eruption phases that produced different eruptive units, which due to the intensive mining is difficult unequivocally to relate to a certain eruptive phase. The first eruptive phase was phreatic to phreatomagmatic followed by effusive lava flow with columnar appearance, which subsequent filled up a depression that formed a lava lake like unit. The third eruptive phase is characterized by typical Strombolian activity that ejected bombs up to 50 cm in diameter. Finally the last event is the formation of dykes up to 10 m thick cross-cutting the Strombolian eruptive products.

Intercalate layers of ashes and lapilli in the Strombolian volcanic products indicate the temporary change of the eruptive mechanism to phreatomagmatic within the Strombolian volcanism. While the intensive mining, mainly in the NE part of the volcano, revealed the structure of the Strombolian crater, the extrusive center of the lava flow has not been localized but presumably, it is in the southern part where the thickest columnar lava flow exists.

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# NEW HINTS OF VARYING PROVENANCE AND PROTOLITH AGES OF DIFFERENT METASEDIMENTARY COMPLEXES OF THE KORALPE-WÖLZ NAPPE SYSTEM (EASTERN ALPS)

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The Koralpe-Wölz nappe system is part of the Upper Austroalpine unit of the Eastern Alps (SCHMID et al., 2004). The individual nappes of the Koralpe-Wölz nappe system are composed of different metasedimentary complexes with mono-, bi-, or polymetamorphic history (HABLER & THÖNI, 2001; THÖNI & MILLER, 2009). They are characterized by medium to high grade (amphibolite and eclogite facies) Eo-Alpine (Cretaceous) metamorphism contemporaneous or subsequent to nappe stacking. Most of the complexes were also affected by Permian high-temperature – low-pressure metamorphism, basically related to lithospheric thinning subsequent to the Variscan orogeny. While the metamorphic conditions of most of the complexes are well constrained, very little is known about the protolith ages of the metasediments of the Koralpe-Wölz nappe system.

Based on U/Pb data of detrital zircons of these different metasedimentary complexes, we can give an overview about maximum ages of sediment deposition and about potential areas of provenance. Data records of additional locations, already sampled, will define this study more precisely in future and will give information about the structural and tectonic evolution of the Austroalpine nappes.

Zircon age spectra (based on $^{206}$Pb/$^{238}$U data) of sampled metasediments of the Koralpe, Rappold and Millstatt complexes indicate post- Variscan sedimentation of parts of these units with maximum ages of 308 Ma & 312 Ma (Koralpe), 328 Ma (Rappold) and 359 Ma (Millstatt). Zircon ages of the Koralpe Complex show main peaks at Ordovician and Carboniferous times. The age distribution of metasediments within the Rappold Complex and the Millstatt Complex is dominated by zircons with Cadomian ages. One micaschist sample from the Saualpe (Koralpe Complex) is dominated by zircons with an age of around 90 Ma. This age proves zircon growth during the Eo-Alpine metamorphic event.

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# DARK EARTH -
# DIE SCHWARZE SCHICHT

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Das Phänomen der "Dark Earth", im deutschsprachigen Raum auch "Die Schwarze Schicht" genannt, tritt europaweit in der Stratigraphie archäologischer Grabungen auf.

Die Bezeichnung Dark Earth wurde von der britischen Forschung geprägt. Erstmals tauchte der Begriff Anfang des 20. Jahrhunderts zur Beschreibung von Schichtbefunden in London auf. Dieser bezeichnet im Allgemeinen eine Trennschicht zwischen römischen oder spätantiken und frühmittelalterlichen oder mittelalterlichen Siedlungsbefunden in einem urbanen Kontext. Es handelt sich um eine Bodenbildungsschicht, die meist eine dunkle bis schwarze Färbung und einen hohen humosen Anteil aufweist und sich schwer oder gar nicht stratifizieren lässt (MACPHAIL et al., 2003; GAISBAUER, 2006).

Die Dark Earth birgt außerdem einige Besonderheiten in sich, die ihr einen geheimnisvollen Anstrich verleihen. Die Aktivität der Bodenorganismen etwa führt zum "Auffressen" von Befunden oder Schichten, die innerhalb oder direkt unter der Dark Earth liegen. Diese wächst also in zwei Richtungen an, sowohl nach oben als auch nach unten hin. So werden also Befunde und Strukturen, oftmals sogar wenn sie in Stein- und Mörtelbauweise errichtet sind, soweit homogenisiert, dass sie schlussendlich unkenntlich sind. Dieses Phänomen führt in weiterer Folge auch zu sogenannten "schwebenden" Befunden, die dann auftreten, wenn Befunde, wie zum Beispiel Mauern oder Gräber den Homogenisierungsprozessen standhielten, aber die zugehörige, umgebende Stratigraphie eben diesen zum Opfer fiel (LEHNER, 2009; GAISBAUER, 2006).

Um dieses Phänomen europaweit vergleichen und näher beleuchten zu können, und so die unterschiedlichen Erklärungsansätze zur Enstehung dieser Schicht in Einklang zu bringen, werden unterschiedliche naturwissenschaftliche Methoden zu Hilfe gezogen. Anhand einiger Beispiele von mehreren Fundorten innerhalb Europas wird die Verschiedenartigkeit der untersuchten Schichten und die gleichzeitige Einheitlichkeit der Dark Earth als Phänomen betont. Zusammenfassend sollen die gewonnenen Erkenntnisse miteinander in Einklang gebracht werden, um so zu einem besseren Verständnis der Dark Earth beizutragen.

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# CHARACTERISATION OF HEAVY MINERAL SANDS BY PORTABLE X-RAY FLUORESCENCE (PXRF)

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Heavy mineral sands (HMS) are a potential resource of zircon, apatite and monazite, and therefore, of critical elements such as rare earth elements, Hf, and P. While major minerals of HMS can often be identified in the field, minor mineral components that host critical elements and the proportions of the various mineral groups are commonly more difficult to determine on-site. Hence, portable X-ray fluorescence (pXRF) analysers that yield geochemical information may improve identification and quantification of mineral constituents of HMS. In this study, we test the applicability of pXRF for the characterisation of garnet-magnetite HMS from the Namibian coastline.

Forty-six samples of HMS were collected from a c. 230 km long stretch of the northern Namibian coast in the Erongo and Kunene regions. The samples contain between a few and > 80 % heavy minerals, the major heavy constituents are garnet, Fe-oxides and Ti-minerals. Elements of interest ($SiO_2$, Ti, Mn, Fe, Zr, Th, Y, V and Hf) were measured by pXRF in powdered and unground HMS samples to test whether minimal sample preparation yields reliable results. Comparing pXRF to conventional laboratory analyses showed that pXRF results of unground sands scatter widely, likely due to sample preparation and resulting inhomogeneity. In contrast, homogenized powdered sands can be measured precisely and their systematic deviation from the conventional laboratory value can be corrected with simple linear regression equations.

To determine proportions of heavy mineral groups in the sands, HMS samples with various heavy mineral contents were selected to calibrate corrected pXRF element concentrations and XRD Rietveld data. Manganese, Fe, Ti and Zr concentrations were used to estimate the amounts of garnet, Fe-oxides, Ti-minerals and zircon in the samples, respectively. Geochemical and mineralogical data correlate well for garnet and moderately for Fe-oxides and Ti-minerals. While the presence of accessory minerals such as zircon, apatite and monazite is indicated by Zr, Hf and Th concentrations, a quantification is not possible with the current data set. Concluding, pXRF analysers are a useful tool for HMS characterisation and yield valuable information that may even be collected directly in the field.

# PHOSPHOROUS-RICH PHILIPSBURGITE, A NEW MINERAL SPECIES FROM LAVRION, GREECE

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Recently, philipsburgite with a high content of phosphorous was found at the 1st level of the Christiana 132 area, Kamariza Mines, Lavrion, East Attica, Greece. This mineral phase was studied by electron microprobe analysis and by single crystal X-ray diffraction. The empirical formula is $(Cu_{5,05}Zn_{0,99})_{\Sigma=6.04}(AsO_4)[(AsO_4)_{0,40}(PO_4)_{0,60}]_{\Sigma=1,00}(OH)_6{\cdot}H_2O$ and the simplified one is $Cu_5Zn(AsO_4)(PO_4)(OH)_6{\cdot}H_2O$. The structure was refined to $R1 = 0.035$ in space group $P2_1/c$ ($a = 12.3291(6)$ Å, $b = 9.2189(4)$ Å, $c = 10.7011(5)$ Å, $\beta = 97.249(2)^{\circ}$, $V = 1206.57(2)$ Å$^3$, Z = 4).

This mineral belongs to the framework structure type of kipushite $Cu_5Zn(PO_4)_2(OH)_6{\cdot}H_2O$ and philipsburgite $Cu_5Zn(AsO_4)_2(OH)_6{\cdot}H_2O$. These isotypic structures are characterized by the two distinct tetrahedrally coordinated $XO_4$ positions, which are either occupied by P or As. CIESIELCZUK et al. (2016) indicated the presence of a solid-solution series between both end-members. In the case of our studied sample the As atoms occupy the *X*(2) site, while the *X*(1) site is dominantly occupied by P. In the literature (cf. KRIVOVICHEV et al., 2018) the possibility of such an ordered arrangement, representing a separate mineral species, was already predicted.

Due to the preferred incorporation of P and As in the respective structural sites the mean P-O distance is 1.580 Å, while the mean As-O bond length is 1.684 Å. KRIVOVICHEV et al. (2018) reported at the *X*(1) position (site occupancy ~$As_{0.63}P_{0.37}$) a mean value of 1.610 Å and for <As-O> of 1.694 Å, respectively.

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# EXPERIMENTAL DETERMINATION OF SULFATE INCORPORATION IN CALCITE, Mg-CALCITE AND ARAGONITE

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The incorporation of trace elements in carbonate minerals provides key information to unravel past chemical-physical conditions of the Earth's surface environments. Sulfate is the second most concentrated anion in modern seawater and is readily incorporated as an impurity in marine carbonate minerals. This fraction of sulfate is commonly referred to as carbonate-associated sulfate (CAS) and it is presumed that the tetrahedral sulfate ion substitutes the trigonal-planar carbonate ion in the respective crystal lattice. CAS is used as a proxy for reconstructing the primary sulfur isotopic composition of oceanic sulfate and the evolution of the marine sulfur cycle in the geological past. Its sulfur isotopic composition (given as $\delta^{34}S_{CAS}$ value) equals that of the dissolved marine sulfate whose $\delta^{34}S_{SW}$ (SW = seawater) value reflects the redox conditions, input-output balance (e.g. evaporates, sulfur-containing ores, leaching/weathering of rocks), and biological activity of the ancient ocean (BURDETT et al., 1989; KAMPSCHULTE & STRAUSS, 2004). However, a mechanistic understanding of the mode and the extent of sulfate incorporation into carbonate minerals is largely lacking.

In this study, we investigate the sulfate incorporation into calcium carbonate minerals and their sulfate partitioning coefficients ($D_{SO4} = (SO_4/CO_3)_{solid} / (SO_4^{2-}/CO_3^{2-})_{fluid}$). To shed light on the mineral growth rate dependence of $D_{SO4}$ we performed steady-state precipitation experiments at varying growth rates, but at constant temperature, pH and sulfate concentration of the reactive fluid (30 mM $SO_4$). The overgrowth experiments were carried out using synthetic calcite or aragonite seeds at 23 ± 1 °C and pH 6.3 ± 0.1 or 8.3 ± 0.1 and in the presence or absence of aqueous magnesium.

Preliminary results from experiments at pH 8.3 suggest that increasing growth rates promote sulfate incorporation in both calcite and aragonite. At low growth rates the extent of incorporated sulfate in calcite and aragonite is similar, whereas with increasing growth rate the sulfate uptake in calcite is much higher compared to aragonite. Calcite grown at pH 6.3 in the presence of sulfate and magnesium exhibits a 3.5 to 5 times higher sulfate content than calcite, which was grown at pH 8.3 at a similar growth rate. The obtained results improve our fundamental understanding on controls of mineral growth rate, pH and aqueous complex formation on sulfate incorporation in (Mg-)calcite and aragonite, and allow determining apparent partitioning coefficients of sulfate between precipitated mineral and reactive fluid for individual precipitation environments.

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# GEOPOLYMER CONCRETE – POTENTIAL APPLICATIONS IN CHEMICALLY AGGRESSIVE SANITATION AND WASTE INFRASTRUCTURE

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The degradation of concrete infrastructure due to the interaction with chemically aggressive gases and solutions from e.g. waste deposits and sewage transport facilities is a globally unresolved economic issue. The vast majority of the damages are caused by biotic metabolic reactions occurring during fermentation processes. This results in the production of various acids, such as sulfuric acid, lactic acid or formic acid, and subsequent interaction with the concrete. Conventional Portland cement based construction materials, mainly composed of Ca-hydrates and Ca-silicate-hydrates, cannot guarantee expected service life in such acidic environments, which raise the demand for alternative materials. In this perspective, distinct types of geopolymer concrete (GPC) might be chemically more resistant in the latter environments. Geopolymers are formed via polycondensation of alumosilicates to form a highly stable polymer network of Si – Al – tetrahedrons with O, thereby avoiding the formation of acid dissolvable hydrates. Additionally, their nano-structural similarity with zeolites enables GPC to have analogous applications, such as the long lasting carrier of antimicrobial cations.

This study presents the critical assessment of GPC performances exposed to a biogenic acid corrosion environment and to a corroding biowaste facility within two long-term field exposure campaigns of up to 24 months. Material performances were characterized using a holistic approach including advanced mineralogical, microbiological and hydro(geo)chemical analytical tools. Additionally, exposure sites specific environmental conditions, such as $H_2S$ and $CO_2$ concentrations, temperature and relative humidity were monitored. GPC performances were compared to standard Portland cement (PC) concrete, as well as to calcium aluminate concrete, simultaneously exposed. Up to 8 times lower corrosion rates could be observed on distinct GPC mixtures compared to the standard PC concrete exposed to the biogenic acid corrosion environment, while no signs of corrosion could be detected on the GPC exposed to the biowaste facility.

# GONDWANA FRAGMENTS IN THE EASTERN ALPS: A TRAVEL STORY FROM U/PB ZIRCON DATA

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We compare detrital U / Pb zircon age spectra of Carboniferous and Permian / Lower Triassic sedimentary rocks from different structural positions within the Austroalpine nappe pile of the Greywacke Zone with published ages of magmatic and metamorphic events in the Eastern Alps and the West Carpathians. Similarities between sink and possible sources are used to derive provenance of sediments and distinct frequency peaks in sink and source age pattern are used for paleogeographic plate tectonic reconstructions. From this, travel paths of Austroalpine and West Carpathian basement units are traced from the Late Neoproterozoic to the Jurassic. We place the ancestry of basement units on the northeastern Gondwana margin, next to Anatolia and the Iranian Luth-Tabas blocks. Late Cambrian rifting by retreat of the Cadomian Arc failed and continental slivers re-attached to Gondwana during a late Cambrian/ early Ordovician orogenic event. In the Upper Ordovician crustal fragments of the Galatian superterrane rifted off Gondwana through retreat of the Rheic subduction. An Eo-Variscan orogenic event at ~ 390 Ma in the Austroalpine developed on the northern rim of Galatia, simultaneously with a passive margin evolution to the south of it. The climax of Variscan orogeny occurred already during a Meso-Variscan phase at ~ 350 Ma by double-sided subduction beneath Galatia fragments. The Neo-Variscan event at ~ 330 Ma was, unlike previously considered, mild in eastern Austroalpine units. This orogenic phase was hot enough to deliver detrital white mica into adjacent basins but too cold to create significant volumes of magmatic or metamorphic zircon. Finally, the different zircon age spectra in today's adjacent Permian sediments disprove original neighbourhood of basins. We propose lateral displacement of major Austroalpine and West-Carpathian units along transform faults transecting Apulia. The intracontinental transform system was released by opening of the Penninic Ocean and simultaneous closure of the Meliata Hallstatt Ocean as part of the Tethys.

# ARCHAEOMETRIC INVESTIGATION ON THE TEMPER OF COARSE POTTERY SHARDS FROM ROMAN-TIMES SETTLEMENT AREAS IN STYRIA AND BURGENLAND, AUSTRIA

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Coarse pottery shards (41 fragments) from the first and second centuries that were found in five Roman sites in Styria and Burgenland (Gleisdorf, Hörbing, Retznei, Saazkogel and Sankt Martin/Raab) were subjected to mineralogical and chemical investigations to test the hypothesis that even coarse ceramics in the Roman period were produced in special centres and then traded like fine ware with people in other locations. Apart from minor variations, the mineralogical and chemical compositions of the investigated ceramic fragments are highly uniform. In addition, it is interesting to note that quartz was used exclusively as a temper material, whereby the grain size and shape varies, depending on the ceramic type. Thus, quartz in ceramic fragments from the dolia is extremely coarse-grained, and often poorly sorted; however, quartz is very finely graded in the cup shards and the grain sizes are well sorted, while the particle sizes and sorting of quartz in the tripod bowls are intermediate between the other two groups. To obtain more information about the production site of the ceramics, quartz temper and quartz samples taken from the nearby rivers as reference samples were subjected to cathode luminescence (CL) analyses. This method is often used in sedimentary geology to determine the origin rocks of the sediments and was adapted for use as an additional method in archaeological provenience analysis (PICOUET et al., 1999). The colour of CL of quartz is observed; blue, red and purple are common colours. Blue is typically indicative of quartz from pegmatite rocks, red is often detected in volcanic rocks and purple to brownish (the most common colour) is found whenever the rock has undergone a regional metamorphosis event (GÖTZE et al., 2001). The result of the CL analysis illustrates that, other than the ceramics from Hörbing, all the other samples displayed purple to brownish coloured CL. The Hörbing samples – both quartz samples from the river and quartz temper in the shards – initially displayed a strong blue CL, hinting at a pegmatite origin for quartz. This evidence combined with the geological information about the region around the sites support the hypothesis that at least the Hörbing shards were produced locally. This is also supported by the fact that at least three pottery kilns have been excavated in the area of the possible vicus of Deutschlandsberg-Hörbing. Combined with the other analytical results and the available archaeological information, the first conclusions regarding the provenience of the analysed shards could be made. The evaluation results show that at least three different production sites for Roman coarse pottery ware existed during the first and second centuries in the regions of Styria and Burgenland: one in Hörbing, one for Retznei, maybe in Flavia Solva, and one for the others, possibly in Gleisdorf.

