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ABSTRACTS

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THE MBC $_{(1.7)}$: A VISUAL BASIC PROGRAM TO CALCULATE BULK COMPOSITION OF ROCKS FROM CHEMISTRY AND THE VOLUME PROPORTIONS OF THE PHASES

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The MBC $_{(1.7)}$ is a Microsoft® visual basic 6.0 program that enables the user to calculate the model bulk composition of the rocks, the chemical formula of different phases and the volume percent of the phases (modal analysis). The bulk composition plays an important role to identify the rocks, origin of the rocks and its tectonic environments. The X-ray fluorescence spectroscopy (XRF) is the method of choice for analysis of major elements and some trace elements. Erroneous analytical results may arise for a variety of reasons, such as, contamination, calibration and peak overlap. In many petrological problems, the scientists interpret the rocks in scale smaller than a typical XRF sample size. Therefore, the XRF is unsuitable for such studies. The MBC program can calculate the model bulk composition of such small scale samples based on the volume of the phases and the molar amount of each oxide per the formula unit of the phases. The program has the ability to calculate the chemical formula of the phases. The output results can be printed out in the form of A4 papers. The program code and the necessary support files are approximately 1.5 MB as a self-extracting setup file and can be downloaded from http://wegener.uni-graz.at/group/tabualam/mbc.

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FLUID INFILTRATION AND METASOMATISM PROCESSES IN WADI SOLAF CALC-SILICATE, EGYPT

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Fluid flow during the metamorphism has important consequences for the thermal and chemical structure of the metamorphosed rocks. Here we study calc-silicate rocks of Wadi Solaf, Egypt to infer the role of the fluid which infiltrated through the Najd fault system. The Najd fault system is the best exposed and possibly the largest pre-Mesozoic zone of transcurrent faulting on Earth. This system was developed during the interval 540–620 Ma (Pan-African Orogeny). High-temperature, low-pressure calc-silicates in the upper amphibolite facies terrain of Wadi Solaf area consist of calcite, grossular, wollastonite, diopside, scapolite, anorthite, albite, andradite, chlorite, epidote, quartz and magnetite. Two metamorphic cycles are recognized: the first cycle is regional metamorphism, while the second one is contact metamorphism. The pro-grade metamorphism of the first cycle is characterized by continuous iron-silica rich fluid infiltration process through an early foliation. During this stage of the metamorphism, the activity of CO_2 was between 0.1–0.128. The rocks after the peak metamorphism subjected to isothermal exhumation with CO_2 activity reached to 0.17–0.26 and oxygen activity was around 0.465–0.485. At depth equivalent to 5.5 kbar, the calc-silicate at higher structural level was metamorphosed under temperature condition above 855°C by the intrusion of syntectonic granites (second cycle). This study shows that the Najd fault system has important consequences for the thermal and chemical structure of the crust during the Pan-African Orogeny.

THE FEIRAN METAMORPHIC COMPLEX OF SINAI: ITS RELATIONSHIP TO THE CORE COMPLEXES OF THE ARABIAN-NUBIAN SHIELD

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The high-grade metamorphic rocks of the Arabian-Nubian Shield are exposed in a series of tectonic windows which are exposed from underneath a low grade arc assembly. In the Eastern Desert of Egypt, these basement complexes have been interpreted as metamorphic core complexes exhumed in extensional settings. In Sinai, the exhumation mechanism of Feiran-Solaf complex is difficult to reveal on the basis of structural arguments as all of its margins are obliterated by post-tectonic granites. Here we use metamorphic methods to investigate its tectonic history and show that the Feiran-Solaf complex was characterised by a single metamorphic cycle experiencing peak metamorphism around 700–750°C and 7–8 kbar and subsequent isothermal decompression to about 4–5 kbar, followed by near isobaric cooling to 450°C. Correlation of this metamorphic evolution with the deformation history shows that peak metamorphism occurred prior to the compressive deformation phase D_2, while the compressive D_2 and D_3 deformation occurred during the near isothermal decompression phase of the P-T loop. We interpret the concurrence of decompression of the P-T path and compression by structural shortening as evidence for the Najd fault system exhuming the complex in an oblique transpressive regime. However, final exhumation from 14.5 km depth must have occurred due to an unrelated mechanism. In the Arabian part of the Arabian-Nubian shield no metamorphic studies exist for the high-grade metamorphic complexes which have more or less the same geometry as the Feiran-Solaf complex. The Arabian complexes need further studies to draw an overview for the evolution of the high-grade metamorphic rocks of the Arabian-Nubian Shield during the Pan-African Orogen.

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TITANITE-BEARING PEGMATITES FROM ARKAROOLA, SOUTH AUSTRALIA

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The sillimanite-bearing Mesoproterozoic metagranites and metasediments of the Mt. Painter Inlier, Arkaroola (northern Flinders Ranges) contain a variety of unusual titanite-bearing pegmatites: a) Kfeldspar – quartz – actinolite – titanite (5%, up to 1 cm); b) scapolite (marialite) – actinolite – titanite (7%, up to 1 cm) – quartz; c) megacryst diopside – titanite (10%, up to 40 cm). Pegmatite (a) is zoned, with euhedral titanite crystal on one side (rim), whereas actinolite dominants on the other rim, Kfeldspar and quartz are mainly in the centre of the pegmatite. Pegmatite (b) contains mainly large elongated crystals of marialite, intergrown with titanite and actinolite, accessories minerals are epidote (secondary), biotite, zirkon and magnetite. The diopside-titanite veins (pegmatite c) are NW–SE striking and up to 5 m in thickness and contain minor amounts of quartz, hematite, calcite and apatite (BAKKER & ELBURG, 2006). Diopside is partly hydrothermally altered to actinolite.

Fluid- and melt-inclusions are abundant in diopside, titanite, and quartz, and are used to examine the formation conditions of these pegmatites. Diopside contains irregular shaped inclusions of calcium-depleted pyroxenes (melt inclusions), which occasionally also includes magnetite crystals and a highly saline fluid phase in the presence of a vapour bubble. Titanite contains trails of dark inclusions with a strong re-equilibration texture (“implosion haloes”). A brine and a vapour bubble are observed in some of these inclusions. Titanite have similar inclusions in the three pegmatite types: a, b, and c. The fluid inclusions in quartz are highly variable in phase assemblages. Most of them contain variable sized cubic salt crystals and vapour bubbles (up to 30 vol%). Additional hematite, magnetite, and other minerals are accidentally trapped in some inclusions.

Electron-microprobe analyses show that the titanite is enriched in LREE and Y, whereas those elements are absent in diopside. Furthermore, titanite contains a variety of sporadic exotic minerals, such as Th-rich minerals, Nb-rich minerals, Ca-Th-U-rich crystals, Nb-Y-Ti-Th-U crystals, Si-Th crystals, monazite, zircon, baddeleyite, uraninite, thorianite.

These preliminary results are used to obtain a genetic model for all types of pegmatites in relation to the adjacent metamorphic rock and regional setting of the Mesoproterozoic basement of the Mt. Painter Inlier. This research will be extended to obtain complete data on the fluid activity in the studied area, based on melt- and fluid-inclusion studies.

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THE USE OF NATURAL HYDRAULIC LIME MORTARS IN RESTORATION; TRANSFORMATION PROCESSES OF BINDER HYDRAULIC COMPONENTS DURING RAPID AND SLOW AIR SLAKING

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Marly limestones are an excellent raw materials to produce Natural Hydraulic Limes (NHL). NHL are produced by firing natural occurring raw materials, such as marly limestones, at temperatures lower than the temperature used in the manufacture of cement clinker. During firing, silica reacts with CaO to form calcium silicates which provide hydraulic properties to the end products. NHL contain mainly portlandite $Ca(OH)_2$ and larnite (Ca_2SiO_4). NHL based mortars are very important for the restoration and conservation of archaeological monuments and historical buildings. Materials for restoration purposes should match those used originally as closely as possible in order to provide some continuity with the past and to age in a similar way as the original.

This paper presents the importance of transformation of larnite during air slaking in NHL based mortars used for restoration purposes and the significance of crystallite size on the portlandite carbonation process. The raw materials used were marly limestones from Crete and a pure fine crystalline calcitic marble, fired at 900 °C for 12 hours. Each of the produced NHL and NL (natural lime) were divided in two parts. The first part was slaked in open air with RH 55-60% (slow hydration), and the second part was rapidly slaked with water. Sampling took place for different periods of time and mineralogical analysis was carried out by X-ray powder diffraction, while quantitative analysis was performed by the Rietveld method using the TOPAS software program.

The NHL binder components are: larnite, vaterite, gehlenite, portlandite, brownmillerite, calcite and minor amounts of quartz, wollastonite and periclase, while NL binder consists only of portlandite. The amount of larnite decreases with time and the amount of vaterite increases simultaneously. The decomposition of larnite offers higher amounts of amorphous SiO_2 and vaterite to the binder. The increase of amorphous SiO_2 improves the pozzolanic activity of the binder during reaction with portlandite.

The rapid or slow hydration of CaO of NHL or NL influences significantly the crystallite size of portlandite. Rapid hydration produces a well crystallized portlandite with crystallite size > 1800 Å, while slow hydration forms a poor crystallized portlandite with crystallite size < 250 Å. It is observed that the speed of the carbonation process of portlandite is a function of crystallite size. The carbonation of the low crystalline portlandite is 1.5 time faster than of high crystalline portlandite. The carbonation is inversely proportional to the crystallite size.

Cubic mortar specimens were produced with different binder/aggregate ratio. The aggregate was quartzite sand. After curing for 28 days to 6 months, the compressive strength of the mortar specimens reaches 10 MPa. The increase of the compressive strength was due to the carbonation of portlandite, the hydration of larnite, the decomposition of larnite to vaterite as well as to the reaction of amorphous SiO_2 with portlandite. Furthermore the presence of amorphous SiO_2, which appears in the fired product, probably contributes to the increase of strength with time.

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MAGNESIUM PHOSPHATES: FROM MOLECULAR STRUCTURES TO STRONGLY CONDENSED MINERALS

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Magnesium-phosphate minerals are structurally very special because in contrast to calcium phosphates they comprise on one hand highly hydrated molecular structures, in which PO_4 units are kept in position by hydrogen bonds originating from $Mg(H_2O)_6^{2+}$ octahedra, and on the other hand they form densely packed orthophosphate structures. As examples for highly hydrated minerals, structure and formation conditions of e.g., cattiite ($(Mg(H_2O)_6)_3\,[PO_4]_2 \times 4\,H_2O$, CATTI et al., 1981; BRITVIN et al., 2002) and struvite ($Mg(H_2O)_6NH_4[PO_4]$, FERRARIS et al., 1986) are discussed. As examples of densly packed magnesium-phosphate minerals, special emphasis is placed on the modulated series of triplite–wagnerite group minerals (ARMBRUSTER et al., 2008). The space group for wagnerite $(Mg,Fe)_2PO_4(F,OH)$ was considered to be $P2_1/c$ with $a = 9$, $b = 12.6$, $c = 11.9$ Å, $\beta = 108°$ until REN et al. (2003) reported a new polytype (space group Ia, $a = 9$, $b = 31.5$, $c = 11.9$ Å, $\beta = 108°$) named wagnerite-5*b* as it has a five-fold superstructure along **b** relative to triplite Mn_2PO_4F and zwieselite Fe_2PO_4F (space group $I2/a$, $a = 9$, $b = 6.5$, $c = 12$ Å, $\beta = 106°$). Single-crystal X-ray and chemical data were obtained on 38 wagnerite samples (ARMBRUSTER et al., 2008) formed under conditions ranging from near surface in sediments to high temperatures (granulite facies) and ultrahigh-pressures. We found five "pseudo"-commensurate modulated structures (polytypes) in decreasing abundance: 5*b* (21 examples), 2*b* (12), 7*b* (3) and 9*b* (2) and 3*b* (1). Five additionally studied triplite–zwieselite samples from pegmatites showed the 1*b* type structure. The crystal structures of all 6 polytypes have been refined from single-crystal X-ray data and imaged by HRTEM. The main structural difference among the various polytypes is modulation of the (F,OH) arrangement giving rise to different space groups and periodicity along **b**. F-dominant triplite–zwieselite (mean octahedral radius: > 0.79 Å) has the 1*b* polytype. The 5*b* polytype prevails in F-dominant, Fe,Mn-rich wagnerite (mean octahedral radius: 0.74-0.79 Å) and in Mg-rich samples (octahedral radius = 0.72 Å) with near F end-member composition. The single 3*b* wagnerite plots among the 5*b* samples but close to the triplite–zwieselite (1*b*) boundary in terms of X_F and mean octahedral radius. Mg-rich wagnerite (octahedral radius = 0.72–0.73 Å) is characterized by the 2*b* polytype, whatever the OH content. 7*b* and 9*b* polytypes are found for compositions stradling the boundary of the 5*b* and 2*b* fields with X_F between 0.84 and 0.98. These broad relationships suggest a major role for compositional control in determining modulation periodicity.

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$K_2Ca_4Si_8O_{21}$ – AN UNUSUAL LAYER SILICATE CONTAINING Q^2 AND Q^3 UNITS

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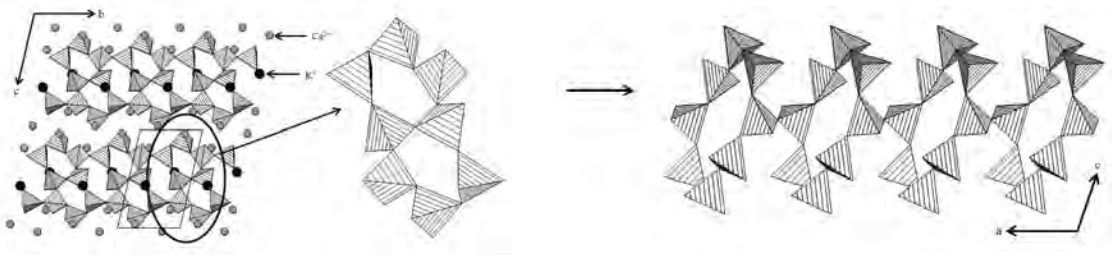
The system K_2O-CaO-SiO_2 has not been investigated in great detail. So far only one comprehensive study focussing on the SiO_2-rich part of the system has been published (MOREY et al., 1930). The authors reported the existence of seven different potassium calcium silicates.

In the course of an ongoing research project on this ternary system, single crystals of $K_2Ca_4Si_8O_{21}$ were synthesized in an experiment with the initial aim to produce $K_2Ca_3Si_6O_{16}$ according to the phase diagram given by MOREY, KRACEK & BOWEN (1930). The compound adopts space group $P\overline{1}$ with $a = 6.8052(3)$ Å, $b = 7.1049(3)$ Å, $c = 11.2132(5)$ Å, $\alpha = 96.680(4)°$, $\beta = 105.280(4)°$, $\gamma = 109.259(4)°$ and $Z = 1$. The refinement of the atomic parameters resulted in a residual of $R1 = 0.0279$ ($wR2 = 0.0652$) for 1736 observed reflections ($I > 2\sigma(I)$). IR- and Raman spectroscopy complete the structural characterization. The observed bands were interpreted by means of density functional theory (DFT) calculations.

