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HIGH-TECH METALS IN SPHALERITE AND CHALCOPYRITE FROM LEAD-ZINC-COPPER ORE IN THE ÖTZTAL-STUBAI COMPLEX

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Despite the strong interest in rare "high-tech" metals Ga, Ge, In, Sn, Sb in hydrothermal sulphide deposits, there is a dearth of studies on metamorphosed ore types (LOCKINGTON et al., 2014). The dominant host for rare metals in sulphide ore is sphalerite, but also chalcopyrite is a significant host to some "high-tech" metals, especially in metamorphic ore. We present 423 sphalerite and 110 chalcopyrite laser ablation ICP-MS spot analyses acquired from Pb-Zn and Cu-Fe-(Pb-Zn) ore samples (VAVTAR, 1988) from throughout the metamorphic Ötztal-Stubai complex (OSC). The aim is to understand controls and enrichment processes of trace metals in those ores. Financial support is kindly provided by BmWFW.

In order of their average abundance in sphalerite, Fe, Cd, Co, Mn, Hg, Ga, In, and Cr are primarily in structural solid solution. Primarily hosted in tiny inclusions are Cu (chalcopyrite), Pb (galena, sulfosalts), Sn (stannite, sulfosalts, cassiterite?), as well as Sb, Ag, Ge, As, Ni, and Bi (sulfosalts such as tetrahedrite). Fe can be present in small pyrrhotite-pyrite inclusions. Ge, Mn, Ni, Cr, and V seems to be incorporated also into silicates or carbonates.

In case of chalcopyrite, Zn, Sn, Pb, Se, Ag, and In can be enriched (>100ppm), both as inclusion-hosted and in solid solution.

Despite very heterogeneous data across the OSC region, there are distinct elemental patterns allowing a robust discrimination of most ore occurrences. Especially Hg concentrations in sphalerite show remarkably low standard deviations within ore occurrences. With respect to sphalerite, all Tösens district ore (except Hochjoch) defines a low-Mn/high-Hg group. Most Nauders district ore (Knappental, Knappenkar, Tscheyjoch) define (with Tösens Hochjoch) a medium-Mn/medium-Hg group. Nauders/Sattelalpe is exceptionally high in Mn and low in Co. Schneeberg shows variable Hg, while Mn/Co is stable, suggesting that Hg chemistry is zoned across this complex deposit. For chalcopyrite, the initial dataset does not allow a robust discrimination.

While sphalerite is a significant host for Ga, Ge, Co, Sn, and In, chalcopyrite seems to host only Sn and In. Sb and Ag are mostly carried by various sulfosalts. Following rare metal "sweet spots" are determined: Hochjoch and Tscheyjoch for Ga, Tösens/Unterbergler Gang and Tscheyjoch for Ge, Knappenkar (sphalerite) and Glücksgrat (chalcopyrite) for In, Tösens/Oberbergler Gang (chalcopyrite), Hochjoch and Sudelskof (sphalerite) for Sn, Tösens and Tscheyjoch for Co (all sphalerite), Sudelskopf for Sb (as sulfosalt inclusion in sphalerite).

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MANTLE XENOLITHS FROM THE LETHLAKANE DIAMOND MINE, BOTSWANA

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Kimberlite pipes are one of the best sources to sample and explore the subcontinental lithospheric mantle (SCLM) due to their abundant incorporation of mantle xenoliths. In Botswana several large kimberlites are mined for diamonds but produce also a variety of xenoliths. Here we present different types of mantle xenoliths from the Lethlakane mining site, northeastern Botswana. Lethlakane is underlain by a thick sedimentary cover and unknown basement at the projected junction of the Kaapvaal and the Zimbabwe Craton and the Magondi and Limpopo proterozoic collisional belts. Although modern mining techniques do not allow the sampling of large pieces of peridotite - as is the case for the old mining dump sites in the Kimberley area, South Africa - a large number of c. 5 cm sized different mantle xenoliths could be sampled from an old recovery pile.

In total 50 samples were taken which can be subdivided in: (1) spinel-lherzolite, (2) spinel-harzburgite, (3) garnet-harzburgite, (4) porphyroclastic (sheared) garnet-lherzolites and harzburgites, and (5) spinel-dunite. All samples are infiltrated by melt veinlets, which are associated with newly formed minerals such as calcite, serpentine, phlogopite and clinopyroxene.

Spinel-lherzolithe contains disseminated spinel crystals up to 1 mm in size distributed in a equigranular matrix consisting of olivine, clinopyroxene and orthopyroxene. Spinel-harzburgite is comparable in texture with spinel-lherzolite. Clinopyroxene is absent or very scarce but usually newly formed along the melt veinlets.

Garnet lherzolite consists of purple garnets with thick kelyphitic rims and in some cases with round olivine inclusions. The main modal composition is equigranular olivine, hypidimorphic intensely green clinopyroxene with spongy rims and orthopyroxene that forms colourless elongated crystals, with occasional round olivine inclusions. In one case garnet overgrowth of spinel is observed.

Garnet harzburgites bear garnet crystals up to 5 mm with thick kelyphitic rims. Equigranular olivine is the main modal component. Clinopyroxene is absent or rarely formed next to garnet. Some samples contain intergranular spinel.

Porphyroclastic (sheared) peridotites have a bimodal distribution in grain size. The fine grained olivine matrix contains orthopyroxene and garnet clasts, which are also affected by shearing and smaller in size compared to granular samples. Clinopyroxene is a rare fine-grained matrix constituent. Undulatory extinction and kink bands are typical for olivine.

Spinel-dunites contain equigranular olivines up to 98 % and small spinel grains in between.Phlogopite is not observed in all samples other than in close proximity to garnet as part of kelyphitic rims.

THE POLYMETAMORPHIC EVOLUTION OF THE AUSTROALPINE BASEMENT UNITS (MATSCH NAPPE, ÖTZTAL COMPLEX) IN THE VINSCHGAU/SOUTH TYROL

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The currently mapped sheet Schlanders (CARG 012) offers the chance to carefully investigate the above mentioned units and their tectonic contacts and to implement them into a tectonic model based on new petrological, geochronological and structural data. The Austroalpine nappe stack in the investigated area, located in the Vinschgau area (Southern Tyrol), comprises from bottom to top the Campo-Ortler (COC), the Texel (TC), the Ötztal (ÖC) complexes and the Matsch (M) nappe. These Austroalpine basement units in the Vinschgau valley (e.g. Matsch Nappe, Ötztal Complex) show a clear polymetamorphic evolution history which can be well reconstructed using the spatial distribution of the alumosilicates, the chloritoid-isograd and the observation of chemical zoning patterns in garnets, which depending on the geographical position and the geological setting, exhibit single-phase, two-phase or even three-phase compositions. Especially in the Matsch Unit, a clear spatial distribution of garnet zoning can be observed: in the west, the garnets show only a Variscan composition (Grt I) with a very small eo-Alpine growth rim (Grt II). Further to the east, into the Ötztal Complex, the proportion of this Grt II rim increases until only a residue of the older core Grt I remains. Special attention must be paid to the eastern part of the Matsch Unit where the garnets surprisingly show a third very low calcium generation (Grt Ib), which occurs between the Variscan core Grt I and the eo-Alpine rim Grt II. Since this Grt Ib distribution spatially correlates well with the occurrence of leucocratic othogneisses and pegmatites, a Permian age is supposed (still needs to be confirmed).

All three aluminum silicates also occur in the mapped area. Andalusite and sillimanite show a clear geographical distribution, where andalusite occurs in the western part and sillimanite occurs in the eastern part of the Matsch Nappe. Relic kyanite occurs only isolated in the western part of the region and is thought to represent a relic from the Variscan metamorphic event. The geographical distribution of the aluminum silicates indicates a change of Permian P/T conditions from west towards east, which also correlates well with the occurrence of these leucocratic orthogneisses. Geothermobarometry yielded a strong increase in eo-Alpine temperature conditions of 500°C to 650°C at pressures of 0.80-1.2 GPa in accordance with previous estimates from HAAS (1984) and HABLER et al. (2009).

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THE ANTARCTIC IRON METEORITE STEINGARDEN NUNATAKS (STG) 07009: PRELIMINARY RESULTS OF A MULTI-DISCIPLINARY STUDY

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In 2007, the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR, Hannover, Germany) carried out a reconnaissance survey of a hitherto unexplored area in Queen Maud Land, Antarctica, to assess the regional potential of meteorite accumulations. As a result of the search campaign 15 meteorites were found and later officially named after the Steingarden Nunataks (STG), being the nearest geographical feature (DELISLE et al., 2015). Here we report the first results of a multi-disciplinary study of the iron meteorite STG 07009, including optical microscopy (OM), analytical scanning electron microscopy (ASEM), electron microprobe analysis (EMPA), instrumental neutron activation analysis (INAA), and accelerator mass spectrometry (AMS). STG 07009 was found as one complete individual specimen weighing ~ 32.6 kg. The main mass (32.2 kg) is stored at the BGR, the type specimen (37.3 g) is kept at the Natural History Museum, Vienna. Macroscopically, the meteorite appears well preserved, displaying a greyish-black surface with numerous cm-sized regmaglypts and does not show any oxidation features in its interior. OM investigation of polished and etched platelets revealed that the meteorite is a plessitic octahedrite with almost all kamacite spindles (apparent diameter = 0.08±0.03 mm, N = 30) having nuclei of schreibersite. Compositionally, kamacite and schreibersite are rather uniform with averaged compositions (6.42 wt% Ni, 0.78 wt% Co) and (45.32 wt% Fe, 39.60 wt% Ni, 0.13 wt% Co, 15.28 wt% P), respectively. However, a detailed EMPA investigation revealed that in places, the spindles contain schreibersite-metal intergrowths, exhibiting complex textures and compositions. Based on bulk chemistry data obtained by INAA, STG 07009 is classified as ungrouped iron with no close relatives (J. T. WASSON, UCLA, personal communication). The corresponding INAA data are 20 µg/g Cr, 6.76 mg/g Co, 131.9 mg/g Ni, 282 µg/g Cu, 10.4 µg/g Ga, 166 µg/g Ge, 14.8 µg/g As, 74 ng/g Sb, 0.29 µg/g W, 16 ng/g Re, 0.129 µg/g Ir, 4.4 µg/g Pt, and 1.606 µg/g Au. AMS measurements (performed by K. NISHIIZUMI and M. CAFFEE at PRIME Lab, Purdue University, USA) of the cosmogenic radionuclides ^{10}Be, ^{26}Al, and ^{36}Cl gave saturation activities (dpm per kg meteorite) of 4.28±0.13, 3.44±0.23, and 17.55±0.72, respectively. Corresponding age calculations gave for STG 07009 a ^{36}Cl/^{36}Ar cosmic-ray exposure age of 780±100 Myr and a ^{10}Be-^{36}Cl/^{10}Be terrestrial age of 75±33 kyr. The latter is rather young when compared to the overall terrestrial age distribution of Antarctic meteorites (JULL, 2006).

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STANDARD ENTROPY AND ENTHALPY VALUES FOR PETROLOGICAL CALCULATIONS: RESULTS FROM RELAXATION CALORIMETRY AND FROM DENSITY FUNCTIONAL THEORY

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Relaxation calorimetry (RC) is a relatively new experimental method that enables the measurement of low-temperature heat capacities (C_p). Its commercial implementation is the physical properties measuring system (PPMS) from Quantum Design®. A major advantage of RC is that *small sample amounts in the mg range* can be studied as compared to other calorimetric techniques that require at least several grams of material (e.g. adiabatic calorimetry). RC thus opens up a new field for measuring low-T C_p for the first time on many phases that can only be synthesized in small amounts in high-pressure devices or occurring in nature as small or fine-grained crystals. For handling powdered samples, specific techniques have been developed.

The impact of RC on petrologic thermodynamic calculations is twofold:

● Mineral end members: *The standard entropy S^o can now be determined* with an accuracy of 0.7-1.0%. Examples that will be discussed include the garnet end members spessartine and andradite and the biotite end members annite and eastonite.

● Solid solutions: PPMS measurements made on solid solutions allow the *calorimetric excess entropy* to be determined. Examples that will be discussed are garnet and feldspar solid solutions, as well as the (Li,Na)$FeGe_2O_6$ pyroxene solid solution.

The enthalpy of formation (usually from the elements), $\Delta H^o_{f,elements}$, is another important thermodynamic quantity required in petrological calculations. It is either measured via some solution calorimetric method, or derived from phase equilibrium experiments resulting in an internally consistent thermodynamic data set. As will be shown by BENISEK & DACHS (in prep.) calculations using density functional theory (DFT) can be another useful source for gaining reliable $\Delta H^o_{f,elements}$ values. The new procedure requires (a) the computation of the enthalpy of formation of a specific phase from the oxides, $\Delta H^o_{f,oxides}$, using DFT and (b) the conversion of this value to a corresponding $\Delta H^o_{f,elements}$ based on $\Delta H^o_{f,elements}$ values of the oxides taken from published literature (e.g. an internally consistent thermodynamic data set or JANAF tables). DFT calculations testing this method have been made for alumosilicates, feldspars, garnets, olivines, pyroxenes, layer silicates, perovskite and amphibole. The so calculated $\Delta H_{f,elements}$ values of relevant end members do not deviate more than 1 % from reference values, most agree to within 0.5 %. This method thus seems to be a new promising tool for calculating $\Delta H_{f,elements}$ values of petrologically relevant mineral end members, especially in cases where experimental data are lacking or the end member in question does not exist physically, because the compositional range is restricted to the solid solution (e.g. eastonite in the case of the biotite solid solution).

ANOMALOUS AS-ENRICHMENT IN GERSDORFFITE IN A REALGAR-RICH ENVIRONMENT: LOJANE, MACEDONIA

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The abandoned Sb–As–Cr mine near Lojane (HIESSLEITNER, 1951; GRAFENAUER, 1977) in northeast Macedonia is a substantial source of arsenic and antimony pollution. The mine and flotation dumps present one of the major environmental problems for Macedonia and are considered a very serious human health risk given high concentration of arsenic-rich wastes (ALDERTON *et al.*, 2014 and references therein).

During a detailed mineralogical study of realgar-stibnite and chromite ore assemblages and their secondary alteration products (collected on ore and waste dumps) by SEM-EDS, EPMA, Raman spectroscopy, single-crystal and powder XRD, we detected a larger number of phases not previously recorded for the deposit (e.g. annabergite, arsenic (or arsenolamprite), baryte, chalcopyrite, coffinite, duranusite, galena, gersdorffite, gypsum, hydroxylapatite, laurite, maucherite(?), millerite, naldrettite(?), parkerite(?), pentlandite, picropharmacolite, pyrrhotite, roméite-group minerals, scorodite, senarmontite, siderite, sphalerite, ullmannite, valentinite, violarite and an unidentified Bi-As-S-Cl-(O?) phase), as well as partly amorphous, small-grained arsenates of Ca, Fe, Sb, Ni etc., including probable arseniosiderite. Grains of chromite-group species are scattered throughout the As-Sb mineralisation.

Nearly all of the observed sulphides contain trace to minor amounts of As, reflecting the As-rich environment. Rounded, commonly finely zoned (concentric or patchy) gersdorffite aggregates up to 20 µm occur in realgar, stibnite and quartz. They often show an anomalous composition with strong As-enrichment and S-depletion and a clear negative correlation between As and S. Only minor Co and Fe contents were measured. Patchy small areas in some aggregates are strongly enriched in Sb, representing As-rich ullmannite.

The previously unrecognised occurrence of several Ni(-As) minerals (apart from already reported Ni-bearing pyrite and vaesite, both also observed in our studies), adds another, albeit small, toxic component to the environmental pollution.

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MINERALOGICAL CHARACTERIZATION OF ANOXIC MARINE OIL SHALES DEPOSITS: A CASE STUDY FROM CENTRAL EASTERN DESERT OF EGYPT

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Upper Cretaceous oil shales are accumulated on the stable shelf within intracratonic sedimentary basins at the central and southern part of Egypt. We present integrated mineralogical analyses for three oil shale horizons from the Duwi and Dakhla formations in the Central Eastern Desert of Egypt. The nannofossil biostratigraphy study confirm that oil shales were deposited during Maastrichtian between ~ 70.63 to 67.7 Ma. Carbonates, phyllosilicates, quartz, fluorapatite and sulphides are the main inorganic constituents in the studied Maastrichtian oil shales. The Duwi oil shales contain calcite (up to 87 wt.%) as a main carbonate mineral. The phyllosilicates and quartz content ranges from 4 to 64 wt. % and from 3 to 37 wt.%, respectively. Fluorapatite also fluctuates between 0 to 14 wt. %. Pyrite (up to 9 wt.%) is the common sulphide mineral, whereas sphalerite is recorded in some samples (up to 6 wt. %). Meanwhile, the mineralogical composition of the Dakhla oil shales, is represented by calcite (47-67 wt.%), phyllosilicates (22-32 wt.%), quartz (3-5 wt. %), fluorapatite (up to 3 wt.%), pyrite (4-6 wt.%) and sphalerite (up to 4 wt.%). Smectite is the most significant clay mineral within Duwi oil shales, varying from 80 to 97 wt. % with minor amounts of kaolinite (~ 3-20 wt.%). Whilst, Dakhla oil shales are characterized by dramatically decrease of smectite content (~59-7 wt.%), which are coincide with enhanced kaolinite contents (up to 93 wt. %). Based on detailed optical studies, chemical composition analysis of clay minerals and bulk geochemistry of shale, the majority of studied clay minerals were inherited from the parental basement material and eroded to marine environment (detrital origin), with minimal authigenic inputs. The relatively variation in mineralogy in both formations reflects changes in intensity of weathering and erosion sediment source under arid and humid climates, composition of source rock, the variable influx of terrigenous sediments into the Tethyan Ocean during high and low sea levels and oxygen availability.

DEBYE-EINSTEIN MODELS FOR HEAT CAPACITIES OF CRYSTALLINE SOLIDS

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Low temperature experimental data of the heat capacities of carbonates (e.g. BISSENGALIYEVA et al., 2012), molybdates (e.g. MORISHITA et al., 2016) and hollandites (WU et al., 2016) are assessed by means of semi-empirical models. Previous studies frequently present fit functions with a large amount of coefficients resulting in almost perfect agreement with experimental data. It is, however, demonstrated in this work by both local and global minimization tools that special care is required to avoid overfitting. The temperature dependent heat capacities are described by relatively simple Debye-Einstein integrals with sufficient accuracy. In case that experimental data below 50K are lacking heat capacities can be extrapolated reasonably well to lower temperatures, i.e. from 50K to absolute zero by the Debye-Einstein integral (GAMSJÄGER et al., 2016). It is suggested to establish the Debye Einstein integral fit as standard method to describe molar heat capacities in the low temperature range between almost 0K and 300K. Thereby, the derived thermodynamic functions are obtained on the same theory-related semi-empirical basis.

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EXPERIMENTAL RECONSTRUCTION OF BRONZE AGE CHALCOPYRITE SMELTING

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Since 2012 archaeo-metallurgical experiments are conducted within the FZ HiMAT research program (History of Mining Activities in the Tyrol and adjacent areas – impact on environment and human societies, University of Innsbruck) with the aim to reconstruct Bronze Age smelting techniques by employing traditional methods from the Himalaya region, Nepal. Starting point are well documented archaeological records of Bronze Age copper ore smelting sites in the Eastern Alps (GOLDENBERG, 2004), ethno-archaeological records of contemporary copper ore smelting in Nepal (ANFINSET, 2011) and mineralogical analysis of smelting products. The applied method combines the knowledge of the involved disciplines in order to approach as close as possible the reconstruction and reproduction of Bronze Age smelting technologies.