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PICOUET, P., MAGGETTI, M., PIONNIER, D., SCHVOERER, M. (1999): Journal of Archaeological Science 26, 943-949.

# ARCHAEOMETRIC INVESTIGATIONS OF COARSE POTTERY FROM ROMAN-TIMES SETTLEMENT AREAS IN STYRIA AND BURGENLAND, AUSTRIA

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In general, coarse pottery of the Roman period has been believed to have been produced at the place where it was used, but recent evidence based on the optical similarity of the potteries suggests that even these ceramics were made in production centres specialized for coarse ware and were traded like fine ware (LAMM, 2011). This hypothesis has also been postulated for coarse ceramics produced during the first and second centuries and found at the Roman sites of Gleisdorf, Hörbing, Retznei, Saazkogel and Sankt Martin an der Raab. To scientifically test this hypothesis, 41 ceramic fragments from these five sites were analysed more closely using mineralogical and chemical methods (CL, EMPA, FTIR, OM, XRD, XRF). The samples were subdivided into three types of pottery: Fragments of dolia (storage containers), tripod bowls and cups. However, cup fragments from the Saazkogel and tripod bowels as well as cup fragments from Hörbing were not analysed, as they were not available from these localities. In contrast to the results of earlier investigations on Roman coarse potteries (PICHLER et al., 2017), the results of this mineralogical investigation show that all ceramic fragments from these regions have similar compositions. Quartz, mica and feldspar minerals, mainly of plagioclase composition, are the main components, but the quantitative content of these minerals in the shards differs, especially that of the plagioclase. The chemical compositions of the fragments specifically differ depending on the type and the sites in which they were found. By applying the Principal Component Analysis (PCA) method, three different chemical groups were determined: a $SiO_2$-rich group with slightly higher amounts of $Fe_2O_3$, MgO and $K_2O$; a second group with a slightly lower $SiO_2$ content but slightly higher CaO, $Na_2O$ and MnO contents; and at least a third group characterised by its low $SiO_2$ content and higher $Al_2O_3$ and $TiO_2$ contents. The minor and rare element contents also supported the formation of these groups but with less precision. To collect more information about the provenience of the analysed shards, the Optimal Foraging Theory model, used in Stone Age archaeology, was also used. By combining the results of these analyses with the available archaeological information, initial conclusions about the provenience of the analysed shards could be made. The evidence shows that at least three different production places for Roman coarse ware existed during the first and second centuries in the regions of Styria and Burgenland: one in Hörbing, one for Retznei, perhaps in Flavia Solva, and one for the others, possibly in Gleisdorf. In addition, it seems as though no standardized formulation for all ceramics existed, although formulations existed for certain equal types of ceramics (cup, dolia and tripod bowl). In contrast, all the ceramics were fired at temperatures between 700 and 800 °C.

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PICHLER, R., HASPL, E., LAMM, S., KLAMMER, D. (2017): Mitt. Österr. Miner. Ges., 163, 71.

# MODAL AND CRYPTIC MANTLE METASOMATISM IN XENOLITHS FROM CENTRAL AND SOUTHERN VIETNAM

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Mantle xenoliths, clinopyroxene, zircon and sapphire xenocrysts occur commonly within the basalt plateaus in central and southern Vietnam. The different basalt flows/eruptions belong to a tholeiitic and an alkaline suite and have Neogene to Quaternary age (HOANG & FLOWER, 1998). The mantle xenoliths are exclusively found in the alkaline basalts and are typically a few cm to tens of cm in size, consist of spinel lherzolites as well as some spinel harzburgites and pyroxenites. Samples from Pleiku, Da Lat, Nui Trai, Xuan Loc and the off shore locality Ile de Cendres were recovered and investigated in detail.

Most samples display the simple lherzolitic mineral assemblage Ol–Opx–Cpx–Sp. The Ol, Cpx and Opx crystals are equigranular, Sp occurs usually as smaller sized intersertal phase or as oriented inclusion in Cpx. Clinopyroxene is found in two generations: (1) primary Cpx I has a uniform composition with a typical $X_{Mg}$ (=Mg/(Mg+Fe$^{2+}$) of 0.92 to 0.98, a $X_{Na}$ (=Na/(Na+Ca) of 0.10 to 0.16, a $Cr_2O_3$ content of 0.6–0.9 wt. .% and $Al_2O_3$ values of 6 to 8 wt. %. (2) Cpx II recrystallized as “spongy rim” around Cpx I, has a lower $X_{Na}$ and $Al_2O_3$ content as well as higher $X_{Mg}$ and $Cr_2O_3$ content compared to Cpx I. Orthopyroxene typically has a $X_{Mg}$ of c. 0.90 to 0.93. The $X_{Mg}$ values for Ol differ slightly between different samples but are within 0.84 to 0.94. Spinel grains have a variable composition with $X_{Mg}$ from 0.65 to 0.92 and $X_{Cr}$ (Cr/Cr+Al+Fe$^{3+}$) of 0.08 to 0.25. The use of the Cpx-Opx thermometer (BREY & KOEHLER, 1990) and the Al and Cr in Ol thermometer (DE HOOG et al., 2010) allowed to calculate temperatures of 800 to 1100 °C at a pressure of 1.5 to 2.0 Gpa. Clinopyroxene I trace and rare earth element pattern are slightly depleted in light rare earth elements (LREE), typical for average depleted mantle compositions, some samples are strongly enriched in LREE indicating mantle metasomatic processes by carbonatitic melts. The variation in LREE as well as LIL element concentration in Cpx from different xenoliths is evidence for the heterogeneous nature of the mantle beneath Indochina. In addition elongated apatites as well as carbonate droplet inclusions in olivine are found in some samples indicating metasomatic influence from carbonatitic melts.

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# PETROCHRONOLOGY OF TEMPERATURE-DOMINATED METAMORPHIC PROCESSES: PETROLOGY AND DATING OF ACCESSORY MINERALS FROM THE IVREA VERBANO ZONE, ITALY

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The emerging field of petrochronology relates absolute ages with petrological information derived from the same minerals. Modern U-Th-Pb in-situ-dating techniques of accessory minerals (AM) allow to gain age information from multiple episodes of crystal growth, dissolution and reprecipitation if these features are preserved within single crystals. Provided that the petrology of these AM, their evolution through metamorphism is well understood, the U-Th-Pb in-situ dating methods can be used to unravel rates of processes in Earth's crust.

Petrological observations and ages are presented for monazites and zircons from migmatic metapelite samples from the Val Strona di Omegna transsect in the Ivrea Zone, Italy.

The Ivrea Zone is part of the pre-Alpine basement located in the Southern Alps of NW Italy and represents an almost complete section from mid- to lower continental crust (e.g. ZINGG, 1980; HANDY et al., 1999). The Val Strona di Omegna shows a 14 km long transect with amphibolite facies in the SE and granulite facies in the NW (REDLER et al., 2012). In all samples monazites exhibit complex zonation patterns. Several monazite-domains from amphibolite to granulite facies samples were dated in-situ by EPMA-CHIME.

A granulite facies metapelite sample (IV 20/05) shows vermicular-shaped metamorphic zircons in proximity to rutile and ilmenite. SIMS in-situ U-Pb dating reveals Permian ages (286.2 ± 2.0 Ma) thus tentatively dating the post-granulite facies peak, Zr-exsolution of rutile or rutile breakdown to ilmenite.

P-T-pseudosections are presented for metapelitic and metabasic rocks from Val Strona di Omegna. P-T-forward modelling was performed in the MnNCKFMASHT-System for metapelites and in the NCKFMASHT-system for metabasites using the Software THERIAK-DOMINO (deCAPITANI & BROWN, 1987; deCAPITANI & PETRAKAKIS, 2010) and the HOLLAND & POWELL (2011) database with updates from WHITE et. al. (2014) and GREEN et al. (2016) for metabasites.

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# FLUID-INCLUSIONS FROM PERMIAN PEGMATITES OF THE EASTERN ALPS

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Fluid inclusions (FIs) in garnet, spodumene and tourmaline from Permian pegmatites were investigated. Samples, taken from the area at St. Radegund (Rappold Complex: RC), the Koralpe Complex (KC), the Millstatt Complex (MC) and the Polinik Complex (PC), represent pegmatites from the Koralpe-Wölz high-pressure nappe system. They consist of K-feldspar, quartz, plagioclase, muscovite, garnet, tourmaline ± spodumene and in rare cases also beryl.

Garnets were characterized using BSE imaging, semiquantitative X-ray elemental maps as well as quantitative EPMA measurements and represent almandine-spessartine solid solutions, dominated by low Ca-contents in the core areas. A "jump" to increased Ca-contents at the rim areas is interpreted as effect of Eo-Alpine Cretaceous overprint.

FIs in garnets from cores with low Ca-contents reflect variations in chemistry. In the RC, $CO_2$+$H_2O$ FIs dominate whereas $CO_2$±$N_2$ fluids predominate in the KC. The MC an PC are dominated by $CO_2$±$CH_4$±$N_2$ fluids accompanied by the rare presence of $H_2O$±$CO_2$+$N_2$ FIs. The occurrence of daughter crystals (i.e. calcite, rutile, muscovite and apatite), especially in the RC and KC, indicate post-entrapment in-situ mineral reactions between the fluid and the garnet host, thus enable the reconstruction of the chemistry of an early $H_2O$+$CO_2$ dominated Permian fluid.

FIs in spodumene hosts from the RC, KC and MC characterize a $CO_2$+$H_2O$- and, in rare cases, an aqueous system. Daughter crystals are frequent (calcite, cassiterite, smithsonite, sinhalite? and unidentified minerals). Graphite solid inclusions in the host occur in the KC as well as in FIs from the MC. FIs are entrapped parallel to the c-axis of the spodumene crystals and exhibit extensive necking, leading to differences in their phase proportions. As suggested for garnets, established daughter phases indicate in-situ reactions between the spodumene host and an early Permian $CO_2$+$H_2O$ fluid.

FIs in tourmaline from the RC and MC consist of $H_2O$+$CO_2$+$N_2$ chemistry and differ to FIs from the KC where pure $CO_2$ or $CO_2$+$N_2$ dominate. Separate $H_2O$+$CO_2$+$CH_4$±$N_2$ FIs and aqueous FIs are entrapped in tourmaline of the PC. FIs are free of daughter crystals, presumably representing the Permian entrapped $H_2O$+$CO_2$-dominated fluid. Reducing conditions after entrapment are indicated by the presence of graphite in the FIs.

To conclude, FIs in the magmatic minerals of the Permian pegmatites underwent intense post-entrapment modifications due to cooling and melt fractionation processes including the presence of Permian minerals like mica as additional nitrogen source along with the $H_2O$-$CO_2$ dominated Permian magmatic fluid. The investigated fluids from pegmatite minerals, which crystallized from different stages during pegmatite formation, enable this reconstruction even though pegmatites were affected by Cretaceous high-pressure overprint.

# NEWS FROM REFRACTORY LAND – TWO NOVEL PHASES IN THE SYSTEMS $CaO-Al_2O_3-Cr_2O_3$ AND $CaO-Al_2O_3-MgO$

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The ternary systems $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-Cr_2O_3$ are of fundamental importance for refractories industry. Apart from previous experimental studies, thermodynamic assessments using the Calphad technique have been also employed to get a holistic picture of the relevant phase relationships. However, as pointed out by HALLSTEDT (1995), the computational results have to be treated with care as long as there is still a lack of data on solid-phase relations. This is surprising because one should assume that both systems have been studied in great detail and are well understood. In the course of our own investigations we were able to finally proof the existence of the compounds $Ca_3Al_4MgO_{10}$ and $CaAl_2Cr_2O_7$.

$Ca_3Al_4MgO_{10}$ was first mentioned more than 50 years ago by MAJUMDAR (1964) to be a stable calcium magnesium aluminate. Its existence, however, was later challenged by DÓDONY & BUSECK (2001) based on electron microscopy data. In a sequence of temperature dependent solid-state reactions the formation of the ternary phase $Ca_3Al_4MgO_{10}$ has been studied. Whereas the compound could not be prepared at 1200 °C, a yield of 85 % of $Ca_3Al_4MgO_{10}$ was obtained at 1320 °C (melting point: 1330 °C). Single crystals could be retrieved from the sinter pellets. Basic crystallographic data are as follows: orthorhombic symmetry, space group *Pbcm*, $a = 5.14073(8)$ Å, $b = 16.7576(2)$ Å, $c = 10.70977(16)$ Å, $V = 922.61(2)$ Å$^3$, $Z = 4$. Using synchrotron radiation it was possible to solve the crystal structure. It contains $[(Al,Mg)O_4]$-tetrahedra forming a three-dimensional network whose topological characteristics have been determined. Al-Mg distributions on the different T-sites have been investigated. The calcium cations are located in voids of the network.

When a 1:1:1 molar composition of the three components CaO, $Al_2O_3$ and $Cr_2O_3$ was reacted at 1500 °C, a previously unknown phase with composition $CaAl_2Cr_2O_7$ formed. Diffraction experiments at ambient conditions on a crystal with composition $CaAl_{2.13}Cr_{1.87}O_7$ yielded the following crystallographic data: space group *P*3, $a = 7.7690(5)$ Å, $c = 7.6463(5)$ Å, $V = 399.68(6)$ Å$^3$, $Z = 3$. $CaAl_2Cr_2O_7$ represents a new structure type. It belongs to the group of double layer structures where individual double layers contain octahedrally and tetrahedrally coordinated cation positions. Linkage between neighboring sheet packages is provided by calcium cations. Thermal expansion has been studied between 29 and 790 °C using in-situ single-crystal diffraction. No indications for a structural phase transition were observed. The thermal expansion tensor has been obtained. A pronounced anisotropy is evident.

DÓDONY, I., BUSECK, P.R. (2001): Phys. Chem. Minerals, 28, 428-434.
HALLSTEDT, B. (1995): J. Am. Ceram. Soc., 78, 193-198.
MAJUMDAR, A.J. (1964): Brit. Ceram. Trans. J., 63, 347-363.

# STRUCTURAL INVESTIGATIONS ON BREDIGITE ($Ca_7Mg(SiO_4)_4$) FROM THE HATRURIM COMPLEX

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Bredigite (idealized chemical composition $Ca_7Mg(SiO_4)_4$) is a rare mineral that has been described from petrological settings related to pyrometamorphism. It has been observed, for example, in contact-metamorphized rocks or in altered carbonate-silicate xenoliths within volcanites based on siliceous limestone-dolomite protoliths.

In pyrometamorphic rocks of the Hatrurim Complex, consisting of products of combustion metamorphism, the existence of small bredigite grains, mainly in larnite rocks, was repeatedly noted (SOKOL et al., 2010). The Hatrurim Complex is distributed over a wide area along the Dead Sea rift zone in the territories of Israel, Palestine and Jordan. Its formation was driven by combustion processes of a sedimentary protolith, however, its detailed genesis is still under discussion (SOKOL et al., 2010; VAPNIK & NOVIKOV, 2013).

Bredigite samples from ternesite-gazeevite-larnite pyrometamorphic rocks of the Hatrurim Complex have been studied by electron probe microanalysis as well as single-crystal diffraction using synchrotron radiation (X06DA beamline at the Swiss Light Source, Paul-Scherrer-Institute). They are characterized by a relatively uniform composition. The empirical formula calculated on the basis of 16 oxygen atoms per formula unit is:

$(Ca_{7.006}Na_{0.015}Ba_{0.014})_{\Sigma 7.035}Mg_{0.938}(Si_{4.000}P_{0.014})_{\Sigma 4.014}O_{16}$.

Basic crystallographic data of a sample studied by X-ray diffraction are as follows: orthorhombic symmetry, space group *Pnnm*, $a$ = 18.38102(17) Å, $b$ = 6.74936(7) Å, $c$ = 10.90328(11) Å, $V$ = 1352.66(2) Å$^3$, $Z$ = 4. Structure solution and subsequent least-squares refinements resulted in a residual of $R(|F|) = 0.023$ for 2584 independent observed reflections with $I > 2\sigma(I)$ and 149 parameters. To the best of our knowledge this is the first detailed structural investigation on natural bredigite. In contrast to previous studies on samples retrieved from metallurgical slags there was no need to describe the structure in the acentric space group *Pnn*2 (MOORE & ARAKI, 1976).

Furthermore, the problem of barium incorporation into the bredigite structure is discussed. Data on the composition of Ba-bearing bredigites from pyrometamorphic rocks of the Hatrurim Complex from Jordan with simplified formula $Ba_{0.7}Ca_{13.3}Mg_2(SiO_4)_8$ (based on 32 oxygen atoms) are provided for the first time, pointing out perspectives of finding new Ba-bearing minerals isostructural with bredigite in nature.

MOORE, P.B., ARAKI, T. (1976): Am. Mineral., 61, 74-87.
SOKOL, E., NOVIKOV, I., ZATEEVA, S., VAPNIK, Y., SHAGNAM, R., KOZMENKO, O. (2010): Basin Res., 22, 414-438.
VAPNIK, Y., NOVIKOV, I. (2013): Basin Res., 25, 115-120.

# ATOMIC-SCALE CRYSTALLIZATION AND RESTRUCTURING OF TWO-DIMENSIONAL $MOS_2$

Kaindl, R.[1], Bayer, B.C.[2,3], Monazam, M.R.A.[2], Susi, T.[2], Kotakoski, J.[2], Gupta, T.[3], Eder, D.[3]
Waldhauser, W.[1] & Meyer, J.C.[2]

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Atomically resolved and element-specific transmission electron microscopy (STEM) gave *in situ* insight in the crystallization and restructuring process of two-dimensional (2D) molybdenum disulphide ($MoS_2$) films (BAYER et al., 2018). Thin amorphous $MoS_2$ films on freestanding graphene membranes crystallized restructured from the energy input of the scanning electron beam into crystalline $MoS_2$ domains. This emulates widely used elevated $MoS_2$ synthesis and processing conditions.