Corresponding to LIEBAU (1985), $K_2Ca_4Si_8O_{21}$ belongs to the group of single layer silicates. An appropriate topological analysis has been performed using the program CRYSTANA (2008). As shown in Fig. 1, the layers parallel to (001) are composed of loop-branched *fünfer* single chains. One discrete chain has a translation period of about 6.8 Å and runs parallel to [100]. In summary, the structural formula can be written as $K_2Ca_4\{\mathbf{\mathit{lB}},5,1^2_\infty\}[Si_8O_{21}]$. Contrary to almost all known single layer silicates, which are exclusively built of ternary $[SiO_4]$-tetrahedra, the layers in the present compound are made up of Q^2 and Q^3 tetrahedra at the ratio of 1:3. Charge balance is provided by K and Ca ions, which are distributed among a total of three general *M* positions. Since one *M* cation is octahedrally coordinated, the whole structure can also be described as a stuffed mixed tetrahedral-octahedral framework.



(a) **(b)** **(c)**

Figure 1. The layers parallel to (001) **(a)** are made up of loop-branched *fünfer* single chains **(b)**, which are successively linked along [010] **(c)**.

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NATURAL DISSOLUTION FEATURES OF SULPHIDES FROM MADAN Pb-Zn ORE DEPOSITS, SOUTH BULGARIA

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Representative specimens from the hydrothermal Pb-Zn deposits of the Central Rhodopes, important parts of the Alpine-Carpathian-Balkan-Dinaride province, were studied. The economically significant deposits of the Madan district include both veins and metasomatic ore bodies enclosed in high-grade metamorphic rocks of the Rhodope massif. The main stages of hydrothermal mineralization are: pre-ore skarn; main sulphide; and late quartz-carbonate stage (VASSILEVA et al. in this volume and references therein). The main ore deposition took place at high temperature (350-330-280°C), and low pressure (~100 bar), from low-concentrated (4-5 wt% salinity) Cl-Na-K containing fluids (BONEV & PIPEROV, 1977).

It is well known that polyhedral sulphide crystals and druses with varied morphology are widespread in the deposits of the Madan district. Sulphide crystals are frequently affected by selective natural hydrothermal dissolution. Especially interesting are the dissolution morphology of galena, sphalerite and chalcopyrite and the various local differences.

Morphological studies on galena dissolution (BONEV, 2007) revealed that rounded, fine-layered corrosion surfaces, starting from the crystal edges and corners, are produced at low undersaturation, whereas at larger undersaturation single etch pits, grooves along the subgrain and twin boundaries, pores and channels, relict pyramidal bulges, etc. formed under the control of the main surface defects, are important. Characteristic dissolution forms of sphalerite from Krushev Dol are rough skeletal formations with smooth edges and triangular islands separated by very fine layers on the tetrahedral faces. In these formations, skeletal depressions occupy the undeveloped centers of crystal faces. Microtopography of the dodecahedral faces is formed mainly by circular etch pits. Chalcopyrite often occurs as well-formed tetrahedral or pseudo-octahedral crystals (RADULOVA & BONEV, 1993). Intensively corroded large chalcopyrite crystals are characteristic examples of chalcopyrite dissolution from the Shumachevski Dol deposit. Sometimes only crusts, which grew autoepitaxically on the early large crystals, are selectively affected by the dissolution.

Based on these observations the etching features formed by selective natural dissolution of sulphides are described, which are different from growth patterns. The differences in the degree of dissolution are evaluated on representative samples from the Madan ore deposits. The naturally dissolved sulphides exposed to weathering conditions undergo fast alterations resulting in formation of highly soluble phases. Mostly, such minerals determine the exceptional reactivity and environmental impact of sulphide-bearing mine wastes.

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A GENETIC MODEL FOR BANDED MAGNETITE-BARITE DEPOSITS IN MOOTEH AREA, WEST-CENTRAL IRAN

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Several iron ore bodies occur to the southwest of the Mooteh gold district, ~50 km East of Golpaygan, Isfahan province, West-Central Iran. The ore bodies are located in the Sanandaj-Sirjan metamorphic-plutonic belt. The country rocks include various schists (chlorite-sericite schist, mica schist, tremolite-actinolite schist), gneisses, quartzite, calc-silicate assemblages, calc-schist, and metavolcanic rocks. The metamorphic series were intruded by a series of mafic dykes, after the main metamorphism and/or during uplift; this is supported by retrograde reactions and lack of metamorphic fabrics.

Outcrops of the Mooteh granite occur to the north of the ore bodies. The granite has been dated, by U-Pb method, to be 578 ± 22 Ma (HASSANZADEH et al., 2008). The country rocks are thermally metamorphosed, implying an older age for the Mooteh metamorphic complex. An Infracambrian age is proposes for the protoliths of the metamorphic rocks.

The iron ores occur as layers and lenses of massive magnetite, magnetite-hematite, and banded magnetite-barite, magnetite-quartz, as well as magnetite-rich skarns.

The textural relationships indicate that magnetite is of pre-metamorphic origin. The banded and massive ores were recrystallized during the greenschist-grade metamorphism, while the iron-rich rocks were transformed into skarn-type assemblages.

The skarn-type ore is relatively enriched in W, Sn, Au and Ag. The Mooteh granite is a highly fractionated, Fe-Mg poor intrusion, and cannot be a potential source for the iron ore bodies and the Fe-rich skarns. The Fe-rich skarns, formed through isochemical reactions during greenschist grade metamorphism, with little introduction of materials from external sources.

The $\delta^{34}S$ values fall in the range +19/5 to +27/9 permil, implying a marine source for the sulphur. Considering the isotopic curves for marine sulfate through geologic time, an Infracambrian-Cambrian age is proposed for the ores and the country rocks.

The Mooteh iron ores are enriched in base metals, Au and Ag, and depleted in REE, and U, Th, V, Ni, Ti, implying a dominant chemical deposition for the ores, with little detrital inputs into the sedimentary basin (LOTTERMOSER & ASHLEY, 1996; NYSTRÖM & HENRIQUEZ, 1994). The ore constituents were provided by submarine hydrothermal vents, associated with episodic volcanic activities; inputs from lands can not be ruled out.

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THE HOHENTAUERN/SUNK DEPOSIT – A KEY FOR UNRAVELLING SPARRY MAGNESITE FORMATION IN THE GRAYWACKE ZONE/EASTERN ALPS, AUSTRIA

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The Carboniferous of the Veitsch nappe in the Graywacke Zone (Eastern Alps/Austria) is the type region of the “Veitsch type” sparry magnesite. The numerous deposits/occurrences of sparry magnesite and talc are integrated in the Minerogenetic Map of Austria as the “Veitsch nappe magnesite-talc district”. The Hohentauern/Sunk deposit, at the structural base of the Veitsch Nappe, is one of the best known magnesite deposits in this district. The stratiform magnesite display distinct metasomatic structure at the contact to the host rocks with distinct sedimentary and diagentic features. Sparry magnesite of the Hohentauern/Sunk deposit is characterized by pinolite, rosette and banded (zebra) textures.

The magnesite contains irregulary distributed mikroinclusions of fine-grained dolomite and evaporate minerals (sylvite). On the other hand magnesite formation is followed by several generations of late dolomite. The bulk composition of sparry magnesite of the deposit has lower MgO and higher CaO contents in comparison to stoichiometric magnesite crystals. The elevated CaO/MgO ratio derives from relics of the dolomite microinclusions and various types of late dolomite formed by redolomitization of the magnesite. The concentrations of some trace elements (Sr-Ba, Ti, Fe-Mn and Cr-Ni-Co) illustrate a Mg^{2+}-metasomatism origin of magnesite mineralization. In the Hohentauern/Sunk deposit the sparry magnesite displays REE pattern with low LREE/HREE, depletion of LREE and a negative Ce anomaly. The stable isotopes ($\delta^{18}O$ and $\delta^{13}C$) data of the sparry magnesite overlap with those typical for magnesite formed by metasomatic dolomite replacement (SCHROLL, 2002). Strongly scattering $^{87}Sr/^{86}Sr$ ratios are affected by several processes. Therefore they are not significant for the magnesite formation. However Nd-Sr isotopes chemistry show that the mineralizing fluid percolated through crustal rocks. Fluid inclusion studies on the sparry magnesite indicate a high salinity of the Mg-rich fluid which transformed the dolomite protoliths. Sm-Nd geochronology of the sparry magnesite show a range of Late Carboniferous to Early Permian. All geological, petrographical and geochemical features of the Hohentauern/Sunk deposit support a diagenetic dolomitization of carbonate host rocks and an epigenetic formation of the magnesite deposit, via metasomatic replacement of a dolomitic protolith by high-salinity Mg-rich solutions. The age of mineralization, however, is still the subject of intensive discussion.

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INVESTIGATION OF PLATINUM-GROUP MINERALS (PGM) IN CHROMITE OF IRAN (KHOY OPHIOLITE) USING ELECTRON MICROPROBE

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Chromitite associated with ophiolite represent a potential target for platinum-group elements (PGE) recovery since they are extremely rich in these strategic metals, especially in Os, Ir and Ru, compared to their host peridotite. This geochemical anomaly was ascribed to the fact that PGE occurred in solid solution in chromite lattice. However, it has been recently demonstrated that the PGE form specific phases, the so called PGM. The PGM are very small (generally less than 10µm) and occur mostly in the chromite crystals. Owing to their small size and to the fact that are often composed of more than one phase, nowadays the most useful technique to investigate PGM is the electron microprobe. The eastern ophiolitic belt of Turkey extends into Iran, forming the so called Khoy Ophiolite, that is the equivalent to the inner group of Iranian ophiolites. More than 70 chromite occurrences have been documented from different ophiolites of Iran. Therefore this country has a potential for PGM presence. In this work we report, for the first time, the discovery of PGM in the chromitite of the Khoy ophiolite, located in NW of Iran. Chromitites form lenticular or irregular pods and occur associated with serpentinized peridotite. Selected samples of chromitites from three different occurrences were investigated at the E. F. Stumpfl microprobe laboratory (University of Loeben, Austria). Some chromitites are fresh, whereas others are altered, showing a rim composed of magnetite and ferrian chromite (Fig. 1a). The magmatic composition (wt%) of the chromite varies in the following ranges: Cr_2O_3 = 30–42, Al_2O_3 = 24–33, Fe_2O_3 = 14–17, MgO = 13–15. TiO_2 is always less than 0.25 wt%. The efficiency of this technique for detecting micrometer scale PGM was demonstrated also in the investigated chromitites that proved to contain different type of PGM. The identified PGM form very small (about 6 microns in size) polyphase grains and, similarly to other ophiolitic chromitite, they are laurite (L), erlichmanite (E) and osmium (O) (Figure 1B). The results presented here, although preliminary, suggest that the Iran chromitites have a potential for the presence of PGM that should be investigated in more detail.

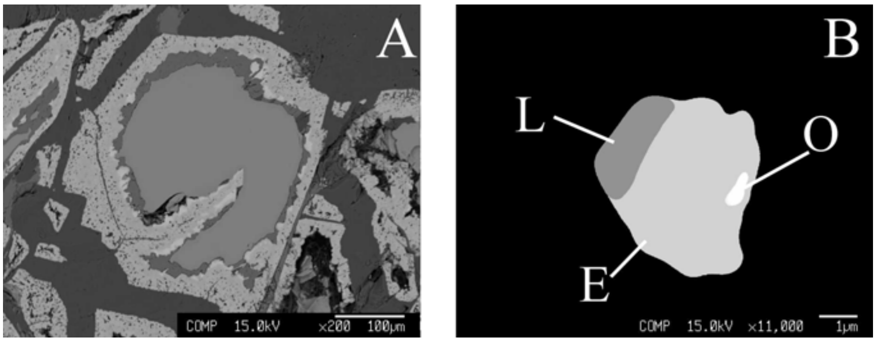

Figure 1. Electron images of an altered crystal of chromite (A) and of a PGM enclosed in fresh chromite (B).

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MUKHINITE, "TAWMAWITE" AND DISSAKISITE: CRYSTAL CHEMISTRY OF THE V-, Cr- AND REE-RICH EPIDOTE-GROUP MINERALS

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Epidote group represents a wide group of minerals with variable chemical composition. Dissakisite ($CaREEAl_2Mg[Si_2O_7][SiO_4]O(OH)$), and mukhinite ($Ca_2Al_2V^{3+}[Si_2O_7][SiO_4]O(OH)$) are rare minerals occurring in the special genetic environment enriched in REE and V, respectively. "Tawmawite" ($Ca_2Al_2Cr[Si_2O_7][SiO_4]O(OH)$) is the theoretical Cr-rich end-member, yet not valid, but considered in this work as a "tawmawite" molecule.

Crystal chemistry of V-, Cr- and REE-rich epidote-group minerals (EGM) is controlled by specific substitution mechanisms, different to the common EGM. Vanadium mostly substitutes for Al in monovalent substitution VAl_{-1}. The content of V_2O_3 in mukhinite from the Tashelginsk, Russia attains 11 wt% (SHEPEL & KARPENKO, 1969). Mukhinite from Pezinok – Rybníček, Slovakia contains up to 10 wt% V_2O_3. Moreover, it is enriched in REE (locally more than 13 wt%) verging to dissakisite.

Incorporation of REE into the EGM structure is carried by complex multivalent and multi-site substitutions. REE are included in the $Fe^{2+}REEFe^{3+}_{-1}Ca_{-1}$ substitution in the epidote–allanite solid solution (ERCIT, 2002) but in Fe-poor environment its influence is limited. Clinozoisite-dissakisite substitution ($REEMgCa_{-1}Al_{-1}$) as an alternative to the epidote–allanite substitution was suggested by ENAMI & ZANG (1988) who described allanite with more than 6 wt% MgO from the Donghai district, China. Moreover, REE-rich mukhinite and V-rich dissakisite from Pezinok – Rybníček show a new, mukhinite-dissakisite type of substitution, $REEMgCa_{-1}V_{-1}$.

Behaviour of Cr in dissakisite and mukhinite is obscured by the Al-Cr disorder in the both *M*3 and *M*1 sites (ARMBRUSTER et al., 2006). Consequently, the clinozoisite–"tawmawite" substitution ($CrAl_{-1}$) influences both sites. On the other side, the substitution of Cr for V is limited only to the *M*3 site. "Tawmawite"–dissakisite substitution ($REEMgCa_{-1}Cr_{-1}$) appears to be present in Cr-rich dissakisite from Outokumpu (TREOLAR & CHARNLEY, 1987). The influence of the both substitutions was observed also in dissakisite and mukhinite from Pezinok – Rybníček enriched in Cr (up to 7 wt%).

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CALCIC TO SODIC-CALCIC AMPHIBOLES OF LAMPROPHYRES FROM THE DITRĂU ALKALINE MASSIF

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Lamprophyres are alkali-rich igneous rocks containing essential amphibole and/or biotite with no feldspar or quartz phenocrysts and form subvolcanic dykes, sills or vents (ROCK, 1991).

The Ditrău Alkaline Massif (DAM) is a Mesozoic alkaline igneous complex situated in the S-SW part of the Giurgeu Alps belonging to the Eastern Carpathians (Romania), and it is composed of hornblendite, diorite, nepheline syenite, syenite, monzonite and alkali granite. The whole complex is cut by late-stage lamprophyre and tinguaite dykes.

This paper reports new results on the amphibole mineralogy of lamprophyres which were not discussed yet in former works of the DAM.

Amphibole compositions were determined by Cameca SX-50 electron microprobe at the Department of Earth Sciences, University of Uppsala, Sweden. Operating conditions were probe current of 15 nA and acceleration voltage of 20 kV.