Smelting and roasting experiments were performed during several workshops in Jochberg, North Tyrol. The camp locality has been chosen because of its original situation in the midst of a Bronze Age copper ore mining and smelting district. In preparation of the experiments local copper ores from historic mining dumps were collected. The smelting hearth (rather than furnace) was set with local stones and completely covered interiorly with clay. Several portions of the ore concentrate (chalcopyrite + pyrite + quartz) were smelted with charcoal, using two leather bellows, each one attached to a bended tuyère. The aim of the first smelting was to produce matte. The matte was grinded into powder with stone tools and mixed with cow/horse dung. Pellets of this mixture were roasted in an open wood fire (roasting hearth, about 2 hours) and then left over night until the ongoing reaction was completely terminated and the material showed a dark red colour as a sign of successful roasting. The roasted matte was then smelted again with charcoal under the tuyères in order to obtain copper like it happens in Nepal. To date, this last step of the process could not be reproduced in a satisfying manner during the experiments. To identify the reasons for the failure the products from the experiments as well as from the Nepalese smelting process are analysed and compared using microscopy, RDA and electron microprobe analysis. The results of the experiments are presented in this paper, which also raises the issue of how several methodological approaches may be combined in order to better understand ancient copper smelting technology. (Project funding: Tyrolian Science Fund, TWF, Austrian Science Fund, FWF).

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MAGMATIC CHROMIAN SPINEL IN METABASITE FROM THE LATIMOJONG MOUNTAINS, SULAWESI, INDONESIA

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In metavolcanic rocks of the Latimojong Mountains, central Sulawesi, Indonesia, chromian spinel spans a wide compositional range in Cr/(Cr+Al). Spinel occurs in the matrix of metamorphic silicates (Chl+Act+Pmp) and as inclusions in magmatic clinopyroxene phenocrysts (Fig. 1). Two types of chromian spinel are observed in metabasites and volcaniclastic rocks, including (i) high-Al chromite (100xCr/(Cr+Al) = 40 – 60) and (ii) high-Cr chromite (100xCr/(Cr+Al) > 70). The values for 100xFe/(Mg+Fe) range from 32 to 52, and TiO_2 concentrations vary from 0.1 to 1.7 wt.%.

Based on the spinel compositions obtained from electron microprobe (EMPA) analyses, it is inferred that the Cr-rich chromites within mafic metavolcanic rocks are derived from a suprasubduction zone (SSZ) environment, whereas Al-rich chromite formed in a mid-ocean ridge (MORB) setting (ZHOU & ROBINSON, 1997). The chromian spinels may have originated from different tectonic settings that were later amalgamated in one region. These results are confirmed by analysis of clinopyroxene showing that parent magmas were generated in IAB and MORB environments. The Cl-chondrite normalized REE patterns of metabasite and volcaniclastic rocks are flat, similar to MORB.

Alternatively, chromian spinel may have crystallized from a single batch of magma, but at different stages of fractional crystallization. Growing clinopyroxene phenocrysts in a MORB-type melt trapped floating chromite crystals that developed through time to progressively more-Al depleted compositions and forming chromite of higher #Cr. In the example illustrated below, Al-rich chromite may have been trapped in the clinopyroxene rim by turbulent magma movement where cumulus material has been brought up from deeper parts of the chamber (Fig. 1).

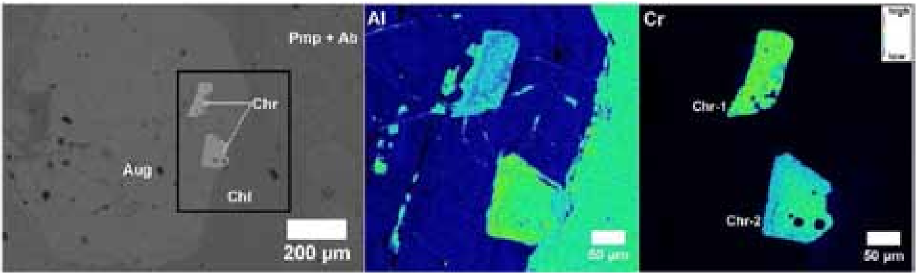

Figure 1. Quantitative element map of chromian spinel hosted by clinopyroxene in metabasite. Area on the left image is enlarged in the Al and Cr element maps. Chr-1 has 13 wt% Al_2O_3, 0.14 wt% TiO_2, 51 wt% Cr_2O_3; Cr# of 73; in contrast, Chr-2 has 18.5 wt% Al_2O_3, 0.7 wt% TiO_2, 38.9 wt% Cr_2O_3, Cr# of 59.

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NoScale - CHARACTERISATION OF THERMAL DEEP GROUNDWATER FOR THE PREVENTION OF SCALING AND CORROSION IN GEOTHERMAL PLANTS

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During the exploitation of thermal water for the use in a geothermal plant a series of hydrochemical reactions such as solution and precipitation processes (scaling) or corrosion processes can be caused by pressure and temperature changes and degassing of the thermal water. Operators of hydrogeothermal plants are often confronted with precipitations in water-bearing parts of their plant, such as heat exchangers and pipes, which result in considerable costs for cleaning or remediation or the use of inhibitors. In the worst case, scaling and corrosion can lead to the abandonment of the system. The effects of the fluids on the technical facilities of hydrogeothermal plants are usually difficult to predict. This applies in particular to the long-term effects in the exploitation and use as well as the aspect of the reinjection of the fluids. In publications and guides for thermal water use in Austria, it is emphasized that the hydrochemical conditions have to be checked during the operation of geothermal plants, but precise directives and thus guidance for operators as well as a scientific investigations on this topic are almost completely missing today. The aim of the research project NoScale was the assessment of deep thermal water bodies in different geological reservoirs in Austria and Bavaria and therefore different hydrochemical compositions with regard to their scaling and corrosion potential in geothermal use. In the course of parallel chemical and mineralogical laboratory investigations, conclusions were drawn about the effects of thermal water on different technical components of hydrogeothermal plants and on the other hand a data basis for the model simulation of the relevant hydrochemical processes was developed. Subsequently, on the basis of detailed hydrochemical model calculations, possible effects of the use of the thermal waters on the technical components of the geothermal plants were shown. This approach of complex process modeling, detailed laboratory studies and experimental approaches has not been followed in Austria so far. The research results contribute significantly to the increased visibility of potential risks of the exploitation and use of thermal water. Thus, the project NoScale supports the operators of hydrogeothermal plants to assess risks of scaling in corrosion already in the pre-drilling phase, which leads to a much more energy and cost efficient operation.

CONTRASTING LOWER CRUSTAL PROCESSES DOCUMENTED IN GRANULITES FROM THE EAST AFRICAN OROGEN AND THE BOHEMIAN MASSIF

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Deeply eroded orogens such as the East African Orogen (EAO) and the Variscan Orogen offer the unique opportunity to study lower crustal processes documented by mineral assemblages and textures, chemical zoning of major and trace elements in minerals, especially garnet, as well as different styles of deformation. HARLEY (1989) presented a detailed compilation of granulite occurrences, PT conditions and differing PT-paths as well as documented the differences in granulites experiencing isobaric cooling (IBC) or isothermal decompression paths (ITD). These contrasting PT paths are typically the result of different tectonic settings and processes.

In the last 25 years ultra-high temperature (UHT) metamorphism has been recognised within more and more granulite facies domains, such as the Saxon and Moldanubian granulites. PERRAKI & FARYAD (2014) postulated an ultra-high pressure stage prior to the UHT overprint based on Grt-peridotite and eclogite occurrences, preserved prograde garnet zoning pattern as well as the finding of diamond and coesite in zircon and garnet, respectively, in the investigated granulites from the Kutna Hora Massif.

Recent work in granulites from the Dunkelsteinerwald, St. Leonhardt and Blumau granulites also points to a possible UHP event before UHT metamorphism followed by a retrograde, locally occurring granulite facies overprint at lower PT conditions as well as hydration of the former dry granulites. Well preserved zoning pattern in felsic and mafic granulites are a clear evidence that the UHT event and probably also the prior occurring UHP event are extremely short lived processes. Based on available age data, zoning pattern and field relationships a time span of about 5 million years is proposed for the UHP and UHT cycles.

In contrast to the short lived granulite facies metamorphic event documented in Saxon and Moldanubian granulites, lower crustal basement rocks from the East African Orogen exhibit partly extremely slow cooling processes of 1-5 °C/my. The EAO is a complex collage of collisional belts involving different orogenic phases and metamorphic overprints starting from around 750 Ma and ceasing around 530 Ma. The granulite facies rocks are exposed in parts of Kenya, Tanzania, Mozambique, Malawi, Madagascar, Sri Lanka, Southern India and Antarctica. The commonly occurring charnockitic and enderbitic gneisses in S-Kenya and Tanzania developed typical coarse grained corona textures during the slow cooling period. In all rocks prograde garnet zoning patterns in major elements are erased while retrograde diffusional modification is widely observed. Detailed 2D mapping of Fe-Mg distribution within garnet and along grain boundaries and neighbouring grains revealed that diffusion along grain boundaries was hampered probably due to the very dry conditions during the high grade event. Trace element diffusion in garnet is considered to be significantly slower compared to major element mobility and thus these elements are useful for defining the metamorphic evolution.

HT/UHT metamorphism as well as slow cooling from these conditions aggravates the reconstruction of a full PT-path and consequently the understanding of the liable tectonic framework. Petrological modeling tools combined with information from relict phases and trace element distribution between phases as well as changes during mineral growth my reveal parts of the obscured prograde history in granulite facies rocks.

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MINERALOGY STUDY IN THE NWF-PROJECT “RUSTY IRON”

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The restoration of iron is a very complex part of the archaeological restoration studies. From the time of the recovery, and the associated change in environmental parameters, decay occurs. The experience of the Archaeology Institute from the University Innsbruck has shown, that proper storage from metals after recovery and desalination with sodium sulphite is not enough for minimizing the damage of the archaeological objects. The goal of this NWF (Nachwuchsförderung) project is the careful mineralogical characterization of artefacts and the development of a fast and controlled workflow beginning at the transfer of the find and its initial treatment up to conservation measures. The focus of the mineralogical investigations is on the occurrence of Cl-bearing phases. The reason for this is the formation of the rust-phase “akaganeite”. Akaganeite, β-FeOOH(Cl) forms in presence of chloride and low pH (STÅHL et al., 2003). It forms rust coatings and loose coverings on the archaeological objects (KELLER, 1969). In our study, we characterized the mineral assemblage of an artefact by wavelength-dispersive electron microprobe analysis and Raman-Spectroscopy. Fig. 1 shows a backscattered electron (BSE) image and a Cl-map of part of a cross section of a nail. At the border from an “inner area” (iron core) and “outer area” akaganeite can be found. These investigations in turn provide the basic data for further experimental investigations.

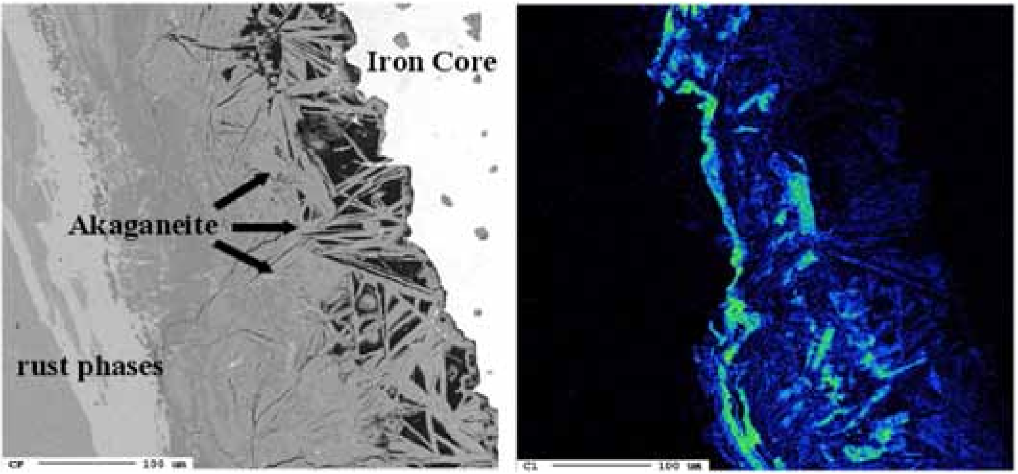

Figure 1. BSE image (left) and Cl-map (right) of a nail.

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LOW-TEMPERATURE BEHAVIOUR OF $K_2Sc[Si_2O_6]F$: DETERMINATION OF THE LOCK-IN PHASE AND ITS RELATIONSHIPS WITH FRESNOITE- AND MELILITE-TYPE COMPOUNDS

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A new (3+2)-dimensional incommensurately modulated (IC) structure has been recently described for $K_2Sc[Si_2O_6]F$ in superspace group $P4_2/mnm(\alpha,\alpha,0)000s(-\alpha,\alpha,0)0000$ with a = 8.9878(1), c = 8.2694(2) Å, V = 668.01(2) Å^3, modulation wave vectors $\mathbf{q_1}$ = 0.2982(4)(**a***+**b***) and $\mathbf{q_2}$ = 0.2982(4)(**-a***+**b***) (HEJNY et al., 2016). In the structure, $[ScO_4F_2]$ octahedral chains and $[Si_4O_{12}]$ rings are interconnected to form a mixed octahedral-tetrahedral framework where large open voids are filled with K in variable coordination ranging. The structure of $K_2Sc[Si_2O_6]F$ is related to that of the melilite- and fresnoite-type compounds, $X_2Z[T_2O_7]$ and $X_2Z[T_2O_8]$, respectively (BINDI et al., 2006). Although melilite- and fresnoite-type compounds have a different structure with layers of $[Si_2O_7]$ dimers and layers of large X cations, they display remarkable similarities to $K_2Sc[Si_2O_6]F$, i.e. (1) tetragonal symmetry with two modulation wave vectors $\mathbf{q_1} = \alpha(\mathbf{a^*}+\mathbf{b^*})$ and $\mathbf{q_2} = \alpha(-\mathbf{a^*}+\mathbf{b^*})$ with α being an irrational value, (2) a modulation-dependant variability in the coordination of a large cation, (3) similar behaviour of corresponding inter-tetrahedral angles and (4) the observed high- and low-temperature behaviour. As concerns point (4), it is remarkable that all of the above mentioned structures transform to the so called normal structure N (a commensurate structure equivalent to the average structure of the modulated structure) with increasing temperatures. On temperature decrease, an increase of the modulation wave-vectors with a subsequent lock-in phase transition has been observed for Co- and Zn-åkermanite (SAZONOV et al., 2015). In order to search for an equivalent lock-in phase for $K_2ScSi_2O_6F$ the low-temperature behaviour has been studied by single-crystal X-ray diffraction. Up to 45 K the irrational component α of the modulation wave-vectors is quite constant varying from 0.2982(4) (RT), throughout 0.2955(8) (120 K), 0.297(1) (90 K), 0.298(1) (75 K), to 0.299(1) (45 K). At 25 K it approaches the commensurate value of 1/3 [i.e., 0.332(3)], thus indicating that the incommensurate-commensurate phase transition takes place between 45 K and 25 K. The commensurate lock-in phase of $K_2Sc[Si_2O_6]F$ has been solved and refined with a 3 × 3 × 1 supercell compared to the tetragonal incommensurately modulated structure stable at room temperature. This corresponds to a 3 × 1 × 3 supercell in the monoclinic, pseudo-orthorhombic setting of the low-temperature structure, space group $P2/m$, with lattice parameters a = 26.786(3), b = 8.245(2) c = 26.824(3) Å, α = 90.00(1)°.

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CHEMICAL GARNET ZONATION: A COMMON CHARACTERISTIC OF THE UPPER AUSTROALPINE MILLSTATT COMPLEX AND LAAS UNIT

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Garnets from micaschists of the northwestern Texel Complex west of the Tauern Window, usually known as Laas Unit, show a distinct garnet zonation pattern with a grossular rich plateau-like core overgrown by a grossular poor rim (HEINISCH, 2014). This “Laas type”- pattern is in close accordance with zonation patterns from the Millstatt Complex east of the Tauern Window (CIRIELLO, 2017), fitting well to a common tectonometamorphic evolution of the Millstatt Complex and Laas Unit before formation of the Tauern Window in the Oligocene (KRENN et al., 2011). Both complexes experienced eo-Alpine staurolite facies metamorphism but additionally an earlier Permian metamorphism is concluded from the frequent occurrence of Permian pegmatites.

“Laas type” zonation patterns are also observed in garnets from the southern Ötztal Complex north of the Laas Unit and Schneeberg Synform where decreasing eo-Alpine metamorphic conditions below staurolite stability are evident (HOINKES, 1981). However, in this region the “Laas type”- garnet patterns exhibit an additional outermost discontinuous rim zone starting with a grossular-rich composition which continuously decreases towards the outermost rim. This feature was already interpreted by PURTSCHELLER et al. (1987) as an eo-Alpine garnet generation overgrowing pre-Alpine garnets and fits to dated garnet zonation patterns in micaschists of eo-Alpine greenschist facies grade below staurolite stability from the northern Wölz Complex east of the Tauern Window (SCHUSTER & FRANK, 1999).

The “Laas type”- garnets from the southern Ötztal Complex were observed in micaschist layers incorporated in steep vertical fold structures connecting the southern Ötztal Complex with the northern Texel Complex (Laas Unit) and possibly represent micaschists of the Laas Unit. This interpretation is supported by Permian monazite-ages obtained from the same micaschists of the southern Ötztal Complex (HEINISCH et al., 2015).

The absence of an eo-Alpine growth zone in garnets from the Northern Texel Complex (Laas Unit) and the Millstatt Complex may be explained by eo-Alpine staurolite formation on the account of pre-Alpine garnet. The stepped texture of the pre-Alpine “Laas Type” zonation pattern may indicate a two-stage formation most probably due to a change of garnet producing reactions in course of Permian and/or Variscan (?) metamorphism. However, the exact interpretation of the pre-Alpine metamorphic history needs support by further age dating.

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THE EFFECT OF WATER ON THE FLUORINE PARTITIONING BEHAVIOR BETWEEN OLIVINE AND SILICATE MELT, FLUORINE CONCENTRATIONS AND F/H_2O RATIOS DURING PARTIAL MELTING IN THE UPPER MANTLE

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Halogens show a range from moderate (F) to highly (Cl, Br, I) volatile and incompatible behavior, which makes them excellent tracers for volatile transport processes in the Earth’s mantle.

In this study, we investigated experimentally the effect of small amounts of water on the F and Cl partitioning behavior between olivine and melt at 1280°C and 0.3 GPa. Results show that there is, within uncertainty, no effect of water on the chlorine partitioning behavior for bulk water contents ranging from 0.03 to 0.33 wt% H_2O ($D_{Cl}^{ol/melt} = 2.2\ (11) \cdot 10^{-4}$). In contrast, fluorine partition coefficients increase linearly in this range and may be described with $D_F^{ol/melt} = 3.6(4) \cdot 10^{-3} \cdot X_{H2O}$ (wt%) $+ 6(4) \cdot 10^{-4}$.

Our findings are consistent with the formation of clumped OH/F defects in forsterite (Crépisson et al. 2014), which increase the defect stability compared to solely hydrolytic weakening and thus the partitioning of fluorine into olivine.

Results of this study further imply that water may have a strong effect on estimates of OIB source fluorine concentrations and fluorine recycling rates in subducting slabs.

Beyer et al. (2016) suggested that multiple episodes of small degree partial melting are required to generate magmas with a high F/H_2O ratio between 0.1 and 0.9 in the upper mantle. Our results indicate that addition of small amounts of water to a dry peridotitic system may potentially lead to a significantly stronger increase in the F/H_2O ratio of the residue during a single small degree partial melting event. Thus, the effect of water on the F partitioning behavior may explain the generation of high F/H_2O ratios and high F concentrations in the upper mantle without the requirement of multiple partial melting episodes.