From that direct observation of nucleation, growth, crystallization and restructuring events in the evolving $MoS_2$ films at the atomic scale was possible (Fig. 1). This suggests that during $MoS_2$ processing various $MoS_2$ polymorphs co-evolve and dynamically transform into each other in parallel. Transitions from in-plane to out-of-plane crystallization of $MoS_2$ layers indicate diffusion of Mo and S species and suggest that in this system and depending upon conditions crystallization can be influenced by weak $MoS_2$/graphene support epitaxy.

This atomic-scale *in situ* technique visualizes multiple fundamental processes that underlie the diverse $MoS_2$ morphologies observed in previous *ex situ* growth and processing work. It opens up an approach for studying growth and restructuring mechanisms of other 2D and probably virtually any layered materials.

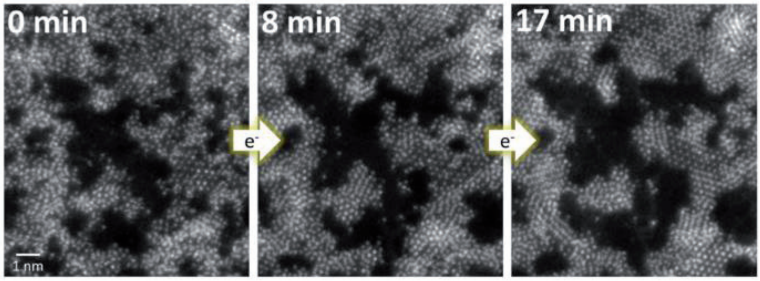

Figure 1. STEM image series of ~2 nm $MoS_2$ on graphene during continuous exposure to e-beam after 0, 8 and 17 minutes, which lead to crystallization from amorphous to nanocrystalline domains.

BAYER, B.C., KAINDL, R., MONAZAM, M.R.A., SUSI, T., KOTAKOSKI, J., GUPTA, T., EDER, D. WALDHAUSER, W., MEYER, J.C. (2018): ACS Nano, 12, 8758-8769.

# THE DANGKHAR BRECCIA: INSIGHTS ON THE FORMATION FROM REMOTE, FIELD AND LABORATORY BASED INVESTIGATIONS

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Remote, field and laboratory investigations revealed the spatial extent, internal structure and mineralogic-petrologic properties of the Dangkhar breccia, Spiti Valley India. The breccia formation is related to the availability of large quantities of carbonate rich debris provided by the Dangkhar Landslide and glacial meltwater lakes on the slope. The breccia clusters about 100 m above the floor and deposition initiated during a valley glaciation (Fig.1a). The breccia was deposited in several cycles with a compact bottom layer of lodgment till of subrounded blocks within a fine grained matrix, followed by proglacial outwash material. A crudely stratified mid layer exhibiting wet sediment deformation and flow structures characteristic of a flow till (BENN & EVANS, 2010), and the top layer with inverse grading and large angular blocks representing a debris flow deposit follow (Fig.1b). Cathodoluminescence imaging showed dark, zoned calcite cement growth characteristic for near surface meteoric cementation (FLÜGEL 2010; Fig.1c). Stable carbon and oxygen isotope values of cements range from $\delta^{18}$O -22.78 to -20.23 ‰ VPDB and $\delta^{13}$C 2.37 to 2.82 ‰ VPDB, respectively, support a freshwater influence. The clasts exhibit values of $\delta^{18}$O -10.25 to -17.45 ‰ VPDB and $\delta^{13}$C 2.37 to 3.51 ‰ VPDB. The three layers represent changes from glacial to paraglacial conditions. Contemporary debris flows are being deposited in an analogous way to the paleo-debris flows through the ephemeral stream channels.

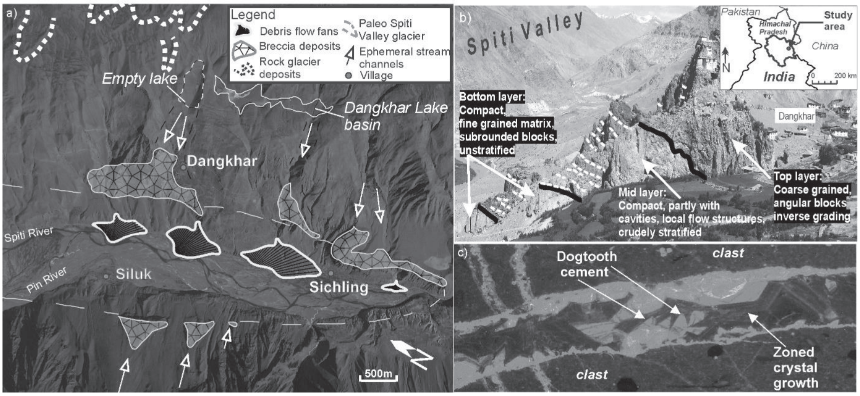

Figure 1. Setting of the Dangkhar breccia. a) satellite image; b) field outcrop; c) cathodoluminescence image.

BENN D.I., EVANS D.J.A. (2010): Glaciers and Glaciation, 2nd edn. Taylor & Francis, London, 816p.
FLÜGEL E. (2010): Microfacies of carbonate rocks–analysis, interpretation and application, 2ndedn. Springer.

# KINETICS OF COMPOSITIONAL AND STRUCTURAL MATURATION OF DOLOMITE AND MAGNESITE (150 - 220 °C) – AN EXPERIMENTAL APPROACH

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Dolomite is an abundant Ca-Mg-carbonate phase throughout ancient carbonate platforms, however, is scarce throughout modern carbonate-depositional environments and seemingly impossible to precipitate experimentally at ambient temperature; this summarizes a geological enigma commonly referred to as “the dolomite problem”. A similar “problem” exists for the much less abundant Mg-carbonate mineral magnesite ($MgCO_3$), which is often associated with dolomite. Natural and synthetic dolomites exhibit significant differences in their compositional and structural properties of stoichiometry (i.e., the relative abundance of $Ca^{2+}$ and $Mg^{2+}$occupying cation sites within the crystal lattice) and cation ordering degree (i.e., “COD”: a measure of the distribution of the $Ca^{2+}$ and $Mg^{2+}$ ions within the crystal lattice). The physicochemical parameters controlling these properties along with the absence of or the presence and abundance of magnesite precipitation, however, are still poorly understood.

In this study, dolomite and magnesite were synthesized in batch reactors at temperatures of 150 °C, 180 °C and 220 °C by reacting $CaCO_3$ (aragonite or calcite) with an artificial solution containing $MgCl_2$ and $NaHCO_3$ over a 360-day reaction period. The obtained results on the maturation of the stoichiometry of dolomite and magnesite and on the COD of dolomite indicate that the formation of ideal, stoichiometric and well ordered, dolomite and of stoichiometric magnesite follow a ripening process and proceed through dissolution and re-precipitation of a sequence of intermediate phases, such as Ca-magnesite, huntite, very-high-Mg-calcite and disordered dolomite. The occurrence and metastability of the precursor phases formed are dependent on temperature and the $CaCO_3$ phase being altered. Temperature is the major rate-controlling parameter of the maturation of dolomite and magnesite stoichiometry and COD of dolomite, corroborating results from prior experiments and natural deposits.

From our data, we determined kinetic rates for the stoichiometric ripening of magnesite and dolomite and for the COD of dolomite for the first time using a first-order reaction kinetic approach. The kinetics increase with temperature following the linear Arrhenius equation, in turn allowing for activation energies of the respective processes to be determined (44.0, 57.4 and 9.3 $kJ \cdot mol^{-1}$, respectively). Interestingly, we found the reaction rate for magnesite stoichiometric ripening is approximately one third of that for dolomite regardless of the temperature, carbonate alkalinity or $CaCO_3$ phase used for reaction. Extrapolation of the obtained dolomitization rates indicates that about 1.4 and 6.8 Myr are required to approach ideal dolomite at 50 °C and 25 °C, respectively, explaining the large absence of ordered dolomite in modern sedimentary successions. The present dataset provides new insights into dolomitization pathways and rates and contributes to a better understanding of the wide range of stoichiometries and COD values of dolomite and its evolution versus magnesite observed in the geological record and in laboratory studies.

# *CoRL* – EINE NEUE TECHNIK IN DER MATERIALANALYTISCHEN MULTISPEKTRALFOTOGRAFIE

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In der traditionellen Multispektralfotografie, welche beispielsweise in der Archäometrie wertvolle Informationen über Art und Verteilung von Materialien in Artefakten erschließt, werden standardmäßig verschiedene Aufnahmetechniken im Wellenlängenbereich zwischen ca. 300 nm und 1100 nm eingesetzt, die sich in zwei große Gruppen unterteilen lassen: Jene bei denen die Aufnahme reflektierten Lichts im Vordergrund steht (z.B. *IRR* – infrared reflected imaging) und jene bei denen durch Lumineszenzeigenschaften emittiertes Licht aufgezeichnet wird (z.B. *UVL* – ultraviolet-induced luminescence imaging). Hier vorgestellt wird eine neue, aus der Praxis heraus entwickelte Methode für spezielle Fragestellungen, in der eine kombinierte Aufnahme von reflektiertem und emittiertem Licht erfolgt: Bei dieser Technik wird eine LED-Lichtquelle gewählt, deren Emissionsmaximum möglichst nahe der höchsten Energie liegt, die noch Lumineszenz in der Probe anregt. Das auf eine geeignete Kamera treffende Licht wird durch einen Langpassfilter gefiltert, der im Bereich des Lichtquellenmaximums eine geringe und im Bereich des Lumineszenzmaximums eine hohe Durchlässigkeit aufweist. Die derart aufgenommenen Bilder eignen sich besonders gut zur Verortung von Pigmenten mit starker Infrarot-Lumineszenz – wie vor allem Cd-Sulfiden, Ägyptisch- und Han-Blau – und Darstellung ihrer Verteilung im Gesamtkontext von Malereien. Sie erscheinen auf derartigen Aufnahmen meist weiß (hohes Detektorsignal), jedoch im Vergleich zu klassischen „reinen“ Lumineszenzaufnahmen nicht auf dunklem (nicht bis schwach emittierendem) Hintergrund, sondern aufgrund des namhaften Anteils reflektierten Lichts in sehr gut sichtbarem Umfeld (siehe Fig. 1). Als bisher nicht vorhandener Name für eine derartige Aufnahme bzw. Technik wird *CoRL* vorgeschlagen – eine Abkürzung für *Co*mbined *R*eflectance *L*uminescence-image bzw. -imaging.

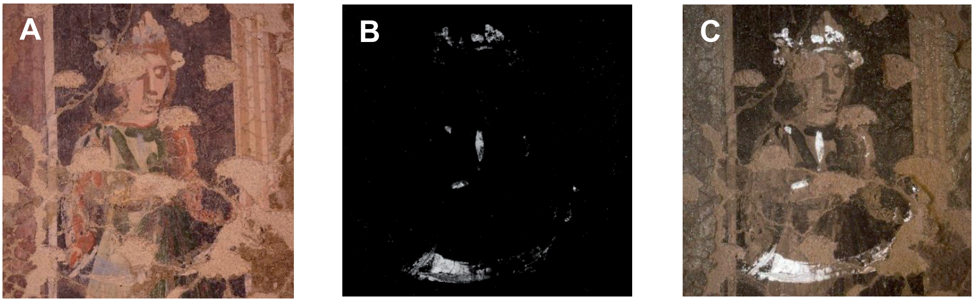

Figure 1. Vergleich zwischen einem traditionellen sichtbaren Reflexions- (A) und Infrarot-Lumineszenz-Bild (B), sowie der hier vorgestellten *CoRL*-Aufnahmetechnik (C) einer römerzeitlichen Wandmalerei (Museumverein Lauriacum, Enns). Bei letzterer ist die Verteilung des Pigments Ägyptisch-Blau aufgrund dessen starker Lumineszenz (im Bild weiß) besonders gut im Kontext der gesamten Bildkomposition ersichtlich.

# KERAMIK ALS PROZESSARCHIV: MINERALOGISCH-PETROGRAPHISCHE UNTERSUCHUNGEN VON FRÜHBRONZEZEITLICHER SCHLACKENGEMAGERTER KERAMIK VOM BUCHBERG BEI WIESING

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In der vorliegenden Arbeit wird das bisher nur inneralpin bekannte Phänomen der Schlackenmagerung an frühbronzezeitlichen Keramikfragmenten vom Buchberg bei Wiesing untersucht, einem bekannten Metallverarbeitungsplatz der Frühbronzezeit (FB). Schlackengemagerte Keramik – ein spezieller Fall der künstlichen keramischen Magerung, bislang bekannt nur aus dem Alpenraum. Dabei wird Schlacke, Nebenprodukt aus der Kupferverhüttung, zerkleinert und dem Ton zugegeben, bevor dieser gebrannt wird. Ziel dieser künstlichen Magerung ist es, die Keramik für den Brennprozess beständiger zu machen, da Schlackenfragmente eine geringe thermische Ausdehnung aufweisen. Die Keramikfragmente, die in der vorliegenden Arbeit untersucht wurden, stammen vom Buchberg bei Wiesing aus den Grabungsjahren 1999-2004 und werden archäologisch in die frühe Bronzezeit datiert. Für diese Untersuchungen wurden 21 Keramikfragmente für eine Untersuchung ausgewählt. In 6 der 21 Fragmente konnte mithilfe eines Polarisationsmikroskopes eine Schlackenmagerung festgestellt werden, diese wurde mittels Elektronenstrahlmikrosonde genauer charakterisiert. Weiters wurden Mikro-Computertomographie (Mikro-CT) Analysen verwendet, um die volumetrische Menge der Schlackenbestandteile in den Fragmenten quantitativ zu erfassen.

Die mit der Mikrosonde untersuchten Schlackenmagerungsbestandteile enthalten als Metallphasen reines Kupfer (Cu), Tenorit (CuO), Cuprit ($Cu_2O$), Covellin (CuS), Chalkosin ($Cu_2S$), Kupfer(II)-sulfat ($CuSO_4$), Kassiterit ($SnO_2$) und Antimon(III)-oxid ($Sb_2O_3$). Bei den festgestellten Kupfersorten sind meist auch kleine Konzentrationen von Fe, As, Sb und Zn dabei. Es lassen sich zwei Sorten Kupfer klar voneinander unterscheiden: eine mit recht hohem Arsen- und Antimon-Gehalt sowie teils noch Silber, und eine mit fast reinem Kupfer und manchmal sehr geringen Gehalten von Eisen. Diese Kupfersorten treten teilweise sogar im selben Keramikfragment auf. Die Datierung der Keramikfragmente vom Buchberg in FBIIa ist nun insofern interessant als dass die Verwendung von Kupferkieskupfer ihren Aufschwung eigentlich erst später mit FBIIb erlebt. Dazu kommt noch der erstaunliche Fund von Kassiterit in der Schlacke: die Legierung von Kupfer mit ca. 10% Zinn zu Bronze kommt ebenfalls eigentlich erst später in FBIIb auf. Damit wären nun sowohl der Beginn der Verhüttung von Kupferkies zu Kupfer als auch die Verwendung von Kassiterit früher anzusetzen, als bislang gedacht. Ebenfalls bemerkenswert ist der Fund von Kupferkieskupfer-Schlacke am Buchberg: In der Nähe des Buchbergs befindet sich keine Kupferkieslagerstätte, sowohl nur die Vererzungen der Schwazer Trias als auch der Grauwackenzone welche von Fahlerz dominiert sind.

# GEM-QUALITY BLACK SPINEL FROM BO PHLOI, THAILAND

Kruzslicz, Á.B.[1], Nasdala, L.[1], Wildner, M.[1], Škoda, R.[2], Redhammer, G.[3], Hauzenberger, C.[4]
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Since the descent of gem corundum production in the Kanchanaburi and Bo Phloi mining fields, western Thailand, local gem cutters have increasingly used black spinel to produce jewellery (SAMINPANYA & SUTHERLAND, 2008). The chemical composition of the Bo Phloi spinel, under due consideration of Mössbauer spectroscopy results, converts to an approximate formula of ${}^{[IV]}(Mg_{0.72}Fe^{2+}_{0.29}Fe^{3+}_{0.04})^{[VI]}(Al_{1.80}Ti_{0.01}Fe^{3+}_{0.11})O_4$, characterising the material as (Fe-bearing) Mg-Al spinel. Nevertheless, the Raman spectrum is not reminiscent of that of "normal" Mg-Al spinel, but rather similar to spectra of Mg-Fe or Mg-Cr spinel (Fig. 1A). This is assigned to the "inversion" degree of the Bo Phloi spinel (compare LENAZ & LUGHI, 2017). The fairly high iron content controls the strong optical absorption (Fig. 1B). Only at a thickness well below 0.1 mm the sample's greyish brown colour is observed.

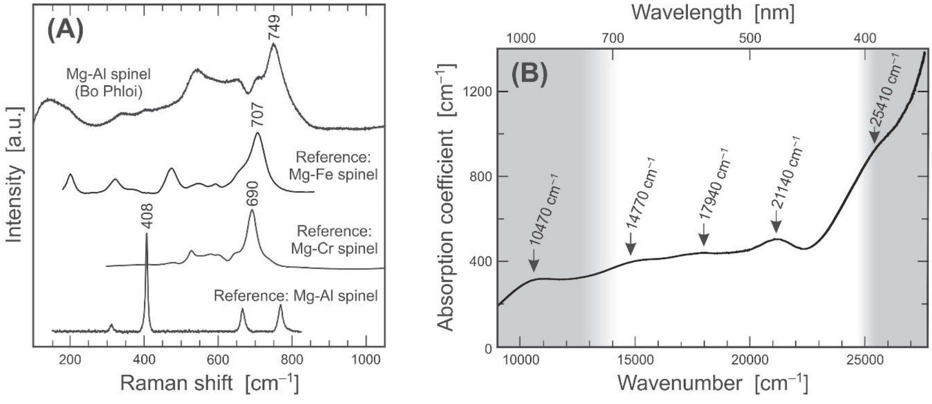

Figure 1. Spectroscopy of the Bo Phloi black spinel. A) Raman spectrum in comparison with three references (Mg-Fe spinel: D'IPPOLITO et al., 2015; Mg-Cr spinel: SHUKLA & RAY, 2017; Mg-Al spinel: NASDALA et al., 2001). B) Optical absorption spectrum, obtained in transmission mode from a 27 μm thick slab.