Three types of amphiboles are determined in the lamprophyres from the northern part of the DAM. They form nearly euhedral prisms and needles. The first type is hornblende with kaersutite core and magnesiohastingsite rims. The second type of amphiboles is elongated hastingsite to magnesiohastingsite which is green in colour. The third type is subhedral crystals of ferro-richterite which are also green coloured.

The composition of amphiboles was recalculated using 13eCNK estimation (LEAKE et al., 1997). The kaersutite cores are Si-poor and Ti-rich (Ti = 0.58–0.76 apfu) with mg# = 0.63–0.67 while toward the rims the Si, Fe^{tot} content of the hornblendes increases, and the Al^{IV}, Mg and Ti content decreases (mg# = 0.50–0.64). The hastingsites-magnesiohastingsites are Fe-rich (Fe^{2+} = 1.78–2.04, Fe^{3+} = 0.46–0.70 apfu, mg# = 0.49–0.55) and potassian (K = 0.23–0.40 apfu). Ferro-richterites [$(Ca + Na)_B$ = 2.85–3.08 and Na_B = 0.86–1.41] are Al-poor and Na-rich.

The estimated crystallisation pressure based on Al-in-hornblende barometry (SCHMIDT, 1992) for kaersutite cores are 7.4–8.4 kbar, for magnesiohastingsite rims are 5.8–6.8 kbar and for hastingsites-magnesiohastingsites are 6.6–9.2 kbar. For estimating the pressure of sodic-calcic amphibole crystallisation Brown's geobarometry (1977) was applied. Based on this method ferro-richterites crystallised above 5.8 kbar.

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TEXTURAL FEATURES OF ZEOLITIC ROCKS FROM MUNELLA, NORTHERN ALBANIA

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Textures, that represent the geometrical relationships among the component crystals of a rock and any present amorphous materials (glass or gas cavities), comprise the following properties: i) crystallinity, ii) granularity, iii) crystal shapes and iiii) mutual relations or arrangement of crystals and any amorphous materials (MACKENZIE et al., 1999).

In studied samples from Munella region, the following texture types are evidenced (BEQIRAJ GOGA, 2005): a) *hypocrystalline textures* (according to crystallinity) that is represented by partly recrystallized glass, quartz and albite phenocrysts; b) *microcrystalline-cryptocrystalline texture* consisting of microlites of zeolite, quartz, chlorite and calcite which filled the vesicles that, in turn, are cemented by zeolitic matrix not well crystallized; porphyric texture consisting of albite, quartz or pyrite phenocrysts within a non crystallized mass; c) *vesicular texture* where round, avoid, or elongate irregular holes (vesicles) formed by expansion of gas, in a magma (MACKENZIE et al., 1999); d) *amygdaloidal texture* where former vesicles are fully or partially occupied by authigenic minerals such as zeolites, quartz, chalcedony, chlorite and/or glass; e) *orbicular texture "orbs"* consisting of concentric shells of rhythmically alternating of zeolitic constitution. Within the shells the texture may either be granular or elongate zeolite, chlorite crystals or glass, may be radially arranged; e) s*pherulitic texture* where the spherulite consists of a dense mass of very fine intergrown needles of chlorite, quartz and zeolite radiating from a common nucleus; f) *corona texture* where quartz crystals are surrounded by a rim of a re-crystallized amorphous chalcedony, probably formed through an incomplete reaction between quartz and a fluid; g) *pseudo-poikilitic texture*, where inclusions of glass-zeolite assemblage are observed in the centre of the quartz crystal. They represent corrosive cavities subsequently filled by glass and zeolite. Their texture complexity reflects the successive phases of palagonitisation process through which they have passed.

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GEOCHEMISTRY AND PETROGENESIS OF BULQIZA PERIDOTITES

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The peridotites of the Bulqiza ophiolitic complex suffered a partial melting that, from the bottom to the top of the section, ranges from 17 to 30% (BEQIRAJ, 1997), as it was shown by the following upward trends: i) the increase of dunite intercalations, ii) the disappearance of clinopyroxene and reduction of orthopyroxene content in harzburgites and iii) the increase of the Cr/(Cr + Al) ratio in accessory chromite. The extremely low content of magmatofile elements (Ca, Al, Na and Ti) along with high content of compatible transitional elements (Ni, Co and Cr) show their extremely residual nature which is similar with that of analogous rocks from Troodos, Vourinos and New Caledonia (PRINZHOFER & ALLEGRE, 1985). Their U-form of the condrite-normalized REE contents is probably due to both partial melting (BECCALUVA et al., 1984) and metasomatism (BODINIER et al., 1988) that caused the Light Rare Earth Element depletion and enrichment, respectively. The residual harzburgites consist of forsteritic olivine (90.40–93.30 mol%) and enstatitic orthopyroxene (Xmg = 90.60–92.20%). The residual clinopyroxene of the basal harzburgites is rich in Mg (Xmg = 95%), too. The report Cr/(Cr + Al) > 0.6 of accessory chromite from harzburgites classifies these later as peridotites of type III (DICK & BULLEN, 1984). The similar MgO content of olivine and orthopyroxene, as well as the same content of orthopyroxene in both basal and uppermost harzburgites and, finally, the abundance of pyroxenite dykes in the vicinity of chromite ore bodies could be probably consequences of the melt/rock interaction. The presence of interstitial clinopyroxene and plagioclase in the upper tectonite harzburgites was explained as a result of the later magmatic impregnation by a magmatic fluid (CANNAT et al., 1990) or as trapped melts at the end of partial melting (BOUDIER & NICOLAS, 1977). The serpentinisation represents the main process that altered the rock composition due to the reaction of ophiolitic rocks with sea water during the complex emplacement on the carbonate periphery.

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THE METAMORPHIC EVOLUTION AND THERMOBAROMETRY OF AMPHIBOLITES FROM THE PFLERSCH-METADIORITE COMPLEX (PFLERSCH VALLEY, SOUTH TYROL, ITALY)

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The Ötztal Complex is a polymetamorphic Austroalpine basement complex. The Variscan and Eo-Alpine metamorphic events in the central and northern Austroalpine Ötztal Complex (ÖC) and the Schneeberg Complex (SC) were studied by TROPPER & RECHEIS (2003) on a regional scale by means of interpretations of different zonation types in garnets in combination with *P-T* estimates, based on multi-equilibrium methods. The Eo-Alpine *P-T* conditions obtained from the ÖC north of the SC range from 469°C and 4.2 kbar in the northern ÖC to 556°C and 8.8 kbar in the southern ÖC adjacent to the SC. Since these *P-T* estimates were all obtained from garnet-bearing metapelites, it was the aim of this study to obtain *P-T* conditions from adjacent metabasites and hornblende-gneisses from the southernmost ÖC north of the SC for comparison with metapelite thermobarometry, using conventional thermobarometry, semi-empirical methods and trace-element thermometry (Zr-in-rutile). The area of investigation is located in the innermost Pflersch Valley. In this field area, massive metadiorite, hornblende-gneiss and amphibolite bodies containing the mineral assemblage garnet + hornblende + plagioclase + rutile + ilmenite + titanite +epidote + chlorite + quartz occur. Since the Ti-Phases also show a growth sequence where rutile grew first and titanite last, it was also attempted to use these Ti-phase succession as an indicator for the *P-T* evolution. Garnet, amphibole and plagioclase show discontinuous growth zoning in agreement with the polymetamorphic evolution of these rocks, where the composition of garnet II and plagioclase II, show higher calcic components, indicate a *P*-accentuated Eo-Alpine metamorphic overprint. The zoning in the calcic amphiboles show a prograde transition from actinolitic cores to hornblende rims. New thermobarometric calculations using the software PET (DACHS, 1998) for the metabasites and the software TWQ (BERMAN, 2007) for the metapelites yield Eo-Alpine *P-T* conditions of 550-620°C and 0.80-0.95 GPa, placing the rocks in the epidote-amphibolite facies domain in accordance with the data of TROPPER & RECHEIS (2003) and other studies from this area. Trace-element thermometry (Zr-in-rutile) reaffirms previously obtained temperatures of around 550°C.

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GEOHAZARDS ASSOCIATED WITH BROWN COAL MINING IN CENTRAL SLOVAKIA

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Brown coals of Central Slovakia are known for their high amounts of arsenic that may reach 1,500 ppm (KEEGAN et al. 2006). Burning of these coals in thermal power plants produces arsenic-rich fly ash and clinker, which can be a risk for the environment and the human health. In 1965, a dam failure of an ash impoundment released the ash into the flood plain of the Nitra River at Zemianske Kostoľany near Nováky where the brown coal is being mined until today. An estimated area of 19,000 ha became polluted. In our work, we tried to monitor the fate of the ash and the element arsenic in the ash and the contaminated soils. We combined electron microprobe analysis (EMPA) and graphite furnace atomic absorption spectrometry (GF-AAS) to identify and separate the arsenic-containing phases. A total digestion and analysis with GF-AAS has shown up to 1,100 ppm arsenic in the ashes and more than 1,300 ppm in the soils of the Nitra flood plain. Sequential extractions (after TESSIER et al. 1979) have shown the affinity of As to iron and manganese oxides and carbonates in the fresh ashes. Arsenic in the soils contaminated by the ashes, however, is mostly iron- and manganese-oxide bound. This indication is supported by electron microprobe analysis (EMPA).

In the fresh ashes, five phases could be identified by EMPA. Mineral fragments, mainly quartz and plagioclase, showed no As at all. Low amounts of arsenic, 0.00-0.02 weight percent (wt%) were found in carbonaceous particles between 50 and 400 µm in size. Although their As content is low, their abundance may give them an important role as arsenic carriers. Porous calcite particles up to 200 µm showed larger amounts or arsenic with 0.00-2.94 wt% As; their occurrence is, however, rare.

Porous glassy particles of variable size are the dominant phase of the ash and their composition is highly heterogeneous; some regions show large amounts of arsenic up to 1.51 wt% As, others none. The highest As concentration was measured in a few of the omnipresent spheroidal glass particles in the ash with up to 12.66 wt% As. The As-bearing spheroids are tiny, their size not exceeding 20 µm. Their composition varies strongly between Fe- and Ca-dominated. Si, Mg, Al, Ti, P and S also appear, albeit in quite variable amounts. The ash in the contaminated soils contains the same phases except for calcite, which is in line with the GF-AAS results of the sequential extraction.

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PECULIARITIES OF THE GASEOUS PHASE OF THE MINERAL FORMING FLUIDS OF METAMORPHIC ROCKS OF THE BERLEBASH SUITE, MARMAROSH MASSIF, UKRAINIAN CARPATHIANS, ACCORDING TO FLUID INCLUSION STUDIES

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Marmarosh massif is an important structural element of the Eastern Carpathians, which differs by the geological features from the other structural-facial zones of the Carpathian fold belt. Metamorphic rocks of the massif have been formed under the influence of the processes of medium- and low-temperature metamorphism and metasomatism. Within the Marmarosh massif stratiform gold ore has been found (polygenic Saulyak field), polygenic stratiform ore shows of pyrite-polymetallic ores, shows of iron-manganese ores and sub-graphite as well as the existence of traps and accumulations of hydrocarbons in them is forecasted. That is why the actual task is to reveal the genesis of prospective shows of mineral resources, related to metamorphic rocks.

Fluid inclusions in quartz of the metamorphic rocks have been investigated in the Berlebash suite (V-$Є_1$*br*), which has been penetrated by four wells (Bp-5, Bp-6, Bp-7 and Bp-8) along the river-bed of Bilyi Stream.

Because of the small dimensions of the fluid inclusions mass spectrometry has been used for chemical analysis. The results of these investigations showed that the prevailing component of the gas phase of the inclusions is methane (59.7–98.6 vol%). Its composition decreased to 7.5–33.1 vol% only in solitary cases. Carbon dioxide and nitrogen are in subordinate amount (1.9–35.4 vol% and 0.6–5.4 vol%, respectively). In some samples the carbon dioxide content is 62.9–92.9 vol%. It should be mentioned that N_2 (0.6–5.4 vol%) appears only when the CO_2 content of the volatile phase reaches or exceeds 23 vol%. This regularity is recognized in the sequence of all the four wells.

The obtained results on the volatile content of fluid inclusions of the vein mineralization within the metamorphic rocks of Berlebash suite of the Ukrainian part of the Marmarosh massif generally complement the existing data (NAUMKO & BONDAR, 2008; NAUMKO et al., 2008) about the prevalence of methane within the gaseous phase of the mineral forming fluids and point out the important role of hydrocarbon compounds in the mineral and ore forming processes. Further investigation of hydrocarbons in fluid inclusions will facilitate the establishment of the migration pathways and the reconstruction of the evolution scheme of fluids, thus contributing to a better understanding of the metamorphogene-hydrothermal mineral genesis in the rock and ore complexes of the Marmarosh massif.

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HYDROCARBON VOLATILE COMPONENTS OF FLUID INCLUSIONS IN HYDROTHERMAL MINERALS OF THE TROSTYANETS VOLCANOGENIC COMPLEX (UKRAINIAN CARPATHIANS)

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For the first time the results of studies of fluid inclusions in hydrothermal minerals of the Trostyanets volcanogenic complex of the Ukrainian Carpathians were analysed.

Rocks of the Trostyanets complex are represented by basalts, clastic lavas of basalts, andesite-basalts of subalkaline series and trachytes, which form rocky outcrops over the length of 2 km in the riverbed and edges of the valley of the Trostyanets Stream.

In the volatile phase of the fluid inclusions of hydrothermal minerals of different type the predominance of methane and higher hydrocarbons with complete or partial absence of carbon dioxide and nitrogen was determined. Such regularity, as well as the availability of the organic matter in veinlets, may suggest the deep-seated genesis of the hydrocarbon constituents of the fluid inclusions.

Experimental investigations of volcanic processes in conditions of high temperatures and low pressures (GULBRANSEN, 1966) clearly testify the stability of hydrocarbons under such conditions. Their formation could be caused by Fischer-Tropsch type dynamic reactions (the formation of hydrocarbons by the interaction of CO, H_2 and H_2O with the participation of ferrous, nickel or silicate catalysts).

Thus, obtained results of studies of volatile components of the fluid inclusions of veinlet mineralization on the whole supplement data (NAUMKO et al., 2009). From the point of view of deep-seated genesis of the hydrocarbon volatile components in the fluid inclusions of the hydrothermal minerals of the Trostyanets volcanic complex completely confirm this fact. To this also testifies the availability of veinlets of quartz-calcite-zeolite composition with the organic matter and earthy discharge of the same organics in the volcanic rock. Such associations of minerals probably were discharged as a result of postmagmatic physical-chemical transformations of the deep-seated fluid saturated with the hydrocarbon constituents.

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STRUCTURAL INVESTIGATIONS ON A SULPHATE APATITE

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Apatite is a generic term for compounds with the general formula $M_6M'_4(ZO_4)_6X_2$, which mainly crystallize in the hexagonal space group $P6_3/m$. The most abundant composition in nature corresponds to $Ca_{10}(PO_4)_6(F,OH)$, the "calcium phosphate apatite". However, extensive isomorphic substitutions can occur in all atomic sites. The coupled substitution $Ca^{2+} + (PO_4)^{3-} \rightarrow Na^+ + (SO_4)^{2-}$, for example, has been studied by PIOTROWSKI et al. (2004).
In the course of the present investigation polycrystalline material of the pure fluor sulphate apatite end-member $Na_6Ca_4(SO_4)_6F_2$ has been prepared by repeated solid state reactions. A Rietveld analysis proofed that the compound is isostructural with calcium phosphate apatite. The distribution of the Ca and Na cations on the crystallographically independent *M* sites has been determined. Furthermore, the high temperature behaviour of $Na_6Ca_4(SO_4)_6F_2$ has been studied by thermal analysis (DTA) and X-ray powder diffraction. Both experimental techniques indicate that the material undergoes a phase transition at about 617.7°C upon heating (see Fig. 1). The phase transformation is reversible. However, rapid quenching allows the preservation of the HT-phase at ambient temperatures. A high-resolution X-ray powder diffraction data set of the quenched high temperature polymorph could be successfully indexed with a primitive orthorhombic unit cell. An *ab-initio* structure determination based on simulated annealing is under progress. The melting point of $Na_6Ca_4(SO_4)_6F_2$ has been determined to be 776.8°C. A mass loss of 0.53 wt% at 850°C (melt) can be attributed to a release of SO_2 from the system.