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STRUCTURAL REINVESTIGATION OF BENTORITE

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Bentorite, with idealized formula $Ca_6Cr_2(SO_4)_3(OH)_{12}\cdot26H_2O$, a Cr-analogue of ettringite, was accepted as valid mineral species by IMA in 1980. However, its crystal structure was never investigated. The only report on this mineral (GROSS, 1980) states that the powder diffraction pattern of bentorite was satisfactorily indexed from the analogy with ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O$. Therefore, the most probable unit cell is hexagonal *P6/mmc* with parameters a = 22.35 Å and c = 21.41 Å.

New bentorite crystals with dark violet colour were found in late low-temperature veins of spurrite rocks associated with ettringite and calcite. The rock specimen was found in pyrometamorphic rocks belonging to the Hatrurim Complex and collected in Arad Stone quarry in the Negev Desert, Israel. The main rock-forming minerals are spurrite, shulamitite-sharyginite, brownmillerite, ye'elimite and mineral of fluorapatite-fluorellestadite series. Baryte, gibbsite, hydrocalumite and sphalerite are accessory minerals.

A careful re-examination of single crystals from the Arad Stone quarry, was done using X-ray single crystal diffraction (SCXRD) on room and low temperature conditions (-100 °C). Bentorite is isostructural with ettringite. It crystallizes in the space group $P31c$ and have unit cell parameters a = 11.1825(8) Å, c = 21.5475(13) Å. Crystal structure was refined up to R = 4.3% starting from atomic coordinates of ettringite (MOORE & TAYLOR, 1970). The refined chemical composition of our crystal $Ca_6(Cr_{1.681}Al_{0.319})(SO_4)_3(OH)_{12}\cdot26(H_2O)$, matches the chemical analysis of bentorite reported by GROSS (1980).

Moreover, a stepwise substitution of Al^{3+} by Cr^{3+}, was found in ettringite crystals from Ma'ale Adummim in Palestinian Autonomy. This hexagonal prismatic crystals show distinct colour zoning from dark violet over pale rose to transparent. For the purpose of SCXRD investigation, they were cut in three parts, or rather three zones along c-axis. Full crystal structure refinements of all three crystals (zones) resulted in different chemical compositions. The colourless basis of the crystal has average chemical formula $Ca_6(Al_{1.602}Cr_{0.398})(SO_4)_3(OH)_{12}\cdot26(H_2O)$ with 20% Cr^{3+} and 80% Al. Intermediate part has 32% Cr + 68% Al or $(Al_{1.355}Cr_{0.645})$. Finally the top of the crystal has ≈ 60% Cr and 40% Al and average chemical formula $Ca_6(Al_{0.821}Cr_{1.179})(SO_4)_3(OH)_{12}\cdot26(H_2O)$.

The substitution of Al^{3+} in ettringite by Cr^{3+} could have important implication in wastewater treatment technology. Thus, formation and temperature stability of Cr^{3+}- bearing ettringite were investigated by WIECZOREK-CIUROWA et al. (2001).

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SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY OF $Cs_2Er[Si_6O_{14}]F$ AND $Cs_2Er[Si_4O_{10}]F$

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Single-crystal growth experiments in the system CsF-Er_2O_3-SiO_2 resulted in the simultaneous crystallization of two chemically related compounds within the same run: $Cs_2Er[Si_6O_{14}]F$ (phase I) and $Cs_2Er[Si_4O_{10}]F$ (phase II). They represent the first examples for cesium erbium silicates containing fluorine.

Basic crystallographic data of the two structures at ambient conditions are as follows: phase I: space group *Cmca*, a = 17.2556(6) Å, b = 24.6565(7) Å, c = 14.4735(5) Å, V = 6157.9(3) Å^3, Z = 16; phase II: space group *Pnma*, a = 22.3748(7) Å, b = 8.8390(2) Å, c = 11.9710(4) Å, V = 2367.5(1) Å^3, Z = 8. The structures were determined by direct methods and refined to residuals of $R(|F|)$ = 0.0229 for 2920 (phase I) and 0.0231 for 2314 (phase II) independent observed reflections with $I > 2\sigma(I)$.

The structure of phase I forms a three dimensional tetrahedral framework consisting of Q^3 and Q^4 groups in the ratio 2:1. Basic building units of the network are unbranched *sechser* single-chains running parallel to [001]. The network can be conveniently built up from the condensation of tetrahedral layers parallel to (010) or (100), respectively.

The crystal structure of phase II can be classified as a *tubular* or *columnar* chain silicate indicating that the backbones of the structure are multiple chains of silicate tetrahedra. The multiplicity of the loop-branched chains is two. The periodicity of the chains has a value of four which is also reflected in the translation periods parallel to the chain direction: $t_{[010]}$ = 8.839 Å.

Alternatively, both compounds can be described as mixed octahedral-tetrahedral frameworks, which can be classified according to their *polyhedral microensembles*. A topological analysis of both nets is presented.

REFINEMENT OF IRON ORE SINTER PHASES: A SILICO-FERRITE OF CALCIUM AND ALUMINIUM (SFCA) AND AN AL-FREE SFC, AND THE EFFECT ON PHASE QUANTIFICATION BY X-RAY DIFFRACTION

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Iron ore sinters are produced by adding lime to fine-grained iron ore and reacting these at temperatures of ~1250°C, by propagating a flame through a bed of intimately mixed ore, lime and carbonaceous char. The sinters are the preferred feedstock for the production of iron in blast furnaces and millions of tons are produced worldwide each year. The sintering reaction takes place at the flame front and redox conditions vary from reducing at the flame to oxidizing during cooling.

Silico-ferrite of calcium and aluminium (SFCA) is an important binding phase that imparts improved strength and reducibility to the sinters produced from iron ores containing variable amounts of Fe, Al, Mg, and Si. As a result the SFCA is variable in its composition and variable in its proportions in the sinters.

The amounts of the different phases, mainly hematite, magnetite, SFCA and a dicalcium silicate are contributing factors to a number of important sinter properties such as extent of sintering, tumble index (strength) and reduction index (reducibility) and are also indicators of temperature and redox conditions during sintering. Phase quantification by powder X-ray diffraction methods is therefore an important method for the correlation of the phase quantities with the different indices. Reliable phase quantification using the Rietveld method is dependent on accurate crystal structure data for the constituent phases being available from the literature for all the phases.

It was however found that the calculated diffraction pattern of SFCA using crystal structure data from HAMILTON et al. (1989) and used by the programme Autoquan (KLEEBERG & BERGMANN 2002) differs substantially from the observed pattern of pure synthesized material. Especially, the calculated peaks at low angles are significantly overestimated as compared to the experimental peaks.

To resolve this discrepancy it was decided to re-investigate the structure of SFCA. Also, because of the complex cation distribution of SFCA, containing Fe, Ca, Mg, Al and Si on 15 different cation sites, it was deemed necessary to include also a structure analysis of SFC, which contains only Fe, Ca, and Si, as this would simplify the allocation of cations on the various sites considerably. The present contribution reports the results of these investigations.

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THE SYSTEM Na_2O-CaO-SiO_2: 90 YEARS OF RESEARCH, BUT DO WE REALLY KNOW EVERYTHING ?

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In their landmark paper from 1925 MOREY & BOWEN presented the first comprehensive description of the phase relationships and melting behavior of the compounds belonging to the ternary system Na_2O-CaO-SiO_2. Due to its fundamental importance for many fields of industrial inorganic chemistry and technical mineralogy this system has been in the focus of a large number of subsequent studies dealing with both basic and applied aspects of silicate science (SEGNIT, 1953; SHAHID & GLASSER, 1971; WILLIAMSON & GLASSER, 1965; ZHANG et al., 2011). After more than 90 years of research activities one should assume that no problems remain to be solved.

In the course of an ongoing project on the high-temperature chemistry of compounds in the systems M_2O-RO-SiO_2 (M: Na, K; R: Ca, Sr, Ba) we realized that even for the most intensively studied Na-Ca-silicates suspicion has to be attached not only to what concerns their melting characteristics but also to what concerns the number of existing phases. Despite the compounds whose existence has been unequivocally proofed by a combination of chemical analysis and crystal structure determination there is still a large number of phases mentioned in the literature which, at best, have been characterized by unindexed powder diffraction patterns. Furthermore, in many cases even the compositions have not been thoroughly studied after synthesis. This information, however, is definitely of great importance when dealing with volatile components such as Na_2O or K_2O at temperatures above 1000°C.

We were able to demonstrate that $Na_2Ca_6Si_4O_{15}$, for example, which has been first synthesized via hydrothermal methods by ARMBRUSTER & RÖTHLISBERGER (1990) can be also obtained under dry conditions using Na_2CO_3, $CaCO_3$ and SiO_2 as educts. Therefore, the ternary phase diagram, where this compound has not been taken into consideration, has to be revised. In-situ high-temperature powder diffraction experiments were used to determine the thermal expansion tensor of $Na_2Ca_6Si_4O_{15}$ between ambient temperature and 1100°C. Furthermore, the crystal structure of a new high-temperature polymorph of the compound has been determined.

Finally, comprehensive synthesis experiments using solid state reactions as well as re-crystallization studies from glasses revealed that several previously described sodium calcium silicates such as $Na_8Ca_3Si_5O_{17}$, $Na_2Ca_3Si_2O_8$ and $Na_2CaSi_5O_{12}$ could not be reproduced indicating that a question mark has to be put on their existence.

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SYNTHESIS, SYNCHROTRON DIFFRACTION STUDY AND TWINNING IN $Na_2Ca_4Mg_2Si_4O_{15}$ – A HETEROPOLYHEDRAL FRAMEWORK COMPOUND

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The formation of polycrystalline $Na_2Ca_4Mg_2Si_4O_{15}$ from solid state reactions has been studied between 800 and 1050 °C. Single crystals of the compound have been grown in a closed platinum capsule by slow cooling in the temperature range between 1300°C and 1000°C. Basic crystallographic data are as follows: monoclinic symmetry, space group $P12/c1$, a = 7.1717(3) Å, b = 5.3512(2) Å, c = 16.4789(7) Å, β = 90.911(4)°, V = 632.33(4) Å^3, Z = 2.

A conspicuous feature of the crystals is an intensive lamellar non-merohedral twinning clearly observable already under a petrographic microscope. The diffraction pattern can be explained as a superposition of two reciprocal lattices with a two-fold axis parallel to [001] being the twin element. Using synchrotron radiation (X06DA beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland) it was possible to solve the crystal structure of $Na_2Ca_4Mg_2Si_4O_{15}$ from a twinned data set. Least-squares refinements resulted in a residual of R(|F|) = 0.031 for 2899 observed reflections with $I > 2\sigma(I)$ and 127 parameters. The crystal structure contains both [Si_2O_7]-dimers and insular [SiO_4]-moieties. Tetrahedra and [MgO_6]-octahedra form a three-dimensional framework whose topological characteristics have been studied. The remaining calcium and sodium cations are distributed among four crystallographically independent positions located in voids of the network.

On a microscopic scale the twinning observed in the diffraction experiments could be explained by the existence of 2_1-screw axis parallel to [001] in (¼,0,z) mapping both domains onto each other. A comparison with related compounds having an $A^+_2B^{2+}_6Si_4O_{15}$ stoichiometry is presented.

More than 25 years after its first observation in refractories (HAUSNER & SUPPANER, 1992) our investigation clarifies the crystal structure of a silicate that is of relevance for both Materials science and high pressure research (BINDI et al., 2015).

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MICROSTRUCTURE AND PHYSICAL PROPERTIES OF THERMALLY SPRAYED MULLITE BARRIER COATINGS

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Chemistry, structure and thermal diffusivity of thermally sprayed mullite coatings with a thickness of about 0.5 mm were investigated by scanning electron microscopy with energy-dispersive X-ray spectroscopy, ex- and in-situ X-ray diffraction from room temperature up to 800 °C and by laser flash method up to 600 °C. The bulk composition of the coating is close to the pristine powder and to stoichiometric 3/2- ($3Al_2O_3{\cdot}2SiO_2$) mullite. Individual splats are variable in their aluminum to silicon ratios and contain traces of calcium and iron. The XRD diffractogram of the as-deposited coating fitted best with a 3/2-mullite with the composition $Al_{4.9}Si_{1.1}O_{9.6}$ beside cubic γ-Al_2O_3 and a pronounced amorphous phase. In-situ high-temperature XRD analysis up to 800 °C showed the appearance of minor amounts of an unidentified crystalline phase at the highest temperature. The amorphous fraction displays almost no changes during the experiment. The thermally induced lattice expansion is around 2.6% for the lattice constants a and b and 7% for c, accompanied with a decreasing crystallite size from about 70 to 40 nm. The thermal conductivity λ of the coatings changes between 2.75 and 3.02 $W{\cdot}(m{\cdot}K)^{-1}$ in the temperature range 20 - 600 °C. This is significantly lower than for single crystal and dense mullite ceramics. Such extremely low values can be achieved by both increasing the porosity, number of microcracks and fraction of the amorphous phase and reducing the grain size and coating thickness.

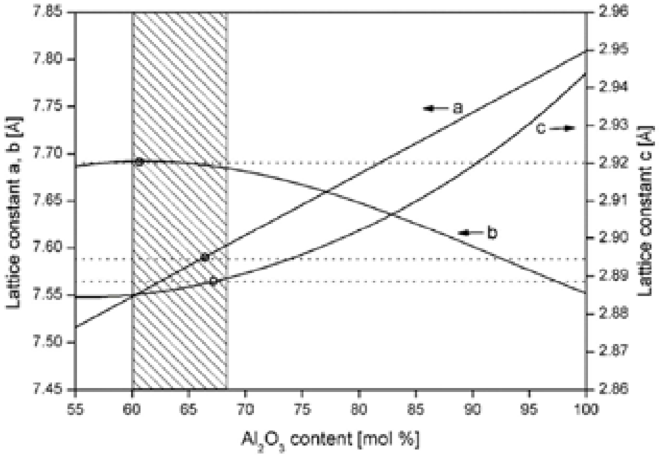

Figure 1. Lattice parameters of the compositional series $Al_2(Al_{2+2x}Si_{2-2x})O_{10x}$ versus Al_2O_3 content.

PETROLOGY AND GEOCHEMISTRY OF APATITE ± WHITLOCKITE-BEARING MANTLE XENOLITHS FROM SOUTHERN LAOS

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Cenozoic basalts are widespread throughout Southeast Asia and form what is called a “diffuse igneous province (HOANG et al., 2013) mostly consisting of shield-building tholeiites that may be replaced by late-stage and small-volume alkali basalts, the latter often containing mantle xenoliths together with sapphire and/or zircon megacrysts. Here we report the results of a petrological and geochemical study of a suite of spinel-lherzolites and ortho/clino-pyroxenites sampled by nepheline±leucite-bearing alkali basalts of the Bolaven Plateau/southern Laos. Both lherzolites (ol+opx+cpx+sp+FeNi-sulfide) and pyroxenites (opx+cpx+FeNi-sulfide) in part show evidence for cryptic or modal metasomatism characterized by a strong enrichment of Li in cpx and opx with respect to ol (cryptic) and by the appearance of apatite rarely associated with minor phlogopite ± calcic amphibole. Two compositional types of apatite are present: (1) apatite characterized by low P_2O_5 (37.9-41.0 wt%) and low analytical totals (93.8-97.4 wt%) combined with high Na_2O (0.9-1.6 wt%) indicative of a significant type-A carbonate-apatite component and (2) apatite with high P_2O_5 (40.5-42.4 wt%) and high analytical totals (97.7-100.9 wt%) combined with low Na_2O (0.3-0.7 wt%). In addition low-P_2O_5 apatites show a much more restricted range in F and Cl (0.2-0.9 wt% F, 0.6-1.6 wt% Cl) compared to high-P_2O_5 apatites (0.3-3.1 wt% F, 0.3-4.1 wt% Cl). One apatite-bearing sp-lherzolite sample contains trace amounts of whitlockite-merrillite solid solution $[Ca_{18}Mg_2(PO_4)_{12}[PO_3(OH)]_2\text{-}Ca_{18}Na_2Mg_2(PO_4)_{14}]$ (HUGHES et al., 2008) in addition to apatite + phlogopite + calcic amphibole. Whitlockite-merrillite is extremely rare in mantle rocks and has been known so far from only one locality in Siberia where its formation was ascribed to a distinct type of ±anhydrous REE-metasomatism (IONOV et al., 2006). In the sample from Laos, whitlockite-merrillite is always intergrown with apatite and was unambiguously identified using EMPA and micro-Raman spectroscopy. It contains 3.5-3.9 wt% MgO and 2.4-3.1 wt% Na_2O, respectively, which is very similar to values reported by IONOV et al., 2006. Thermometry of the apatite-(whitlockite-merrillite)-sample yields ~900-950°C for a pressure of 1.5 GPa.

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CONTINUOUS GROWTH STAGES OF MINERALS IN AN ALPINE CLEFT OF THE GLOCKNER NAPPE SYSTEM (TAUERN WINDOW, EASTERN ALPS)

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A large Alpine cleft was discovered 2012 in the Glocknerwand near Hoffmanspitze at 12° 41’06,2“ E, 47° 04’53,0“ N, 3575m sea level. The cleft mineralization hosts in prasinite interlayered by calcschists and consists of early quartz mobilisates (milky quartz) followed by large crystals of smoky quartz, covered by adularia+hematite+chlorite and finished by two calcite generations, a first rhombohedral and a late scalenohedral.

Fluid Inclusions (FIs) have been investigated from a quartz layer in prasinite host, milky quartz, smoky quartz and calcite. In prasinite quartz, aqueous FIs with additional solid inclusions like albite, rutile and magnesite, characterized by Raman spectroscopy, occur. FIs with eutectic temperatures (T_e) around -28°C homogenize to the liquid phase between 250-270°C. Data are in close relation to primary FIs with negative crystal shapes in smoky quartz with homogenization temperatures (T_h) between 248-272°C, showing some lower T_e around -22.0°C that is indicative for a dominant H_2O-NaCl±KCl±$MgCl_2$ system. Based on last ice melting temperatures (T_m) around -1.0°C, lowest salinities are observed. Rhombohedral calcite shows two groups of FIs, an early primary generation of negative rhombohedral shape with T_h from 240 to 250°C followed by a second generation of irregular shaped FIs arranged as clusters with T_h from 110 to 160°C. This second generation is related to latest crack healing (necking down) and associated with the growth of late scalenohedral calcite. Late stage fluid system is characterized by decreasing T_e around -40 to -45°C indicative for a more complex system like H_2O-NaCl-$MgCl_2$±$CaCl_2$. Total salinities are <3 mass% with NaCl/$MgCl_2$ = 0.7/0.3.

Considering fluid inclusion density isochores of all studied FIs, an increased geothermal gradient (≥45°C/km) is required as previously suggested for the metasediments of the Glockner Nappe System (e.g. DACHS, 1990). This high temperature evolutionary path is the effect of isothermal decompression from peak conditions (ca. 7kb/500°C) down to <2kb/~300°C, representing growth conditions of early mineral phases like smoky quartz and rhombohedral calcite. Late fluid overprint is linked to scalenohedral calcite growth and fluid re-equilibration in milky quartz as an effect of fracturing under isobaric cooling conditions near shallow (ca. 3km) crustal levels.