D'IPPOLITO, V., ANDREOZZI, G.B., BERSANI, D., LOTTICI, P.P. (2015): J. Raman Spectr., 46, 1255–1264.
LENAZ, D., LUGHI, V. (2017): Am. Mineral., 102, 327–332.
NASDALA, L., BANERJEE, A., HÄGER, T., HOFMEISTER, W. (2001): Microsc. Anal., Eur. Edn., 70, 7–9.
SAMINPANYA, S., SUTHERLAND, F.L. (2008): Austr. Gemmol., 23, 242–253.
SHUKLA, A.D., RAY, D. (2017): EPSC Abstracts, 11, EPSC2017–183.

# POTENTIALLY NEW Ba, Fe-MELILITE FROM GURIM ANTICLINE, HATRURIM COMPLEX, ISRAEL

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The potentially new Ba, Fe-melilite ($Ba_2Fe^{2+}Si_2O_7$) is the first barium mineral belonging to the melilite group. It was found in the veins of coarse-grained andradite-gehlenite-rankinite paralava hosted by gehlenite hornfels of the Hatrurim Complex (Mottled zone), Gurim Anticline, Negev Desert, Israel (SHARYGIN et al., 2008). The type locality is situated in vicinity of Arad city, in the central part of Israel's largest pyrometamorphic rock area, named the Hatrurim Basin.

Ba, Fe-melilite occurs in small enclaves accompanied by other barium minerals, such as fresnoite, walstromite, celsian, zadovite and baryte. Rock-forming minerals of this paralava are titanium-enriched andradite, minerals of the gehlenite-alumoåkermanite series, rankinite, fluorapatite, kalsilite, wollastonite and flamite. In this rock we also found magnetite, cuspidine, gurimite, native copper and perovskite. Secondary minerals are zeolites, tacharanite, afwillite and tobermorite-like Ca-hydrosilicates.

Ba, Fe-melilite usually forms light yellow crystals, app. 10-15 μm in size. Very rarely their size reaches 50 μm. It occurs exclusively in fine-grained aggregates in rankinite and gehlenite together with other barium minerals, such as fresnoite ($Ba_2(TiO)Si_2O_7$), celsian ($BaAl_2Si_2O_8$), zadovite ($BaCa_6[(SiO_4)(PO_4)](PO_4)_2F$) and walstromite ($BaCa_2Si_3O_9$). The crystal structure of Ba, Fe-melilite [$a$ = 8.2334(14) Å; $c$ = 5.2854(8) Å] was refined in space group $P\bar{4}2_1m$ with a final $R_1$ value of 0.045. The empirical formula of Ba, Fe-melilite is $(Ba_{1.712}Ca_{0.250}Sr_{0.043}Na_{0.015}K_{0.011})_{\Sigma 2.031}(Fe^{2+}_{0.808}Mg_{0.088}Al_{0.052}Mn^{2+}_{0.019}Zn_{0.015}Fe^{3+}_{0.004})_{\Sigma 0.986}Si_{1.985}O_7$ (calculated based on seven oxygen atoms). The following main bands were observed in the Raman spectrum (cm$^{-1}$): 129, 168, 238, 272, 308, 411, 469, 585, 611, 635, 669, 702, 823, 912, 970 and 1015.

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# INCORPORATION OF ME IONS (Co, Cr AND Zn) DURING CALCIUM-ALUMINIUM-SILICATE-HYDRATE AND TRIOCTAHEDRAL SMECTITE FORMATION

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The contamination of ground and surface water by heavy metal (Me) ions is a global issue, as most of these potentially carcinogenic and/or cytotoxic components pose a significant health hazard. Consequently, the demand for cost-efficient natural and synthetic materials with a high Me ion removal capacity for water treatment applications is highly increasing.

Therefore, we assessed the mineralogy, crystal chemistry and nano-structure of calcium-aluminum-silicate-hydrate (C-A-S-H) and trioctahedral smectite precipitated at low to extremely high concentrations (1.9 to 188.5 mmol) of aqueous cobalt ($Co^{2+}$), chromium ($Cr^{3+}$) and zinc ($Zn^{2+}$). For this purpose, hydrous aluminosilicate phases were synthesized by a sol-gel process with and without Me ions at different initial molar ratios of Ca/(Si+Al) (0.6, 1.0 and 1.6) and Me/Si (0.0, 0.02 0.2 and 2.0), but constant Al/Si ratio of 0.05, at ambient temperature. The chemical evolution of the experimental solutions during aluminosilicate synthesis was analyzed by ICP-OES, whereas the characteristics of the precipitates were studied by ATR-FTIR, XRD and high-resolution TEM methods. At Me/Si ratios of ≤ 0.2, C-A-S-H with a 14 Å tobermorite-like structure emerged, while at a Me/Si ratio of 2.0, either trioctahedral Co- and Zn-smectite or amorphous Cr-gels formed. The Me ion removal potential varied in the range from 99.99 % to 22.47 %, depending mainly on the initial Me ion concentration, type of Me ion used, evolution of pH and nature of the experimental precipitates. The immobilization capacities for $Co^{2+}$, $Cr^{3+}$ and $Zn^{2+}$ ions by C-A-S-H, Cr-gels and trioctahedral smectite were determined as 3-40 mg/g, 30-152 mg/g and 122-141 mg/g, respectively (BALDERMANN et al., 2019). The removal mechanism for Me ions from solution was based on a combination of isomorphous substitution in the octahedral layer, cation exchange in the interlayer sites, surface adsorption and surface precipitation. It is concluded that the hydrous aluminosilicate phases reveal a high detoxification potential for Me ions, particularly under alkaline conditions, which is important, e.g., for assessing the Me ion mobility in engineered systems, such as in underground concrete structures and in waste disposal facilities.

BALDERMANN, A., LANDLER, A., MITTERMAYR, F., LETOFSKY-PAPST, I., STEINDL, F., GALAN, I., DIETZEL, M. (2019): J. Mater. Sci., 54, 9331.

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# MONAZITE DATING AND PETROLOGY OF CORDIERITE BEARING GNEISSES FROM THE HIGHLAND COMPLEX - WANNI COMPLEX BOUNDARY, SRI LANKA

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The basement rocks of Sri Lanka can be subdivided from NW to SE into the Wanni Complex (WC), the Highland Complex (HC) and the Vijayan Complex (VC) based on differences in metamorphic grade and isotope model ages (MILISENDA et al. 1994). While the PT conditions of the HC were studied extensively and UHT conditions are well constrained, PT data from the WC and VC are less abundant but the common occurrence of migmatites and pyroxene bearing gneisses place the metamorphic grade into the granulite facies as well. Only few recent petrological and geochemical work has been done in the WC-HC boundary area (KITANO et al., 2018; WANNIARACHCHI & AKASAKA, 2016) which is ill defined but the SW of Sri Lanka displays cordierite and lower temperatures than the UHT HC. Age of the main metamorphic phase is ca. 580-570 Ma in the HC (SAJEEV et al., 2010) and ca. 580 Ma in the VC (KRÖNER et al., 2013). With U-Th-Pb monazite ages of around 530 Ma, the cordierite bearing assemblages from the WC are significantly younger representing post-peak thermal events (WANNIARACHCHI & AKASAKA, 2016). In this study, U-Th-Pb monazite dating combined with a petrological study including pseudosection modelling and thermobarometry was done focused on cordierite bearing migmatic biotite-garnet gneisses located at the WC – HC boundary in the SW to reconstruct its P-T-t path. The migmatic ortho- and paragneisses with the mineral assembly cordierite + garnet + biotite + plagioclase + k-feldspar + quartz + ilmenite + magnetite + spinel + silimanite contain monazites as garnet inclusion (Group1) and in the matrix (Group2). Group1 monazite ages cluster around 575 ± 5 Ma and 561 ± 5 Ma whereas ages of Group 2 cluster at 550 ± 3 and 527 ± 3, both groups showing complex chemical zoning. Based on the different ages and the textural occurrence of monazite we suggest that two thermal events at ca. 550-575 Ma and ca. 530 Ma are recorded in this rock type indicating a complex evolution during the late stage of the pan African orogeny. Obtained PT conditions are 700-750 °C and around 7 kbar. It is unclear if the main metamorphic phase in the WC belongs to the older or younger overprint and therefore more age data are needed.

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# TWO DIFFERENT BASALT PROVINCES (MORB VS. WPB) IN THE EVAPORITIC PERMIAN HASELGEBIRGE FORMATION (EASTERN ALPS, AUSTRIA) AND POSSIBLE TECTONIC IMPLICATIONS

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The evaporitic Haselgebirge Formation hosts in many places small occurrences of basaltic rocks. The geochemistry of these basalts can potentially provide information about the tectonic setting of the Haselgebirge Formation and the evolution of the Meliata ocean, respectively. We present here 50 new XRF analyses of these basaltic rocks from various localities (Pfennigwiese, Annaberg, Wienern, Hallstatt, Moosegg, Lammertal) and compare the results with previous data from local studies (GRUBER et al., 1991; KIRCHNER, 1979; KIRCHNER, 1980a; KIRCHNER, 1980b; KRALIK et al, 1984; LEITNER et al., 2017; SCHORN et al., 2013; ZIEGLER, 2014; ZIRKL, 1957). Based on the concentrations of immobile trace elements (Zr, Nb, Y, Ti), a predominance of MORB-like compositions is observed for the Lower Austrian occurrences and for the locality Wienern (Grundlsee). On contrast, basalts from the localities Lammertal, Moosegg and Hallstatt have predominantly within-plate-type compositions.

We discuss this striking regional (east-west) difference of basalt types in terms of existing palinspastic models for the Haselgebirge formation (LEITNER et al., 2017; STAMPFLI & BOREL, 2002; McCANN et al., 2006).

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# THE LOWER AUSTRIAN DROSENDORF UNIT – THE TRAILING EDGE SIDE OF THE AVALONIAN SUPERTERRANE?

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The Bohemian Massif consists of various peri-Gondwana terranes that amalgamated in the course of the Variscan orogeny. The Saxothuringian and the Moldanubian Zones are considered to belong to the Armorican Superterrane which has an African affinity (TAIT et al., 1997). Characteristic for the Armorican Superterrane is the absence of zircons with ages between ca. 1.0 and 1.8 Ga (NANCE & MURPHY, 1996). The Moravian Zone, on the other hand, is considered to be part of the Avalonian Superterrane which is of South American ancestry (FRIEDL et al., 2000) and characterized by the presence of Mesoproterozoic zircons. Lithological similarities between the Lower Austrian Drosendorf Unit and the Moravian Zone have already been pointed out many years ago (FRASL, 1970). MATURA (1976), FRITZ & NEUBAUER (1993) and FINGER & STEYRER (1995) interpreted the Drosendorf Unit as a Moravian element that was tectonically incorporated into the Moldanubian Zone during the Variscan orogeny. This interpretation is complimented by recent geochemical and geochronological data which show that the Moravian Bittesch orthogneiss and the bulk of the Dobra orthogneiss of the Drosendorf Unit (Dobra Gneiss Type B; LINDNER & FINGER, 2015) are correlative. Both are ~580 Ma old, I-type granitoids with volcanic arc characteristics. A second, geochemically distinct type of Dobra Gneiss (Dobra Gneiss Type A) is preserved in the easternmost part of the Dobra orthogneiss body. This rock has a much older, Mesoproterozoic protolith age (GEBAUER & FRIEDL, 1994). We thus speculate that the Drosendorf Unit represents the trailing edge side of the Avalonian Superterrane, which was formerly in contact with South American cratonic basement. The Avalonian ancestry of the Drosendorf Unit is further corroborated by abundant Mesoproterozoic zircons recorded in paragneisses that overlie the Dobra Gneiss in the east.

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# IMPACT OF $Li_2CO_3$ ON PHASE DEVELOPMENT DURING HYDRATION OF CALCIUM ALUMINATE CEMENT WITH CALCITE

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During long-term hydration of calcium aluminate cement (CA-cement) conversion of metastable hydrates (e.g. $C_2AH_8$ & $CAH_{10}$) to stable $C_3AH_6$ is observed in many cases. KUZEL & BAIER (1996) found that conversion can be evaded by introducing a carbonate source (e.g. $CaCO_3$), leading to primal formation of stable monocarbonate ($C_3A\ CaCO_3\ 11H_2O$, MC).
$Li_2CO_3$ is used to shorten the induction period of CA hydration leading to acceleration of the nucleation rate (RODGER & DOUBLE, 1984).
To gain insight into the long-term impact of $Li_2CO_3$ on the hydration of CA-cement with $CaCO_3$ a reference mixture of 70 wt. % CA-cement and 30 wt. % $CaCO_3$ with a w/s ratio of 1 was compared to the same mixture with 0.05 wt. % $Li_2CO_3$ addition (abbr.: Li-mix). Phase formation within 28d compared to expected phase development, obtained by thermodynamic modelling with GEMS (WAGNER et al., 2012) was our focus of research.
Early hydration behaviour was already investigated by MANNINGER et al. (2019) and showed that changes of pore solution composition can be correlated with phase composition.
In Fig. 1 the comparison of the long-term behaviour is shown. Addition of $Li_2CO_3$ leads to faster formation of thermodynamic stable hydrate phases (MC, $Al(OH)_3$ mic.) during 10h and 1d while the phase content is nearly levelled out at 28d.

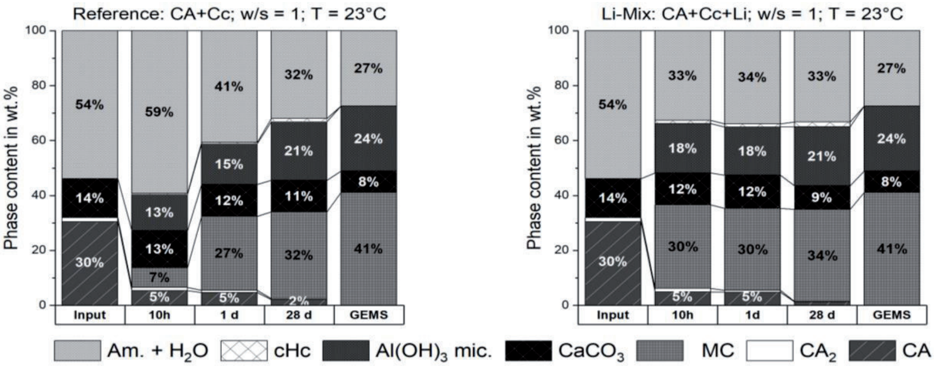

Figure 1. Comparison of phase development of reference & Li-mix to thermodynamic stable phases.

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# PETROLOGY AND GEOCHEMISTRY OF MAGMATIC GNEISSES FROM THE WANNI COMPLEX, SRI LANKA

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Sri Lanka is composed of three main tectonic units: (1) Vijayan Complex; (2) Highland Complex; (3) Wanni Complex. The Vijayan Complex is exposed in the southeast of Sri Lanka and comprises mainly migmatitic orthogneisses with PT-conditions of 800 to 900 °C and 8-9 kbar (PETSCHNIG, 2015). The Highland Complex in central Sri Lanka experienced UHT metamorphism up to ~1150 °C at 8-12 kbar (SAJEEV & OSANAI, 2004). It contains a variety of different rock units which include marbles, calcsilicates, charnockitic gneisses, khondalites and migmatites.

The boundary between the Highland and the Wanni Complex extends from the southwest to the northeast of Sri Lanka and is not clearly defined. Along the southwestern border area cordierite bearing rocks are commonly found. In the central and northern parts of the Wanni Complex, magmatic orthogneisses with subordinate amounts of nearly undeformed granitoids dominate. The migmatic gneisses contain small grains of garnet and pyroxene and in some cases spinel within a matrix of potassium feldspar, plagioclase, quartz, and biotite. Sometimes cm-sized garnets occur. The metamorphic grade is thought to be lower compared to the Highland Complex. Garnet-pyroxene bearing gneisses allow to constrain the PT-conditions with 800-1000 °C and 7-9 kbar.

The orthogneisses display a mainly meta- to peraluminous granitic composition and follow a high-K calcalkaline to shoshonitic magmatic trend. Most samples fall into the volcanic arc granite (VAG) and syn-collision granite (Syn-COLG) fields according to the tectonic discrimination diagrams from PEARCE et al. (1984).

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# RHENIUM SULPHIDES AND PLATINUM-GROUP MINERALS AT HAIDBACH/PINZGAU – RECENT RESULTS

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The copper-nickel-cobalt sulphide mineralization at Haidbachgraben/Felbertal (Salzburg) is hosted by amphibolite and chlorite schist of the Habach Group in the Subpenninic nappe system of the central Tauern Window (MELCHER et al., 2017). Orebodies occur as highly deformed lenses and stringers within a hornblendite unit chemically resembling ultramafic pyroxenite. Mineralization consists of major pyrrhotite, chalcopyrite, pyrite, pentlandite, and minor sphalerite and Ni-Co-Fe sulpharsenides (gersdorffite-cobaltite series) associated with a large number of accessory minerals. According to quantitative analysis of grain mounts, Fe sulphides (pyrrhotite > pyrite) make up about 75 to 92 % of the sulphide assemblage. Chalcopyrite accounts for 1.4 to 19.2 %, and pentlandite for 6.3 to 6.8 %. Pyrite is the major carrier of Co (median 0.37% by LA-ICP-MS) and As (0.29%), while Ni is hosted by pentlandite and pyrrhotite (0.57%). Copper and Fe sulphides all have elevated Se concentrations (maximum of 287 ppm, median 88 ppm). Chalcopyrite hosts significant Zn (median 568 ppm) and some Ag (34 ppm), but low In and Sn.