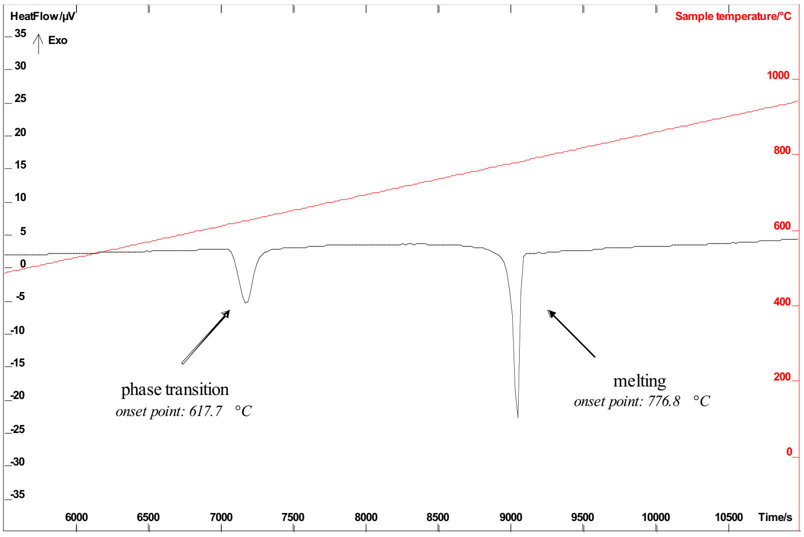

Figure 1. DTA measurement (phase transition and melting point)

PIOTROWSKI, A., KAHLENBERG, V., FISCHER, R.X. (2004): Eur. J. Mineral., 16, 279-284.

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Fe-Ti OXIDES OF WEST CARPATHIAN GRANITOIDS: INDICATORS OF MIXING PROCESSES AND A TOOL FOR REGIONAL GRANITE MAPPING

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The ferromagnetic susceptibility values above K $2{\cdot}10^{-4}$ (SI) discriminate West Carpathian granites with I-type affinity from other granitoids. Strong input and assimilation of mafic rocks occurring in these granites indicate the presence of abundant microgranular mafic enclaves and increase the whole rock magnetic susceptibility. Enclaves show natural remanent magnetisation often around $16{\cdot}10^{-3}$, host I-type granites around 10^{-3}. In these sense the I-type granites can be considered as the composite granites formed from the crustal and assimilated mantle material. It can be concluded that the measurement of rock magnetic susceptibility index in the field is a useful tool for regional geological mapping of I-type granites.

Principal contributors of SI in I-type granites are Fe-Ti oxides which present: (1) as an early-orthomagmatic stage of magnetite rich in ulvöspinel component which became unstable during cooling and preserved usually as relic inclusions in accessory and rock-forming minerals, (2) late magmatic/high temperature hydrothermal phase of magnetite with low content of impurities precipitating along with other silicates from primary titanomagnetite, biotite and anorthite formed in intergranular space and (3) low temperature hydrothermal phase (hematite, rutile) which are extended during the cooling regime in subsolidus stage.

Inter-oxide re-equilibration of primary titanomagnetite released titanium to form ilmenite oxy-exsolutions following rutile precipitation, locally along with Ti-hematite. Oxythermometry of Fe-Ti oxides reveals a relatively smooth evolution from orthomagmatic to late-magmatic/high-temperature hydrothermal or subsolidus/solidus stages with equilibrated temperatures of 860–400°C and oxygen fugacity values approaching those of the FMQ buffer +0.5 $\Delta\log fO_2$ (~860°C) and –5.2 $\Delta\log fO_2$ (~400°C) indicating decrease of oxygen fugacity during cooling. Late magmatic differentiates (dikes), due to higher volatile activity, show the opposite trend or an increase in the oxygen fugacity: the value –0.22 $\Delta\log fO_2$ (~738°C) during late-magmatic stage is buffered by FMQ, while the later system is buffered by Ni-NiO - value 0.2 $\Delta\log fO_2$ (~ 630°C). The iron, present in both oxidation states (Fe^{2+} and Fe^{3+}), is mainly incorporated into the magnetite at the expense of silicates. The association of Ti-magnetite, pure magnetite and discrete hematite shows that crystallization and evolution of Fe-Ti oxides in granitic magma. It is a long termed process from orthomagmatic to a low-temperature subsolidus/solidus stage showing a gradual decrease in oxygen fugacity except in late magmatic differentiates, where the opposite trend is possible.

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PSEUDOSECTION MODELLING OF A LOW-Mg ECLOGITE FROM THE TYPE LOCALITY (KORALPE, EASTERN ALPS)

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In the Kor-Saualpe and Pohorje regions of the Eastern Alps several eclogite bodies occur within metapelitic gneisses. The bodies are between 1 meter and several hundreds of meters in size and some of them were defined by HAÜY (1822) as the type locality for the rock type "eclogite". A growing body of petrological work has documented the metamorphic evolution of the metapelites surrounding the eclogites, including studies of the *PT* paths, studies of the evolution of water content and geochronological work documenting the cooling and heating rates. Moreover, there are many petrological, geochemical and geochronological studies on eclogites, but very little work has been done on phase diagrams for the eclogite bodies themselves. Here we use recently available activity models for amphiboles to present new thermodynamic pseudosections for the Koralpe eclogites that can be used to constrain their *P-T* path and general metamorphic evolution. The modelling of these rocks using THERMOCALC, results in estimates for the conditions of metamorphic peak (between 16.5 and 20.5 kbar and 600°C to 720°C) that are discussed and compared with earlier studies which used conventional thermobarometers. Furthermore, interpretation of the metamorphic evolution using *PT* and P-M_{H2O} pseudosections indicates that the *PT* path of the eclogites happened in H_2O-saturated conditions. Thus, the pseudosection modelling provides additionally information on the prograde and high-pressure evolution and permit to conclude that eclogite and metapelite surrounded have certainly undergone the same metamorphic peak in Eo-Alpine time. Moreover, the different *PT* estimates on the eclogite from Pohorje, always matter of debate, compare to our results suppose that a *PT* gradient from Koralpe to Pohorje is likely.

HAÜY, M. (1822): Traité de minéralogie. Seconde edition. Deuxième tome, Bachelier et Huzard, Paris.

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TWO MAIN TYPES OF VARISCAN GRANITOIDS IN THE TISIA COMPOSITE TERRANE (HUNGARY).

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Two main types of Variscan granitods were identified in the Tisia Composite Terrane. Both have the similar ages about 340–360 Ma (U/Pb, K/Ar, Sr/Rb). Granitoids of Kunságia Terrane outcrops in Mórágy Mts. whereas in the Battonya unite of the Békésia Terrane granitoids occur 1000–1500m below the surface. The first one is metaluminous (A/CNK $\leq$ 1), I-type magnesio-potassic microcline megacryst-bearing amphibole-biotite quartz monzonite and monzogranite, with several chromite-bearing high potassic mafic enclaves (melamonzonite, melasyenite, locally named vaugnerite/durbachite), and with some peraluminous microgranite dikes. Granitoids of Mórágy Mts. contains microcline occurring as megacrysts (Δ = 0.9) as well as in the groundmass (Δ = 0.5). Plagioclases are mostly zoned, "spike" zonation can be observed (An_{35-45}, spike: An_{60}), quartz forms knots with common undulatory extinction. Mg- and actinolitic hornblende are common. In the main granitoid body the hornblende is richer in Fe than in enclaves where it forms "pilites" with tiny chromite grains. Mg-rich (calc-alkaline-type) biotite is common; they are richer in Mg in enclaves. Whole intrusive body belongs to the calc-alkaline K-rich monzonitic series**.** K, Mg and Ca enriched with low Al, Si ($D_{granitoids}$ = Na + K + 2Ca/Al(Si + Al) = 1.2, $D_{encl.}$=1.7, MONTEL, 1993). Due to the high D, mostly the Ca activity beside of apatite, titanite, high amount of allanite crystallised in the enclaves as well as in the enclosing granitoids. Allanite is the major REE-rich mineral that controls the whole-rock REE patterns (ΣREE_{encl} = 350 g/t, $\Sigma_{granitoid}$ = 250 g/t, $\Sigma_{microgr}$ = 120 g/t). They are oxidised ($Fe^{3+}/Fe^{tot} \approx 0.4$) characteristic of the igneous allanite in the I-type granitoids (BROSKA et. al., 2000). Altered allanites are enriched in ΣREE and depleted in Al and Ca. In microgranite allanite was not identified (D = 1.1). The basic melt (enclaves) originated from the upper mantle, acidic melt (granitoids) formed by partial melting of the continental crust and probably crystallised in the same time after collision.

The majority of the Battonya granitoids are two-mica granodiorite and granites rarely with amphiboles. They are peraluminous (A/CNK > 1, ΣREE = 112 g/t), S-type and belong to the granodioritic series**.** The amphibole-bearing variety contains calc-alkaline-type and the two-mica-bearing one contains peraluminous-type biotite. The plagioclases (An_{25-40}) are slightly zoned. K-feldspar is microcline (Δ = 0.76). The only REE-rich minerals are monacite ($D_{granitoids}$ = 0.9) and tiny grains of xenotime crystallised after apatite. REE pattern is controlled by zoned monacite. The core is slightly richer in HREE than the outer zone. Granitoid formed from melting of "wet" crustal rocks where two continental lithospheres underplated after the collision.

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Nb-Ta OXIDE MINERALS FROM THE JEZUITSKÉ LESY GRANITIC PEGMATITE, BRATISLAVA MASSIF, WESTERN CARPATHIANS, SLOVAKIA: COMPOSITIONAL VARIATIONS AND EVOLUTION

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The newly discovered Jezuitské lesy granitic pegmatite, situated in muscovite-biotite granodiorites to granites of the Bratislava Massif, Malé Karpaty Mountains, contains a variety of Nb-Ta oxide minerals. Studied pegmatite dyke is at least 1-2 m thick; it is located approximately 6 km NW of the Bratislava castle. The border part of the pegmatite is represented by a quartz-microcline (± muscovite) zone followed by intermediate coarse-grained quartz-microcline-muscovite zone with fan-shaped platy albite (cleavelandite) and slightly developed blocky quartz core. Moreover, fine-grained saccharoidal albite aggregates (± quartz, muscovite) form abundant irregular bodies, which replace the former zones. The accessory minerals include beryl (locally Na,Cs-rich), phenakite, bertrandite, garnet (almandine-spessartine), Mn-rich fluorapatite, monazite-(Ce), cheralite, Hf-rich zircon, gahnite, uraninite, pyrite, galena, graphite (?), and Nb-Ta oxide minerals.

The columbite-tantalite group minerals are the main Nb-Ta-bearing phases of the pegmatite. They can be divided into a primary and a secondary association. The primary columbite-tantalite association occurs in the quartz-microcline-muscovite zone whereas the secondary association is hosted by the saccharoidal albite. The primary association is represented by ferrotantalite, rarely manganotantalite with Ta/(Ta + Nb) = 0.52–0.79 and Mn/(Mn + Fe) = 0.32–0.69. They form discrete tabular crystals up to 10 mm in size, often as intergrowths with ferrotapiolite and ferrowodginite, with concentric, rarely coarse oscillatory zoning as a result of primary magmatic crystallization. The secondary columbite-tantalite association is represented by smaller (0.3–2 mm) crystals of ferrocolumbite to ferrotantalite and manganocolumbite with relatively low Ta/(Ta + Nb) = 0.10–0.54, and Mn/(Mn + Fe) = 0.30–0.67. The crystals commonly show complex irregular patchy zoning which indicates a late magmatic to subsolidus dissolution-reprecipitation phenomena.

Ferrotapiolite forms discrete crystals (up to 5 mm in size) or irregular intergrowths with ferrotantalite; it occurs with the primary columbite-tantalite association in the coarse-grained quartz-microcline-muscovite zone. Ferrotapiolite is rather homogeneous with Ta/(Ta + Nb) = 0.88–0.95 and Mn/(Mn + Fe) = 0.06–0.10.

Ferrowodginite from the Jezuitské Lesy pegmatite represents the first known occurrence of this mineral in the Western Carpathians. It forms subhedral to anhedral intergrowths (up to 0.7 mm) with ferrotantalite and ferrotapiolite. The Sn content in the ferrowodginite attain 13–15 wt% SnO_2 (0.56–0.65 apfu Sn); Ta/(Ta + Nb) = 0.76–0.86 and Mn/(Mn + Fe) = 0.33–0.41.

Microlite occurs as irregular up to 2 mm long and 100 µm wide rim along ferrotapiolite, as irregular filling in ferrotapiolite fissures, or small irregular patches (generally < 10 µm) in ferrocolumbite. The Ta/(Ta +N b) ratio in microlite attains 0.90–0.95, F content reaches 2.4 to 3.3 wt% (0.70–0.94 apfu). Microlite represents the youngest Nb-Ta phase, which originated probably during a low-temperature, hydrothermal overprint of the Jezuitské Lesy pegmatite.

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MINERAL TRANFORMATIONS DUE TO COMBUSTION METAMORPHISM IN A COAL WASTE DUMP IN WOJKOWICE, UPPER SILESIA, POLAND

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The coal waste dump in Wojkowice, Upper Silesia, Poland is a good example of a dump, where processes of mineral transformation can be investigated. The dump was affected by fire but, today, there is no sign of thermal activity and a part of the dump has been exploited and used for road building. As the interior of the dump is now accessible, making observation and sample collection easy, three sections of the dump showing different degrees of fire influence have been distinguished: (1) a central fire core, characterized by the presence of glassy slag which cements strongly sintered and fused coal waste rocks; (2) its external aureole, affected by high temperature and hydrothermal leaching, where the coal wastes are porous because of degassing; (3) a zone unaffected by the fire where the wastes are grey or black and still contain tiny laminae of coal. Three petrographically different kinds of waste rocks were collected, namely slag, sandstone, and siltstone, and their mineralogy and radioactivity investigated.

Mineral transformations and actinide transport in the fire field reflects the thermal decomposition of primary phases in the high-temperature, oxygenated environment of the central zone, active transport in the steep thermal gradient of the external aureole of the fire core and hydrothermal leaching by steam and boiling water. The final precipitation of newly formed mineral phases is possible in the external zone and, as the fire wanes, due to condensation of volatiles and crystallization from cooled oversaturated percolating water. Chemical redox conditions related to oxygen availability are crucial factors influencing transport and precipitation. The strongly oxidized, red-stained fire core is surrounded by unaffected coal and a pyrite-rich reductive zone which act as a chemical barrier or trap, especially for migrating uranium and some of its decay daughters.