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ZUR ETYMOLOGIE DES VERMICULITS

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Vermiculit ~$Mg_2(Mg,Fe,Al)[(OH)_2|(Si,Al)_4O_{10}]\cdot Mg_{0.35}(H_2O)_4$ (monoklin; fide STRUNZ & NICKEL, 2001) ist ein bedeutendes Industriemineral und mannigfaltiger Gegenstand material- und erdwissenschaftlicher Forschung. Auch aus etymologischer Sicht ist das Mineral interessant, stellt es doch eines der wenigen dar, die direkt in Anlehnung an ein Tier benannt wurden (KRICKL, 2010). Eine Analyse der Literatur zeigt jedoch, dass bezüglich der Herleitung des Mineralnamens eine sehr weit verbreitete, feine Fehlinterpretation vorliegt: Sehr häufig und an prominenter Stelle der naturwissenschaftlichen (z.B. SCHRÖCKE & WEINER, 1981; LIBAU, 1985, FALBE & REGITZ, 1999; MARINI, 2007), etymologischen (z.B. LÜSCHEN, 1979; SENNING, 2007) und für SammlerInnen verfassten Literatur (z.B. ĎUD'A et al., 1997), erfolgt der Hinweis, dass sich der Name direkt vom lateinischen Wort *vermiculus* ableite – den Diminutiv zu *vermis* für *Wurm*. Dies erscheint auf den ersten Blick durchaus sinnvoll, da die Kristalle durch thermische Behandlung eine sehr charakteristische, würmchenförmige Expansion zeigen (siehe Abb. 1). Die scheinbar stimmige Ableitung wurde bereits sehr früh von namhaften und einflussreichen Autoren vertreten (z.B. DANA, 1837; WITTSTEIN, 1847; CRAIG, 1869) und folglich wenig hinterfragt. Bei gründlichem Studium der Erstbeschreibung offenbart sich jedoch die eigentliche Absicht des Autors, den Namen auf "*Vermiculor*" zurückzuführen, was er mit *"to breed or produce worms*" übersetzte (WEBB, 1824). Beim lateinischen *vermĭcŭlor* (*vermĭcŭlārī, vermĭcŭlātus sum*) handelt es sich um ein Deponens, das in antiken Texten zumeist im Sinne von *wurmig sein* verwendet wurde. Entgegen der heute verbreiteten Meinung geht der Name des Vermiculits folglich nicht auf ein Nomen, sondern ein Verb zurück und übersetzt sich gemäß der ursprünglich intendierten Bedeutung nicht zu "Würmchenstein", sondern "Würmer hervorbringender Stein".

Abb. 1. Thermisch expandierter Vermiculit zeigt häufig eine charakteristische "Würmchenform" – der Grund seiner Namensgebung (Bildbreite 2 cm).

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ARIEGILATITE, A NEW MINERAL WITH MODULAR STRUCTURE

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The new mineral ariegilatite $BaCa_{12}(SiO_4)_4(PO_4)_2F_2O$ (IMA 2016-100; GALUSKIN et al., 2017) was found in spurrite pyrometamorphic rocks of the Hatrurim Complex in the Negev Desert, near Arad City, Israel, associated with spurrite, calcite, brownmillerite, shulamitite, CO_3-bearing fluorapatite, brucite, fluormayenite-fluorkyuygenite, periclase, barytocalcite, baryte and another potentially new mineral $Ba_2Ca_{18}(SiO_4)_6(PO_4)_3(CO_3)F_3O$.
Single-crystal diffraction data was collected from a very small (≈ 30µm long) und highly fractured crystal using synchrotron radiation (X06DA, Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland). The crystal structure of ariegilatite was refined to $R1$ = 2.05% ($R\text{-}3m$, a = 7.1905(4), c = 41.251(3) Å, V = 1847.1(2) Å^3, Z = 3).
Ariegilatite is a (PO_4)-analogue of dargaite $BaCa_{12}(SiO_4)_4(SO_4)_2O_3$ (GFELLER et al., 2015). Therefore, it belongs to the arctite – nabimusaite group [arctite: $BaCa_7Na_5(PO_4)_6F_3$ (SOKOLOVA et al., 1984), nabimusaite: $KCa_{12}(SiO_4)_4(SO_4)_2O_2F$ (GALUSKIN et al., 2015)].
This group is characterized by modular structures containing single $\{[WB_6](TO_4)_2\}$ or triple $\{[W_3B_{12}](TO_4)_4\}$ anti-perovskite layers intercalated with single $A(TO_4)$ layers, where A = Ba, K, Sr...; B = Ca, Na...; T = Si, P, V^{5+}, S^{6+}, Al...; $W = O^{2-}, F^{-}$.
The structure of ariegilatite can be described as a 1:1 stacking of the two modules $\{Ca_{12}(SiO_4)_4F_2O\}^{4+}$ and $\{Ba(PO_4)_2\}^{4-}$ along (001). The stacking type of nabimusaite (arctite) (3:1 type) is defined by intercalation of three $[Ca_{12}(SiO_4)_4O_2F]^{3+}$ modules with inserted modules of $[K(SO_4)_2]^{3-}$.

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A POTENTIALLY NEW MINERAL WITH A MODULAR STRUCTURE BASED ON ANTIPEROVSKITE LAYERS

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The potentially new mineral $Ba_2Ca_{18}(SiO_4)_6(PO_4)_3(CO_3)F_3O$ was found in spurrite pyrometamorphic rocks of the Hatrurim Complex in the Negev Desert, near Arad City, Israel, associated with spurrite, calcite, brownmillerite, shulamitite, CO_3-bearing fluorapatite, brucite, fluormayenite-fluorkyuygenite, periclase, barytocalcite, baryte and the recently accepted new minerals ariegilatite $BaCa_{12}(SiO_4)_4(PO_4)_2F_2O$ and stracherite $BaCa_{12}(SiO_4)_2[(PO_4)(CO_3)]F$ (GALUSKIN et al., 2017a, b).

Single-crystal diffraction data was collected using synchrotron radiation (X06DA, Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland). The crystal structure was refined to $R1 = 7.5\%$ ($R\text{-}3m$, $a = 7.12546(11)$, $c = 66.2902(13)$ Å, $V = 2914.78(9)$ Å^3, $Z = 3$).

The structure of the 'new' mineral can be described as a stacking of three different modules along (001): six layers of $\{Ba(PO_4)_{1.5}(CO_3)_{0.5}\}^{3.5-}$, three triple antiperovskite (AP) layers $\{(F_2OCa_{12})(SiO_4)_4\}^{4+}$ and three single AP-layers $\{(FCa_6)(SiO_4)_2\}^{3+}$.

This entire group of minerals is characterized by modular structures containing single $\{[WB_6](TO_4)_2\}$ or triple $\{[W_3B_{12}](TO_4)_4\}$ anti-perovskite layers intercalated with single $A(TO_4)_2$ layers, where A = Ba, K, Sr...; B = Ca, Na...; T = Si, P, V^{5+}, S^{6+}, Al...; $W = O^{2-}$, F^-. Different combinations of modules along (001) result in different c-parameters (GALUSKIN et al., 2017c). Minerals with structures build by a 1:1 stacking of the single AP-layers and single $A(TO_4)_2$ layer have $c \approx 26$ Å. Triple antiperovskite layers intercalated with single $A(TO_4)_2$ layers result in $c \approx 41$ Å.

The structure of our 'new' mineral, with $c \approx 66$ Å, comprises modules of two other new minerals ariegilatite $BaCa_{12}(SiO_4)_4(PO_4)_2F_2O$ (IMA 216-100), with $c \approx 41$ Å, and stracherite $BaCa_6(SiO_4)_2[(PO_4)(CO_3)]_2F$ (IMA 2016-098), with $c \approx 26$ Å (GALUSKIN et al., 2017a, b).

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HIGH-PRESSURE BEHAVIOR OF KALSILITE-*O1* PHASE

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Several polymorphs of $KAlSiO_4$ are known to exist. The "$KAlSiO_4$-*O1*" phase is structurally closely related to the stuffed derivatives of tridymite, however, the topology of the Si/Al-ordered framework is different. The tridymite-framework exhibits UDUDUD rings whereas the framework of the "*O1*"-phase shows two different types of six-membered rings with UUDDUD and UUUDDD configuration that are occurring in a ratio of 2:1. A similar arrangement has been found in the structure of megakalsilite ($KAlSiO_4$; KHOMYAKOV et al., 2002) where the same two types of rings appear in a ratio of 1:3.

The crystal structure of the "*O1*"-phase has been solved and refined from synthesized material (GREGORKIEWITZ et al., 2008; KREMENOVIC et al., 2013). Recently, the first natural crystals of "KAlSiO4-*O1*" have been found in the pyrometamorphic rocks of the Hatrurim Complex, Negev Desert, Israel (KRÜGER et al., 2016).

In this study we present the high pressure (HP) behaviour of kalsilite, performing in-situ high-pressure single-crystal diffraction and Raman spectroscopic investigations in the diamond anvil cell on a natural grown crystal from ambient conditions up to 6.3 GPa. Raman spectra indicate a phase transition between 0.5 GPa and 1.6 GPa on pressure increase. On decreasing pressure the HP-phase was observed on pressures as low as 1.1 GPa. For the HP-phase full-intensity X-ray diffraction data collections have been collected at 1.1, 2.4, 3.0, 4.0 and 5.2 GPa.

In contrast to the HP-behaviour of trigonal kalsilite (GATTA et al., 2011) kalsilite-*O1* performs a HP-phase transition to a larger unit cell with lattice parameter $b_{HP} = 3 \times b_{LP}$ while maintaining monoclinic symmetry. The unit cell dimensions of HP kalsilite "*O1*"-phase at 5.2 GPa are a=15.277(4) Å, b=26.606(6) Å, c=8.1511(16) Å, β=90.18(2)°, V=3313(1)$Å^3$. The pressure induced structural phase transition in kalsilite "*O1*"-phase appears to be completely reversible.

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$Ca_3TiO_4Cl_2$: A NEW COMPOUND WITH FIVE-COORDINATED TITANIUM

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Single crystals of a new calcium oxochloro titanate were discovered as by-products in synthesis experiments using Ca_2Cl_2 as a flux. Analyses revealed, that small amounts of titanium were substituted by iron. Consequently, we performed more synthesis experiments in an iron-free environment and finally obtained $Ca_3TiO_4Cl_2$ as a powder (by solid state reaction), and as single crystals (flux synthesis in sealed Pt-capsules). The crystal structure was determined using X-ray, and refined using synchrotron radiation diffraction experiments (performed at X06DA, Swiss Light Source, Villigen). The compound crystallises in space group *Pnma*, (a = 10.6009(2), b = 3.9246(1), c = 16.3193(3) Å, Z = 4). The crystal structure was refined using 1153 unique reflections. A final fit of R_{obs} = 0.023 was obtained utilising 61 parameters.

The titanium atoms exhibit five-fold coordination polyhedra, which can be described as trigonal bipyramids: Distances are 1.89, 1.79, 1.88 to O1, O2, O3, and 2.01 Å to O4 (2×). The polyhedra are corner-linked (via O4) and form chains parallel to *b*. The structure exhibits a layered character, as sheets with chains and Ca-Cl layers alternate along *c*.

Within the iron-containing synthesis, we also found a monoclinic form of the compound, which was intergrown with the orthorhombic structure. However, the monoclinic cell could be indexed from the composite diffraction pattern, and the structure was solved. Lattice parameters are a = 16.79, b = 3.93, c = 10.56 Å, β = 102.5°, Z = 4, the space group is *C2/m*. The reciprocal lattices of the composite are related by the following transformation:

$\boldsymbol{a}_{mon}^* = \boldsymbol{c}_{or}^*$, $\boldsymbol{b}_{mon}^* = -\boldsymbol{b}_{or}^*$, $\boldsymbol{c}_{mon}^* = \boldsymbol{a}_{or}^* + \boldsymbol{c}_{or}^*/3$

The structures are closely related, and differences are caused by configuration and stacking sequence of the layers.

ON THE PHASE TRANSITIONS OF NASICON-TYPE $Na_3Sc_2(PO_4)_3$

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NASICON-type materials belong to the group of hetero-polyhedral framework compounds exhibiting ionic conductivity. These 'NAtrium Super Ionic CONductors' were first reported by GOODENOUGH et al. (1976) in consequence of a systematic exploration of cubic skeleton structures like pyrochlore and cristobalite-type carnegieite leading to the type material $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$. Nowadays, NASICONs are classified with the general formula $A_xM_2(XO_4)_3$ (A = Li, Na, K, Mg, Ca; M = Al, Sc, Y, Ti, Zr, V, Nb, Cr, Mn, Fe, Ga, In; X = Si, P, As, S). Due to their physical properties they gained interests as a solid electrolyte over decades, followed up by investigations as a potential insertion host for energy storage applications (JIAN et al., 2017).

The ionic conductivity is strongly symmetry correlated. Based on the pseudo-cubic, trigonal framework (ideally *R3c*) of the corner-linked MO_6 and XO_4 polyhedra three polymorphs are known for $Na_3Sc_2(PO_4)_3$, which exhibit up to now the highest sodium ion conductivity. The reversible states are (i) ionic insulator: monoclinic, low temperature α-phase below ~65 °C, (ii) ionic conductor: average rhombohedral, intermediate β-phase, and (iii) 'superionic' phase: rhombohedral, high temperature γ-phase above ~165 °C. All phase changes are induced by sodium ion order / disorder (COLLIN et al., 1986).

DSC measurements, Fig.1, show two distinct and smooth phase transitions (ΔT ~40 °C) at ~10 °C ($\alpha \rightarrow \beta$) and ~160 °C ($\beta \rightarrow \gamma$) during heating. On cooling the $\beta \rightarrow \alpha$ transition is faint, moreover, the unsteady signal from 65 to -20 °C indicates a second β'-type phase. On dT-PXRD patterns, Fig. 2, this temperature range is characterized by the presence of sharp and diffuse incommensurate reflections. The $\beta \rightarrow \gamma$ transition is evident by a discontinuous increase of the ***c***-axis and a small positive anomaly in the basal plane of the trigonal substructure. The general thermal expansion of $Na_3Sc_2(PO_4)_3$ is strongly anisotropic.

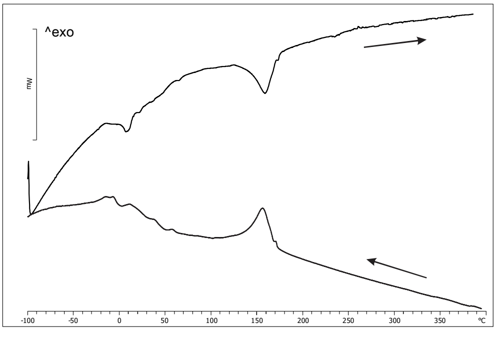

Figure 1. DSC curves of $Na_3Sc_2(PO_4)_3$, (-100 to 400 °C), heating (upper curve), cooling (lower curve).

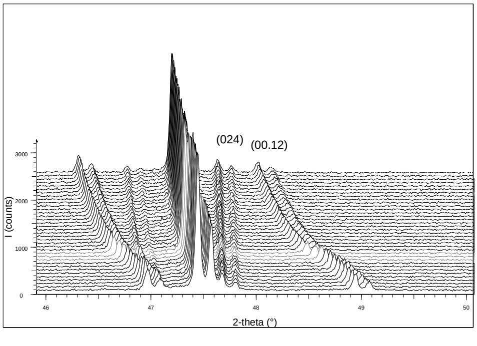

Figure 2. dT-PXRD of $Na_3Sc_2(PO_4)_3$, (50-400 °C), $\beta \rightarrow \gamma$ phase transition (gray patterns).

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OH-INCORPORATION IN SYNTHETIC FLUORAPATITE IN AQUEOUS FLUIDS AT LOWER CRUSTAL CONDITIONS

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Apatite ($Ca_5(PO_4)_3(OH, F, Cl)$) is a ubiquitous accessory mineral in many crustal rocks that is widely used to evaluate petrogenetic processes (SPEAR et al., 2002) and plays a unique role by monitoring fluid-rock interaction as it incorporates halogens and OH from hydrothermal aqueous fluids to form a ternary solid solution of the endmembers F-apatite, Cl-apatite and OH-apatite. The F, Cl and OH contents of apatite, coexisting with a variety of fluids at high P and T, provide better constraints on the chemical composition of aqueous fluids which may exist in the lower crust. In this study experiments of the synthetic fluorapatite single crystals were conducted at 800 °C and 1.0 GPa using the piston-cylinder apparatus under aqueous conditions with moderate KCl (X_{KCl}) and NaCl (X_{NaCl}) mole fractions (X_i = 0.1 – 0.5). The OH-incorporation in synthetic fluorapatite ($Ca_5(PO_4)_3F$) was studied by FTIR-spectroscopy. All IR spectra of experimentally treated apatite crystals showed a maximum absorption band at the same position (3540 cm^{-1}). The OH-contents in fluorapatite were calculated from IR absorption spectra measured on oriented single crystals, expressed as ppm water, using the calibrations of LIBOWITZKY & ROSSMAN (1997) and WANG et al. (2011). According to the calibration of WANG et al. (2011), the calculated OH-contents in fluorapatite treated in moderate KCl and NaCl mole fractions are 2.3 times larger than those of LIBOWITZKY & ROSSMAN (1997). Referring to the calibration of WANG et al. (2011) the OH-concentrations in the system H_2O-KCl decrease with increasing KCl from 244 ± 2 ppm (X_{KCl} = 0.000) to 165 ± 13 ppm (X_{KCl} = 0.520). In the system H_2O-NaCl the OH-concentrations decrease with increasing NaCl from 244 ± 2 ppm (X_{NaCl} = 0.000) to 205 ± 5 ppm (X_{NaCl} = 0.306), but at $X_{NaCl} > 0.3$, the OH-contents increase with increasing NaCl from 205 ± 5 ppm to 253 ± 6 ppm (X_{NaCl} = 0.509). Best fit equations for the OH-content in fluorapatite in the system H_2O-KCl and H_2O-NaCl are: $m_{OH} = - 130 X^2_{KCl} – 82 X_{KCl} + 244$ and $m_{OH} = - 785 X^2_{NaCl} – 380 X_{NaCl} + 244$, where m_{OH} represent OH-contents in fluorapatite in ppm, and $X_{KCl} = n_{KCl} / (n_{KCl} + n_{H2O})$, $X_{NaCl} = n_{NaCl} / (n_{NaCl} + n_{H2O})$ where n is moles.

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NEW SC-RICH PHOSPHATE MINERALS FROM THE TRUTZHOFMÜHLE APLITE, NE BAVARIA, GERMANY

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In addition to the occurrence of kolbeckite in phosphate assemblages of the Bavarian Forest (DILL et al., 2006), primary scandium-bearing phosphate minerals have been discovered in an apatite-rich sample from the Trutzhofmühle aplite, Bavaria (DILL et al., 2008). In polished section AS7848 (BGR collection, Hannover), at least three different Sc-phosphates were characterized using electron beam techniques. All minerals carry high Sc and Zr, besides Ba, K, Ca, Fe, Mn, U and other elements. One of the minerals occurs as grains large enough to produce thin slices using the FIB technique for TEM work. Unfortunately, the original sample specimen was not kept, so that this one polished section now serves as the only reference source of the new minerals.

The specimen contains three grains of a Sc-Ba-K-Zr phosphate (informally named “oberpfalzite”) and several grains of a Sc-Zr phosphate-silicate phase informally termed “trutzhofmuehlite”. The three “oberpfalzite” grains are all euhedral, up to 80 µm in size, compositionally zoned and hosted by Mn-rich hydroxyl apatite. They show a reflection behaviour similar to apatite in reflected light and thus are not easily visible under the reflected light microscope. “Trutzhofmuehlite” occurs as smaller, roundish, partly zoned grains in a matrix of secondary Fe-Al silicate, and as rims around zircon. Phase 3, Ca-Na-Sc-Fe-Mn-(Zr) phosphate, was only observed forming rims around apatite.