Accessory minerals include discrete phases of the noble metals Au, Ag, Re, Ir, Pt and Pd. Gold is present as electrum (13-39 % Ag) and rare petzite [$Ag_3AuTe_2$]. Hessite is the most common Ag phase, accompanied by argentopentlandite, empressite and acanthite/argentite. Iridium is present as very rare irarsite, whereas abundant sperrylite and Pt(-Fe) alloy phases are hosts to Pt. Palladium minerals include Pd-melonite as the most common Pd phase, merenskyite [$PdTe_2$], michenerite [PdTeBi], and the rare mineral testibiopalladite [PdTe(Sb,Te)]. Keithconnite [$Pd_{20}Te_7$], kotulskite [PdTe] and sudburyite [PdSb] are rare and either associated with petzite and Pd-melonite, or occur as late-stage crack-fillings in Fe and Cu sulphides.

Rhenium minerals comprise abundant tarkianite [$(Cu,Fe)(Re,Mo)_4S_8$] and as yet unidentified Re-Pb sulphides of approximate [$RePbS_3$] and [$(Re,Pb,Mo)_2(Fe,Cu)_3S_6$] composition. Tarkianite is a cubic phase crystallizing in the linneite group and characterized by high hardness (KOJONEN et al., 2004); it invariably occurs as minute (max. 8 µm) euhedral, singular inclusions in pyrite. The Re-Pb phases are either new minerals, or varieties of dzhezkazganite [$ReMoCu_2PbS_6$], a trigonal phase having a structure similar to molybdenite-3R (GENKIN et al., 1994).

The polymetallic mineral assemblage at Haidbach is interpreted as an orthomagmatic sulphide deposit overprinted by metamorphic processes.

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# RÖMISCHE GOLDMANUFAKTUR AM MAGDALENSBERG (KÄRNTEN): MINERALOGISCHE UNTERSUCHUNG ZUR HERKUNFT DES GOLDES

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Die anlässlich der 60-Jahrfeier der Ausgrabungen auf dem Magdalensberg im Jahre 2008 der Öffentlichkeit zugänglich gemachten Bereiche der so genannten „Unteren AA-Bauten“ boten Einblicke in ein im Imperium Romanum einzigartiges Befund- und Fundensemble einer kaiserlichen Goldbarrengießerei und dokumentierten die archäologischen und naturwissenschaftlichen Erkenntnisse im Kleinmuseum AA/43 (DOLENZ, 2015). Zwei bereits 1993 gefundene Marmorgussformen aus lokalem Kraiger Marmor wurden einer mikroskopischen Untersuchung unterzogen, die zeigte, dass metallisch glänzende Partikel sowohl im Inneren der Gussformen, an den Wänden und auch auf der Oberfläche der Marmorblöcke außerhalb der Gussform auftreten.

Einige der metallisch glänzenden Bestandteile wurden rasterelektronenmikroskopisch untersucht. Die Goldpartikel erreichen bis zu 0.4 mm Größe. Insgesamt wurden 20 Goldpartikel im Größenbereich von 10 µm bis 400 µm untersucht. Es treten sowohl hochreine Partikel (99.8 % Au), die eindeutig aus einer Schmelze stammen, als auch Goldpartikel mit blättrigem Habitus auf. Die Goldpartikel weisen teilweise einen signifikanten Cu-Gehalt von bis zu 6.4 % und maximal 3.2 % Ag auf. Die Gussfomen enthalten noch weitere metallische Phasen, z.B. Platin, Galenit, Bronze, Eisen-Chrom Späne und metallisches Eisen. Bei den Platinpartikeln (< 20 µm) handelt es sich um goldfreies Platin mit bis zu 0.3 wt. % Palladium.

Die Herkunftsfrage des Goldes der „norischen Taurisker“ wird kontrovers diskutiert (vgl. DOLENZ et al., 2018). Im Vergleich der neu gewonnenen Daten mit jenen zu Goldvorkommen in Kärnten und Steiermark (SCHMIDERER, 2008) erscheint klar, dass sich die Partikel aus der Gussform nicht direkt aus Tauerngold oder lokalem Klieninggold ableiten lassen. Da ein hoher Reinheitsgrad des Goldes in den Barrengussformen vorliegt, ist zuvor geläutertes Gold eingebracht worden. Aufgrund der zur Füllung der Gussform notwendigen großen Goldmenge ist außerdem davon auszugehen, dass hier Gold verschiedener Herkunft eingeschmolzen wurde. Dies könnte Flussgold, Berggold, aber auch bereits verwendetes Gold einschließen. Flussgold ist in der Regel ärmer an Silber als Berggold, speziell jenes aus den Hohen Tauern, in denen die Ag-Konzentrationen häufig zwischen 10 und 15% bei <0.1% Cu liegen (SCHMIDERER, 2008). Auch die Platinpartikel können als Hinweis auf Beimengung von alluvialem Seifengold gewertet werden.

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# GROUNDWATER AND LAND USE STRATEGIES FOR THE TOS, MOROCCO, INFERRED FROM MINERALOGICAL, HYDROCHEMICAL AND ISOTOPIC INVESTIGATIONS

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The Quaternary terrestrial sedimentary deposits of the Tafilalet Oasis System (TOS) in the south of Morocco's High Atlas are very important for the local water supply and land use in this Saharan oasis, particularly under the aspects of global climate change. Two ephemeral streams, Ziz and Rheris, drain the mountainous areas of the High Atlas, which are thought to provide the main water source of TOS ground- and well waters. However, due to the complex regional geology and the lack of data, the potential source of the well waters as well as the water-sediment/rock-interactions in the TOS are not yet fully understood. We therefore aim to gain a mechanistic understanding of the climatic and anthropogenic processes affecting the TOS system, in order to (i) evaluate the vulnerability of the ground- and well waters and (ii) to develop sustainable strategies for future water and land use management. The overall project therefore follows a multi-disciplinary approach integrating geographical, mineralogical as well as hydrogeochemical investigations. In one attempt, we studied the mineralogical composition of the Quaternary sediments of the TOS using X-ray diffraction, focusing on the spatial distribution of silicate phases (e.g., quartz, clay minerals) and carbonates across the TOS. Complementary, we investigated the strontium isotopic ($^{87}Sr/^{86}Sr$) and the hydrogeochemical composition of several well waters and of the ephemeral stream waters of Ziz and Rheris.

For all mineralogical and hydrogeochemical aspects analyzed, we reveal distinct spatial distribution patterns, displaying a gradual trend from north to south along the TOS basin axis. Moreover, mineral phase distribution exhibits a lateral trend related to present-day river channels and ambient floodplains. Isotopic and hydrogeochemical signatures on the other hand mimic the north-south trend. We observe low Mg/Ca ratios and low Sr concentrations in the north, which are anticorrelated to the respective $^{87}Sr/^{86}Sr$ ratios. Especially the latter isotopic ratios indicate significant and unexpected water-rock interactions with the underlying Paleozoic rocks of the Antiatlas. To summarize, this study shows the importance of understanding the dynamic processes within the TOS, such as sediment provenance and genesis in relation to hydrogeochemical and environmental conditions, because of the limited contribution of rain and stream waters to the ground- and well waters within the TOS, a fact that directly influences long-term water supply and land use.

# X-RAY FLUORESCENCE (XRF) AND INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) FOR THE GEOCHEMICAL ANALYSIS OF ROCKS, PRESENTED ON IN-HOUSE CONTROL SAMPLES

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After more than two decades experience in major and trace element analysis of rocks using wavelength dispersive X-ray fluorescence analysis at the Department of Lithospheric Research (University of Vienna) the laboratory was upgraded by the installation of a PANalytical PW2404; the preparation lab got a PANalytical EAGON2 fusion system replacing the formerly used Philips PerlX'3 fusion bead machine.

The aim of the presented study is the production of in-house control samples for geochemical analysis at the Department of Lithospheric Research for monitoring analytical processes and also for the teaching of students. Therefore three different rock types (acidic, basic, ultramafic) from Austrian localities were selected for the analyses by XRF and INAA; those were sampled in larger quantities, crushed, homogenized and splitted to equal sub-samples.

Major elements were determined on fused beads, trace elements on pressed powder pellets; a description of the used method in WDXRF is given in DUBOC et al. (2019). The analytical methods of INAA is described in MADER & KOEBERL (2009).

The comparability of sub-samples was checked by repeated measurements and statistical evaluation; by comparing the results of XRF and INAA it could be shown, that both types of analysis can complement each other sufficiently in geochemical whole rock analysis.

The selected rock samples can be used for teaching and research purposes and for monitoring the processes following the laboratories' SOP.

For the future it is planned to expand the suite of available in-house control samples by adding some sedimentary rock types (e.g. carbonate, shale, sandstone).

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# CHALLENGES AND NEW TECHNOLOGIES IN THE FIELD OF REFRACTORY MATERIALS

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Refractories are indispensable for industrial high-temperature production processes in key-industries like steel, cement, non-ferrous or glass industry. Depending on the field of application there are different requirements on refractory material and design or the need for particular refractory system solutions. Based on the specific operation conditions at the customer, important demands to achieve customized solutions are e.g. performance improvement, safety and ergonomics optimization, environmental issues, improvement of the customers product quality (e.g. by purging technologies), rise of customers production capacity (increase steel yield etc.). Also adaption of refractories to new processing technologies and products in the customers industries is a basic issue. Major elements to reach customer requirements are engineered microstructures, raw materials and additives, alternative bonding systems, materials with reinforced zones, shape design engineering and unique system solutions. Sophisticated laboratory testing methods including customer specific laboratory wear trials as well as computerized simulation methods (FEM, CFD, DEM, use of water modeling), completed by thermochemical simulations support target-oriented product and system development. Recycling as green technology represents another great opportunity for the refractory industry. A further focal point is development and application of non-destructive testing methods in line with quality assurance and R&D. Furthermore the use of Big Data approaches, digitalization and automation is strongly growing. The presentation outlines some examples for new technologies in the broad field of refractories.

# GEOCHEMISTRY AND ZIRCON U-PB GEOCHRONOLOGY OF IGNEOUS ROCKS FROM SOUTHWESTERN VIETNAM AND SOUTHEASTERN CAMBODIA

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Main subduction-related magmatism occurred in Vietnam from the Late Paleozoic to the Late Mesozoic which is related to two significant tectonomagmatic periods: (1) the opening and closure of the Tethyan Ocean and (2) the subduction of the Paleo-Pacific Ocean beneath the Eurasian continent. Two main distinct groups of Mesozoic igneous rocks, based on their zircon U-Pb ages, were found in southwestern Vietnam–southeastern Cambodia (SWVN-SEKH). The igneous rock suite related to the first event (Honkhoai suite) displays an Early Mesozoic age (ca. 210-180 Ma) and is mainly composed of biotite-hornblende granodiorite dispersedly outcropping at small islands in southernmost Vietnam. The latter event resulted in the emplacement of voluminous basic to felsic rocks (i.e. gabbro-diorite to granite) in the SWVN-SEKH during the Late Mesozoic (ca. 108-78 Ma). Within the SWVN-SEKH area, four different igneous suites can be distinguished based on their petrological and U-Pb age features: (1) the Dinhquan intrusive magmatic suite comprises mainly gabbro-diorite, monzodiorite, monzonite, and syenite, which are visibly altered by intensive K-feldspar metasomatism leading to a noticeably high amount of potassium; (2) the Deoca-Phnom Den magmatic suite is the major magmatic group, consisting mainly of granodiorite and granite; (3) the Ankroet-Ba Phnom suite is composed of fine to medium-grained granite; and (4) the Pha Aok-Tamao suite comprises muscovite-bearing granite and coarse-grained biotite granite. The Honkhoai rocks point to a calc-alkaline series typical for a plutonic arc-related nature. Their U-Pb zircon age yields 195 ± 2.1 Ma coincident with the Early Mesozoic magmatism which is linked to the Indosinian Orogeny driven by accretion of the Sibumasu terrane to the Indochina–South China block. The Dinhquan and the Deoca-Phnom Den rocks are metaluminous to peraluminous and usually contain the minerals amphibole, sphene, and allanite. The observed trends in trace and rare earth elements indicate a close genetic relationship of those and are typical for arc magmatism. The obtained ages are 105.0 ± 0.6 for the Dinhquan suite and 86.5 ± 1.9 to 94.4 ± 1.9 Ma for the Deoca-Phnom Den suite, compatible with the subduction event which existed along the eastern margin of the Eurasian continent during the Late Mesozoic, referred to as the Late Yanshan Orogeny. The slightly younger Ankroet-Ba Phnom suite, 89.3 ± 0.9 Ma, shows a peraluminous composition and higher contents in heavy rare earth elements. Their strong negative Eu, Sr, Ba, Ti anomalies suggest high fractionation, indicate a transition from arc magmatism to a subsequent extension regime compatible with a within-plate tectonic setting. Rocks from the Pha Aok-Tamao suite display a pronounced peraluminous nature, reveal a distinctly young age of 78.0 ± 0.4 Ma which might be related to the collision tectonic setting between the Indochina and Luconia block marking the halt of the Mesozoic subduction event in the SWVN-SEKH area.

# ROCK-MELT REACTION AND SMALL SCALE HETEROGENEITIES IN THE LITHOSPHERIC MANTLE UNERNEATH N. PATAGONIA, ARGENTINA

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The Patagonian Lithosphere represents the southernmost part of the South American Plate. It has been shaped by the ongoing subduction of the Nazca and Antarctic oceanic plates responsible for the formation of the Andean continental arc and the back arc region. The back-arc region is characterized by voluminous, late Miocene “main plateau” tholeiitic basalts and less-voluminous Pliocene “post plateau” alkali basalts. The latter frequently carry mantle xenoliths up to 30 cm in diameter.

The xenoliths in the “post plateau” alkali basalts closest to the Andean arc SE of the village Comallo in N. Patagonia are mainly foliated spinel harzburgites frequently with disseminate amphiboles and/or cm thick veins. One xenolith, a fine-grained amphibole-free spinel harzburgite, shows unique features. In a 2.5 cm long profile along the foliation the Fo content of the individual olivine grains decreases from 91.5 to 79.5, whereas NiO remains constant at ~ 0.40 wt.%. The opx and cpx follow the same trend with Mg# ranging from 92.2 to 83.0 and 93.5 to 86.2 respectively. Furthermore, the Cr# of spinel ranges from 63.4 to 32.5 following the same trend as the pyroxenes. The cpx have concave downward LREE patterns indicating intergranular melt percolation and fractionation with increasing (La/Sm)N along the foliation from 1.5 in the grains with low Mg# to 4.1 in the high Mg# grains.

Based on the assumption of local equilibrium, the Fe-Mg partitioning between opx and cpx (opx-cpx geothermometer) would yield a dramatic temperature increase from 760°C in the high Mg# pairs to 1000°C in the low Mg# pairs over a distance of 2.5 cm. Such a temperature gradient is unfeasible and the observed Fe-Mg partitioning rather indicates grain-scale disequilibrium due to different rates of Fe-Mg exchange of opx and cpx during the metasomatic event.

The extreme compositional gradient in a mantle xenolith, which otherwise exhibits a well equilibrated microstructure, indicates interaction with a metasomatic agent not related to the host basalt. The most likely metasomatic agent is a melt e.g. from an upwelling vein. Emanating from the vein, the melt percolated into the wall rock preferably along the foliation leading to the most intense metasomatism closest to the melt source (low Mg#). The unusual constant Ni concentration in the olivine, independent of the Mg#, could be attributed to very low oxygen fugacity of the interacting melt. The metasomatic front is well defined by the highest Mg#, whereas the contact to the melt source is not preserved. This gives us a handle on the life-time of this geochemical perturbation via inverse diffusion modelling.

# A MODEL FOR MULTICOMPONENT DIFFUSION IN IONIC CRYSTALS

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This contribution deals with diffusion in ionic crystals that are solid-solutions and feature more than two end-member components. The interdiffusion of ionic species is of crucial importance, e.g., for (1) assessing the preservation potential of growth zoning and element partitioning during changing P-T conditions and (2) diffusion-chronometry via analysis of secondary compositional zoning in minerals.

We theoretically address ionic diffusion in the situation when both *binary exchange* of cations between neighbouring lattice sites and *vacancy mediated self-diffusion* of cations are important. The model equations are derived from linking expressions for the system's free energy with Onsager type reciprocity relations. The resulting diffusion equations are non-linear: The diffusive flux of each component depends on the concentrations and concentration gradients of all components and, of course, on all self-diffusion and binary exchange coefficients. The dependence is neither postulated nor fitted, it is directly derived from the model.

The suggested model is solved numerically and is verified using experimental data for diffusion in the Na-$^{39}$K-$^{41}$K three-component system of isotopically doped alkali feldspar. Among other things, the model is applied for constraining the proportions among the self-diffusion coefficients of Fe, Mg, and Ca in garnet from complex secondary compositional zoning, as observed in partially resorbed garnet from a mafic granulite.

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# REHYDROXYLATION OF CERAMIC TILES AND ITS INFLUENCE ON CURVATURE EFFECTS AFTER FIRING

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In the 1980s, rapid firing technology enabled a significant step forward in the development of tile production in roller kilns. The firing times as well as the energy consumption could be reduced to a fraction of those of the tunnel firing process in a very short time. However, a sintering time of only a few minutes does not enable a complete thermal conversion of clay minerals, resulting in disequilibrium of sinterphases and thus leads to a limited sintering activity. Thus, time-dependent rehydroxilation of transition phases (X-ray amorphous clay minerals) by water absorption from the ambient takes places, resulting in deformation of the ceramic product. Deformations are more noticeable with increasing product dimension; hence large-format products like tiles or laboratory benchtops are affected. Standard specifications, measured at kiln exit do not assure that these are being kept on a long term basis. In order to counter this problem, a process-controlled convex pre-curvature has been established, which is eliminated by concave delayed deformation effects after firing. However, this is accompanied by process uncertainty and high storage costs.