The radioactivity of the samples measured by gamma- and alpha spectrometry is variable but in a patterned way. For example, sandstone samples from zones 2 & 3 are three times less active than the remainder of the samples; coarse-grained waste rocks contain much less actinides than do siltstones and slag. However, averaged radioactivity values for samples representing the three thermally-different zones in the dump reveals a significant increase from that least affected by fire (zone 3) to the fire core. This can be explained as due to secondary remobilization. However, the $^{238}U/^{234}U$ ratio is constant and independent of grain size or thermal influence. This is confirmed by the general mineral composition of the zones and where high-temperature mineral phases, e.g., spinel, hercynite, pyroxene, indialite, anorthite, cristobalite and glass, occur in the central fire zone.

The thermal and physicochemical conditions for actinide dynamics in such a "wet" fire field are similar to those characterizing natural, organic-matter rich fission reactors such as that at Oklo in Gabon.

Ni-RICH COBALTITE–NICKELINE AND COBALTITE–ALLOCLASITE ASSEMBLAGES FROM OPHIOLITE COMPLEX OF ALBANIA

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The geology of Albania is distinguished by the presence of a widespread middle Jurassic ophiolite complex named Mirdita zone. This exhibits the features of mid-oceanic ridge (MOR) and supra-subduction zone (SSZ-) type ophiolites (SHALLO et al., 1995). The metallogeny of this complex is distinguished by high potential, mainly of chromite and Cu mineralization. A widespread vein-type and lenticular quartz-sulphide and massive sulphide type mineralization occurs within the gabbro-plagiogranitic sequences and close to the gabbro-ultramafic contacts. Among them, the Ni-rich cobaltite–nickeline–native gold and the cobaltite–alloclasite mineral assemblages have interesting mineralogical peculiarities (ÇINA, 2004). The first assemblage is characteristic of the lenticular massive sulphide ore bodies, mainly of Co-Au type. This mineralization is related to gabbroid rocks close to the contact with the ultramafic Kam-Tropoja ultramafic massif. Euhedral polygonal crystals of Ni-rich cobaltite are situated within a chalcopyrite–pyrrhotite groundmass. These crystals are partly corroded and intersected by chalcopyrite veinlets. By textural etching the cobaltite crystals show zoning. The fine single or polyphase inclusions of nickeline, hedleyite (Bi_7Te_3) and native gold are situated within the host of Ni-rich cobaltite crystals. This mineral is a special variety, distinguished by high Ni content (9.20 wt%), corresponding to a 26.03 mol% NiAsS component (Table 1). The cobaltite–alloclasite assemblage belongs to the Cu ores–quartz–sulphides vein-type ore body related to gabbros, in the vicinity of plagiogranites. The main minerals are chalcopyrite and pyrrhotite with small amounts of cobaltite, alloclasite and late-formed pyrite and marcasite by sulphurization of pyrrhotite. Euhedral alloclasite crystals with prismatic habit are intersected by chalcopyrite veinlets. Polysynthetic twinning of alloclasite crystals is a characteristic feature. Some parts of these crystals are replaced by cobaltite, which contains relics or parts of the twins of alloclasite (MAUREL & PICOT, 1973; ÇINA, 2004). The chemical composition of these two minerals is nearly the same (0.08 wt% Ni). The presence of the Ni-rich cobaltite–nickeline mineral assemblage suggests that it has been formed by the interaction between hydrothermal fluids and ultramafic rocks.

Minerals	Co	Ni	Fe	As	S	Sb	Total	CoAsS	NiAsS	FeAsS
Ni-rich cobaltite	24.28	9.20	1.87	47.28	18.02	0.02	100.67	68.40	26.03	5.57
Cobaltite	34.17	0.08	1.97	45.52	18.88	0.05	100.67	94.03	0.24	5.73
Alloclasite	35.62	0.09	0.90	45.37	19.65	0.03	101.66	97.16	0.24	2.60
Ni-rich cobaltite: $Co_{0.699}Ni_{0.262}Fe_{0.056}As_{1.055}S_{0.939}$, cobaltite: $Co_{0.959}Ni_{0.002}Fe_{0.059}As_{1.005}S_{0.974}Sb_{0.001}$, alloclasite: $Co_{0.986}Ni_{0.002}Fe_{0.027}As_{0.987}S_{0.998}$										

Table. 1 Microprobe analyses and formulae of Ni-rich cobaltite, cobaltite and alloclasite, Albanian ophiolite

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SHALLO, M., ÇINA, A. & TURKU, I. (1995): Outline of the metallogeny of the Albanian MOR and SSZ-type ophiolites. Workshop on Albanian ophiolites and related mineralization. Doc. BRGM, 244, 27-46.

QUARTZ-BEARING BASALTS FROM KARADAG STRATOVOLCANO, CENTRAL ANATOLIAN EXTENSIONAL SETTING: OXYGEN ISOTOPIC EVIDENCE FOR CRUSTAL CONTAMINATION

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Quartz-bearing and quartz-free Pliocene basaltic lavas have been examined from Karadag stratovolcano, Central Anatolian Extensional Setting. Quartz-bearing basalts, mineralogically, include Cr-spinel-bearing olivine, clinopyroxene, phlogopite, calcic amphibole and opaque minerals. Partially resorbed grains of quartz are surrounded by reaction rims with groundmass. $\delta^{18}O$ values for single grains from the basaltic lavas are 9.50–10.74‰, respectively, indicating that the quartz is of crustal (probably metamorphic) origin. Accordingly, the $\delta^{18}O$ values (7.42–7.54‰) for pyroxenes also record the moderate crustal contamination, respectively. These preliminary results suggest that crustal contamination played an important role in the evolution of Pliocene (mantle-derived) continental basalts from Karadag Mountain, Central Anatolian Extensional Setting.

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OXYGEN AND STRONTIUM ISOTOPIC EVIDENCE FOR THE EFFECT OF CARBONATE METASOMATISM ON THE GENESIS OF INNER ISPARTA ANGLE POTASSIC VOLCANISM, SW ANATOLIA

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Inner Isparta Angle is a typical example of intra-plate alkaline potassic magmatism. Plio-Quaternary volcanic products comprise silica–saturated (trachytic, trachyandesitic and basaltic trachyandesitic) and silica-undersaturated (lamproitic, trachybasaltic, minette-type lamprophyric and leucite-tephritic) rocks. In general, cpx and phlogopite are the common mineral phases, together with groundmass calcite. Volcanics have high abundances of LILE and high LILE/HFSE ratios, and their incompatible element patterns Except for alkaline silicate magma/carbonate-wall-rock interaction around the Golcuk maar crater conduit, Cpx ^{18}O and whole-rock ^{87}Sr/^{86}Sr isotopic ratios of volcanics clearly indicate that magmatic (mantle) carbonate metasomatism played a significant role on the genesis of inner Isparta Angle alkaline potassic magmas, rather than sediment carbonates. Features such as high Zr/Hf (35–50) and low Nb/Ta (15–25) fractionations, and mantle-like low Sr isotopic ratios support that carbonate-rich melts/fluids are generated at high pressure by low-degree melting of mantle sources. The occurrence of undersaturated alkaline rocks also requires magma generation at high pressures and X_{CO2}. All these data demonstrate that the geochemical and isotopic imprints of phlogopite- and carbonate-bearing metasomatic agents are important factors, playing role on the source domains of inner Isparta Angle potassic volcanism.

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CLASTS OF VARISCAN ROCKS WITHIN THE KOŘENEC AND RAČICE CONGLOMERATES (RHENOHERCYNICUM, BOHEMIAN MASSIF), Th-U-TOTAL Pb EVIDENCE FROM AN ELECTRON MICROPROBE MONAZITE STUDY

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Synorogenic Carboniferous flysch sedimentation was linked with the Variscan orogeny, and culminated during exhumation at about 330 Ma. Sediments of the Drahany Uplands are subdivided into the Protivanov, Rozstání and Myslejovice Fm. (from older to younger). The age of sedimentation and provenance of the sediments of the Protivanov to lower part of the Myslejovice Fm. is poorly known. Conglomerates (older Račice and younger Luleč conglomerates) are largely restricted to the southern part of the basin – Myslejovice Fm. Thin conglomerate layer (<50 m, Kořenec conglomerate) occurs in the Protivanov Fm.

The changes of rock pebbles composition from the Kořenec and lowermost part of the Račice conglomerates (orthogneisses with common muscovite, rhyolites and dacites > I/S-type granitoids, contact hornfelses, clastic sediments) through major part of the Račice conglomerates (orthogneisses with common muscovite, I/S-type granitoids > volcanic rocks, contact hornfelses) reflects propagating erosion level within the same source. Major rock types of the both Kořenec and Račice conglomerates (biotite granites, leucocratic orthogneisses and two-mica deformed orthogneisses) were used for CHIME monazite dating.

Biotite granites yielded age 333±8 Ma, leucocratic orthogneisses 331±7 Ma and two-mica deformed orthogneisses 332±22 Ma. Based on rock structure, chemical composition of rock-forming minerals, and whole rock chemistry, the pebbles of biotite granites to granodiorites show ~~close~~ similarity to I/S type Variscan granitoid rocks of the Nasavrky massif. The results of the CHIME monazite dating of biotite granite pebbles (333±8 Ma) correspond well to the CHIME dating (334±12 Ma), and to the U-Pb zircon dating (332.2±1.2 Ma; SCHULMANN et al., 2005) of the granites from the Nasavrky massif. Metamorphic event close to the 330-335 Ma (corresponding to LP-MP/HT metamorphism and migmatization) took place in the eastern part of the Bohemian massif (Moldanubian Zone, eastern part of the Orlica-Snieznik Dome; BÜTTNER & KRUHL, 1997; GORDON et al., 2005).

Monazite dating suggests similar stratigraphic range of the Protivanov, Rozstání and Myslejovice Fm., and therefore the starting of sedimentation at the boundary of Tournaisian and Viséan (345 Ma) proposed by DVOŘÁK et al. (1990) is unlikely.

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CRYSTALLIZATION AND PHASE TRANSITION OF MACKINAWITE (FeS)

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Nanocrystalline iron sulfides typically form in the oxygen-free layers of marine sediments. The iron sulfide is initially mackinawite (FeS) that converts to greigite (Fe_3S_4) (LENNIE et al., 1997) which, in turn, converts to pyrite (FeS_2) (HUNGER & BENNING, 2007). Depending on the particular conditions, the phase transitions may not be completed and ferrimagnetic greigite remains in the sediment. When the iron sulfide precipitates, several potentially toxic metals may be incorporated into the structure (HOLMES, 1999). Therefore, the formation of iron sulfides is used in bioremediation procedures. It is important to know whether the incorporated metals stay in the crystal or are remobilized during the phase transitions. Neither the nanometer-scale structural details of the phase transitions from amorphous iron sulfide to pyrite, nor the fate of the incorporated metals are satisfactorily known (WOLTHERS et al., 2003). Our goal is to study the structural, chemical and morphological changes of nanocrystalline mackinawite, as it converts to greigite.

We synthesized mackinawite by precipitation from hydrous solutions. The reactants were iron (II) and (III) chloride, Mohr's salt or iron (II) sulfate and sodium sulfide or thioacetamide. The structure of the product was studied using high-resolution transmission electron microscopy and selected-area electron diffraction. Freshly precipitated iron sulfide is typically poorly crystalline, and consists of disordered sheet- and ribbon-like features. Few-nm-sized crystalline islands occur in the material, the structure of which can be identified in most cases as either mackinawite or greigite. However, some lattice spacings are inconsistent with either structure. As the material is aged in solution for several days or cured in an autoclave for several hours, the crystalline islands grow to tens of nanometer sizes, and their structures are consistent with that of greigite. In the future we plan to study the structure of iron sulfide precipitated in the presence of various metals, and to follow the fate of these metals when mackinawite converts into greigite.

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CRUSTAL THICKENING DURING THE ALPINE OROGENY: INSIGHTS FROM MAFIC GRANULITE XENOLITHS OF THE PANNONIAN BASIN

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Blocks in the basement of the Pannonian Basin went through large scale juxtaposition and several drastic changes due to the tectonic processes during the Miocene extension of the basin (18–11 Ma). The material of the deep lithosphere has been sampled by post-extensional alkali basaltic volcanism in five areas within the ALCAPA block. Crustal xenoliths are the most abundant in the Bakony-Balaton Highland Volcanic Field located in the central region of the Pannonian Basin, which was mostly effected by extension. We have studied mafic lower crustal granulite xenoliths from this area in order to identify deep lithospheric processes acting associated with the geodynamic evolution.

Peak metamorphic conditions are shown by the granulite facies rock-forming mineral assemblage (clinopyroxene, plagioclase, garnet, ± orthopyroxene ± amphibole ± biotite). In most of the xenoliths, the peak metamorphic mineral assemblage shows equilibrated granoblastic microstructure, while in some samples non-equilibrium poikiloblastic microstructure is present. Petrographic observations and fluid inclusion studies of the latter samples suggest that biotite was destabilized in the presence of CO_2-rich fluids by the reaction Bt + Pl + Qtz = Opx + Grt + melt. Melt was extracted from the rock, and orthopyroxene, garnet and plagioclase remained as restitic phases. Careful geothermobarometric investigations have shown that the granoblastic xenoliths represent a complete crustal section with equilibrium temperatures and pressures between 800–1150°C and 0.9–1.7 GPa, which corresponds to 35–60 km depth. Granoblastic Grt-Opx-Pl granulites give 900–1070°C and 0.9–1.5 GPa as equilibrium conditions, which completely overlaps the formation conditions of the granoblastic mafic granulite xenoliths. This corresponds to the overthickened orogenic root of the Alps, where CO_2-rich fluid input led to the partial melting of the lower crust may be at the beginning of the extension of the Pannonian Basin.

According to mineral reactions observable in the rock, peak metamorphic conditions were followed by significant pressure decrease to 0.7–0.8 GPa (25–28 km), which corresponds to the depth of the present day crust-mantle boundary. This can be correlated with significant crustal thinning during the extension. Melting of high Ti amphiboles and reactions of rock-forming minerals with melts at lower pressures indicate that partial melting of the lower crust was continuous during the extension. Accessory Fe-Ti oxides have preserved the traces of interaction of the xenoliths with the host basalt. By the modelling of diffusion profiles in the oxide grains we have estimated that the interaction lasted a few days.

Our results on the metamorphic evolution of lower crustal xenoliths have shown a series of lithospheric processes during the extension of the Pannonian Basin, which can be used for refining models of basin extension.

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HYDROGEN ISOTOPE COMPOSITIONS OF HYDROUS COMPONENTS IN CARBONADO DIAMOND

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Among the most intriguing questions of geochemistry in the last decades is the origin of carbonado diamond, a special microcrystalline diamond variety that is found only in placer deposits in Brazil and Central Africa. Carbonado has a number of unique features that distinguishes it from other diamond types: restricted to a particular time interval and locality; porphyroclastic and highly porous microstructure in which the pores are filled with crustal minerals (like florencite, kaolinite, quartz, etc.); narrow stable carbon isotope composition range of about –27 ± 3 ‰ (relative to V-PDB) and a high 4-He signal. Diamond formation from organic matter due to subduction-related metamorphism or extreme nuclear irradiation, precipitation from carbonic fluids in the mantle, or an impact origin either by transforming terrestrial organic matter into diamond, and transport of extraterrestrial diamondiferous material have been suggested for the origin of carbonado.