The chemical composition of “oberpfalzite” is complex. Besides the major elements Sc, Ba, K, Zr and P, minor amounts of Na, Mg, Al, Ca, Ti, Mn, Fe and Pb were detected. The composition, calculated from the median of 31 EMPA and SEM analyses and based on 48 oxygen, corresponds to $(K_{3.5}Ba_{1.5}Sc_{7.4}Zr_{1.4}Fe_{0.9}Mn_{0.3})_{15}[(PO_4)_{12}]$. Taking heterovalent substitutions into account, a simplified structural formula of $(K,Ba,Ca,Pb)_5(Sc,Zr,Fe,Mn)_{10})[(PO_4)_{12}]$ is considered reasonable. Raman spectroscopy using a 532 nm laser showed fluorescence and two broad peaks at 435 and 1055 cm^{-1}, respectively. No vibrational bands indicative for the presence of OH-groups or water were detected. The TEM investigation at GFZ Potsdam showed that “oberpfalzite” is a cubic phase with a = 10.1297 Å, space group I-43d (220).

The mineral assemblage in the manganoan apatite sample consists of zircon, monazite, quartz, chlorite and various phosphates. Phase 1 (“oberpfalzite”) is interpreted as a primary magmatic phosphate. During reaction with quartz and silicates, this mineral becomes unstable forming phase 2 (“trutzhofmuehlite”). In addition, phase 2 may also form via reaction involving zircon and apatite. Phase 3 may have formed by reaction of apatite with phase 1 or another Sc-rich precursor mineral.

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HIGH-PRESSURE COMPRESSION BEHAVIOUR OF ORTHORHOMBIC $LiScGe_2O_6$

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Pyroxene-type phases are subject to systematic investigations of the thermomechanical behaviour and related structure-property relationships for various reasons (e.g., HOFER et al., 2015). Therefore, several stable orthorhombic and monoclinic pyroxene polymorphs at various temperature and pressure were identified. Regardless of whether silicon or germanium based phases, the relative sizes and the interplay of the ions at T, M1 and M2 positions in the $M2M1T_2O_6$ compounds appear to control the structural stabilities and transformations. To support the understanding of phase transition driving parameters, the high-pressure behaviour of germanium compounds is in the current focus of systematic compressibility studies.

In this study we investigate the structural compression of an orthorhombic lithium-scandium-germanate end-member (with M2 = Li, M1 = Sc and T = Ge) and determine the equation of state (EoS) using a STOE AED2 four-circle X-ray diffractometer and Mo-$K_{alpha1,2}$-radiation. For each pressure point about 15 unique diffraction peaks were used for each LSG and quartz (pressure standard, e.g., SCHEIDL et al., 2016) in order to refine high-precise lattice parameters. Then, EoSFIT7-GUI (e.g., GONZALEZ-PLATAS et al., 2016) was used to fit a third order Birch-Murnaghan EoS onto the derived unit cell volume (Fig. 1) clearly indicating a structural phase transition near 9 GPa.

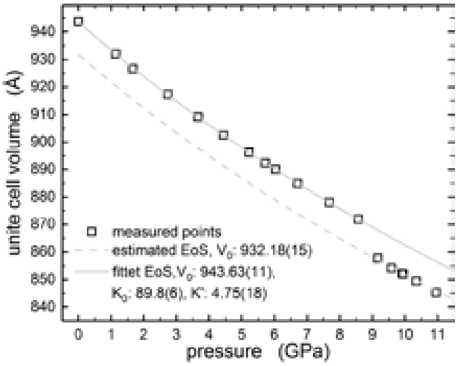

Figure 1. Unite cell volume determined by single-crystal X-ray diffraction experiments on a synthetic $LiScGe_2O_6$ crystal within a diamond-anvil cell. A probable first order phase transition is clearly visible around 9 GPa.

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IRREGULAR COMPRESSION BEHAVIOUR OF SOLID CO_2 - A VOLUMETRIC AND ULTRASONIC STUDY AT -75°C

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Carbon dioxide is the most abundant volatiles of the Earth beside H_2O and of fundamental relevance in rock forming processes. A re-appraisal of the melting curve of CO_2 and the determination of the stability boundary of silver oxalate ($Ag_2C_2O_2$) by MIRWALD & SCHOTTENBERGER (2004) suggested anomalous changes in dP/dT-slope at 400, 1200 and 2500 MPa. In addition, isothermal runs within the liquid and solid phase field (at 225°, 140° and 13°C) insinuated anomalous compression behaviour at similar pressures. This raised the question whether these anomalies may occur independently of the state of matter and thus may become also relevant for rock-forming processes under fluid conditions. Volumetric pressure experiments on "dry ice" (0.5 cm^3) were undertaken in a piston cylinder vessel (bore: 8 mm) at -75° C. The piston displacement was monitored by two transducers (resolution: ± $0,5 \cdot 10^{-6}$m). Simultaneously, ultrasonic (us) measurements were performed (through-transmission, probe 150 MHz, 250V), that rely on the determination of the relative time shift of the zero-crossing positions of the wave train. Figure 1 shows the relative compressibility of solid CO_2 revealing three anomalies. No pressure hysteresis is observed. Structurally the cubic structure of CO_2 seems only slightly affected by these volume effects, thus no phase transition is triggered (LIU, 1983). The volumetric data are fully supported by the us-measurements. Generally, these irregular changes in the compressibility of solid and liquid CO_2 may potentially be related to not uniform changes in the intermolecular interaction of the CO_2 molecule at high pressure.

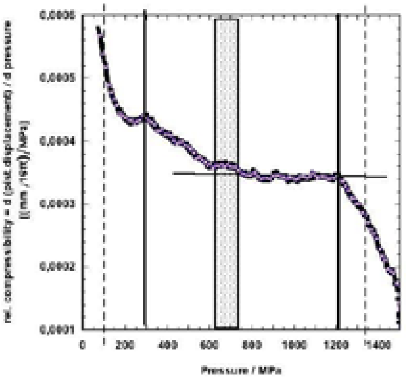

Figure 1: Relative compressibility of solid CO_2 indicating three anomalies at 300, 600-750 and 1200 MPa at -75°C. The two dashed lines at 100 and 1350 MPa confine the pressure ranges where the stress–strain behaviour of the vessel is not steady at compression and decompression.

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POTASSIUM IN CORDIERITE, A GEOBAROMETERIC INDICATOR

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Cordierite, $(Mg, Fe)_2Al_4Si_5O_{18}\cdot n(H_2O, CO_2, Na^+, K^+)$ grouped among the framework silicates is a characteristic mineral in low-medium grade metapelites. The orthorhombic structure is characterized by c-parallel channels that are formed by pseudohexagonal Si/AlO_4 rings, where small amounts of alkalis may be hosted. The channel component sodium has been experimentally shown to exhibit a pressure independent but temperature-inverse behaviour (MIRWALD, 1985) useable as a geothermometer (TROPPER et al., 2017). Incorporation experiments in synthetic Mg-cordierite (800 – 1000° C, 300 - 700 MPa) by THOMPSON et al. (2002) suggested to possible use of the potassium content as a thermometer for melts. An extended experimental study on two natural pelitic rock materials ("W-" and "SP5-cordierite") by Wyhlidal (2008) and TROPPER et al. (2017) allows to study the crystal chemical evolution of Mg-Fe-cordierite ($X_{mg} = 0{,}5 \pm 0{,}1$) as a function of T (MIRWALD & TROPPER, 2015). The data also provided some insights into the problem of potassium incorporation in cordierite. In the course of this study long duration experiments (1225 hrs.) at 600° and 700° C at 20 MPa were conducted to investigate the incorporation of K_2O as a function of pressure. Figure 1 shows that the K_2O-content of cordierite is strongly correlated with low pressures (<300 MPa). This suggests that high potassium contents in natural cordierites, e.g. that one of the Blaue Kuppe (SCHREYER et al., 1990) are related to incorporation processes at very low pressures at intermediate temperatures lasting over a certain geological time span.

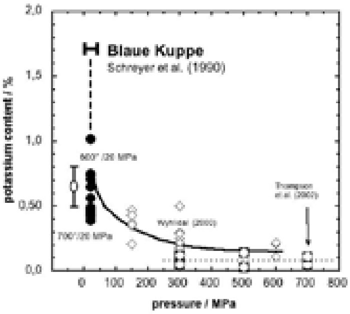

Figure 1: Potassium content of Mg-Fe-cordierite as function of pressure, temperature range 580-780° C.

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PERICLASE AN IMPORTANT INDUSTRIAL MINERAL FOR REFRACTORIES

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Magnesite named after its chemical composition respectively according to the Greek landscape magnesia has been named by Dietrich Ludwig Gustav Karsten in 1808 (RÖSLER, 1983). The discovery of magnesite deposits in Austria led to intensive industrial use and today magnesia based refractories are indispensable materials. By heat treatment magnesite and synthetic brucite can be transformed to periclase which is also called magnesia. Before the use of magnesia beneath alumina-silica products natural rocks like dunites and serpentinites have directly been used for various applications.

Refractory materials can be classified as coarse ceramic materials consisting of refractory aggregates in different grain sizes which are bound together and pores. They are designed to protect people and equipment in order to enable high temperature processes.

The world production of all magnesia grades (caustic-, sintered- and fused magnesia) is estimated to have totalled 13Mt in 2012. In Austria approximately 870 000t magnesite have been mined in 2012 (ROSKILL REPORT, 2013). From this by far the main portion has been used to produce refractories. During use refractories undergo significant changes which lead to modified properties and finally wear of the materials. Improvements can be achieved by careful consideration of the mineralogical and chemical composition as well as the physical constitution (crystal size, porosity of grains) of the materials. This also has some implications with respect to raw material selection for magnesia production. One important issue is the combination of magnesia and other oxides which in certain amounts or ratios result in materials showing unique thermal and physical properties. Due to the various and unique properties of the natural resources and complex process steps still there is need to gain knowledge which gives rise for further research activities.

RÖSLER, H. J. (1983): Lehrbuch der Mineralogie, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig.
ROSKILL REPORT (2013): Magnesium Compounds and Chemicals: Global Industry Markets and Outlook, Roskill information services Ltd., ISBN 978 0 86214 597 2, twelfth edition

W-SN MINERALISATION IN CALC-SILICATE ROCKS OF THE BASAL AMPHIBOLITE UNIT AT MESSELINGSCHARTE (FELBERTAUERN AREA, AUSTRIA)

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An unusual W-Sn mineralisation occurring at Messelingscharte in Early Palaeozoic amphibolites of the Basal Amphibolite unit in the Tauern Window was re-investigated as part of an ongoing exploration programme by WBH AG. Four types of scheelite mineralisation are distinguished. (1) Scheelite-bearing calc-silicate pods, (2) Discordant, deformed scheelite-quartz veins, (3) Scheelite in concordant mylonitic quartz-amphibolite layers, (4) Scheelite on joint surfaces. Type 1 and 2 are assumed to be pre-Alpine (Variscan?) formations.

The mineralised calc-silicate rocks occur as metre-sized irregular shaped pods. They are composed of major clinozoisite, quartz, and plagioclase with minor to accessory scheelite, titanite and chlorite. Bulk geochemistry reveals high concentrations of W (≤7.74 mass% WO_3), Sn (≤1254 ppm SnO_2), Be (≤41 ppm) and transition metals (Cu, Pb, Zn; $\sum \leq 2500$ ppm) in these rocks.

Three scheelite generations are distinguished based on micro-textures, zoning, Mo-content and luminescence colour. The first generation is coarse-grained and Mo-rich (0.82-1.7 mass% MoO_3) and normally preserved in the cores of large scheelite porphyroblasts. It is interpreted as primary pre-Alpine (Variscan?) scheelite. Scheelite generations 2 and 3 are Mo-poor/free and are interpreted as metamorphic mobilisations and recrystallisation products formed during Variscan (?) and/or Young Alpine regional metamorphism. Hence, similar to Felbertal scheelite deposit (Scheelite 1 and 2 there), pre-Alpine Mo-rich scheelite was overprinted by two stages of metamorphism.

A unique feature of scheelite mineralisation at Messelingscharte is the association of W with Sn. Clinozoisite and titanite were identified as the main Sn-bearing phases (clinozoisite ≤3.00 mass% SnO_2, =0.09 apfu; titanite ≤6.48 mass% SnO_2). Sn-bearing clinozoisite (large anhedral grains with irregularly shaped Sn-rich lamella) was also affected by metamorphic recrystallisation; the later formed fine-grained, euhedral metamorphic clinozoisite is Sn-free. Substitution of $(Al, Fe)^{3+}$ by $(Sn, Ti)^{4+}$ in clinozoisite is explained by simultaneous incorporation of divalent cations like Fe^{2+}. Titanite shows patchy irregular zoning defined by Sn-content and rarely hosts very small (<3 µm), roundish cassiterite grains.

Mineralogy, bulk geochemistry and mineral chemistry point to a magmatic hydrothermal source of fluids causing calc-silicate alteration (cf. ALDERTON & JACKSON, 1978). The studied calc-silicate rocks clearly differ from metamorphic clinozoisite segregations known in the Tauern Window and from clinozoisite-rich calc-silicate patches in the Felbertal tungsten deposit. Future exploration and research must test the hypothesis that Messelingscharte is a type of distal skarn associated with a so far unidentified granite (Felbertauern augengneiss?).

ALDERTON, D.H.M., JACKSON N.J. (1978): Mineralogical Magazine, 42, 427-434.

THERMAL EXPANSION, MECHANICAL AND OPTICAL PROPERTIES OF GALLIUM AND ALUMINUM SUBSTITUTED Zn_2TiO_4 SPINELS

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Polycrystalline samples of new $Zn_{1.75}Ti_{0.75}Ga_{0.5}O_4$, $Zn_{1.5}GaTi_{0.5}O_4$, and $Zn_{1.75}Ti_{0.75}Al_{0.5}O_4$ spinel were prepared by solid-state reactions in platinum crucibles and closed platinum capsules at 1523 K and 1623 K, respectively. The chemical composition of the colorless crystals was determined by wavelength-dispersive X-ray spectroscopy. Phase analysis and structural investigations were carried out by high-resolution powder X-ray diffraction and Raman spectroscopy. Crystal structure refinements of the inverse spinels $Zn_{1.75}Ti_{0.75}Al_{0.5}O_4$, $Zn_{1.5}GaTi_{0.5}O_4$, and $Zn_{1.75}Ti_{0.75}Ga_{0.5}O_4$ resulted in the following basic crystallographic data: cubic, $Fd\text{-}3m$, a = 8.37810(1) Å, V = 588.079(3) Å^3; a = 8.405473(8) Å, V = 593.863(2) Å^3 and a = 8.44015(1) Å, V = 601.244(2) Å^3, Z = 8. In addition, *in situ* high-temperature powder X-ray diffraction experiments enabled the investigation of the thermal expansion of the new spinel-type compounds. For sample preparation, required for further material analysis, the sintered tablets and fragments were embedded in epoxy resin and polished to a mirror-like surface finish. To determine the mechanical properties, nanoindentation experiments were performed with a Berkovich diamond indenter tip. Analyses of the load–displacement curves revealed a high hardness ranging from 10.2 ± 0.4 GPa to 11.8 ± 0.5 GPa and a reduced elastic modulus of 162 ± 5 GPa up to 178 ± 6 GPa. Furthermore, the optical properties of the spinel-type materials were studied by spectroscopic ellipsometry in the wavelength between 250 and 1000 nm. All materials exhibit a high refractive index ranging from n = 2.20 to n = 2.10 at 430.8 nm (Fraunhofer G line) with a similar low dispersion (0.09 to 0.07, n_G–n_B).

ARCHAEOMETRIC INVESTIGATIONS ON SELECTED ROMAN DOMESTIC POTTERY OF THE VILLA GRÜNAU, STYRIA, AUSTRIA – A MULTI TECHNIQUE APPROACH

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The archaeometrically investigated Roman domestic pottery fragments originate from various excavations carried out in the years between 1988 and 1997 in the area of the Villa Grünau. Above all parts were exposed in the western area of the villa, where a part of the main building was located as well as the courtyard of the villa (POCHMARSKI, 2005). The fragments are from the 1st to 3rd century, with a focus on the second century. An archaeological arrangement in groups was performed with reference to the vessel shape, the size of the temper particles and the pore size. No detailed studies have so far been carried out on the firing temperature and the raw material used. With respect to the firing temperature of the ceramic fragments there is only an estimate which assumes a temperature between 700 ° - 800 ° C. The firing conditions had been both oxidizing as well as reducing whereby mixed fires also existed. (LAMM, 2011). For the study, 29 different ceramic fragments were selected with the archaeological grouping of LAMM (2011) served as a basis. The study aims to achieve through the application of different mineralogical, petrological and chemical methods new insights with respect to the raw materials used, the firing temperature and a potential differentiation of the ceramic fragments into different groups. In addition, the aim is to determine the provenance of the domestic pottery of the Villa Grünau. For this reason, two ceramic fragments from Kalsdorf and eight more from Lassenberg were additionally included in the study. Analytical methods were used, the optical polarization microscopy, X-ray powder diffractometry, X-ray fluorescence spectroscopy and the micro probe.

The summarized results of the study are: The mineralogical and chemical composition of the ceramic shards is quite similar, with few exceptions. The main mineral phases are quartz, mica/illite, feldspar, in some shards additionally calcite and dolomite and in very few cases amphibole, pyroxene and garnet. Based on the mica / feldspar ratio, 3 different groups can be detected. The estimated firing temperatures for most of the ceramic shards are between 650° to 850°C whereby the ceramic samples form Kalsdorf display indicators for a higher firing temperature (> 900°C). Ceramic fragments form the sites Villa Grünau, Karlsdorf and Lassenberg, with just a few exceptions, are CaO-poor ceramics supposedly with illitic based clay material and rock fragments and/ or sand used for tempering. With regard to the provenance the study shows, that the ceramics of the Villa Grünau could come partly from the Vicus von Gleisdorf (KLAMMER et al., 2000).

KLAMMER, D., KOLLMER, H., SCHINDLER-KAUDELKA, E. (2000): In JESCHEK, G. (eds) Die grautonige Keramik aus dem Vicus von Gleisdorf, 73-82.
LAMM, S. (20011): Dissertation, Karl-Franzens-Universität Graz.
POCHMASKI, E. (2005): SchSt., 18, 79-91

FLUID EVOLUTION OF THE CU-NI±PGE-SULFIDE MINERALIZED BATHTUB INTRUSION (DULUTH COMPLEX, MINNESOTA, U.S.A)

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The troctolitic Bathtub intrusion (Duluth Complex, NE-Minnesota) hosts the sub-economic Cu-Ni-sulfide Babbitt deposit, which is characterized by disseminated sulfide ores (pentlandite, pyrrhotite and chalcopyrite) that locally contain anomalous platinum-group element (PGE) concentrations. Platinum-group minerals (PGMs) are either hosted by primary magmatic sulfides (first generation PGMs) or associated with areas of hydrous silicate alteration (secondary generation PGMs). Petrographically two apatite generations are observed in these samples, which were used to track magmatic and metasomatic processes: (i) earlier crystallized apatite I inclusions in clinopyroxene; and (ii) later formed, LREE-enriched apatite II along grain boundaries of cumulus and intercumulus silicates, associated with hydrous mineral assemblages (such as sericite + chlorite + amphibole). Based on fluid inclusion studies in cumulus phases and apatite II, as well as textural and compositional variations of apatite, the following predominant fluid systems, which were active during magmatic, subsequent metamorphic and late metasomatic events, are reconstructed:
(i) An early fluid evolution stage, characterized by a homogeneous H_2O-CO_2-CH_4 fluid, indicated by negative-crystal shaped CH_4-CO_2-rich fluid inclusions (FIs) in cumulus plagioclase and multiphase solid inclusions (MSIs) in igneous olivine (e.g. graphite, REE+Y-bearing phosphate minerals, hydrous silicates and carbonates). Identified MSIs represent early FIs that show modifications after entrapment.
(ii) A later fluid system is documented by two types of FIs in LREE-enriched apatite II (types A and B): Heterogeneous aqueous, saline type A FIs, aligned parallel to the crystallographic c-axis, with end-member homogenization entrapment temperatures around 280°C. The close association of apatite II with hydrous mineral assemblages of greenschist- to amphibolite-facies conditions suggests a metamorphic origin for type A FIs. Type B FIs define secondary unmixed carbonic-aqueous fluids entrapped along cracks. This later fluid generation can be correlated with the bright REE-enriched domains in apatite II. During cooling, fluid phase separation into aqueous and carbonic inclusions generated a modified fluid system [H_2O–$NaCl(\pm CaCl_2 \pm MgCl_2)$–$CO_2$] near solidus conditions.
(iii) The latest fluid-induced processes include the nucleation of monazite along apatite II rims or in cracks, and Cl-rich domains (up to 4.93 wt.% Cl) in altered apatite II. Since secondary generation PGMs and other precious phases are abundant in these alteration patches, we suggest the presence of a Cl-rich fluid phase, which may have served as a transporting medium during PGE remobilization.