Rehydroxilation reactions of ceramics and the associated mass gain occur in two distinct steps. Stage I is characterized by transient equilibration, whereas Stage II reactions refer to rehydroxylation. RHX reactions in stage II are linear with time$^{1/4}$ – Power-law model (INCE & DEROGAR, 2014; WILSON et al. 2014). In order to gain more detailed information about the influence of raw materials and ceramic mixes on the curvature effects after firing, RHX-Process, several experiments (DTA-IR, FTIR, mass gain after autoclave treatment) have been performed.

It has been observed that the mass gain is directly related to temperature, sinterkinetics and phase composition, with a completed conversion at temperatures above 1000 °C (no Stage II reactions after autoclave treatment). Furthermore clays from different deposits with no relevant differences in mineralogical composition show a different behavior under firing and RHX. These effects are still not yet fully understood and are a matter of an ongoing research project.

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# INCORPORATION OF HEAVY METALS (Co, Cu, Zn) IN SYNTHETIC CALCIUM-ALUMINIUM-SILICATE-HYDRATE (C-A-S-H) GEL STRUCTURES: ENVIRONMENTAL IMPLICATIONS FOR METAL ION TRANSPORT IN AQUEOUS MEDIA

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Concrete is one of the most important building materials of our time. During cement hydration, exposure of cementitious materials to heavy metal (Me) ions can cause severe environmental risks, taking that novel cement supplements (slag, fly ash, etc.) can carry much higher levels of potentially hazardous Me ions than ordinary Portland cement (ACHTERNBOSCH et al., 2003). The focus of our study is to investigate the immobilization mechanisms and thresholds of Me ions during the co-precipitation with calcium-aluminium-silicate-hydrate (C-A-S-H) gels, as well as revealing apparent changes in the physicochemical properties of such Me-doped phases. Therefore, C-A-S-H bearing Me ions were synthesized from Si-, Ca-, Al- and Me-salts by a sol-gel process with given molar ratios of Ca/Si (1.0) and Al/Si (0.05), but varying molar ratios of Me/Si (0 to 0.6). During C-A-S-H phase precipitation and maturation, monitoring of the reactive fluid chemical composition was performed by pH and ICP-OES analyses. The crystal chemistry-structure relationships of the precipitates were characterized by FTIR, XRD, ESEM, TEM and thermogravimetric analyses. The formation of poorly crystallized, nano-sized (40 to 60 nm) C-A-S-H particles with a homogeneous chemical (gel-like) composition in the range from 0.87 to 0.99 of molar (Ca+Me)/(Si+Al) was observed at Me ion concentrations lower than 0.4 M. At higher Me ion loads of copper ($Cu^{2+}$) (> 0.4 M) the co-precipitation of reaction by-products, such as atacamite ($Cu_2Cl(OH)_3$), has been observed, which denotes the upper level of Me ion immobilization by synthetic C-A-S-H gel structures. The removal mechanism is based on isomorphous substitution of the respective Me ion for the Ca position in the CaO layer of the C-A-S-H structure (1 to 40 mol% substitution of Me for Ca), though a minor amount of interlayer ion exchange is possible (BALDERMANN et al., 2019). This indicates that Me ions preferentially substitute for Ca in the C-A-S-H structure, thus reducing the risk of contamination of the environment. Further efforts will focus on calculating respective solubility products in order to shed light on the physicochemical properties and chemical reactivity of C-A-S-H bearing low to extremely high loads of heavy metals.

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# MARBLE PROVENANCE ANALYSIS OF ROMAN PERIOD ARTEFACTS FROM VILLACH – STADTMUSEUM, AUSTRIA

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Marble, one of the most widespread and commonly used materials, has been utilised for a very long time during human history, with the earliest marble objects dating as far back as the Neolithic Period. In fact, throughout history, marble was used for a variety of purposes, including art, architecture and religion. Currently, the Museum of Villach in Austria hosts a large Roman collection of archaeological artefacts dating back to dates scattered between the 1st and 3rd century AD, most of which were discovered in different regions of the Drau River between the 1970's and 2003. Out of this collection, 26 marble artefacts, ranging from epitaphs, tomb portraits, torso statues and grave altar inscriptions to fragments of reliefs, pillars, architraves, grave steles, aediculae and base/corner blocks of burial structures amongst others, were sampled.

The provenance of the material of these artefacts was investigated. Based on the general location within the river Drau at which the artefacts were found, the samples were divided into two main categories, the Villach group and the Frög group. The analytical methods applied to these samples included petrographic investigations, chemical and isotopic analysis as well as fluid inclusion analysis (crush-leach analysis). Statistical treatment for each sample was applied. Given that most artefacts sampled were found in the Drau river close to the Villach area, preliminary hypotheses consider the option that the marble artefacts originate from local quarries. The ancient Roman marble quarries at Gummern and Treffen, both of which are located relatively close to the Drau river bank, were the main quarry candidates considered for the provenance of these 26 artefacts.

# MODERATE MELT DEPLETED ANHYDREOUS MANTLE XENOLITHS UNDERNEATH CENTRAL VIETNAM: EVIDENCE FOR STABILIZATION OF THE LITHOSPHERIC MANTLE BEFORE MESO-PROTEROZOIC TIMES

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The Vietnam Cenozoic basalts belong to the Western Pacific "diffuse" igneous province (HOANG et al., 2013). They contain mantle xenolith-bearing alkali basalts, basanites and rarely nephelinites. The volcanism has been attributed to continental extension caused by the collision of the India-plate with the Eurasia-plate and by subduction of the Pacific Ocean below Asia.

A collection of 24 mantle xenoliths from Ia Bang Lake, Dak Doa district and Bien Ho, Pleiku city in Central Vietnam has been studied in detail. They are predominantly spinel lherzolites (19) but spinel harburgites (3) and two garnet pyroxenites are present as well. The size of the xenoliths ranges from 5 to 40 cm in diameter with medium to coarse-grained protogranular textures.

The whole rock Mg# for spinel lherzolites and spinel harzburgites vary from 89.5 to 90.7 and from 91.4 to 91.6, respectively. Most of the xenoliths have $CaO/Al_2O_3$–ratios of 0.8-0.9, which is slightly higher than the Primitive Mantle ratio. Both CaO and $Al_2O_3$ correlate with MgO most likely indicating that the sampled rocks were derived from a common mantle source having experienced variable degrees of partial melting. The rock forming minerals are chemically homogeneous. The Fo contents of olivine vary between 89.2 and 91.2 and the Mg# of orthopyroxene and clinopyroxene range from 89 to 92 and 89 to 94, respectively. The range of Cr# for spinel is 0.06-0.26. Model calculations in both whole rock and clinopyroxenes show that lithospheric mantle underneath Central Vietnam experienced melt extractions that vary between 2-15 % for most samples.

Most of the primitive mantle-normalized whole rock and clinopyroxene REE patterns are parallel indicating that clinopyroxene is the main repository of the trace elements. Clinopyroxenes are divided into two groups: group A with concave upwards REE and $(La/Yb)_N < 1$ suggesting various degrees of melt extraction and group B with $(La/Yb)_N$ ranging between 1 and 53. Group B in a mantle normalized trace element diagram shows negative Pb and Sr anomalies, which together with the general absence of hydrous phases, suggest variable interaction with percolating silicate melt(s).

The primitive-mantle normalized highly siderophile element (HSE) patterns show insignificant fractionation among Ir, Ru and Pt with only slight depletion in Os. On the other hand, all samples have a $(Pt/Re)_N$ ranging from 1.4 to 4.5, which is an evidence for melt depletion. Some samples display clear Re addition from percolating melts preventing calculation of reliable rhenium depletion ages ($T_{RD}$). However, one sample with a depleted Pd and Re signature yields $T_{RD}$ of 1.9 Gy which can be interpreted as a minimum SCLM stabilization age in this area.

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# NANO-SCALE INVESTIGATION OF AMORPHOUS Ca-Mg CARBONATE BY STEM

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Amorphous calcium carbonate (ACC) is a highly soluble mineral phase that commonly occurs as a precursor of calcite and aragonite in modern biotic and abiotic precipitation environments (ADDADI et al., 2003). Considering that the formation of ACC is of high relevance in many natural surroundings and of eminent concern for medical and industrial applications (MATSUNUMA et al., 2014), the effect of environmental factors, such as temperature, pH and organic and inorganic additives, on the stability and transformation pathway of ACC was investigated in numerous studies. Special focus therein was given on investigating the incorporation of $Mg^{2+}$ ions in ACC, because $Mg^{2+}$ plays an important role in the temporal stabilization of both natural and synthetic ACC. Although the molecular structure of amorphous calcium magnesium carbonate (ACMC) was recently studied, significant gaps in knowledge exist with respect to the distribution of $Mg^{2+}$ and $Ca^{2+}$ ions in the ACMC structure on the nano-scale. Thermogravimetric results of a previous study on synthetic ACMC by RADHA et al. (2012) point towards the presence of discrete $MgCO_3$ phases in the ACMC crystals. Such heterogeneity could be induced during the heating process (thermally driven $MgCO_3$ segregation), but may also be valid for the amorphous nano-particles.

In order to assess the chemical heterogeneity of ACMC on the nano-scale, amorphous $Ca_{0.89}Mg_{0.11}CO_3\cdot0.46H_2O$ (ACMC_11) and $Ca_{0.46}Mg_{0.54}CO_3\cdot0.60H_2O$ (ACMC_54) materials were synthesized by a batch method using $(Ca,Mg)Cl_2$ and $Na_2CO_3$ solutions and analysed by STEM coupled with EDX. TEM images of ACMC_11 and ACMC_54 reveal spheroidal particles with a size range from 30 to 90 nm. Based on TEM observation, ~14 individual spheroidal particles of ACMC_11 and ACMC_54, respectively, were examined by EDX. The EDX results reveal that the average Mg content of the spheroidal particles is 12.7 ±3.6 mol% for ACMC_11 and 63.4 ±7.7 mol% for ACMC_54, which is in good agreement with the Mg content determined by ICP-OES analyses of the digested solids of ACMC_11 (11.4 ± 0.6 mol%) and ACMC_54 (53.9 ±2.7 mol%). Overall, the results did not confirm the presence of discrete $MgCO_3$ and $CaCO_3$ particles in the ACMC solids. In contrast, our findings suggest that the distribution of $Ca^{2+}$ and $Mg^{2+}$ ions in the ACMC solids is compatible with the concept of an “amorphous solid-solution”, which has significant implications for developing transformation mechanisms as well as strategies for industrial applications.

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# THERMAL BEHAVIOR OF CLAY MINERALS BEYOND THERMODNAMIC EQUILIBRIUM

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Detachment of glazed stoneware tiles from the bonded surface and further architectural ceramics as a consequence of concave curvature or moisture expansion is a recent problem of silicate ceramic industry. Theses phenomena seem to be directly related to fast firing process of modern kilns, where the whole firing cycle takes place in less than 40 minutes.

Within this context, rehydroxilation of dehydroxilated clay-related compounds such as metakaolinite, dehydroxilated montmorillonite or illite, is considered a main driving force. In order to get an insight into the sinterkinetic behavior, the relevant mineral reactions at high heating rates have been studied in more detail. Therefore, several in-situ DTA-MS/DTA-IR and ex-situ firing experiments using rates of 5, 30 and 50 K $min^{-1}$ in the temperature regime between 1100 °C and 1250 °C have been performed on 1.) individual separated clay minerals (kaolinite, montmorillonite, illite) as well as on 2.) two different mixtures (consisting of quartz, feldspar, kaolinite and illite) close to industrial compositions.

Preliminary results show that compared to equilibrium studies all mineral reactions are shifted to higher temperatures by 10 to 30 K, in certain cases up to 76 K. With increasing temperature, the content of amorphous material increases according to XRPD evaluation. DTA experiments on kaolinite with a heating rate of 30 K $min^{-1}$ showed a significant exothermal signal at ~ 1000 °C which is allocated to the formation of spinel. This phase, however, could not be identified using XRPD. Thus, an amorphous or at least highly disordered structure has to be considered. In montmorillonite, the formation of $\gamma$-cordierite was observed at 1200 °C, a phase first described by DIMITRIJEVIC & DONDUR (2007).

Further studies will include the quantification of the exact amounts of each phase and the total amorphous content using the Rietveld method. HT- in situ XRPD experiments with the separated clay minerals and the two aforementioned mixtures will be performed to obtain an overview of the structurally traceable reactions in the systems. In order to determine which phases (ordered and amorphous) contribute to the assumed rehydroxylation reactions, actual case examples of deformed tiles will be analyzed with XRPD and vibrational spectroscopy.

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# EFFECT OF $SiO_2$ ADDITION ON THE MINERALOGY OF EAF SLAGS

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Steel slags can be used as building materials due to their beneficial mechanical properties, e.g. for road construction (PASETTO & BALDO, 2011). However, steel slags also contain certain environmentally relevant elements, such as F, Cr, Mo and V. The project MiLeSlag connects the leachability of major and trace elements with the mineralogical composition of electric arc furnace (EAF) steel slags, since it is known from various studies that the leaching behaviour is linked to the mineralogy (HÖLLEN & POMBERGER, 2014). Therefore, pH dependence leaching tests have been conducted to evaluate the leachability of certain elements present in the slag. Furthermore, the leaching controlling phases have been modelled using the program LeachXS™ and were additionally compared with microscopic results of the investigation of the mineralogical phases composing the steel slag. Figure 1 illustrates the pH-dependent leaching of silicon of a re-melted original slag sample (A) and a conditioned re-melted slag sample (B). For conditioning, additional $SiO_2$ was added to the melt to tailor mineralogy for decreased leachability of V. Higher amounts of $SiO_2$ in the melt resulted in the formation of pyroxenes and olivine phases and the absence of larnite (i.e. belite: β-$Ca_2SiO_4$). The modelled results confirm the XRD analyses.

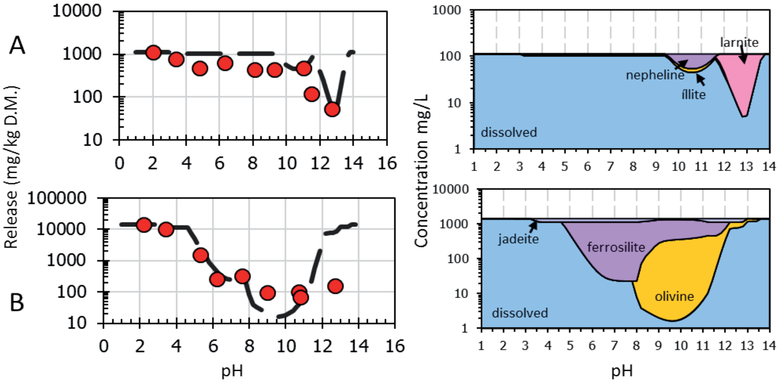

Figure 1: Left: pH-dependent release of silicon; Right: modelled phases controlling the leachability, A: re-melted original slag, B: conditioned re-melted slag.

PASETTO, M., BALDO, N. (2011): Constr. Build. Mater., 25, 3458-3568.
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# ECLOGITES AND GARNET BEARING PYROXENITES IN THE OSTRONG UNIT OF THE MOLDANUBIAN ZONE (LOWER AUSTRIA): GEOCHEMISTRY AND PETROLOGY

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The petrology and geochemistry of the most southern mafic to ultramafic metamorphic rocks from the Ostrong Unit in the Moldanubian Zone, Lower Austria have been investigated. Based on petrography and bulk-rock geochemistry, eclogites and garnet bearing pyroxenites are clearly distinguishable and show affinity to mid-ocean ridge basalts and non-oceanic continental basalts, respectively. In addition, compositional zoning in garnet from eclogites (Fig. 1) provides crucial information for a two-stage garnet growth including a prograde eclogite-facies and a subsequent granulite-facies stage. Beside of sharp changes of other trace elements (P, Ti, Zr, V, Cr, Ga), the two distinct growth phases are best documented by low Y + HREE concentrations in the garnet core and a sharp increase of these elements at the core-mantle boundary. The core of the garnet crystals contain well preserved omphacite inclusions and have increasing grossular contents from the centre outwards indicating prograde growth during the eclogite-facies stage. Isothermal decompression during exhumation of the rock leads to partial decomposition of the garnet and formation of retrograde phases, probably as kelyphitic rim around the garnet. The newly grown garnet mantle with high Y + HREE content has a chemically heterogeneous composition and is most likely the result of the consumption of the heterogeneous kelephitic rim during the granulite-facies stage. In addition, this HT imprint results in the decomposition of REE-bearing zoisite and the partitioning of Y + HREE into the newly formed garnet mantle. The outermost part of the garnet is chemically homogenous and formed by a different reaction mechanism compared to the garnet mantle. Following the granulite-facies peak, decompression during initial uplift resulted in the development of a symplectitic rim consisting of clinopyroxene + plagioclase ± orthopyroxene ± spinel. The presence of coarse-grained amphibole within the rocks indicate a late amphibolite-facies overprint.

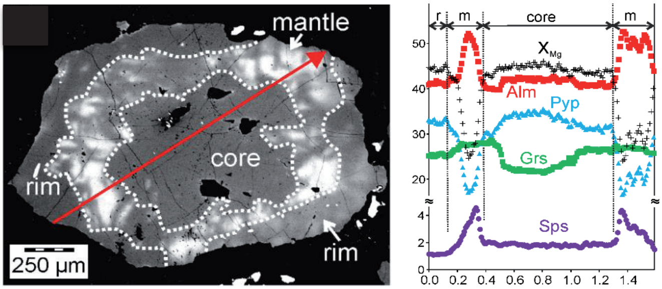

Figure 1. BSE image and major element zoning profile of a representative garnet from an eclogite. Y-axes indicates mol. % of garnet endmembers; x-axes indicate distances in millimetres.

# THE PRE-METAMORPHIC HISTORY OF MOLDANUBIAN GRANULITES AND GFÖHL GNEISS IN LOWER AUSTRIA (BOHEMIAN MASSIF): CONSTRAINTS FROM TRACE ELEMENTS AND U-PB AGES OF ZIRCONS AND WHOLE-ROCK GEOCHEMISTRY

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The Gföhl Unit in the Austrian sector of the Molanubian Zone (Bohemian Massif) exposes large volumes of high- to ultra-high-grade Variscan metamorphic rocks of granitoid composition, mapped as "Gföhl Gneiss" and "granulite". In an attempt to better understand the pre-metamorphic evolution history of these prominent rocks, we combined whole-rock geochemical (major, trace element and isotope data) with a LA-ICP MS zircon study (trace element and U-Pb analysis).