The carbonado grains show a smooth "glassy" surface, which has been interpreted as "fusion crust" and evidence for an extraterrestrial origin. Our textural observations using cathodoluminescence microscopy and SEM/EMPA analyses suggest that the carbonados were formed in a fluid-rich environment and subsequent processes resulted in partial recrystallization of the surface. The recrystallization caused no change in the chemical compositions of pore-filling minerals, in the textures of the pores, and in the cathodoluminescence colour. This suggests that the conditions of the post-formation history of the carbonados were not much different from those prevailing during their formation. Pore-filling mineral florencite has a typical crustal Sr isotope composition, indicating that secondary post-formation processes, independent from those related to carbonado diamond formation, produced the present mineral assemblages in the carbonados' pores.

New evidence advanced for an extraterrestrial origin is the H–C bonds in carbonados not found in other terrestrial diamonds. If such H–C bonds are evidence for an extraterrestrial origin, D/H ratios may be used to infer the ultimate origin of the H component. One of the main aims of this study was to determine the amount and hydrogen isotope composition of the H compounds in carbonados. For this purpose carbonado samples from Brazil and Central Africa were studied. Hydrogen of bulk carbonado yielded ~ –80 ‰, consistent with an origin from either crustal or mantle-derived fluids. However, there is a hydrogen component bound to the diamond showing a D-depletion of –200 to –150 ‰. The H isotope data combined with textural and Sr isotope evidence are explained with a mantle origin and from reduced C-H fluids, although an extraterrestrial origin cannot be excluded.

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THE OCCURRENCE OF MAGNESITE AND HYDROMAGNESITE IN MEDIEVAL DOLOMITIC LIME MORTARS

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A study of medieval mortars from historical buildings in Tyrol/Austria and South Tyrol/Italy that excel by a remarkable weathering resistivity reveals an unexpected mineralogical complexity. Magnesite, hydromagnesite and brucite could be identified as crystalline Mg phases in the binder matrix of dolomitic lime mortars by X-ray diffraction analysis (XRD). Furthermore, thermogravimetric analyses (DTA/TG) indicate the presence of additional amorphous or poorly crystalline Mg phases.

Typical for the occurrence of Mg phases are dense areas within the binder from ~20 to 300 µm in size. Under the petrographic microscope (with both parallel and crossed polarizers) they appear as diffuse brownish patches. Elemental mapping reveals an intimate intergrowth of Ca (most likely calcite) and Mg phases, the latter too small and/or fine grained to be unambiguously identified by EMPA. Whereas the concentration of Ca is more or less constant within the binder, Mg is concentrated in these brownish patches. In some cases, concentric rings (Liesegang rings) with alternating higher and lower Mg concentration are present. Occasionally, the brownish patches are even visible in hand specimen appearing as white globules. The XRD-analysis reveals an intermixture of calcite and magnesite. In all samples that show these diffuse brownish patches in thin section magnesite was documented by XRD. This suggests that magnesite is preferentially located within these patches although other Mg phases cannot be ruled out because of the small grain size. Clearly documented was hydromagnesite occurring within the binder as radial aggregates with spherolitic textures ~50 to 250 µm in size. It may also be present as linings growing in open cracks/pores or covering the surfaces of plasters.

The concentration of Mg phases in the brownish patches and the spherolitic arrangement of the hydromagnesite crystals indicate local oversaturation leading to the formation of seed crystals from which magnesite and hydromagnesite progressively grow into the surrounding matrix. This mineral growth took place under disequilibrium conditions as also indicated by Liesegang rings, a formation which is explained by nonlinear reaction-diffusion processes (RODRIGUEZ-NAVARRO et al., 2002). Furthermore, disequilibrium growth is indicated by the coexistence of hydromagnesite and magnesite whose formation is kinetically hindered under atmospheric conditions and the absence of nesquehonite. Therefore, interpretations which base on equilibrium thermodynamic models (KÖNIGSBERGER et al., 1999) may lead to inadequate conclusions (MONTOYA et al., 2003).

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MINOR AND TRACE ELEMENTS IN SOME ORE MINERALS FROM THE CHIPROVTSI ORE DISTRICT, NORTHWESTERN BULGARIA

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Minor and trace elements in some ore minerals (pyrite – coarse-grained and colloform, arsenopyrite, galena, sphalerite and cinnabar) from the Chiprovtsi Ag-Pb hydrothermal stratabound replacement and Martinovo Fe skarn deposits in NW Bulgaria were determined using ICP-MS. The Martinovo and Chiprovtsi deposits are hosted in low-grade metamorphic rocks (marbles and schists) of Precambrian–Early Ordovician age (CARRIGAN et al., 2003). The genesis of the Chiprovtsi deposit remains uncertain (ATANASSOV & PAVLOV, 1983; DRAGOV et al., 1991).

A suite of 53 elements (Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, B, Al, P, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Hf, Ta, W, Re, Au, Hg, Tl, Pb, Pd, Pt, La, Ce, U, Th, As, Sb, Bi, S, Se, Te) was measured compared to standards STD DS7 and BLK in order to reveal minor and trace element pattern amongst them. Major elements in a particular mineral have not been considered in interpretation.

All minerals reveal enrichment in Cu (12.73–3529.13 ppm), Sb (29.18– >2000 ppm), Ag (4.7– >100 ppm) and Au (20.8–7764.2 ppb). With the exception of cinnabar, where Hg is a major element, Hg is detected as trace element in the rest of the minerals, in the range 5.116– >100 ppm. Arsenic is detected as minor element in cinnabar (1705.08 ppm) and in both types of pyrite, as the colloform type in particular, has the highest As contents (>10000 ppm, up to 4.76 wt. %, measured by EPMA). Arsenic is also detected in sphalerite (106.9 ppm) and galena (13.7–288.4 ppm).

It seems that colloform pyrite accumulates many elements in considerable amounts – Cu, Zn, Pb, Ni (23.5–1660.4 ppm), Co, As, Sb, Tl (15.12–878.40 ppm), Hg, even Ag, Au, Pd and Pt. The latter (Pd, Pt), most likely are leached from the host rocks (metamorphosed basic volcanic rocks). Fast crystal growth from oversaturated hydrothermal fluids may favour the incorporation of chemically suitable ions in the crystal structure of colloform pyrite. Cd and Cu are main minor elements in sphalerite (Cd >2000 ppm). Cu is presumably included in tiny chalcopyrite inclusions in sphalerite. Lesser amounts of Ga, Ge, In, Se and Pd are also detected.

These results suggest common hydrothermal fluid source for all minerals, thus substantiating the idea of granite intrusion related origin of the hydrothermal fluids that formed both ore deposits (Martinovo and Chiprovtsi), a matter contested so far.

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POST-MAGMATIC HYDROTHERMAL ALTERATION OF IGNEOUS ROCKS OF TESCHENITE ASSOCIATION (SILESIAN UNIT, OUTER WESTERN CARPATHIANS): EVIDENCE FROM ASSOCIATED FRACTURE AND AMYGDULE MINERALIZATION

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Hypabyssal sills, pillow lavas and pyroclastics formed by igneous rocks of teschenite association are coincident with sedimentation of the Lower Cretaceous Těšín-Hradiště Formation belonging to the Silesian Unit of the Outer Western Carpathian's Flysch Belt. Petrographically, the igneous rocks can be classified as teschenites, picrites, monchiquites and alkaline basalts. The rocks exhibit signs of intense hydrothermal alteration, evidenced by carbonatization, chloritization, serpentinization and/or zeolitization of many rock-forming minerals.

Mineralogical, fluid inclusion and stable isotope studies of associated amygdule and fracture mineralization revealed two stages of post-magmatic alteration which differ in both mineral association and formation conditions.

Stage I is formed by minerals typical for "deuteric" alteration of teschenites which took place immediately after solidification of the host rock. The vein-type mineralization is composed of titanite, aegirine-augite, annite, strontian apatite and analcime. The associated fluids were high-temperature (390–510°C) NaCl-rich, $CaCl_2$-poor brines (total fluid salinities range between 47 and 57 wt%). The source of fluids can be found in residual fluid phase remaining after crystallization of silicic magma in low-pressure environment (<1 kbar).

The superimposed Stage II mineralization is widespread in all rock types. It is typically composed of trioctahedral chlorite (clinochlore-chamosite), carbonates (mainly calcite, locally also dolomite, ankerite, siderite, magnesite and/or strontianite), sulphides (pyrite, marcasite, rarely sphalerite and millerite), celadonite, quartz, chalcedony and/or opal. The total range of homogenization temperatures of aqueous fluid inclusions is relatively wide (56–248°C), but most of the data are between ~80 and ~150°C. Salinities are generally low, between 0.2 and 3.7 wt% NaCl equiv. The fluid systems belong to Na-Cl or Na-Mg-Cl compositions. The calculated fluid $\delta^{18}O$ values range between –1 and +17 ‰ SMOW and fluid $\delta^{13}C$ values are between –17 and +1 ‰ PDB. Both the fluid inclusion and stable isotope data are inconsistent with idea of fluid source in post-magmatic residual fluids and/or seawater. Rather, the data could indicate the dominant contribution of diagenetic waters, produced by dewatering of neighbouring sedimentary sequences during compaction and/or warming-up caused by the intrusions of magma giving rise to igneous rocks.

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TRACE ELEMENTS IN GEM CORUNDUM (RUBY)

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In our study we compare trace element contents of gem corundum (ruby) from different countries in order to evaluate the possibility to constrain their origin. We investigated single grains of rubies from Longido and Mahenge (Tanzania), Mong Hsu and Mogok (Myanmar), Yen Bai and Luc Yen (Vietnam), Chanthaburi (Thailand), John Saul & Aqua Mine (Kenya), as well as corundum crystals from placer deposits from Srí Lanka and Madagascar. To determine the origin of rubies we will create fingerprints of single grains by their trace element content. The rubies of this study mostly occur in granulites, marbles and especially in metasomatic contact areas. Single grains of rubies have been analysed by electron microprobe (EMPA) at the Eugen Stumpfl Laboratory at the Universities of Graz and Leoben. The low concentration of trace elements in corundum limits our investigations by EMPA to the elements Al, Cr, Ti, V, Fe and Ga. The maximum element concentrations in the analysed rubies are 4.019% Cr_2O_3, 1.047% TiO_2, 0.622% V_2O_3, 0.158% FeO and 0.137% Ga_2O_3. The results indicate that we are able to distinguish different groups of rubies on the basis of the chemical composition as well as to determine the geological origin of various rubies. However an overlap in chemical composition occurs and it might be difficult to assign a single corundum crystal to its origin. Zoning patterns can be observed optically and chemically especially in samples from Myanmar. Thus element mapping was performed by EMPA. The acquired data shows an inverse correlation in Ti and Cr as it is indicated in Fig. 1 and Fig. 2. Rims with a relatively high content in Cr are dark red in colour in contrast to high Ti content rims which are greyish in colour.

Additional LA-ICPMS data will be obtained and should help to constrain the origin of corundum.

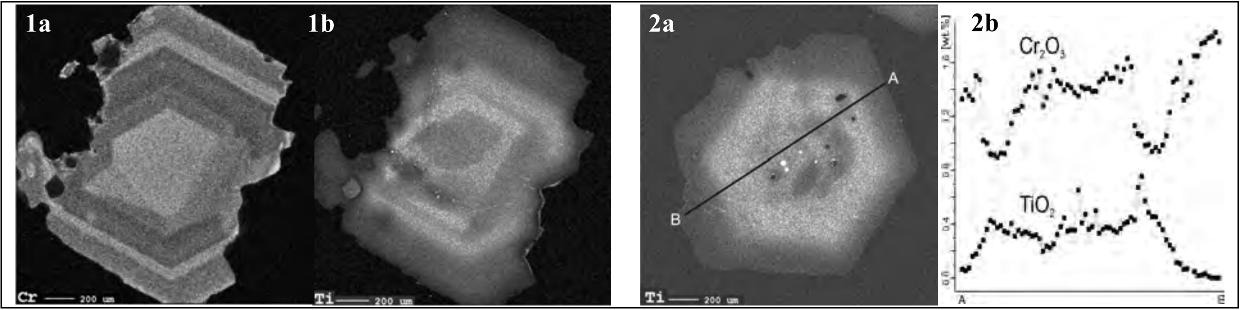

Figure 1. Element mapping images are indicating different chemical zoning rims, which are influencing the colour of the ruby. (a) Element mapping image of Cr in contrast to the Ti concentration in map (b) of the same grain. Figure 2. (a) Element mapping image of Ti in a zoned ruby. (b) Cr_2O_3 and TiO_2 concentration profile along A–B line.

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THE Fe-Mo-Nb-S SYSTEM: PHASE RELATIONS OF EDGARITE

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Niobium has a high affinity to oxygen and, therefore, practically all minerals containing niobium are oxygen compounds. Nevertheless, the sulphide edgarite $FeNb_3S_6$ (BARAKOV et al., 2000) was described from a feldspar-rich fenite in the Khibina alkaline complex, Kola Penisula, northwest Russia. Edgarite was found in association with pyrrhotite, ferroan alabandite, marcasite, and wurtzite. Edgarite is hexagonal, and its crystal structure is related to the crystal structure of molybdenite, as is the crystal structure of NbS_2 (not known from nature). NEWBERRY (1979) discussed the potential influence of Nb on the polytypism of molybdenite.

We decided to study phase relations within the Fe-Mo-Nb-S system in order to determine phase relations of edgarite and to verify the existence and establish the extent of solid solutions between molybdenite and edgarite. Experiments were carried out by means of the standard technique of evacuated silica glass tubes. Because of unfavourable kinetics, some runs were performed in salt fluxes (in NaCl, KCl or KI) or in the presence of a small amount of iodine (HIMODE et al., 1987) – see Fig.1.

Within the ternary Fe-Nb-S sub-system, our experiments indicate a broad $Fe_xNb_yS_2$ solid solution, which embraces the edgarite composition. In the central part of the Fe-Mo-Nb-S system at 400°C, there are two univariant assemblages: molybdenite + pyrite + edgarite + NbS_2 + vapor; molybdenite + pyrrhotite + edgarite + NbS_2 + vapor. In the MoS_2 + $FeNb_3S_6$ assemblage, both phases exhibit only a limited mutual substitution. We could not confirm any influence of Nb on the polytypism of molybdenite. Further research is in progress.

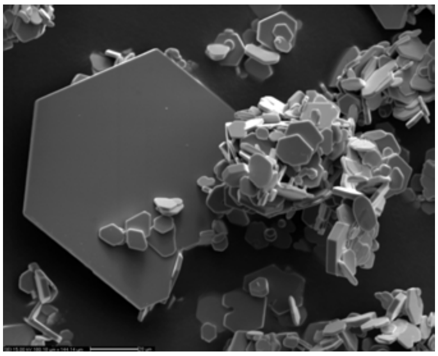

Figure 1.
SEM micrograph of edgarite grown in iodine vapor at 1000°C.

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PETROGRAPHIC CHARACTERISTICS OF THE POTTERY FROM THE EARLY MEDIAEVAL SETTLEMENT IN THE VICINITY OF KAPITAN ANDREEVO VILLAGE, SVILENGRAD MUNICIPALITY, SOUTH BULGARIA

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Data about the pottery complex from the explored archaeological site 27 located in the south-western part of the modern village of Kapitan Andreevo is reported in the present paper. The early mediaeval settlement is an unfortified one, situated on the first non-flooded eastern bank of Maritsa River. In the boundaries of the investigated area, which is approximately 3300 m^2, 13 early mediaeval dwellings and equipment are registered. The importance of the ceramic wares for dating and analyses of the cultural environment is enormous, taking into consideration the fact that this is almost the entire inventory from the settlement area.