STRATA-BOUND SCHEELITE DEPOSITS REVISITED - 50 YEARS OF FELBERTAL

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After its discovery in 1967 Felbertal has long been regarded as the type locality for strata-bound W deposits. Its discovery triggered worldwide exploration for this then new class of W deposits, but so far without any other economic counterpart. Early genetic models for the Felbertal deposit postulated a syngenetic/syndiagenetic formation by exhalative-hydrothermal processes and related mineralisation to Early Palaeozoic mafic volcanism with subsequent reworking and mobilisation during later orogenic events. Later, this model was challenged and various epigenetic, in part granite-related models of ore formation were proposed. A clear decision in favour of one of the genetic models was strongly hampered by the poly-metamorphic overprint of the deposit and lack of precise age data on mineralisation. In this presentation, it will be summarised how absolute age determination of ore minerals and associated host rocks using various isotope systems and modern in-situ dating techniques have changed our understanding on the formation of this scheelite deposit, which remains to be a major global tungsten producer since 50 years.

Some key aspects controlling formation of the Felbertal W deposit in the Eastern Alps are: (1) It is restricted to the lower parts of the Early Palaeozoic Habach Complex (amphibolites, hornblende fels, various orthogneisses) representing a rather exotic terrane in the Alpine orogen. (2) Geochemically specialised and strongly fractionated granites in the deposit („K1-K3 orthogneiss“ and equivalents) were emplaced at c. 336-341 Ma coeval with non-mineralised and granites (e.g, Felbertal Augengneis) during Variscan collision. The melts derived from Mid-Proterozoic continental crustal protoliths. (3) Four different scheelite types are distinguished; two are of magmatic-hydrothermal (types 1, 2) and two of metamorphic origin (types 3, 4). (4) The postulated pre-Variscan ore stage was not confirmed by modern in-situ dating of scheelite. The in-situ U-Pb age of c. 340 Ma for Scheelite type 1 from the finely foliated scheelite-quartz ore („scheelite-rich quartzite“) in the Eastern Ore Zone, previously thought to be c. 520 Ma old, supports the age relationship of tungsten mineralisation with Variscan magmatism. (5) Ore formation is linked with fluids, which are characterised by enrichment in LIL elements (K, Rb, Cs), Nb, Ta as well as in F etc. Mineralising fluids of magmatic-hydrothermal origin precipitated scheelite in quartz-dominated stock work veins, in shear zones and in disseminated form and caused deposit-scale alteration of the host rocks (e.g., low K/Rb; radiogenic Sr-isotope signature). (6) Finley foliated ores, previously interpreted as syngenetic (e.g., meta-exhalites), are best regarded as tectonites; i.e., mylonites. (7) The Felbertal deposit was affected by poly-phase regional metamorphism and deformation (Variscan: c. 330-340 Ma; (?) Permian: c. 270 Ma, Alpine: c. 30-40 Ma) what caused localised mobilisation of tungsten. In the Austroalpine units where a direct link of tungsten mineralisation with specialised granites is lacking only sub-economic tungsten showings were formed. It is concluded that correct genetic models are vital for successful exploration of mineral deposits.

PETROGENESIS OF HIGHLY FRACTIONATED A-TYPE GRANITES IN THE NORTH ARABIAN-NUBIAN SHIELD; EGYPT: CONSTRAINTS FROM WHOLE-ROCK GEOCHEMISTRY AND Sr-Nd ISOTOPES

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The Neoproterozoic highly fractionated calc-alkaline granitoids are widespread in the North Arabian-Nubian Shield (ANS). An integrated study of minerology, whole-rock geochemistry and Sr-Nd isotopes was carried out for a Neoproterozoic granitoids of Gabal Abu-Diab in the Central Eastern Desert of Egypt, to investigate its petrogenesis and geological significances. Petrographically, Abu Diab batholith represent a multiphase pluton consists of two-mica granites (TMGs) as a main phase in the center followed by garnet bearing muscovite granites (GBMGs) and muscovite granites (MGs) at the margin, and intruded into older granodiorite and metagabbro-diorite rocks. The granites are slightly peraluminous with high SiO_2 (>75 wt.%), K_2O+Na_2O (9.3-8.7 wt.%). Petrographic and geochemical features show that they are highly fractionated A-type granites. The TMGs are enriched in light rare earth elements (LREEs) relative to heavy REEs, have weakly negative Eu anomalies and are depleted in Nb, Ba, P and Ti. In contrast, the GBMGs and MGs have tetrad-type REE patterns ($TE_{1,3} > 1.1$) with strongly negative Eu anomalies and are extremely depleted in Ba, Sr, P and Ti. The TMGs (583 ± 29 Ma) are characterized by relatively low initial $^{87}Sr/^{86}Sr$ ratios (0.70382-0.70337) that suggests their derivation from a depleted mantle source, with little contamination from the older continental crust. By contrast, the TMGs and MGs has very high $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios that reflect the disturbance of the Rb-Sr isotopic system and may give an indication for the high temperature magma-fluid interaction. Abu-Diab granitoids are characterized by positive $\epsilon Nd(t)$ values (4.41-6.57), corresponding to young Nd-T_{DM2} ages ranging from 956 to 921 Ma, clearly reflect the juvenile crustal nature and preclude the occurrence of pre-Neoproterozoic continental crust in the ANS. We suggest that Gabal Abu-Diab granitoids were generated by partial melting of pre-existing calc-alkaline I-type granodiorites followed by subsequent fractionations.

PETROGENESIS OF GRANULITES AND GFÖHL GNEISSES FROM THE MOLDANUBIAN ZONE IN THE SOUTHEASTERN BOHEMIAN MASSIF, LOWER AUSTRIA

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The prominent granulites and Gföhl gneisses from the southeastern Moldanubian Zone (Bohemian Massif) in Lower Austria, with the Variscan (~340 Ma) high to medium-pressure and high temperature metamorphic imprint, indicate that both meta-granitoidic rock types have S-type affinity typically related to partial melting of sedimentary source material within the lower crust. The samples represent peraluminous fractionated granites, granodiorites and tonalities in the A/NK-A/CNK plot after SHAND (1943). Variation diagrams of major element oxides and trace elements, such as decreasing TiO_2, FeO^{tot}, MgO, Ba, Zr, Sr and increasing Rb/Sr with increasing SiO_2 reveal typical crystallization trends. Granulites can be characterized as calc-alkaline to high-K calc-alkaline rocks while Gföhl gneisses only represent high-K calc-alkaline rocks on the basis of the SiO_2-K_2O plot of PECCERILLO & TAYLOR (1976). Chondrite-normalized REE plots resemble typical patterns of subduction zone related granitoides, showing moderate to slight enrichment in LREE and negative Eu anomalies. For reconstruct the tectonic setting of the magmatic rocks, element discrimination diagrams such as Rb vs. Y+Nb and Rb vs. Y after PEARCE et al. (1984) were applied. Referring to that, the bulk composition of investigated rocks represent syn-collisional to volcanic arc related granitoides. According to FRIEDL et al. (2011) the emplacement and crystallization of the magmatic rocks is in the range of 450 to 430 Ma, which in turn marks a (late) Ordovician-Silurian stage within the Moldanubian Zone where an active continental margin led to the production of large intrusive rocks.

FRIEDL, G., COOKE, R., FINGER, F., McNAUGHTEN, N., FLETCHER, I. (2011): Mineralogy and Petrology, 102, 63.
PEARCE, J., HARRIS, N., TINDLE, A. (1984): Journal of Petrology, 25, 956-983.
PECCERILLO, R., TAYLOR, S. (1976): Contrib. Mineral. Petrol., 58, 63-81.
SHAND, S. (1943): The Eruptive Rocks, 2nd edn., John Wiley, New York.

TWO STAGE METAMORPHIC HISTORY OF HP-UHT GRANULITES FROM THE MOLDANUBIAN ZONE (BOHEMIAN MASSIF) REVEALED BY GARNET ZONING AND MINERAL INCLUSIONS

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Mineral inclusions and compositional zoning in garnet crystals of felsic and mafic granulites from the Gföhl Nappe System, southeastern Moldanubian Zone, provide detailed information of a two stage metamorphic history of these rocks. The first metamorphic episode is related to deep crustal subduction at eclogite facies conditions while the second one records an UHT overprint that occurred within the orogenic root zone. Both the felsic and mafic granulites contain conspicuous garnet zoning profiles with chemically homogenous high-grossular cores with X_{Grs} values of about 30-35 mol.%. In contrast, the rim parts of the garnets show a pronounced zoning where almandine and pyrope increase but grossular values decrease dramatically. To reconstruct the two stage metamorphic evolution, PT-path modelling was performed by the Gibbs free energy minimization software package Theriak-Domino (DE CAPITANI, 1994) in combination with major and trace element zoning in garnet. In that respect, chemically homogenous garnet cores with high-grossular plateaus suggest formation during a prograde low to medium-temperate eclogite facies event, probably up to UHP conditions. This is documented by columnar shaped inclusions of altered jadeite relics in high-grossular garnet cores from felsic granulites. Pronounced zoning at the garnet rims is compatible with an isobaric heating phase reaching approximately 1000-1100°C and 1.6-1.8 GPa. The common occurrence of polyphase mineral inclusions consisting of K-feldspar + kaolinite (hydrated kyanite) + quartz and melt inclusions in low-grossular garnet rims indicate muscovite-consumption and incipient melting during this granulite facies temperature increase. The observed mineral inclusions and garnet zoning pattern suggest that after the eclogite facies event isothermal decompression was followed by near isobaric heating to UHT conditions. Final exhumation and emplacement within the Moldanubian nappe pile is seen in highly deformed and partly hydrated and retrograded granulites.

DE CAPITANI, C. (1994): Beihefte zum European Journal of Mineralogy, 72, 48.

MINERALOGICAL CHARACTERIZATION OF THE TEISER KUGELN (VILLNÖSS/FUNES, SOUTH TYROL)

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The Teiser Kugeln are found as geodes in basaltic andesites and andesites, both of Lower Permian age and part of the Athesian Volcanic District (VISONÀ et al., 2007), located in the Villnöß/Funes valley, South Tyrol. Their name is derived from the occurrence near the village Teis/Tiso. So far, minerals in the mm- to dm-sized geodes were identified optically only, but never analytically. Therefore, and in order to study the formation of the geodes, their mineralogy and relations of present mineral phases, qualitative analysis of minerals in the Teiser Kugeln was conducted using Raman spectroscopy (RS) and single-crystal X-ray diffraction (XRD).

Typically, the geodes show a chalcedonic rim and a coarse-grained crystalline quartz filling. The quartz filling can be complete or incomplete, the latter leaving space for other minerals to grow. Calcite was identified macroscopically, as well as several different varieties of quartz, i. e. rock crystal, amethyst and milky quartz. Prehnite ($Ca_2Al_2Si_3O_{10}(OH)_2$), datolite ($CaBSiO_4(OH)$) and the zeolites chabazite ($(Na,K,Ca,Na,Mg,Sr)_{1.8-4}Al_{3-4}Si_{8-9}O_{24}\cdot n(H_2O)$) and stilbite ($(Na,Ca)_{5-9}Al_9Si_{27}O_{72}\cdot 28(H_2O)$) were identified by RS and XRD.

Prehnite forms either greenish spheres or greenish-white to yellowish-white aggregates of tabular crystals (Figure 1: A, C). Chabazite occurs as transparent cubes that have the lustre of glass (Figure 1: C). Stilbite is found in columnar-shaped, translucent crystals (Figure 1: B). The milky tabular datolite crystals exhibit a distinct glassy lustre and form a coating in the cavity. Sphere-like hematite inclusions were found sporadically in amethyst crystals.

The crystallization sequence (from outside to inside) starts with chalcedony (agate), followed by coarse-grained crystalline quartz, and calcite. Prehnite, chabazite, datolite and stilbite represent the last crystallization stage and occur frequently as coatings inside the cavities, overgrowing all other phases.

Figure 1. Examples of the analysed minerals. A: Prehnite; B: Stilbite; C: Green prehnite and white cubical chabazite (with a non-visible prehnite coating)

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$K_2CaSi_4O_{10}$ – A PREVIOUSLY UNKNOWN CRYSTALLINE PHASE IN THE TERNARY SYSTEM K_2O-CaO-SiO_2

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In the course of a systematic re-investigation of the ternary oxide system K_2O-CaO-SiO_2 a new potassium calcium silicate with the chemical composition $K_2CaSi_4O_{10}$ was discovered within the products of solid state reactions aimed at the synthesis of $K_4CaSi_6O_{15}$. By applying direct methods the crystal structure of $K_2CaSi_4O_{10}$ was solved from single-crystal X-ray diffraction data. The compound crystallizes in the triclinic space group P-1. Its unit cell is defined by the following lattice parameters: a = 7.0915(7) Å, b = 8.4211(9) Å, c = 10.2779(12) Å, α = 104.491(10)°, β = 100.570(9)° and γ = 113.738(11)°. $K_2CaSi_4O_{10}$ is isotypic with the minerals litidionite, fenaksite and manaksite (BRANDAO et al., 2009). Loop-branched *dreier* double-chains of $[SiO_4]$-tetrahedra running along [100] are connected via dimers of irregularly coordinated edge-sharing $[CaO_5]$-polyhedra. Potassium cations are located within cavities of the heteropolyhedral framework. However, the channels within the silicate double-chains remain unoccupied.

$K_2CaSi_4O_{10}$ further enlarges the knowledge of the system K_2O-CaO-SiO_2, which is of interest for process technology in the fields of biomass combustion (BERJONNEAU et al., 2009).

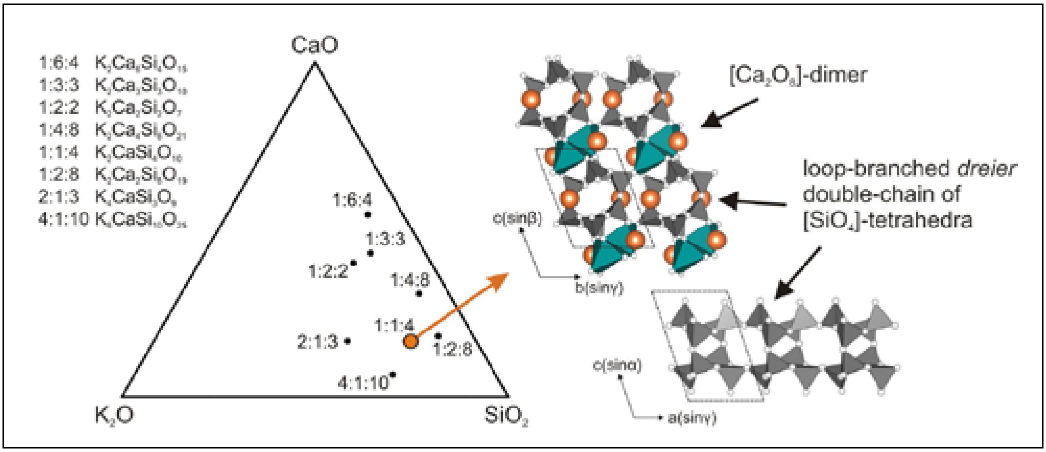

Figure 1. Ternary plot of the system K_2O-CaO-SiO_2 showing the composition [in mol%] of all ternary phases with known crystal structure and details of the crystal structure of $K_2CaSi_4O_{10}$.

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$M^{3+}(H_2AsO_4)_3\cdot5H_2O$ (M = In, Ga), TWO SYNTHETIC ANALOGUES OF THE IRON HYDROGENARSENATE MINERAL KAATIALAITE

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Kaatialaite, $Fe^{3+}(H_2AsO_4)_3\cdot5H_2O$ (RAADE et al., 1984), is a rare iron hydrogenarsenate mineral that typically occurs as a supergene phase at very low pH. Its crystal structure is known from a synthetic analogue (BOUDJADA & GUITEL, 1981), although it appears that the water content of the natural material is variable, with 3-5 H_2O per formula unit (RAADE et al., 1984).

The Ga- and In-analogues of kaatialaite are, similar to kaatialaite itself, secondary phases grown in a highly acidic environment. They were encountered during a reinvestigation of the primary reaction products, stored in plastic boxes in air, of hydrothermal syntheses conducted about 11 years ago during an extensive study of the system M^{1+}-M^{3+}-As-O-H (SCHWENDTNER, 2008).

Previously unknown $In(H_2AsO_4)_3\cdot5H_2O$ grew as tiny subparallel acicular crystals in small droplets of a very acidic solution formed from hygroscopic acid arsenates (syntheses in systems M^+-In-As-O-H). The compound was characterised by a structure refinement (R ~ 5.8%) from single-crystal XRD data (Mo$K\alpha$; 293 K). Since the crystal was gradually decomposing during the measurement, until it was completely X-ray amorphous (probably due to dehydration), additional low-temperature measurements will be conducted.

$Ga(H_2AsO_4)_3\cdot{\sim}5H_2O$ is a fine-grained decomposition product of synthesised Tl_3Ga_2-$(HAs_2O_7)_3\cdot nH_2O$ and formed after immersion and grinding of the latter compound in aceton for several minutes. Comparison of the powder XRD pattern gave a good fit for "$Ga(H_2AsO_4)_3\cdot5H_2O$" ("blank" ICDD-PDF file; RONIS et al., 1972). Using the model of BOUDJADA & GUITEL (1981) as a starting point, a Rietveld refinement led to R_{wp} = 10%.

Most hydrogen bonds in both In- and Ga-analogues appear to be split, in view of multiple possible acceptor atoms (O...O < 3.0 Å). Unit-cell parameters of all compounds are compared in the table below [[1]RAADE et al (1984) for synthetic material, refined from powder XRD data; [2]BOUDJADA & GUITEL (1981), single-crystal structure determination].