Based on whole rock geochemistry, the Gföhl Gneiss represents a felsic peraluminous, S-type granite. Remnant "magmatic" zircon domains with ages of ~ 480 Ma document an Ordovician protolith age for this rock type. Another group of inherited zircon cores are dated at around 550 Ma, indicating that the sedimentary source was deposited in Cambrian or lower Ordovician times. Ti-in zircon thermometry gives crystallization temperatures of ~750-850 °C for the granitic protolith, while "metamorphic" zircon overgrowth shells have higher Ti contents indicating that the Variscan metamorphism of the gneiss occurred at temperatures > 850 °C.

The granulites include predominately felsic and minor mafic variants. The former are leucogranites similar to the Gföhl Gneiss, the latter are peraluminous granodiorites with I-type or I/S transitional type source affinity in terms of their chemical composition. However, remnant magmatic zircon domains with oscillatory zoning show ages of ~ 440–400 Ma in both felsic and mafic granulites, hinting that they represent granitoid rocks that are younger than the Gföhl Gneiss protoliths. There is a marked difference in trace element compositions between the remnant magmatic zircons and the voluminous metamorphically grown zircons, which have lower P, Y and HREE but higher Ti contents. Ti-in-zircon thermometry indicates that the magmatic zircons formed at temperatures of 800–840 °C, whereas significantly higher temperatures of 890–940 °C are obtained from metamorphic zircons.

# CORROSIVE REACTION TEXTURES OF FIRECLAY CAUSED BY $H_2SO_4$ ATTACK

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A crucial factor in producing highly pure titanium dioxide pigments by the sulphate process is the corrosive reaction of the sulphuric acid with the mullite, cristobalite and glassy phase bearing refractory fireclay. Detailed and systematic observations of reaction textures in combination with mineral chemical analyses from the immediate hot face to the cold end of used $Al_2O_3$-$SiO_2$ bricks allow a reconstruction of a two-step thermo-chemical modification of the fireclay grains in the presence of sulphuric acid. In an initial step, mullite decomposition appears at the edges of fireclay grains, resulting in the growth of a blocky amorphous silica corona and aluminium-sulphate. This texture can be explained by the $H_2O$ releasing reaction $Al_6Si_2O_{13} + 9\ H_2SO_4 = 3\ Al_2(SO_4)_3 + 2\ SiO_{2\ (amorphous)} + 9\ H_2O_{\ (g)}$. In a second step, when temperature reaching minimum ~770 °C, the newly formed aluminium-sulphate is transformed to corundum. The formation of this pseudomorphic corundum after aluminium-sulphate occurs through the reaction $Al_2(SO_4)_3 = Al_2O_3 + 3\ SO_{3\ (g)}$ and appears mainly at the hot face of the studied bricks. This interpretation is consistent with decreasing $SO_3$ concentrations from the cold end (~20 wt.%) to the immediate hot face (~3 wt.%) of the bricks. To improve the resistance against sulphuric acid attack on such fireclay bearing refractories, a special impregnation is recommended.

# TRACE ELEMENT CONCENTRATIONS OF QUARTZ FROM ALPINE FISSURES

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In the year 2000 mineral collectors found artefact-like quartz fragments and a flint fragment showing distinct hewing signs in an Alpine fissure near the Riepenkar. The fissure, measuring around 15 m in length and 3 m in depth, is located west of the Olpererhütte at around 2700 m altitude. The findings of blades and bladelet-shaped quartz flakes, partial lateral retouching and signs of usage have led to the conclusion that the quartz crystals show evidence for lithic reduction. Geologically, the fissure at the Riepenkar is located in the "Tux-Gneis-Kern". This unit belongs to the Venediger thrust sheet system of the Sub-Penninicum and consists of various metagranodiorites and metatonalites. The fissure itself is situated in a leucocratic orthogneiss host rock with minor tonalite lenses nearby (at least 200 m distance). The trace elemental concentrations in quartz from this as well as other Alpine fissures were studied using LA-ICP-MS, EPMA, SEM, CL, micro-XRF, micro-Raman spectroscopy, single-crystal XRD and PXRD. The aim of this study was to test the ability of using the trace elemental contents of Alpine fissure quartz as a possible provenance tool in archaeology. Most samples were provided by the mineral collector Walter Ungerank and derive from the Tyrolean part of the Tauern Window. Further samples were collected in various locations in the Tauern Window in South Tyrol. Thus, the sample locations are distributed over large areas of the western part of the Tauern Window, while their host rocks cover various rock types including metagranites, metapelites and metabasites.

The trace elemental concentrations of quartz from these Alpine fissures typically contain only minor amounts of Li, B, Mg, Al, P, Ca, Ti, Fe and Ge. Their abundance depends on the quartz variety and was quantified by applying LA-ICP-MS. Combined with CL imaging these measurements revealed a chemical zonation, which is expressed as sector zoning in the quartz crystals. LA-ICP-MS results indicate that slight differences in the median trace elemental concentrations from Alpine fissure quartz have at least the potential to discriminate between quartz from fissures in different host rocks. The total trace elemental content depends on the quartz variety: amethyst shows high Fe contents; milky quartz shows a tendency towards increasing Al and Li contents. Hence, a use of the quartz trace elemental content as a provenance tool has to take into account the quartz variety. Sector zoning was confirmed through CL imaging and the LA-ICP-MS profiles show that it affects the variability of trace elemental contents (especially for Al and Li) within both single crystals and quartz from Alpine fissures. A relatively clear distinction based on trace elemental contents can be made between samples from outside the Tauern Window and those from within the Tauern Window. Further extensive sampling in the central and eastern part of the Tauern Window should be conducted to confirm these observations.

# ON THE HYDRATION OF HIGH-GRADE METAMORPHIC TERRANES

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Pervasive hydration of previously dry metamorphic rocks is a common process in many metamorphic terranes. However, although hydration reactions are ubiquitous and the `catalysing effect' of water is commonly accepted, the actual processes of catalysis during pervasive hydration remain poorly understood. We suggest that (1) the exothermicity of hydration reactions may provide thermally buffered intervals of near-constant temperature that favour equilibration and that (2) hydration catalyses equilibration mainly due to the dramatic sudden increase of the equilibration volume and the related effective bulk composition. By comparison, the fluid-effect of erasing kinetic barriers may be subordinate. In order to test these two hypotheses, we explore the relationship between temperature (T), bulk composition (B) and time (t) on a new diagram – the TBt diagram. For the 1st hypothesis we model the energetics of metamorphic hydration reactions to predict buffering intervals in T–t space. For the 2nd hypothesis we design non-linear paths through compositional space based on the ratio between intra-grain and grain-boundary diffusivities and chemical potentials to constrain bulk compositional changes through time, temperature and infiltration events: the B axis of the TBt diagram. Ultimately, the predictions of quantitative paths on the TBt diagram will also help to constrain questions on the origin of late stage fluids. Predictions are tested against observations from the Plankogel Unit. This unit forms the hanging wall of the eclogite type-locality in the Eastern Alps and features pervasively re-hydrated greenschist- to amphibolite facies assemblages of Eoalpine age that pervasively overprint drier Permian parageneses.

# PROGRADE TO RETROGRADE MONAZITE (RE)CRYSTALLIZATION IN MEDIUM-GRADE METASEDIMENTARY ROCKS FROM THE ORLICA-ŚNIEŻNIK DOME (CZECH REPUBLIC/POLAND)

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We use textural and geochronological arguments to constrain monazite petrogenesis and the age of metamorphic events in medium-grade metasedimentary rocks from the European Variscan Belt (Orlica-Śnieżnik Dome, Czech Republic/Poland). The relationships between monazite, allanite and other major and accessory phases are characterized for staurolite-, sillimanite- and kyanite-grade, garnet-bearing mica schist samples.

Garnet porphyroblasts with prograde compositional zoning include allanite in the core and monazite at the rim. Allanite is virtually absent from the matrix; it shows replacement textures involving a cluster of Th ± U ± Y-rich silicates or phosphates. Monazite, with frequent micro-cracks or trimmed grain boundaries, abounds in the mica-rich matrix; it occurs as lone grains close to partially resorbed garnet, apatite or staurolite, and as subhedral and compositionally zoned aggregates associated with allanite and xenotime. Electron microprobe analyses of monazite define Pb vs. Th* isochrons (ages = 363–343 Ma) with positive intercepts (Pb 0 = 40–120 ppm) which suggest the presence of initial Pb and age overestimation. Isotopic analyses obtained by laser ablation coupled with mass spectrometry confirm the minor presence of initial Pb which leads to variable discordance in the $^{206}Pb/^{238}U$–$^{207}Pb/^{235}U$ system. Conversely, the $^{206}Pb/^{238}U$– $^{208}Pb/^{232}Th$ system is not visibly affected; analyses are concordant and $^{208}Pb/^{232}Th$ ages range from 358 to 299 Ma (±7–8 Ma) regardless of monazite texture or composition. They define a main group at 330–310 Ma, with few older outliers. All observations suggest that a first monazite generation (MnzI) formed via allanite breakdown at prograde to peak *P–T* conditions (5–7 kbar/575–640 °C). A comparison with previous geochronological results reveals that the age of this prograde reaction is, however, preserved by only few domains yielding 360–340 Ma. Instead, our results emphasize the importance of retrograde processes which built the dominant age population of 330–310 Ma. The latter ages are ascribed to a combination of (1) transient monazite growth after allanite and controlled by P availability, (2) variable recrystallization/replacement of older monazite grains, and (3) minor monazite neoformation due to the resorption of garnet or apatite. The young monazite grains or domains (MnzII) mostly formed during fluid influx and chloritization; they constrain the end of the orogenic history when mid-crustal rocks were exhumed and re-hydrated at temperatures below ~300 °C.

# MONAZITE AGES IN HIGH-GRADE METAPELITES FROM THE AUSTRIAN PART OF THE BOHEMIAN MASSIF: INSIGHT INTO A COMPLEX POLYPHASE METAMORPHIC EVOLUTION

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Polyphase garnet growth, remnant mineral inclusions and textural relations indicate that most high-grade metamorphic rocks in the Austrian part of the Bohemian Massif are polymetamorphic. The method of in-situ EPMA Th-U-total Pb monazite dating provides an effective tool to constrain the age of different metamorphic events.

Monazite in migmatitic paragneiss from the Bavarian Unit in Upper Austria has mostly ages close to 320 Ma. These ~320 Ma old monazite grains formed in connection with late Variscan low pressure, high temperature metamorphism. However, monazite inclusions in zoned garnet porphyroblasts occasionally give older ages of ~ 340 Ma and document a preceding medium- to high-pressure Variscan regional metamorphism in the Bavarian Unit (SORGER et al., 2018).

In the central and eastern Bohemian Massif monazite ages of 335-340 Ma are most common. There is no evidence for an Upper Carboniferous regional metamorphic overprint in these areas (FINGER et al., 2007). However, the Variscan metamorphic evolution was complicated though. A polymetamorphic evolution can be documented for a granulite facies paragneiss from the Drosendorf Unit in Lower Austria (Loya quarry). The rock contains two garnet generations. Monazite inclusions in the older garnet (grt1) give an age of ~ 370 Ma and indicate an Early-Variscan (late Devonian) metamorphic stage. Matrix monazite formed along with the second younger garnet generation (grt2) at 340 Ma. Rare monazite relics of Cadomian age (~ 620 Ma) are preserved in the rock as well.

A polymetamorphic evolution with events at ~ 370 Ma and 340 Ma could also be shown for Moldanubian paragneisses from the Raabs Unit, using monazite in different textural positions. Thus, evidence is mounting that the Variscan evolution of the eastern Bohemian Massif involved two different orogenic events at 340 and ~ 370 Ma. Due to the strong Carboniferous metamorphism, the Devonian event has remained widely unrecognized so far. It may reflect the incipient collision of Armorica and Avalonia.

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FINGER, F., GERDES, A., JANOUŠEK, V., RENÉ, M., RIEGLER, G. (2007): J. of GEOsciences, 52, 9–28

# MAGNESIUM ISOTOPE EVIDENCE FOR ENHANCED CRUSTAL REWORKING IN EARLIEST CAMBRIAN SEDIMENTS – A CASE STUDY FROM KAZAKHSTAN

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The initiation of the Phanerozoic eon was accompanied by a unique (bio-)geochemical revolution in Earth´s history, leading to the rise of metazoan life. Concomitant geodynamic or tectonic changes, such as continent re-organization and collision, is associated with enhanced crustal reworking, affecting the weathering of rocks and consequently the oceanic nutrient balance. Further, changing global ocean currents caused mixing of water masses. A causal relationship between these geological events and timing of the biologic turnovers, however, remains unclear. In this study, we investigated phosphatic shallow water sedimentary rocks from Kazakhstan, key deposits from the Precambrian-Cambrian (Pc-C) boundary. We show that a rapid increase (ca. 1 Myr) in the stable Mg isotope composition within these phosphorites, which we consider representative for ocean chemistry, show co-variations with radiogenic Sr isotope signatures. We interpret this co-variation as a swift and severe response in ocean chemistry to riverine influx from continents, which is directly related to enhanced crustal reworking. Our data strongly suggest that ocean chemistry at the Pc-C boundary, represented through deposits in Kazakhstan, was strongly affected by continent re-organization and subsequent weathering. A rapid recovery of the isotope signatures towards signatures that existed prior to this excursion likely reflects a shift towards ocean-spreading dominated signatures. Thus, a direct link between the coupled positive seawater Sr-Mg isotope excursion to concomitant Gondwana assembly at the Pc-C boundary and the marked change in marine fauna at this time seems plausible.

# COMPARING NEW TESTING METHODS FOR THE SULFATE RESISTANCE OF SHOTCRETE

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Shotcrete is one of the essential building blocks of modern excavation and tunnelling methods. In these underground settings shotcrete frequently comes into contact with aggressive solutions and can be chemically attacked and damaged which may necessitate expensive refurbishing efforts. A deeper understanding of the mechanisms of deleterious chemical attacks on concrete is necessary to better predict long-term performance and durability of newly developed concrete mixes. Sulfate attack is one of the major chemical threats to shotcrete, leading to weakening and in extreme cases disruptive expansion of the cement matrix.

We compare the performances of 7 dry-mix shotcrete mix designs using different amounts and types of supplementary cementitious materials (SCM) in a novel sulfate resistance test for concrete using powdered samples (STEINDL et al., 2019) and in a modified sulfate expansion test specified in SIA 262/1:2013 (SIA, 2013). In the former test, powdered samples are used instead of prisms or drill cores to better decipher alteration reactions and to eliminate and indirectly assess the influence of variations in microstructure or porosity. Chemical (XRF, IC, ICP-OES) and mineralogical (FTIR, XRD) analyses of the reactive solutions and solids show that the mineral reactions during the experiment are dominated by the dissolution of portlandite, Ca-leaching from C-S-H and the precipitation of calcite and ettringite. The test is coupled with thermodynamic modelling of the reactive fluids to understand precipitation mechanisms and assess stability relations between hydrated solid phases. Our results show marked differences in the reactivity of the mixes and the amount of precipitated secondary calcite and ettringite.

In the second test setup, the sulfate-related expansion of drill cores in a 5 wt. % $Na_2SO_4$ solution is measured. The setup revealed the important influence of the type and amount of SCM used, with mixes containing high amounts of blast-furnace slag showing lower expansion than mixes with low amounts of either blast-furnace slag or metakaolin.

Comparing the results of both test methods provides advanced insights into concrete damaging mechanisms in sulfate-loaded environments. This helps to identify the best-performing mix designs to develop more durable and sustainable shotcrete in the research project “ASSpC - Advanced and Sustainable Sprayed Concrete”.

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# APLITE HOSTED REICHENSPITZ-TYPE MOLYBDENITE MINERALIZATION IN THE CENTRAL TAUERN WINDOW, SALZBURG/TYROL)

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Molybdenite mineralization located in the Reichenspitzgruppe at the border of the provinces of Salzburg and Tyrol is hosted by Variscan I-type plutons metamorphosed into gneisses (EICHHORN et al., 2000). The gneisses show S-type affinity due to crustal contamination (FINGER et al., 1993), and are intruded by calc-alkaline aplitic A-type granites (SCHERMAIER, 1993). Mineralogy and geological setting resemble Mo mineralization at the Alpeinerscharte, Tyrol (MELCHER et al., 1996; LANGTHALER et al., 2004). Both occurrences form part of the "Molybdenum Ore District Central Gneiss Supersuite" as defined in the Interactive Raw Materials Information System (IRIS, www.geologie.ac.at/services/webapplikationen/iris-interaktives-rohstoffinformationssystem/).

The Reichenspitz mineralization is controlled by shear zones and the intrusion contacts of the aplitic granites (STEINER, 2018). Molybdenite either appears disseminated in the aplitic granite, often in the vicinity to intrusion contacts, or in sulfide-bearing quartz veins. The ore paragenesis comprises assemblages of molybdenite, pyrite and chalcopyrite, with molybdenite being by far the most abundant. The aplitic and granitic gneisses carry abundant accessory assemblages of zircon, U-Th-phases, apatite, and allanite (i.e., REE-bearing minerals) in the vicinity of the molybdenite mineralization. Strictly associated with, and often within the molybdenite is a mineralization containing Bi sulfides (bismuthinite), native bismuth, Pb-Bi-Ag sulfosalts (cosalite, lillianite, pavonite, and others) and Bi tellurides.

The Mo mineralization likely represents a low-grade low fluorine calc-alkaline molybdenum porphyry system formed during the pneumatolytic stage of the intrusion of the aplitic granites. During the Neoalpine event, remobilization formed various alteration minerals including powellite, wulfenite, betpakdalite-CaCa, ichnusaite, nuragheite, sardignaite, suseinargiuite, and ferrimolybdite. The mineralization can be compared to Su Seinargiu, Sardinia (with a very similar alteration, ORLANDI et al., 2015), and Endako, BC (SELBY et al., 2000).