The main technological groups of the pottery findings were characterised, regarding their mineral and chemical composition, texture and firing temperatures during a complex investigation. The applied methods included crystal optical, X-ray diffraction, AES ICP and RMS analyses of ceramic fragments, clays of the regions and some pottery glaze. The results of this study can be summarised as follows: 1) In the area of the settlement the main part of the pottery has identical petrographic, mineral and chemical composition, which suggest one source of the material. The differences of the ceramic fragments are predominantly in the size of the clastic components – psephitic to aleuritic – as well as in their quantity. The results of the XRD and chemical analyses of the clay from the area and pottery show similar composition. Imported pottery is present in limited amounts (single fragments). 2) On the basis of the results of the XRD analyses of the clay of the region we can conclude that it has polymineral composition. The plasticity and other physical characteristics (impurities, colour) of the clay that are necessary for its use in ceramic production are adequate. 3) The mineral composition and XRD results define the temperature of firing of the main group pottery in the interval of 650–800 (820) °C. 4) The compared fragments of ceramic glaze from the investigated early mediaeval settlement and those from the area of the city of Serdika show identical optical and chemical characteristics. This result correlates to the analyses provided up to now for topography, urban buildings and equipment found in both settlements. We suppose therefore that the investigated settlement near Kapitan Andreevo was populated in the same or in a close period of time as Serdika, between the second quarter or the middle of 7th c. AD and the beginning of 9th c. AD.

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THE SCHORL–ELBAITE SOLID SOLUTION AND USEFUL CORRELATIONS

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In Li-rich pegmatites Na- and Fe-rich tourmalines (schorl) and Na- and Li-rich tourmalines (elbaite) are quite common. Structural and chemical investigations (including light elements) of tourmaline samples of the schorl-elbaite solid solution show that there is a very good inverse correlation between the lattice parameter *a* (for values ≥ 15.84 Å) and the Li content. This correlation can be used in future for a reasonable estimation of the Li content, which can not be measured by electron microprob0e1 analysis. The lattice parameters can easily be determined by single crystal or powder X-ray diffraction. Lower values than 15.84 Å for *a* are typically a result of an increasing $^{[4]}$B content in Al-rich samples that usually have a (Fe^{2+} + Mn^{2+}) content of <0.1 apfu and relatively low Li contents. However, such samples were only rarely observed in nature (e.g., ERTL et al., 1997, 2007, 2008). There is a very high positive correlation between the lattice parameter *a* (for values ≥ 15.84 Å) and the (Fe^{2+} + Mn^{2+}) content in tourmalines of the elbaite–schorl series. Similar to other $^{[4]}$B-bearing tourmalines (olenites), a positive correlation between Al at the *Y* site and $^{[4]}$B and another positive correlation between (Mn^{2+} + Fe^{2+}) and $^{[4]}$Al was found in these tourmalines. These correlations suggest that, in the short-range order configurations, Al at the *Y* site is coupled with $^{[4]}$B, whereas Mn^{2+} and Fe^{2+} are coupled with $^{[4]}$Al. Sometimes mixed occupations, including Si, B, and Al were found at the *T* site in the investigated tourmaline samples. Usually in samples of the elbaite–schorl series the Si content is not lower than ~5.6 apfu (ERTL et al., 2006; HUGHES et al., 2001). The <*T*–O> distances of such samples are typically in the range 1.616–1.622 Å. An accurate assignment of *T*-site occupation is only possible by combining chemical with structural and/or spectroscopic data (magic-angle spinning nuclear magnetic resonance). However, the correlations mentioned before show a general trend, that in tourmalines with a relatively high schorl component pronounced amounts of $^{[4]}$Al, and in samples with a relatively high elbaite-component significant amounts of $^{[4]}$B are common.

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GEOCHEMISTRY OF LALUN SANDSTONES, POSHTE-BADAM BLOCK, IRAN: IMPLICATION FOR SOURCE AREA WEATHERING, PALEO-OXYGENATION, PROVENANCE AND TECTONIC SETTING

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Whole rock major, trace and rare earth elements chemical composition of 12 sandstone samples, from the Early Cambrian Lalun Formation, Poshte Badam block, Central Iran, have been investigated to determine their source area weathering, paleo-oxygenation conditions, provenance and tectonic setting. The Lalun Formation exhibits two types of sandstones: purple sandstones (Litharenite) and white quartzite sandstones (Quartzarenite). White quartzite sandstones are relatively depleted from all major and trace elements (except SiO_2, Zr and Co) in comparison with purple sandstones mainly due to the presence of quartz and absence of other Al-bearing minerals. La/Sc, Th/Sc, Th/Co, Th/Cr and Cr/Th ratios of studied samples were compared with those of sediments drived from felsic and basic rocks, Upper Continental Crust (UCC; TAYLOR & MCLENNAN, 1985) and Post-Archean Australian average Shale (PAAS; TAYLOR & MCLENNAN, 1985) ratios, which reveal that these rocks were derived from erosion of felsic rocks. The La/Sc vs. Th/Co (CULLERS, 2002) and Ni vs. Tio_2 (FLOYD et al., 1989) plot, also suggests the felsic nature of the source rocks. Although, the La-Th-Sc plot of samples fall in the mixed-sedimentary field close to UCC and PAAS, which indicates a parrent rock similar to a mixed sedimentary-metasedimentary provenance. The chondrite normalized REE patterns of samples are similar to UCC and PAAS, with slightly light rare earth elements (LREE) enrichment, negative Eu anomaly and flat heavy rare earth elements (HREE) pattern similar to a felsic and/ or cratonic sedimentary source. The chemical index of alteration in purple and white quartzite sandstones (CIA; NESBITT & YOUNG, 1982) (50% and 68%, respectively), plagioclase index of alteration (PIA; FEDO et al., 1995) (51% and 80%, respectively), and A-CN-K diagram (NESBITT & YOUNG, 1984), indicating intense weathering conditions in the white quartzite relative to purple sandstones, possibly due to climatic variations or recycling. Moreover, there is an increase in mean Th/U values, parallel to CIA values, observed from purple sandstones to white quartzite sandstones. However, the SiO_2 vs. Al_2O_3+K_2O+Na_2O diagram (SUTTNER & DUTTA, 1986) propose trend of climate change from arid to humid during deposition of the Lalun Formation. Plots of the geochemical data on tectonic discrimination diagrams suggest a passive continental margin setting for them. The geochemical parameters such as U, authigenic U, U/Th, V/Cr, Ni/Co and Cu/Zn ratios indicate that these sandstone were deposited under oxic environment.

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MINERALOGY AND CHEMICAL COMPOSITION OF METAL MINING WASTE DUMP SAMPLES

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The concentration of trace metals in a mine waste does not necessarily reflect their potential for release. In order to assess the potential toxic effects, the most widely accepted method is the sequential extraction which is used to operationally define the ease with which constituents are released to solution from the solid phase.

We used the TESSIER et al. (1979) method to assess the potential toxicity of samples from Bányabérc waste dump, Mátra Mts. Hungary. The main ore minerals of the studied site are galena, sphalerite, wurtzite, pyrite, chalcopyrite and some stibnite. Gangue is dominantly quartz with traces of calcite. The host silicate assemblage consists of variable amounts of K-feldspar, quartz, plagioclase, amphibole, pyroxene, chlorite, smectite. The secondary mineral phases are gypsum, jarosites, schwertmannite, goethite, anglesite, covellite, epsomite, alunogen, hexahydrite, rhomboclase, a halotrichite-group member and a copiapite-group member. The chemical fractions obtained with the TESSIER et al. (1979) method are defined as follows: (i) exchangeable, (ii) ions associated with carbonates or specifically adsorbed metals, (iii) ions associated with manganese oxides and amorphous iron oxides (reducible), (iv) ions occurring in sulfide minerals or organic (oxidizable), and (v) ions occurring in silicate minerals (residual). Analyses were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The total metal content was also determined following microwave-assisted digestion with aqua regia. For samples (≤ 2 μm, obtained by settling in ion-changed water) containing only water-soluble sulfates according to XRD data, we used water dissolution (pH 2) instead of sequential extraction. These samples represent the pore-water composition and are analogous with phases precipitated on a waste dump walls after long dry periods.

Mine waste samples contained elevated Zn (178.4–10464.7 ppm), Pb (186–4620 ppm), Cd (0.49–56.2 ppm), Cu (28.7–262.1 ppm), As (606.1–1550.7 ppm) concentrations. The sequential extraction leaching procedure showed how much of these quantities could be released. The possible mobilizable quantities for Zn were found to be: 142.7–4415 ppm, for Pb: 31.49–2823.1 ppm; for Cd: 0.4–23.1 ppm; for Cu: 18.3–231.8 ppm and for As: 429–535.7 ppm. These results demonstrate the importance of sequential extraction procedure when assessing the stability and bioavailability of metals at mine-waste impacted sites. The water dissolution results suggests that we have huge quantities of heavy metals in the water-soluble phases which are totally released in the environment (data exceeding the reference values for water – Zn: 4400–32620 ppm; Pb: 14.3–54.4 ppm; Cd: 1.44–166 ppm; Cu: 437–747 ppm; As: 217 ppm).

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MVT BASE METAL MINERALIZATION IN RUDABÁNYA (NE HUNGARY) – CHANGES OF GENETIC INTERPRETATION

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Rudabánya is a known medieval silver and copper producer and medium size iron ore mine since the 19th century. The bulk of the oxidized iron ores and the primary siderite bodies were removed by open pits and underground mining until 1985. Indications of potentially significant base metal ore mineralization have been repeatedly studied since the abandonment. These enrichments were known to concentrate on the edges of metasomatic siderite blocks tectonically embedded in clay marl (PANTÓ, 1956). Most characteristic minerals of this paragenesis are barite and silver-bearing galena.

Recent explorations revealed new features of this mineralization. Significant Zn content was detected (exceeding Pb in most cases), occurring dominantly in the form of iron-free sphalerite (cleiophane) and less in smithsonite. Sphalerite is not apparent because of its small grain size and characterless colour. Base metal enrichments were found not only in the rims of siderite bodies, but also related to N-S and NE-SW trending thrust zones. Moreover, both galena and sphalerite occur in the clay marl, siltstone and fine-grained sandstone (regarded as barren country-rock by the previous mining) as stratabound lenticular enrichments. Although their continuity is broken and the original spatial arrangement of the ore bodies is overprinted by a polyphase deformation, this stratiform mineralization seems to predate the siderite metasomatism.

The presence of a later large-scale disseminated copper overprint is also obvious although no clear genetic link to these base metal enrichments are found yet.

The recent information about the multi-stage Rudabánya mineralization points to the presence of sediment-hosted Pb-Zn-Cu-Ag base metal mineralization in near-surface position and of economic size.

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MAGMATIC VS. HYDROTHERMAL PROCESSES IN THE SOUTH FILSON CREEK MINERALIZATION, SOUTH KAWISHIWI INTRUSION, DULUTH COMPLEX

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The Duluth Complex (DC) is a series of mafic to ultramafic intrusions related to the 1.1 Ga Midcontinent Rift System (MILLER et al., 2002). The South Filson Creek (SFC) deposit occurs above the basal units of the South Kawishiwi Intrusion (SKI), and represents a unique geological setting of Cu-Ni-platinum-group element (PGE) mineralization within the Duluth Complex. It is located in an approximate stratigraphic high of 1000 m above the basal contact unlike all other known ore occurrences in the DC.

Two types of mineralization have been distinguished in the SFC area. (1) Mineralization, primarily magmatic in origin, appears in the Layered Series as disseminated fine-grained patches and pockets in an area of approx. ½ square kilometer and is not restricted by tectonic lineaments. Pyrrhotite, chalcopyrite, pentlandite and cubanite are the main ore-forming minerals with subordinate amount of other copper-bearing sulfides (bornite, covellite, talnakhite). Sulfides form interstitial blobs between cumulus silicates or fine-grained disseminations and microscopic veinlets. Several platinum-group minerals (PGMs) have been described in the samples, associated both with magmatic and secondary hydrothermal features. Geochemical properties of this type of mineralization helped to correlate it with other ore types within the SKI.

Amphibole, chlorite, sericite, prehnite, pumpellyite and carbonate alteration is connected to brittle structures in the area. This alteration has remobilized metals from the primary magmatic sulfide mineralization in the troctolites and is also responsible for a Cu-dominant mineralization (2) in the Anorthositic Series which has not been described in the area before.

Local remobilization of PGMs probably has occurred as a result of a separate alteration event characterized by mostly serpentinization.

Segregation of a Cl-bearing magmatic fluid has been revealed by variation in the halogen-content of apatite from pegmatoidal rocks.

Based on present study primary magmatic mineralization in the South Filson Creek area has been modified by later fluid-rock interaction on a regional scale which has to be taken into account in further Cu-Ni-PGE exploration in the Duluth Complex.

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GEOCHEMISTRY OF PALEOZOIC BASALTIC ROCKS FROM NORTH OF SHAHROOD, N IRAN

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The study area is located in north of Shahrood in Semnan province, N Iran, and in the east of Alborz structural zone. There are several outcrops of Silurian volcanic rocks in north of Shahrood, North of Iran, that provide a record of the history of the Paleo-Tethys ocean. The volcanic rocks consist of olivine basalt to andesite lavas and associated pyroclastic rocks. The main constituents of the rocks are olivine, plagioclase, pyroxene, and opaque minerals. According to different chemical evidences, basaltic rocks from north of Shahrood have alkaline-subalkaline nature. On the basis of tectonic discrimination diagrams they plot in within-plate setting and generated from continental lithospheric mantle.

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ON THE GEOCHEMISTRY AND MINERALOGY OF PHYLLITE-HOSTED TOURMALINITES – EASTERN ALPS

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Tourmalinites are widespread minor lithologies within a tectonic unit called "Grobgneiss series" at the eastern escarpments of the Alps, some 100 km S of Vienna. This rock series is predominantly composed of quartz phyllites and coarse grained orthogneisses. A phyllite-hosted stratabound arsenopyrite mineralization (GÖD & HEISS, 2006) spatially associated with tourmalinites gave rise to a detailed study of this type of rock. The tourmalinites occur as concordant lenses within the quartzphyllites with estimated thicknesses of approximately 0.5m and lateral extensions of some few 10m. The maximum distance between their westernmost and easternmost occurrences known so far is roughly 50km. The tourmalinites are mainly fine grained more/less massive, black rocks. Their tourmaline content varies between 60 and 80 vol%. Subordinated, a banded variety was observed. Quartz and some minor muscovite are the only other minerals visible with the naked eye. Microscopic investigations of the tourmalinites confirm their small grain sizes (locally below 50μm) and their simple mineralogical composition, displaying just chlorite, garnet, apatite, clinozoisite and zircon as additional and accessory components. Feldspars are absent. The tourmaline individuals are uniformly zoned with greenish to bluish cores and dark brown rims. The bulk chemistry of the tourmalinites is controlled by the mutual relation of tourmaline and quartz as emphasized by the B_2O_3 content varying between 2.9 and 8.9 wt% (n = 11) but resembles, disregarding the boron, the composition of the hosting phyllites. The likewise simple trace element pattern of the tourmalinites is inter alia emphasized by the following concentrations (aver./max., ppm, n = 11): Li 15/20; F 790/1280; Sn 13/20 and W 11/30. Five samples have been analysed for their chlorine, iodine and bromine content yielding the following results: iodine and bromine < 0.5 ppm and chlorine contents of ≈ 20 ppm for three of the analysed samples. The only trace elements geochemically slightly enriched are As 25/85 ppm and Zr 200/290 ppm. Microprobe analyses define the tourmalines as Mg-rich schorls. The tourmalinites yield $\delta^{11}B$ values of $\approx -11‰$ (4 analyses) and one single value of $-9‰$. These data preclude marine evaporites as B sources for the tourmalinites but do not allow to discriminate between granites or sediments respectively as potential boron sources (BARTH, 1993; JIANG & PALMER, 1998). The same is – sensu HENRY & GUIDOTTI (1985) – emphasized by the composition of the tourmalines themselves.