Compound	SG	a [Å]	b [Å]	c [Å]	β [°]	V [Å^3]
$Fe(H_2AsO_4)_3\cdot5H_2O^1$	$P2_1$ or $P2_1/m$	15.363(5)	19.844(5)	4.736(2)	91.77(3)	1443.2(9)
$Fe(H_2AsO_4)_3\cdot5H_2O^2$	$P2_1/n$	15.25(3)	19.60(5)	4.72(5)	91.8(8)	1410.1(1)
$In(H_2AsO_4)_3\cdot5H_2O$	$P2_1/n$	15.514(3)	19.901(4)	4.890(1)	91.51(3)	1509.2(5)
$Ga(H_2AsO_4)_3\cdot{\sim}5H_2O$	$P2_1/n$	15.3206(8)	19.7843(1)	4.6850(3)	91.956(4)	1419.3(1)

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EMPLACEMENT AND TRANSPORT OF FELSIC MATERIAL BELOW THE MOLDANUBIAN CRUST IN THE BOHEMIAN MASSIF. INSIGHTS FROM NUMERICAL MODELING

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The Bohemian Massif is a well-preserved part of the Variscan Orogeny with wide varieties of igneous and metamorphic rocks documenting both subduction and collisional events. Discrepancy exists about the number and forms of the microplates involved in the orogeny and direction of subduction that make it difficult to reconstruct tectono-magmatic evolution of the massif. The pressure–temperature conditions determined for the gneisses and granulites of the Bohemian Massif (Gföhl Unit in the Moldanubian zone) predict continental crust to be buried to mantle depths (> 100 km), than exhumed, shortly underwent ultrahigh-temperature metamorphism at lower crustal depth, and finally be exhumed to middle-to-upper crustal depths. There are two contrasting models explaining formation and exhumation of these rocks: a classical continental crust subduction model with its following exhumation, and a continental crust underthrusting, where the continental crust of the subducted plate penetrates the crust-mantle boundary of the overriding plate, and finally is extruded into middle crust. Few attempts to numerically reproduce the structures of the Bohemian Massif were made on the assumption on the "crustal underthrustig", although none of the models focused on the appearing of this felsic material at the lower crustal level of the Moldanubian zone before the extraction. We investigate this problem using a coupled petrological-thermomechanical tectonic-magmatic numerical approach. The preliminary results show that any appearance of felsic crust with the required characteristics of the Gföhl Unit in the Moldanubian zone at the lower crustal level is possible only if the continental crust subducts to the deep levels and then exhumes upwards in the overlaying crust. There is two ways how the subducted continental crustal material could percolate into the overlying crust: either along the subduction channel or in form of diapir through the lithosphere of the overriding plate weakened by upward percolation of the extracted melts/fluids. In the first case the partially molten continental crust exhumes vertically towards the surface at the boundary between two plates and at the ongoing collision could theoretically expand towards the overlying plate and percolate the overlying crust a bit further. This scenario is quite close to the idea of "crustal underthrustig" for the Bohemian Massif. Nevertheless, it is difficult to explain the preservation of a continental block (Tepla-Barrandian block), and the appearance of ultra-high-temperature eclogites and peridotites in the Moldanubian zone. The exhumed material is composed in this case mostly from the subducted partially molten upper continental crust, including some eclogites and mantle from the low level (max. 2.5 GPa). The experiments with crustal diapirism show contrariwise the complex structures of the perculating diapirs including the blocks of the deeply subducted oceanic plate and the serpentinized mantle from the mantle wedge. Thus, the preliminary results of the numerical experiments do not support the "crustal underthrusting" model, but rather agree with an idea of initial subduction with subsequent exhumation of the felsic crust from the Gföhl Unit in form of a diapir, although none of the models can explain so far all geological-petrological data available.

MULTISTAGE P–T EVOLUTION RECORDED IN GARNET-BEARING MIGMATITES FROM THE BAVARIAN UNIT, BOHEMIAN MASSIF, UPPER AUSTRIA

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The Bavarian Unit in Upper Austria, as part of the Moldanubian superunit of the Variscan Orogen, was formed during a late Variscan (post 330 Ma) LP–HT overprint, probably related to a partial delamination of mantle lithosphere and subsequent asthenospheric upwelling (FINGER et al., 2007). We investigated unusual grt-crd-sil-migmatites with large garnet porphyroblasts, that occur along the Danube valley near Ottensheim. The large garnet porphyroblasts of these rocks preserve chemical zoning which constrains a multistage metamorphic evolution. Elevated homogeneous grossular content in the core (5–6 mol% grs) is followed discontinuously by low grossular content in the garnet mantle (1–1.5 mol% grs) and then again by a discontinuous increase at the rim (3–3.5 mol% grs) defining three distinct stages of garnet growth. The three garnet zones also display different mineral inclusions, i.e., sillimanite, plagioclase and spinel in the core, staurolite, biotite, plagioclase, sillimanite and muscovite in the mantle, and cordierite, sillimanite, K-feldspar and spinel equilibrated with the garnet rim.

Metamorphic conditions were obtained from a microprobe study of the garnet and the enclosed minerals using standard geothermobarometric calculations as well as thermodynamic modelling. A first prograde MP–MT metamorphic event (0.9–1.1 GPa and 740–780°C) is represented by the garnet core. This first metamorphic event was followed by a stage of decompression and cooling. A renewed heating event starting at LP–MT conditions (0.44–0.54 GPa and 580–610°C) led to a regrowth of garnet. The rims of the garnets formed during LP–HT metamorphism (0.60–0.66 GPa and 830–910°C). U-Th-total Pb dating of monazite inclusions in the garnet cores indicates an age of 340 ± 7 Ma for the first MP-MT metamorphic event, relating it to the Variscan collision stage. Dating of matrix monazite yields an Upper Carboniferous age (315 ± 4 Ma) for the LP–HT overprint, consistent with existing geochronological dates from the Bavarian Unit (GRAUERT et al., 1974; KALT et al., 2000;, FINGER et al., 2007).

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EVIDENCE OF A HIGH PRESSURE EVENT IN GRANULITE FACIES ROCKS FROM THE DROSENDORF NAPPE – LOWER AUSTRIA

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Various paragneiss and amphibolite types occur in the Drosendorf nappe in the southeastern Moldanubian superunit. A high grade garnet, K-feldspar and sillimanite bearing paragneiss from the southernmost part of the Drosendorf nappe contains large garnet porphyroblasts, showing a conspicuous zoning pattern. A constant grossular plateau in the core (6–7 mol% grs) and a sharp increase at the garnet rim (9–10 mol% grs) followed by a deacrese to the outermost rim (4–5 mol% grs) indicates a discontinuous garnet growth (Fig. 1). Inclusions of muscovite with a high Si content of 3.20 apfu together with kyanite indicate higher pressure and lower temperature conditions for the initial garnet growth. Calculation of equilibrium phase diagrams obtained 1.5–1.7 GPa for garnet core growth at a temperature of 650–700 °C. For the garnet rim and equilibrated matrix phases conditions of 0.8–1.0 GPa and 800–900 °C could be determined, which are similar to conditions proposed by PETRAKAKIS (1997) for the paragneiss in the southern Drosendorf nappe.

Garnet bearing amphibolites are widespread in the Drosendorf nappe and have the general mineral assemblage amphibole + garnet + plagioclase ± sphene ± epidote/zoisite ± orthopyroxene ± clinopyroxene. Garnet is heavily resorbed and show typical plagioclase coronas or orthopyroxene + plagioclase symplectites, which indicate an isothermal decompression path at high temperature (ITD). Large garnet porphyroblasts in amphibolite show a similar zoning pattern as observed in paragneiss. The grossular content shows a significant increase from the core (24–25 mol% grs) to the rim (28–29 mol% grs) and decreases to the outermost rim (21–22 mol% grs).

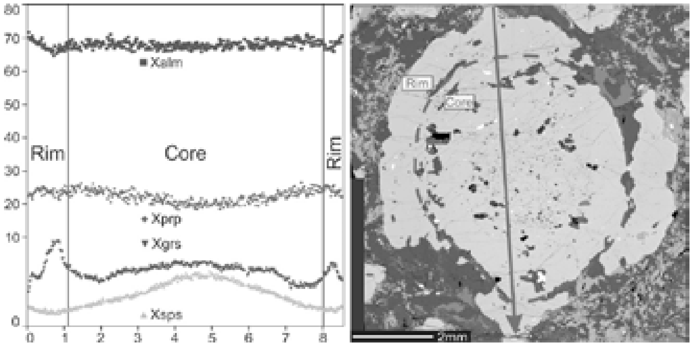

Figure 1. Garnet porphyroblast in a paragneiss sample shows a compositional zoning especially in the grossular component. A backscatter electron (BSE) image shows the garnet and the profile line of the analysed profile.

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OH-DEFECTS IN QUARTZ AS MONITOR FOR PROVENANCE

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OH-defects of more than 500 quartz grains from siliciclastic sediments and their potential source rocks were studied by FTIR-spectroscopy. Sediment samples were derived from the Rhine River at Rhöndorf and from the Baltic Sea coast at Darß. As potential source rocks Hercynian granites from the Black Forest and Proterozoic granites from Sweden were investigated, respectively. Prior to analysis, all quartz grains were manually aligned parallel to the crystallographic c-axis, and polarised measurements were performed in two perpendicular directions in order to erase the IR-signal of fluid and melt inclusions and to minimize the contribution of mica inclusions. IR-absorptions of the hydrous defects were converted into concentrations for water equivalents.

Results show that quartz grains from Darß and Rhöndorf exhibit fundamentally different defect water contents, where quartz grains from Darß are generally low in defect water (in average 4 wt ppm, most grains below 2 wt ppm) compared to grains from Rhöndorf (in average 20 wt ppm with significant populations at 10, 20 and 50 wt ppm). Most granites from Sweden have defect water concentrations around 2 wt ppm water, no grains >20 wt ppm water were observed, and the average value of all analysed grains (N=120) is around 4 wt ppm. Quartz grains from the Black Forest granites cluster around 24 wt ppm water. In addition to the defect water content, IR spectra bear information concerning the OH-speciation of the hydrous defects that occur as characteristic absorption band at 3378 cm^{-1}, 3470 cm^{-1}, and 3595 cm^{-1}, depending on the charge balancing cation (Al, Li, or B, respectively) during H-incorporation. If spectral characteristics are parametrised with respect to absorption band ratios, IR spectra can be used to identify grain cluster from distinct source rocks in their siliciclastic counterparts.

Based on the current data set it can be concluded that detrital quartz derived from the Proterozoic Scandinavian Shield is in average by far less rich in OH-defects than detrital quartz derived from the Hercynian orogeny and may thus be used as tool for provenance analysis in sedimentary basins, where both sources are mixed.

ClinOPT - OPTIMIZATION OF THE AMMONIUM UPTAKE OF NATURAL CLINOPTILOLITE FOR ENVIRONMENTAL APPLICATIONS

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Natural clinoptilolite and other zeolite rocks are used in different industrial applications and present an attractive material for environmental purification processes due to their high abundance and low costs of production. Based on its capability to easily exchange alkaline and earth alkaline cations it is possible to adapt clinoptilolite to special needs in industrial waste water treatment. In this contribution we present how in-situ NaOH-liquid-treatments of natural clinoptilolite can influence mineral chemistry, and therefore enhance ammonium uptake within a new industrial process ("ion-exchanger-loop-stripping"). The effects are compared to conventional treatment with NaCl and/or HCl.

Natural clinoptilolite (2.5 kg) from Romania was treated in column experiments operated in upflow mode for 24 h by continuously recycling 20 L of NaOH-, NaCl-, NaCl & HCl-, HCl-solution and deionized water, respectively. Duplicate subsamples of the treated material were taken for combined mineralogical and chemical analyses (XRD, EPMA, XRF). Additionally, liquid analysis of the feeding solution before and after the treatment process was conducted by ICP-MS to complete mass balances for the liquid phase. Ammonium uptake experiments were carried out by adding 20 g of treated material and 500 ml of ammonium sulphate solution (concentration range 500-5000mg NH_4^+ L^{-1}) into an overhead shaker for 24 h. Ammonium was then analysed before and after ion exchange using Kjedahl method.

It can be demonstrated that NaOH treatment of natural zeolites has a strong influence on the exchangeable cation composition and, to some extent, decreases the Si/Al-ratio of the zeolite. Zeolite particles (1.5-2 mm) changed during the treatment resulting in the formation of an altered outer zone in each particle. This alteration zone is characterized by a measureable change of the composition of the exchanged cations, such as a significant increase of Na and decrease in K. It could be shown that pre-treatment of natural clinoptilolite with NaOH can enhance its performance to exchange ammonium in industrial processes (+25%). Pre-treatment allows to create a semi-artificial material, which can be adapted to specific demands for environmental applications such as the denitrification of liquid effluents from biogas and sewage treatment plants.

TEMPERATURE DRIVEN PHASE TRANSITIONS OF PEROVSKITES WITH THE CHEMICAL COMPOSITION Ca(Fe,Mn,Ti)$O_{3-\delta}$

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Perovskites (ABX_3) have numerous physical, magnetic and electronic properties and offer a wide range of technological applications due to their chemical and structural variability. Most of the perovskites do not exhibit the ideal cubic aristotype structure at ambient conditions but a distorted one of lower symmetry; e.g. the mineral perovskite $CaTiO_3$ is orthorhombic at ambient conditions but undergoes structural transitions to the cubic *Pm-3m* structure at elevated temperatures. A correct determination of these phase transitions as well as a detailed knowledge of the structural development with regard to internal and external parameter variation is essential for technological applications and has therefore been in the focus of research for several decades. The objective of this study is to investigate the structural development of Ca(Fe,Mn,Ti)$O_{3-\delta}$ perovskites as a function of temperature and composition with a special focus on the intra-orthorhombic *Pbnm* to *Cmcm* transition (HOWARD & STOKES, 2005), which has been discussed controversially in the past for several perovskite-type oxides. The crystal structures of $CaFe_xTi_{(1-x)/2}Mn_{(1-x)/2}O_{3-\delta}$.($0.08 \leq x \leq 0.31$) perovskites were therefore refined applying the Rietveld method from high resolution powder X-ray diffraction data collected in-situ from 296 to 1273 K in capillary transmission geometry at a Panalytical Empyran Diffractometer equipped with a Galipix detector and a focussing mirror for Mo radiation. The samples exhibit a series of *Pbnm* → *Cmcm* → *I4/mcm* → *Pm-3m* transitions with increasing temperature (ALEKSANDROV, 1976; GLAZER, 1972). The phase transitions as well as the structural development is characterized by the complex interaction between cell distortion, octahedral tilting and -distortion in dependence of temperature, chemical composition and oxygen vacancies. A method to determine the *Pbnm* to *Cmcm* transition in Ca(Fe,Mn,Ti)$O_{3-\delta}$ perovskites, that depends not solely on the visual inspection of weak peak splittings or R factor comparisons, has been derived by formulating a suitable phase boundary condition for the stability field of *Pbnm* (tilt system $a^-a^-c^+$) based on group-subgroup and unit cell relationships in comparison to the cubic aristotype.

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CRYSTAL CHEMICAL AND IR-SPECTROSCOPIC INVESTIGATION OF THE KIESERITE - SZOMOLNOKITE SOLID SOLUTION SERIES WITH RELEVANCE TO MARS

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The investigation of hydrous sulfate deposits and sulfate-cemented soils on the surface of Mars is one of the important topics in the recent scientific endeavour to retrieve detailed knowledge about the planetary water budget and surface weathering processes on our neighbour planet. Orbiter IR spectra of the Martian surface indicate that kieserite, $MgSO_4 \cdot H_2O$, is a dominant sulfate species at lower latitudes (CHRISTENSEN et al., 2004; CLARK et al., 2005). However, given its presumed formation by weathering of Fe-rich olivines and pyroxenes (CLARK & VAN HART, 1981), it is very probable that the actual composition lies at an intermediate value between the Mg- and Fe-kieserite (szomolnokite) endmembers. Although it is known that lattice parameters and spectral band positions differ significantly between these two endmembers, no detailed crystal chemical or spectroscopic investigation along the entire $(Mg,Fe)SO_4 \cdot H_2O$ solid solution range was done so far.

We hereby present first results on structural and lattice parameter changes from single crystal X-ray diffraction measurements of hydrothermally synthesized crystals with variable Mg/Fe ratio. Furthermore, FTIR spectra reveal changes in the wavenumber positions of prominent bands at ambient and low temperature, as the Fe/Mg ratio progresses towards Fe-dominant compositions. The entire kieserite-szomolnokite solid solution shows Vegard-type behaviour, i.e. lattice parameters as well as spectral band positions change along linear trends with increasing Fe content (a = 6.91-7.09, b = 7.63-7.55, c = 7.64-7.78 Å; β = 118.0-118.6° from kieserite to szomolnokite). The changes observed for several absorption features in the IR spectra enable to roughly estimate the Fe/Mg ratio and its variation in Martian kieserite, by comparison with present and future remote sensing data on a global scale, as well as by in-situ rover measurements. Most suitable absorption features in this respect are the ν_1 vibration of the H_2O molecule, the H_2O bending vibration, the ν_3 and ν_1 stretching modes of the sulfate tetrahedron, as well as a band diagnostic for kieserite at around 850 cm^{-1} (LANE et al., 2015). The symmetric stretching mode of H_2O increases in wavenumber with increasing Fe content, while the SO_4^{2-} stretching modes decrease in energy, along with the H_2O bending vibration and the well-resolved band at ~850 cm^{-1}. However, apart from the band at 850 cm^{-1} and the symmetric stretching mode of H_2O, the changes are likely too small to be effectively interpreted from orbital remote sensing measurements showing a poor signal to noise ratio. We therefore recommend only the aforementioned two spectral features to be used for interpretation of the composition of kieserite on the Martian surface.

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STRUCTURE AND IR-SPECTRA OF MHSH(~3/5) (MAGNESIUM HYDROXIDE SULFATE HYDRATE), A POSSIBLE CANDIDATE TO REPRESENT THE PRESUMED SECOND KIESERITE POLYTYPE ON THE SURFACE OF MARS

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The discovery of various sulfate hydrates on the surface of Mars presents one of the exciting findings in the ongoing exploration of our neighbour planet. Based on spectroscopic data obtained by orbital remote sensing, kieserite, $MgSO_4·H_2O$, represents one of the dominant constituents of the sulfate assemblage at lower and equatorial latitudes (CHRISTENSEN et al., 2004; CLARK et al., 2005). However, the acquired kieserite spectra show some oddities in comparison to patterns observed for terrestric kieserite. Currently, these differences are interpreted in the literature as being due to the existence of a second polytype of the kieserite structure, present on Mars, but having also been observed during laboratory experiments involving controlled dehydration of higher $MgSO_4$ hydrates or re-hydration of $MgSO_4$ at low humidity conditions (‘LH-kieserite’; WANG et al., 2009).

This work presents strong evidence that this ‘Martian kieserite‘ is actually a mixture of kieserite with a tetragonal phase of the MHSH-type (magnesium hydroxide sulfate hydrate), structurally related to the mineral caminite ($MgSO_4·⅓Mg(OH)_2·⅓H_2O$, space group $I4_1/amd$, a = 5.242, c = 12.995 Å; KEEFER et al., 1981) corresponding to MHSH(2/3) (HOCHELLA et al., 1983), but with different lattice parameters and site occupancies. We managed to hydrothermally synthesize single crystals of such a phase close in composition to MHSH(3/5) and analysed it by means of single crystal (a = 5.219, c = 13.108 Å) as well as powder X-ray diffraction. Additionally, IR and Raman spectra of the phase have been measured and compared to kieserite and the results of WANG et al. (2009).

The comparison of our data to the product obtained in epsomite dehydration experiments at very low humidity by WANG et al. (2009) yields a very good match, corroborating that the obtained phase is indeed analogic to the stable product of sulfate dehydration in a low humidity environment and temperatures relevant to the surface of Mars. We therefore postulate the hypothesis that MHSH is not only the explanation for the observed spectral discrepancies seen in ‘Martian kieserite’, but that this mineral may as well represent an abundant constituent of sulfate assemblages on the surface of Mars at lower latitudes, with important implications for our understanding of the sulfate-based surface water budget of the Earth’s nearest neighbour planet.