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# THE TBt-DIAGRAM. AN ALTERNATIVE TO PSEUODESECTIONS?

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The use of thermodynamic *PT* pseudosections to infer pressure–temperature paths of metamorphic rocks is inherently circular: While pseudosections are calculated for a *single* bulk composition (often obtained by XRF analysis), the art of inferring metamorphic *PT* paths is underlain by the fundamental premise that metamorphic parageneses respond only partially to changes in physical conditions and thus contain non-reactive parts of the overall bulk composition (i.e. *multiple* bulk compositions on the paragenesis scale). Although this conflict is increasingly recognized in the literature, there are little efforts to design tools that can be usefully employed to supersede *PT* pseudosections. In this contribution we present a new diagram that may fill this niche: The *TBt* diagram (*T* = Temperature, *B* = Bulk composition, *t* = time). In principle, the *TBt* diagram is akin to the well known *TX* diagrams where bulk composition is plotted on one axis of the diagram. However, in the *TBt* diagram, the *B* axis is not a simple linear axis (e.g. a mole fraction), but is a non-linear path through multi-dimensional compositional space that is externally controlled by processes such as fluid infiltration (sudden and dramatic increase of the equilibration volume giving the paragenesis access to a much larger bulk composition) or cooling (continuous decrease of the equilibration volume and thus decrease of the bulk composition). We argue that the *B* axis of the *TBt* diagram can be constrained by microstructural and/ or diffusion modelling and illustrate applications in the context of the Plankogel series in the southern Kor- and Saualpe.

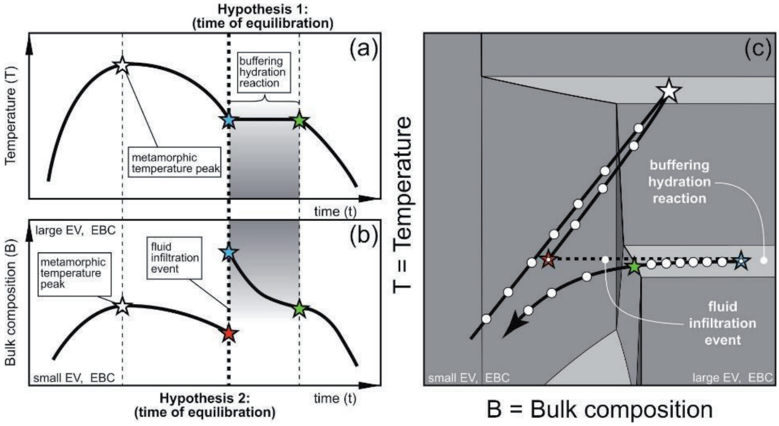

Figure 1. Schematic illustration of a *TBt* diagram. (a) Temperature (*T*) – time (*t*) diagram including fluid infiltration event that causes a hiatus in the cooling history (b) Bulk composition (*B*) – time (*t*) diagram for the same evolution. (c) The *TBt* diagram as a parametric representation of (a) and (b). White circles denote time.

# PHASE RELATIONS AND MICROSTRUCTURES IN A FULGURITE FORMED IN A COARSE SOIL OF WEATHERED GRANITE

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Fulgurites are mostly “branch-like” cylindrically or conically shaped glassy structures that form, when a cloud-to-ground lightning strikes a target material, which is usually soil, sand or rock. The energy dissipated during the fulgurite forming electrical discharge event is between 1 and 30 MJ/m, which is transferred to the target material within several 10s of μs leading to a peak power output of about $10^{13}$ W, heating rates of $10^{3}$ K/s, and peak temperatures on the order of $10^{5}$ K (e.g. PASEK et al., 2012). The conditions prevailing during fulgurite formation are extreme, comparable only to other short-lived high-energy geological events such as hypervelocity impact and induced impact metamorphism as well as frictional heating during seismic slip. Accordingly, the phase content and the microstructures that are observed in fulgurites are peculiar. We present new mineralogical and petrographical data from a fulgurite from the Inyo County, E-California (USA), which was formed in a coarse soil (gravel) of weathered granite as target material.

Several fragments of a fulgurite tube including side branches are available. The largest sample represents a segment of a hollow cylinder with a wall thickness of 1.8 centimeters and an inner fulgurite tube diameter of about 4 centimeters. The fulgurite can be subdivided into five concentric zones. The innermost zone is dominated by a colourless, translucent glass with grey schlieren. In addition, lechatelierite (amorphous $SiO_2$) and cristobalite are present. Moreover, spherical aggregates of metallic Fe and of polyphase of Fe-Si-P alloys with eutectic internal microstructure occur. In the next zone, cristobalite embedded in a translucent glass matrix is the main mineral phase. Further out, cristobalite forms rims around cores of quartz. The next zone contains many relic quartz grains floating in a glassy matrix. The outermost zone contains abundant grains of quartz, feldspar, and opaque phases, whereby magnetite and hematite dominate. In addition, a variety of dendritically grown phases including spinel, Fe-rich olivine, and clinopyroxene occur.

The presence of lechatelierite indicates peak temperatures in excess of 1700 °C at the inner fulgurite wall at extremely reducing conditions as indicated by the presence of Fe-Si-P alloys. A significant outwards decrease of the peak temperatures is indicated by the fact that quartz grains are preserved at the outer fulgurite wall. In addition, the conditions have been far less reducing in the outermost portions of the fulgurite as indicated by the presence of magnetite and hematite. Finally, the flash heating was followed by fast cooling as indicated by the presence of dendritically grown phases, which are considered as evidence for crystallization under the conditions of large undercooling.

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# ANCIENT IRON SMELTING REVISITED BY MODERN TECHNIQUES: WHAT MAKES AN IRON ORE WORK?

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The art of ancient bloomery iron smelting caught the attention of many archaeometallurgists in the past decades, the findings of which have been summarized in several important works (TYLECOTE, 1992; PLEINER, 2000; REHDER, 2000). Despite these accomplishments, none have ever considered conducting a thorough study, spanning across several mineralogy-cally and chemically distinct ores, both pure and diluted by quartz sand, to infer on the precise range of chemical and/or mineralogical ore compositions which render an ore workable, taking into consideration the chemical and physical circumstances dictating the course of the smelting process. The enormous quantities of resources required, like sufficient charcoal, ore, wood and refractory clay for such an endeavour are in themselves self-explaining as to why such an extensive project did not take place until now.

In this contribution, we present the preliminary results of our long-term study (having started in the year 2012) using the results of XRF (X-Ray Fluorescence) data from the slag and ore samples obtained during more than 150 controlled smelting experiments. The results, albeit preliminary, clearly define the region of workable ores (without significant CaO contents) in the ternary system $FeO-Al_2O_3-SiO_2$. The compositions corresponding to 'workable' ore compositions cluster around the cotectic lines joining both eutectic points in the given ternary system. Such compositions have the lowest melting points, indicating that the key factor to a successful iron smelt is indeed that the slag remains sufficiently liquid during the entire smelt to be able to flow down from the region of the air inlet, liberating space for the incoming iron particles from the furnace shaft, while still partially coating the forming iron bloom, preventing its re-oxidation.

Ores with abundant CaO in the gangue form a separate cluster in the $FeO-Al_2O_3-SiO_2$ ternary scheme, since CaO in combination with the other gangue oxides leads to different more complex quarternary eutectic compositions. Regardless, the key factor governing the functionality of any particular ore seems to be independent of its mineral composition and defined entirely by its global chemistry, in accord with the findings of SAUDER & WILLIAMS (2002), which also emphasize the crucial role of a sufficiently fluid bloomery slag.

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# VISUALIZING FLUID-MEDIATED ROCK TRANSFORMATIONS USING MICRO-CT AND MICRO-XRF: THE BÄROFEN METAGABBRO

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The aim of this study is to provide textural and petrographic constraints on the gabbro-eclogite transition from the locality Bärofen in the Koralpe (Styria, Austria) using micro-CT and micro-XRF in comparison with backscatter electron image petrography. Petrographic investigations showed that the primary Permian magmatic assemblage plagioclase + clinopyroxene$_1$ + orthopyroxene reacted during eo-Alpine high-P metamorphism in micro-domains to form clinopyroxene$_2$, garnet, kyanite, hornblende and occasionally corundum. Fluid influx lead to the progression of reactions involving plagioclase and orthopyroxene. The investigations were performed on a hand specimen showing in-situ eclogitization with a length of 13 cm, width of 3 cm and thickness of 1 cm.

Micro-computed tomography (micro-CT) investigations were performed using a XtremeCT 2 (Scanco Medical AG, Brüttisellen, Switzerland). The scans were performed using 900 projections with 4608 samples, resulting in a 30.3 µm isotropic resolution. The tube settings were 68 kV voltage, 1470 µA current and an integration time of 900 ms per projection. In the first step 5 representative rock volumes where defined. Therefore a mask for the rock surface had to be created by segmenting the volume of interest (VOI) using a Gauss threshold algorithm. Afterwards the filter settings for the different materials had to be defined. Based on their density the following minerals could be identified: plagioclase, clinopyroxene (omphacite), orthopyroxene/garnet and pyrite. The resulting threshold widows using the -1000-1000 scaling were: 248-329 for omphacite, 330-431 for plagioclase, 432-609 for orthopyroxene/garnet and 610-1000 for pyrite. Unfortunately due to a similar density it was not always possible to distinguish between magmatic clinopyroxene (augite) and omphacite as well as garnet and orthopyroxene. Nonetheless the mineralogical transformation from gabbro to eclogite is clearly visible and modal amounts of plagioclase and orthopyroxene decrease whereas garnet and omphacite strongly increase.

Micro-XRF element mapping was performed with Bruker Tornado M4 Micro-XRF with a Rh target X-ray tube powered at 50 kV and 600 µA. The beam was focused with polycapillary optics to a spot size between ~15 and ~100 µm, with smaller spot sizes at high X-ray photon energies, and secondary x-ray energies were collected with EDS silicon drift detector at 20 mbar vacuum chamber atmosphere. The map has a size of 1178 mm x 25.5 mm (1573 x 340 Pixel) and a resolution of 75 µm/Pixel. Netto-Measuring time was ca. 15 hrs, which equal 120 ms per Pixel. False colour element maps are normalized representations of cps intensities of characteristic Kα or Lα-lines energies. The phase maps are quantitative results of a semi-automatic numerical discrimination method, which is based on clustering of bins of Na, Mg, Al, Si, K, Ca, Ti, and Fe cps-histogram. In contrast to micro-CT this method leads to a more detailed mineralogical discrimination such as between magmatic clinopyroxene and omphacite as well as garnet and orthopyroxene

# PRELIMINARY STUDY: TECTONIC SETTING OF GRANITOIDS FROM THE SUKHOTHAI TERRANE UTTARADIT PROVINCE, THAILAND

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Within the Uttaradit Province, northern Thailand the Nan Suture occurs between the Indochina and Sukhothai terranes, extending for approximately 150 km in a northeastern-southwestern direction. The rocks associated with the Nan Suture are generally dominated by ophiolitic rocks such as gabbro, pyroxenite, and serpentinised peridotite (PANJASAWATWONG, 1991).

However, this work focuses on the nearby granitoids which are widely exposed in the Uttaradit Province. In general three granitic provinces occur within Thailand, which are designated as western-, central and - eastern- granitoid belts. Granitic plutons in the study area belong to the eastern granitoid belt displaying usually I-type affinity (COBBING, 2011). Outcrops are readily found along both sides of the Nan River. Granitoids occurring along the western side of the Nan river are overlain by silicic clastic sedimentary rocks. In contrast, the eastern side is in contact with limestone and pyroclastic rocks. Part of the limestone was transformed during contact metamorphism to calc-silicate rocks with a mineral assemblage of quartz, clinopyroxene, wollastonite, and plagioclase.

First petrographical observations did not show significant differences in mineral assemblage and texture between the granitoid occurrences from the study area. They typically show a seriate texture, perthitic feldspars and small amounts of micrographic texture. The micrographic quartz-feldspar intergrowth texture is mostly found in the eastern parts. The main mineral assemblage comprises quartz, plagioclase, and some alkali feldspars. Their accessory mineral content includes biotite, apatite, zircon, and hornblende. According to their mineral assemblages the igneous rocks are classified as monzogranite, granodiorite and tonalite. Previous work on a granitic pluton nearby covering a surface area of ~1 km$^2$ gave an emplacement age of is 254.7 ± 4.2 Ma. The Permo-Triassic granites most likely formed within a syn-collisional or post-collisional environment. Further age dating as well as geochemical data are planned and will help to better understand the emplacement of these granitoids during the accretion of the Sukhothai terrane.

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# BAVSIITE, $Ba_2V_2O_2[Si_4O_{12}]$, A NEW SILICATE MINERAL WITH SINGLE 4-RINGS

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Bavsiite from the type locality Gun Claim, Yukon Territory, Canada, occurs as millimetre sized sky-blue, platy crystals in a barium-rich low temperature skarn related to a porphyritic quartz monzonite stock. Associated minerals are alstonite, barite, celsian, diopside, fresnoite, suzukiite, walstromite, witherite and minerals from the cerchiarite group. Electron microprobe analyses yielded the empirical formula $Na_{0.02}Ba_{1.98}Ti_{0.16}Fe^{2+}{}_{0.03}V^{4+}{}_{1.80}Al_{0.05}\,Si_{4.00}O_{14}$ based on 14 oxygens per formula unit; the simplified chemical formula is $Ba_2V_2Si_4O_{14}$. Bavsiite is tetragonal, space group $I4/m$, $a$ = 7.043(1), $c$ = 11.444(2) Å, $V$ = 567.6(2) $Å^3$, $Z$ = 2. Least-squares refinement using anisotropic displacement parameters was carried out with the program SHELXL-2013 (SHELDRICK, 2015) and yielded $R1$ = 0.0159 based upon 312 unique reflections with $I > 2\sigma(I)$. The crystal structure of bavsiite comprises unbranched single $[Si_4O_{12}]^{8-}$ rings connected by $[VO_5]^{6-}$ square pyramids and $BaO_{12}$ polyhedra. It can also be considered as cage-like $[Si_4V_2O_{18}]^{12-}$ clusters built by four $SiO_4$ tetrahedra and two $VO_5$ square pyramids (Fig. 1a). These clusters are cross-linked to form a pseudo-two-dimensional network (2D) parallel to the (001) plane, containing empty channels along the $a$ axis (Fig. 1b). The 2D networks are held together by $Ba^{2+}$ ions located in channels parallel to the $c$ axis (Fig. 1c). Bavsiite is isotypic to synthetic $\beta$-$BaVSi_2O_7$ (LIU & GREEDAN, 1994) and polymorphic to orthorhombic suzukiite ($BaVSi_2O_7$). In the crystal structure of suzukiite (ITO et al., 2014) $Si_4O_{12}$ chains along the $c$ axis are linked by $VO_5$ square pyramids to form layers parallel to the $ac$ plane, which are connected by barium atoms.

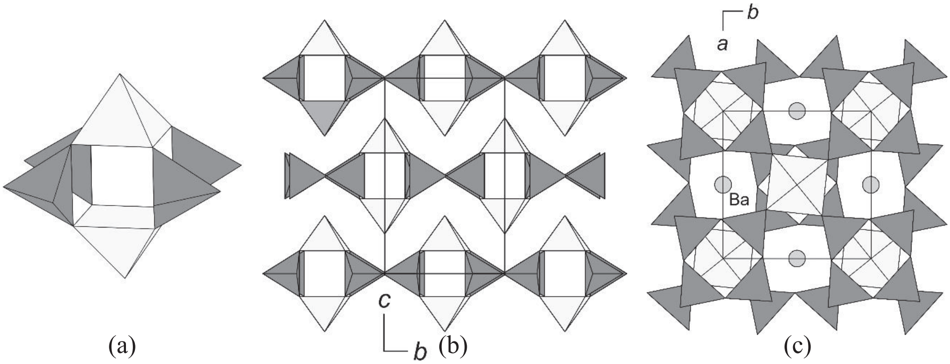

Figure 1. The crystal structure of bavsiite: (a) the cage-like $[Si_4V_2O_{18}]^{12-}$ cluster, (b) cross-linked clusters form a pseudo-two-dimensional network (2D) parallel to the (001) plane, Ba atoms are omitted for clarity and (c) projected along the (001) plane with Ba atoms in the channels along $c$.

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# MONITORING AND MODELING OF CALCITE PRECIPITATION KINETICS INDUCED BY $CO_2$ EXCHANGE DYNAMICS - EXPERIMENTS IN A RAILWAY TUNNEL

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Calcium carbonate precipitation from a supersaturated aqueous solution is one of the main challenges when it comes to clogging of e.g. tunnel drainage systems, which leads to high costs from maintenance and cleaning procedures over its operating lifetime. In order to be able to predict and prevent, or getting ideas how to easily remove $CaCO_3$ scaling, on-site experiments were conducted in an Austrian railway tunnel, where pH, electric conductivity (EC) and temperature of a locally occurring acidulous groundwater were in-situ and continuously monitored.

The experimental setup is based on a 1:1 drainage test track, supported by stationary reactor experiments, where the drained groundwater is monitored by a newly developed online sensor system and time-resolved sampling of solutions and solids. In distinct experimental sets, effects of e.g. flow rate, turbulences and gas exchange on scaling formation were tested. Results support the sensitivity of the monitored master parameters to successfully describe potential and ongoing coupled carbonate precipitation and $CO_2$ exchange with the tunnel atmosphere by fitting the measured pH, EC and solution chemistry with PHREEQC based modelling results using a reaction kinetics approach.

Data obtained from a ~300 days study period and modelling results are presented and discussed with regard to typically occurring physicochemical and precipitation conditions. The study shows that in-situ monitoring coupled with an advanced reaction kinetics modelling approach can be successfully used to detect and follow ongoing calcite formation in the above mentioned environment, i.e. a promising tool to be applied for scaling issues in geotechnical settings.