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THERMODYNAMIC TESTING OF HIGH-T/LOW-P WHOLE-ROCK EXPERIMENTS

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This study represents a comparison between thermodynamic calculations (pseudosections) and the results of the experimental investigations on low-*P*/high-*T* metapelite hornfels formation from the Southalpine domain. Pseudosection calculations were undertaken in the system KNCFMTiASH using the program THERIAK-DOMINO (DE CAPITANI & PETRAKAKIS 2010) with an updated version of the internally consistent data set of HOLLAND & POWELL (1998, data set tcdb55), and extended *a*-*X* models concerning the melt phase after WHITE *et al.* (2001, 2007). The hornfels experiments were conducted in a hydrothermal apparatus at a pressure of 0.3 GPa over a temperature range between 550°C to 780°C in order to experimentally simulate hornfels formation and compare it to metapelitic hornfelses from Franzensfeste/Fortezza and Klausen/Chiusa in the Southalpine domain in northern South-Tyrol. As starting materials two natural Brixen quartzphyllite samples were used. One sample W shows a low content of Na_2O (0.59 wt.%) and the other sample SP5 has a higher content of Na_2O (1.72 wt.%) in its bulk rock composition. The agreement between the calculated and the observed mineral assemblages in both experimental series is satisfactory since the claculations yield much more plagioclase as is actually present and predict an earlier formation of aluminium silicates (580°C instead of 730°C). In both experiments the calculated formation of cordierite is >650°C which is clearly higher than observed in the experiments. On the other hand temperature of melt formation at 680°C agrees very well with the textural observations in both experimental series. It is also noteworthy that muscovite is more stable in both sets of experiments than in the pseudosection calculations. This discrepancy varies between 30°C and 110°C and could be due to minor F and/or Cl contents in the micas which we did not analyse. Major mineral chemical trends could also satisfactorely be reproduced except for Ti-contents in biotite. Overall the results indicate actually satisfactorial agreement between the observed and thermodynamically stable mineral assemblages but some discrepancies still occur which are mostly due to kinetical reasons (complete old garnet resorption did not take place, inhibited growth of andalusite). Nonetheless thermodynamic testing not only helps to constrain equilibrium assemblages but also helps identifying certain non-equilibrium features in the whole-rock experiments otherwise not detected (e.g. garnet, muscovite stability).

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GEOTHERMOBAROMETRY OF EXTREME EVENTS: THE KÖFELS ROCKSLIDE

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Pseudotachylytes are the product of concentrated shearing and partial melting (fusion) of rocks. They typically appear in cataclastic zones as veins of molten rock often in association with a characteristic rock micro-breccia or fault gouge. Petrological investigations of these rocks allow constraints on the physical conditions of their formation. When they occur at the basal part of extremely rapid rockslides they are called frictionites. One of the rare occurrences of these frictionites is the Köfels rockslide in the Ötz Valley. The aim of this investigation was to determine the P-T conditions under which frictionites formed during the Holocene rockslide event of Köfels. To accomplish this goal frictionite samples were analyzed using a broad range of analytical techniques - namely light microscopy, electron probe microanalysis (EPMA) and micro-Raman spectroscopy. The frictionite from Köfels represents molten and subsequently crystallized orthogneiss. Temperatures were estimated using the melting temperatures of apatite (lower limit) and zircon (upper limit) and lie between 1600-1700°C. Based on the shift in the main quartz-Raman band at 464 cm^{-1} pressures of ca. 25 GPa were obtained using the data from MCMILLAN et al. (1992) and KOWITZ et al. (2013). Raman mapping of deformed quartz grains shows that the formation of lechatelierite (SiO_2 glass) is most likely not only temperature-induced but also pressure-induced and requires ca. 30 GPa at ca. 1500°C. Because quartz deformation features are confined to micron-scale domains, this indicates that within the frictionites pressures of 25–30 GPa were attained only at point contacts between grains.

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ENCAPSULATED INDUSTRIAL PROCESSES: SLAG-TEMPERED CERAMICS AND ITS IMPLICATIONS FOR PREHISTORIC METALLURGY IN THE LOWER INN VALLEY

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The use of slag-tempered ceramics is a characteristic feature of prehistoric inner-Alpine settlements associated with Cu-ore deposits. Slag-tempered ceramic fragments from three sites in the Lower Inn Valley were investigated with mineralogical, petrographical and geochemical methods: (1) the hilltop settlement Kiechlberg near Thaur, (2) the gravel quarry Kundl-Wimpissinger and (3) the cemetery St. Leonhard site, latter both in the vicinity of Kundl. The Kiechlberg (1) site is a small hill on the south face of the Karwendel mountain range, a few kilometers northeast of Innsbruck. Superficial finds of artefacts and metallurgical slags led to first archaeological excavations in the frame of the Special Research Programme HiMAT (supported by the Austrian Science Fund FWF). On the Kiechlberg, a huge amount of ceramic and flint artefacts as well as metal objects made of copper and bronze were collected during the investigation of a prehistoric layer of debris, indicating an occupation of the site from Late Neolithic up to Middle Bronze Age. One specific feature was the occurrence of slag-tempered ceramic fragments. The slag fragments are <5 mm in size and often occur greenish due to alteration of Cu-minerals. The slag mineral assemblage is olivine + clinopyroxene + spinel + Cu-droplets. Chemical compositions of the Cu metal droplets are identical to compositions from slag samples from the site itself. At the gravel quarry Wimpissinger (2) near Kundl a Late Bronze Age settlement was discovered with a metal workshop containing slag residues and ceramic fragments. In these ceramic fragments slag temper was also found. The mineralogy of the analysed slag fragments as well as the slag temper indicate that the ore used to produce Cu-metal came from the nearby fahlore-group mineral deposits of Brixlegg (embedded in Devonian dolomites, "Schwazer Dolomit"). Significant amounts of Ni and Co also indicate that ores of Triassic age ("Schwazer Trias") were also used. On the south side of the Inn Valley near the village of St. Leonhard (3) near Kundl (Tyrol, Austria) a few pieces of bronze and pottery have been discovered on a field. Here, a Late Bronze Age (Urnfield period) cremation burial site is suggested. Because of the greenish spots observed on one of the pottery fragments it was assumed that some of the jars could have been tempered with slag sand. Slag sand/grit is a by-product of copper ore smelting processes and can be found in the copper smelting sites Mauk A in the nearby Mauken valley, only two kilometres southwest, as well as at the smelting site in Rotholz (Buch i. T.). Mineralogical investigations of ceramic fragments confirm the first assumption that in the three above mentioned sites primarily slag fragments were used as temper. The slag temper has a characteristic chemical/mineralogical composition. The metal/copper inclusions in the slag have typical “fahlore-signature” containing Sb and As. The chemical composition and textures of the silicate phases are comparable to the Late Bronze Age copper slags from the adjacent site “Mauk A”. Chemical analysis of the slag-tempered fragments from all three sites indicate so far that local fahlore-group minerals from the Lower Inn Valley have been used.

GOLD AND SILVER AT ROTGÜLDEN DEPOSIT - WHERE ARE THEY HOSTED?

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Rotgülden is the largest known Au-Ag-As-Cu-Bi deposit in the eastern Tauern Window and a special type of gold mineralization within the Hohe Tauern area. The host rocks of the stockwork, massive and disseminated ores are Mesozoic metacarbonates of the Silbereck Series and calcareous shales of the Brennkogel Formation. Mineralization is structurally controlled by a shear zone partly forming massive replacement ores linked to a large-scale Alpine fold structure (HORNER et al., 1997).

The different ore types record a poly-phase formation related to the retrograde pressure-temperature-time evolution of Young Alpine regional metamorphism and exhumation of the Tauern Window. Three paragenetic stages are to be distinguished: Stage I) Main sulfide stage (c. 375° - 425°C), Stage II) Gold and sulfosalt stages (>400° (?) - c. 200°C), and Stage III) Low temperature (<200°C) "transformation" stage under rather oxidizing conditions.

Gold is mainly found in the chalcopyrite- and arsenopyrite-rich massive ores. During an exploration campaign in 2013 up to 51.5 g/t Au over 3.9 m and more than 200 g/t Ag were encountered (PAAR, W.H., pers.comm). It occurs in different mineral associations, but is commonly inter-grown with chalcopyrite and various sulfosalts in the paragenetic stages postdating the main sulfide (pyrrhotite, arsenopyrite, pyrite) stage. Gold is normally rich in silver (40 - 70 at.% Ag), but higher gold contents (>70 at.% Au) were found in the cores of some grains. Gold shows a chemical within-grain (growth?) zonation of Au-rich and Ag-rich inner zones. The gold grains are often surrounded by a µm-thin Ag-rich rim.

Gold is commonly associated with Ag-Bi-Pb-sulfosalts, which are important carriers of silver in the deposit. The sulfosalts studied can be classified as members of the galena-matildite solid solution series, the lillianite and pavonite homologous series, and Ag±Cu-rich phases. The most common Ag-rich sulfosalts are gustavite, pavonite, freibergite, stephanite, and matildite. Three types of sulfosalt associations are distinguished: Type 1 sulfosalts are present in symplectitic intergrowths, Type 2 are lath- to prismatic-shaped sulfosalts, and Type 3 sulfosalts are low-temperature decomposition and reaction products of the earlier formed sulfosalts. The minerals of the Type 1 sulfosalt association are characterized by rather higher silver, selenium, and antimony contents compared to the other sulfosalt associations.

The final paragenetic stage is characterized by formation of Ag-bearing sulfides such as acanthite, Ag-rich galena (<10 at.% Ag) and Ag-rich chalcopyrite (<4.5 at% Ag).

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FLEISSTALITE, $Fe^{2+}(SO_3)\cdot 3H_2O$, A NEW SULFITE MINERAL SPECIES

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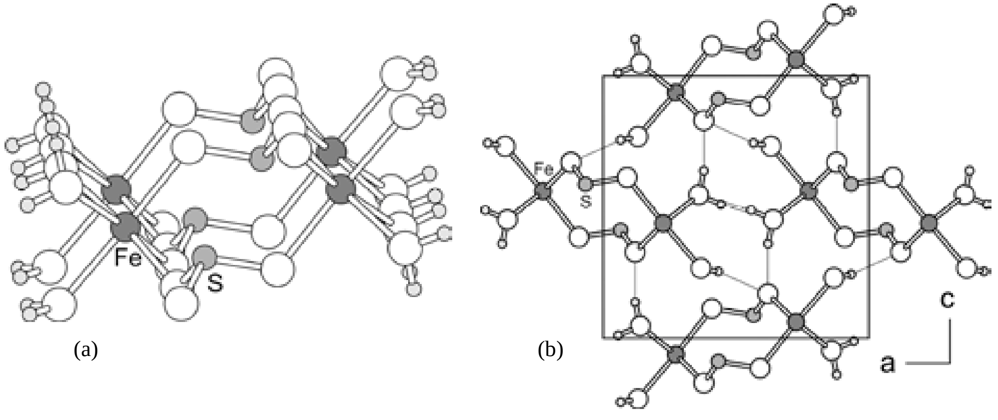
The new mineral fleisstalite was found in an alpine cleft at Mokritzen, Kleines Fleißtal, about 4 km W of the mountain Hoher Sonnblick, Carinthia, Austria. It occurs as spherical aggregates of prismatic, colourless crystals, elongated parallel to [010], up to 0.5 mm long and associated with quartz, muscovite, monazite-(Ce), siderite and pyrite. The mineral (IMA 2016-038) is named after its type locality Kleines Fleißtal.

The empirical formula is (average of 18 spots and based on 6 oxygens apfu) $(Fe_{0.92}Mn_{0.09})_{\square 1.01}(S_{0.99}O_3)\cdot 3H_2O$. Fleisstalite is orthorhombic, space group *Pnma*, and its unit-cell parameters (at 100 K) are: a = 9.554(5), b = 5.534(3), c = 9.429(5) Å, V = 498.4(4) Å^3, Z = 4. X-ray diffraction data indicate the structural relationship of fleisstalite to gravegliaite, the orthorhombic Mn-sulfite trihydrat (BASSO & LUCCHETTI, 1991). Least-squares refinement using anisotropic displacement parameters for all non-hydrogen atoms was carried out with the program SHELXL97 (SHELDRICK, 2008) and yielded $R1$ = 0.057 for 396 unique reflections with $F_o > 4\sigma(F_o)$. The basic structural unit in the fleisstalite structure is the chain built by two isolated Fe - [3O + $3H_2O$] - octahedra connected by two S which build SO_3-groups (Fig. 1a). The chains are running indefinitely along [010] and are crosslinked by hydrogen bonds from 1.792 to 2.158 Å, yielding a three dimensional network (Fig. 1b).

The (Fe^{2+}, Mn)-sulfite trihydrate albertiniite (VIGNOLA et al., 2016) is monoclinic and a polymorph of fleisstalite. The crystal structure of albertiniite is built by a three-dimensional net of Fe-O-S interactions of 6-coordinated Fe atoms and sulfite groups.



(a) (b)

Figure 1. The basic structural unit of the fleisstalite structure is a indefinitely chain built by two Fe-octahedra and two sulfite-groups (a) and its projection along [010] with outlined (single lines) hydrogen bonds (b).

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BAYESIAN STATISTICS APPLIED TO THE RIETVELD METHOD

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A quantitative phase fraction, lattice constant and crystal structure refinement is frequently carried out by means of the Rietveld method. Coherent diffraction length and microstrain can e.g. be deduced by the double Voigt approach. Optimized model parameters are usually obtained by a least square algorithm. However, it is not guaranteed that the global minimum is found by this method when scanning the parameter space. This problem is circumvented by using a global optimization procedure, e.g. Bayes approach with a Markov Chain Monte Carlo (MCMC) algorithm. As a result of this MCMC algorithm not only the global minimum is detected but also probability distributions and correlations of the parameters are revealed. The Rietveld approach combined with the Bayesian statistics is applied to evaluate diffraction patterns of in situ high-temperature X-ray experiments. It has been observed that in contrast to the classical local minimization techniques acceptable results are obtained by means of Rietveld combined with Bayesian statistics even if the signal-to-noise ratio is low. As one of the future goals of this research work numerically stable, highly automated Rietveld algorithms should be established for industrial applications.

A COMPARATIVE STUDY OF X-RAY DIFFRACTION RESULTS OBTAINED 25 YEARS APART: THE CRYSTAL STRUCTURE OF $Co_2(OH)_2(SeO_3)$ FEATURING O–H···*E*[Se^{4+}] HYDROGEN BONDS (*E* = LONE ELECTRON PAIR)

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Only about a century ago, in 1912, Max von Laue and co-workers established the basis for the structure investigation of crystalline materials by demonstrating the diffraction of X-rays at the ordered atomic arrangement in crystals. Naturally, experimental and, later, computational methods have evolved dramatically since then, and, with the wide availability of automatic four-circle diffractometers since the 1980ies, the number of published crystal structures increases exponentially. But also within this later period, experimental methods and refinement strategies were – and constantly are, of course – further developed and improved.

Within the framework of a Bachelor thesis (KREMLICKA, 2017), we reinvestigated the unpublished crystal structure of $Co_2(OH)_2(SeO_3)$, a simple but crystal chemically very interesting compound, using the very same single crystal synthesized and investigated already in 1991 (WILDNER, 1995). Both data sets were obtained on four-circle diffractometers, the earlier using a point detector (3795 reflections measured) with refinement on 1508 unique $F_o > 3\sigma(F_o)$, the new one using a CCD area detector (7156 reflections measured) with refinement on all 1889 unique F_o^2.

$Co_2(OH)_2(SeO_3)$ crystallizes monoclinic ($P2_1/n$, a = 7.724(1), b = 5.829(1), c = 9.568(2) Å, β = 97.37(1)°, V = 427.2(1) Å^3, Z = 4) and is built from complex sheets of two types of strongly distorted face-, edge- and corner-sharing CoO_6 octahedra, which are interlinked via SeO_3 groups and 'standard' O–H···O hydrogen bonds (2.730 Å). A second type of H atom forms no obvious hydrogen bond, but is pointing towards the Se-apex of the pyramidal selenite group, with O···Se = 4.104 Å; however, calculating the position of the Se^{4+} apical lone electron pair *E* (KOSKENLINNA, 1996) yields Se–*E* = 1.38 Å, resulting in a possible, nearly linear, O–H···*E* hydrogen bond with O···*E* = 2.91 Å. Concerning this unusual finding, a literature search is in progress, but so far no comparable cases were found.

The comparison of the two structure analyses from 1991 and 2017 reveals a generally good agreement of the positional atomic parameters for oxygen and heavier atoms; i.e. Se–O and Co–O distances and angles usually match within 1-2σ, whereas, e.g., displacement parameters differ quite dramatically (with much higher values for the data from 1991), albeit showing similar tendencies concerning anisotropy. These findings might indicate that also other non-positional refinement parameters, e.g. atomic site occupancies essential in structure refinements of minerals (and solid solutions in general), could differ significantly for the very same sample throughout 'modern' structure analyses (i.e. based on four-circle diffractometer data) which have been performed around a quarter-century apart.

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FIRST RESULTS OF THE INVESTIGATIONS ON THE SYSTEM Fe_2O_3-CaO-Al_2O_3-MgO (FCAM): THE PHASES FCAM-I AND FCAM-III, TWO NEW HOMOLOGUES OF THE AENIGMATITE STRUCTURE-TYPE (SFCA)

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In analogy with the so-called SFCA series, our investigation in the chemical system FCAM (Fe_2O_3-CaO-Al_2O_3-MgO) showed the existence of a stoichiometric homologous series $M_{14+6n}O_{20+8n}$, where M = Fe, Ca, Al, Mg and n = 1 or 2. In more detail, the two previously unknown compounds $Ca_3MgAl_6Fe_{10}O_{28}$ or FCAM-I (isostructural with SFCA-I, ZÖLL et al., 2017) and FCAM-III (ZÖLL, unpublished data) $Ca_{2.38}Mg_{2.09}Fe^{3+}_{10.61}Fe^{2+}_{1.59}Al_{9.33}O_{36}$ have been synthesized.

Two experimental series in air and under controlled oxygen fugacity using the hematite-magnetite buffer were conducted. Pure polycrystalline FCAM-I formed at 1190 °C in air. Increasing the temperature from 1300 °C to 1400 °C, the FCAM-I phase breaks down forming a variety of new compounds depending on T and fO_2.

Basic crystallographic data of FCAM-I ($Ca_3MgAl_6Fe_{10}O_{28}$) are: space group $P\,\bar{1}$, a = 10.2940(3) Å, b = 10.4393(3) Å, c = 11.5977(6) Å, α = 94.342(6)°, β = 111.611(6)°, γ = 109.617(3)°, V = 1069.81(7) Å³, Z = 2.

In air, the FCAM-III phase forms and co-exists with FCAM-I at 1400 °C. Increasing the temperature up to 1425 °C, FCAM-I disappears completely and FCAM-III co-exists with magnesium ferrite and a variety of calcium iron oxides. At 1450°C FCAM-III breaks down.

Small single crystals of FCAM-III were characterized using electron microprobe analysis and synchrotron X-ray single-crystal diffraction (X06DA beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, CH). The basic crystallographic data of FCAM-III ($Ca_{2.38}Mg_{2.09}Fe^{3+}_{10.61}Fe^{2+}_{1.59}Al_{9.33}O_{36}$) are: space group $P\,\bar{1}$, a = 10.223(22) Å, b = 10.316(21) Å, c = 14.203(15) Å, α = 93.473(50)°, β = 107.418(67)°, γ = 109.646(60)°, V = 1323.85(2) Å³, Z = 1.

Using Schreinemaker's technique to analyse the phase relations in the system Fe_2O_3-CaO-Al_2O_3-MgO as a function of T and fO_2 it was possible to obtain the semi-quantitative stability relations between the participating phases and to construct a topologically correct phase sequence as a function of temperature and oxygen fugacity.

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