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ELECTRONIC AND MAGNETIC STRUCTURE OF PYROXENES I. HEDENBERGITE

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The electronic and magnetic structure of the chain silicate hedenbergite ($CaFe^{2+}Si_2O_6$) has been investigated by a number of experimental methods (neutron diffraction, Mössbauer spectroscopy, low temperature magnetic measurements), as well as by electronic structure calculations for clusters of different size in the local spin density approximation. The calculated size-converged spectroscopic data (*d–d* excitation energies, hyperfine parameters) are in quantitative agreement with the respective experimental values. The calculated magnetic coupling constants are about +25 cm^{-1} and –4 cm^{-1} for intra-chain and inter-chain coupling, respectively. The latter value shows that weak superexchange via edges of silicon tetrahedra is well reproduced by the calculations, and it is in qualitative agreement with an observed metamagnetic transition at 4.2 K in an external magnetic field with an onset around 4 T but saturation is not achieved in fields up to 14.5 T. The large ferromagnetic intra-chain coupling is attributed to a nearly degenerate ground state. The ratio between the two magnetic coupling constants agrees with earlier estimates on similar compounds. Finally, it is demonstrated how the detailed discussion of the various exchange pathways contributes to an improved understanding of the connection between magnetic properties and the geometrical structure.

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NEW U-Pb ZIRCON AGE CONSTRAINST ON THE MAGMATIC AND METAMORPHIC EVOLUTION OF GRANULITE FACIES BASEMENT ROCK FROM SOUTHERN TANZANIA

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Based on detailed geological, petrological and geochronological studies the tectonostratigraphy and geologic evolution of central and north-eastern parts of Tanzania is fairly good known. From structural bottom to top the major units are: (1) the Archaean Tanzania Craton; (2) the Usagaran Belt which consists of eclogites, some granulites, greenschist facies metapelites and associated quartzites as well as abundant granitoids and volcanic sequences; (3) the "Western Granulites", part of the Neoproterozoic Mozambique Belt (MB) including reworked parts of the craton and Usagaran Belt and composed of granulite facies metapsammites, migmatic orthogneisses, and mafic granulites; and (4) the "Eastern Granulites" which are clearly distinct from the "Western Granulites" by the occurrence of a basal unit consisting of migmatic enderbitic gneisses, mafic granulites and meta-anorthosites and a cover sequence consisting of marbles, calcsilicates, and metapelites.

However the geological units change in the S and SW of Tanzania. Here, to the east of Lake Malawi, distinctly different crustal pieces occur that may have derived from the Paleoproterozoic Usagaran Belt, the Mesoproterozoic Irumide Belt and from the MB in north Mozambique. Since there is only limited information on the age of metamorphism and formation of the igneous precursor rocks, thirteen samples were dated by U/Pb zircon LA-MC-ICP-MS. The samples were taken along a traverse from Mbamba Bay, Lake Malawi to Masasi, S-Tanzania. Samples are derived from deformed granitic gneisses and undeformed granitoids as well as from metapelitic samples and Grt-Am-rich gneisses.

One sample from Mbamba Bay, Lake Malawi, gave an upper intercept age of around 2000 Ma, another one a concordant age of c. 720 Ma. All other samples taken from Songea, Tunduru and Masasi show mostly concordant ages around 1000–1100 Ma obtained from magmatic zircon cores. Zircon rims are commonly observed and show also mainly concordant ages of 560-600 Ma. Some magmatic zircons also indicate ages of around 700-800 Ma.

The westernmost part of the studied area is probably a continuation of the 1.8-2.0 Ga old Usagaran Belt. All other samples have different metamorphic and intrusion ages compared to the Western & Eastern Granulites in Tanzania. Similar ages as well as similar lithological units can be found in the Unango and Marrupa Complexes in N-Mozambique. Thus a major tectonic boundary separating the Eastern Granulites (Mahenge Mountains) and the Unango and Marrupa Complexes is proposed between the Mahenge Mountains and the towns of Songea and Tunduru.

PETROLOGICAL INVESTIGATIONS OF TI-PHASE RELATIONS IN THE METARODINGITES OF BURGUM, PFITSCH VALLEY (SOUTH-TYROL, ITALY)

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The focus of this investigation is on the petrology of the metarodingites of Burgum in the Pfitsch-Valley, South-Tyrol, Italy. Geologically, these rocks are part of the Penninc Upper Schieferhülle (Bündnerschiefer) of the Tauern Window.

The samples were collected from heaps of rock debris located next to the Sterzingerhütte. Although this site is known by mineral collectors for its large, idiomorphic crystals of zircon, apatite, diopside, vesuvianite, and titanite, almost no petrological data exist so far. Therefore this study represents the first mineralogical-petrological investigation to deduce the T-$X\mathrm{CO_2}$ conditions of its formation. The metarodingites contain the mineral assemblage garnet, chlorite, ilmenite, magnetite, perovskite, calcite, dolomite, titano-clinohumite. In most samples corona-like reaction textures involving Ti-bearing phases can be found. In the center of these reaction textures ilmenite + magnetite occur. This assemblage is enclosed by a rim of perovskite, which is rimmed by titanite. The matrix shows the assemblage diopside + garnet + chlorite. Electron microprobe analysis shows that ilmenite contains a significant geikielite component (4.1-5.8 wt.% MgO). Peroviskite is very close to end-member composition and titanite contains only minor amounts of F and Al (<0.07 wt.% F, 0.48-1.03 wt.% Al_2O_3). Garnet is essentially a grossular-andradite solid solution with minor amounts of Ti (2.49 – 5.61 wt.% TiO_2).

Schreinemakers analysis of the phase relations in the system CaO-TiO_2-MgO-SiO_2-H_2O-CO_2 involving the phase components geikielite, perovskite, titanite, calcite, quartz yield an invariant point in a T-$X\mathrm{CO_2}$ diagram. The assemblage geikielite + quartz + calcite is restricted to high $X\mathrm{CO_2}$, whereas perovskite requires low $X\mathrm{CO_2}$ at high T. Titanite is stable at low T and high $a\mathrm{SiO_2}$ and thus forms most likely during retrogression. Therefore this mineralogical sequence can be interpreted as being the result of lowering $X\mathrm{CO_2}$ during the prograde path and a decrease in T contemporaneous with an increase in $a\mathrm{SiO_2}$ during the retrograde path.

FORMATION OF AMORPHOUS SILICA AND POLYMERIC SILICIC ACIDS BY CYCLIC FREEZING IN VARIOUS AQUEOUS SOLUTIONS

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Aqueous solutions (100 mL) containing monomeric silicic acid were subjected to cyclic freezing (6 hrs at +20°C, 6 hrs cooling from +20°C to –20°C, 6 hrs at -20°C, 6 hrs heating from -20°C to +20°C) for up to 100 days. Monomeric silicic acid at concentrations of about 1.79 mM was obtained by the decomposition of tetraethoxysilane in the aqueous solutions. The initial pH of the solutions for individual experimental runs was adjusted to 3, 5, 7, 9, and 11 by HCl and NaOH addition, respectively. The ionic strength was equalized by adding 5.0 mM NaCl in all solution. In several experimental runs 0.1 mM of Al (as $AlNO_3 \cdot 9H_2O$), B (as H_3BO_3) and Ge (as GeO_2) were added. After certain periods of experimental time (20, 40, 60, 80, 100 days) solutions were removed from the conditioning cabin et and filtrated through a 0.1 μm cellulose membrane. Subsequently, the concentrations of dissolved components in the filtrated solutions were analysed by ICP-OES.
Results show that during the first 40 days the concentration of silicic acid decreased by precipitation of amorphous silica, whereas other components remained in solution. The amount of silica precipitation increased with the number of freezing-thawing cycles. During the freezing period supersaturation with respect to amorphous silica causes amorphous silica formation and re-dissolution during the thawing period was kinetically inhibited. The decrease of silicic acid concentration was highest at pH 5 and less at elevated and lower pH. For experimental times > 40 days the precipitates partly redissolved. However, a secondary precipitation process occurred up to 100 days. The depletion of silicic acid was stronger in the presence of Al and even more stronger in the presence of Ge compared to pure Si or Si-B containing solutions. A similar elevated decrease of silicic acid concentration by cyclic freezing was also observed in the presence of alkali and earth-alkali metals by DIETZEL (2005).
Analyses of polymerization degree of dissolved silicic acid by β-silicomolybdic acid method show that the presence of Al and Ge led to a nearly complete polymerization of silicic acid. Contrary, silicic acid in respective reference solutions at 25°C remained completely monomeric. The complex behaviour of amorphous silica precipitation by cyclic freezing are discussed, which may contribute to a deeper understanding of dissolution and precipitation processes of silicic acid in the active layer of cryosols including the role of amorphous silica for the formation of secondary minerals like clay minerals and zeolites.

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PETROLOGY OF THE CONTACT BETWEEN THE LITHOLOGIES OF THE Pb-Zn ORE DEPOSITS PFLERSCH VALLEY – SCHNEEBERG (SOUTH TYROL, ITALY) AND ITS POLYMETAMORPHIC HOST ROCKS

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The Pb-Zn ore deposits of the Pflersch Valley and the Schneeberg are situated in the northern part of South-Tyrol, near the Pflersch Valley and the Passeier Valley. Geologically, the ore mineralizations are situated in the polymetamorphic Ötztal Complex. The aim of this study is the detailed field mapping of an area in the Pflersch Valley and the Lazzach Valley, with special emphasis on the contact between the ore horizons and the surrounding country rocks. Petrological investigations focus therefore on samples that contain sulphide as well as silicate mineral assemblages in order to provide Eo-Alpine P-T-fS_2 estimates in addition to the previously obtained P-T data from adjacent metapelites (PROYER, 1989).

In the Lazzach Valley, the major, macroscopically visible ore minerals are sphalerite (marmatite) + pyrrhotite compared to sphalerite + galena from the Schneeberg area. Submicroscopically, galena, gudmundite (FeSbS) and chalcopyrite occur. The ore paragenesis in the Pflersch Valley is similar, except that galena occurs as the major ore mineral. Furthermore fahlore, proustite (Ag_3AsS_3) and boulangerite ($Pb_5Sb_4S_{11}$) are present as submicroscopically components (SCHMITZ, 1974).

The host rocks of the schistosity-concordant metalliferous lodes are muscovite-rich schists and albite-bearing schists. Conspicuous are graphite schists near the metalliferous horizons. Furthermore, the sulphides are often accompanied locally with a garnet-rich paragenesis, containing garnet + quartz + biotite + muscovite + feldspar ± rutile.

Our study focuses on garnet + sphalerite-bearing samples in order to 1) investigate Zn incorporation in garnet and 2) to use these samples for thermobarometry as well as fS_2 evaluations. So far, the sphalerite geobarometer considering the incorporation of the FeS component yielded pressures between 5-10 kbar at a temperature of 550°C. Garnet is known to incorporate almost no Zn, but garnets coexisting with sphalerite, contain up to 1.3 wt% of ZnO! Zn incorporation probably occurs along the Fe-Zn exchange reaction $Fe_3Al_2Si_3O_{12}$ + 3ZnS = $Zn_3Al_2Si_3O_{12}$ + 3FeS. Therefore sphalerite coexisting with garnet contains slightly more Fe (8-10 wt%), compared to the matrix sphalerite (6-7 wt%). In addition, it is planned to model this reaction based on available thermodynamic data as well as thermodynamic approximations as in the case of the Zn-garnet end-member.

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SULPHIDES OXIDATION OF MINE TAILINGS SEDIMENTS FROM ABANDONED Sb DEPOSIT MEDZIBROD (NÍZKE TATRY MTS., SLOVAKIA)

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Abandoned Sb deposits situated in the Ďumbier part of the Nízke Tatry Mts. (Tatric tectonic unit, Variscan pluton with low level of Alpine overprint) were in the second half of the 20th century one of the main producers of antimony ores in central Europe. The ores were milled and Sb minerals were concentrated by flotation and the waste was deposited in one tailing impoundment.

This study describes oxidation processes of sulphidic minerals and Sb and As mobility in impoundment material. The fine-grained material containing sulphides such as pyrite, arsenopyrite less stibnite, jamesonite, berthierite and gudmundite is weathering and toxic elements are released into surface waters and catchments and have negative influence on aquatic environment quality.

The ore minerals and their weathering products were studied in reflected polarized light microscope and consequently analyzed by electron microprobe. Ore minerals, especially arsenopyrite are being replaced by rims in oxidation zone. Content of As in the rims of arsenopyrite varies from 16.73 wt% to 20.56 wt%, Sb up to 4.51 wt%, exceeding Sb content in primary arsenopyrite (highest content – 0.65 wt%).

The most abundant are secondary Sb oxides, which can be divided into two groups. Phases in first group consist mainly of Sb (from 81.76 wt% to 85.73 wt%) with low As content (up to 1.01 wt%). Second group of Sb oxides are phases with dominant content of Sb from 37.40 wt% to 65.02 wt%. Volume of Fe in chemical analyses varies from 10.11 wt% to 24.05 wt%. Content of As is in the range from 0.21 wt% to 5.98 wt%.

Fe oxides occur also frequently and can be divided into two types. In the first one content of Fe varies from 78.19 wt% to 86.99 wt%, contents of As and Sb are close to zero. Second type is characteristic with various content of Fe, Sb and As. In this phases Fe dominate and varies from 24.36 wt% to 47.56 wt%., Sb content is up to 26.00 wt% and As up to 32.28 wt%.

In some samples Pb oxides were observed and consist of variable contents of Fe (from 0.66 wt% to 26.15 wt%), Sb (from 1.88 wt% to 11.89 wt%) and As (from 2.68 wt% to 15.50 wt%).

A large amount of carbonates represented by magnesite and dolomite are present in the tailing material and have an important role in neutralizing of acid solutions generated by sulphides oxidation.

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NEW DATA ON THE SOPOT CHONDRITIC METEORITE (ROMANIA): COMPARATIVE ELECTRON-MICROPROBE AND RAMAN STUDY

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The Sopot meteorite (SM) (fallen on April 27th, 1927, near Sopot village, SW Romania; DUMITRESCU, 1928) is one of the seven officially recognized falls of Romania. Of the eight fragments recovered (in total 958 g), seven are hosted by Romanian museums and one (0.6 g) is in a private collection in Graz (Austria). Only recently (IANCU et al., 2004), the SM was classified as H5 chondritic meteorite. However, little is still known about SM in international references. The official online Database of The Meteoritical Society classifies the SM generically as "ordinary chondrite" (http://tin.er.usgs.gov/meteor/metbull.php).

This contribution provides new Electron Microprobe (EMP) analyses results and, for the first time for a Romanian meteorite, information retrieved by FT-Raman spectroscopy. The studied material (#I.77) belongs to the Museum of Mineralogy of the Babeş-Bolyai University, which hosts the only meteorite collection in Romania. The EMP measurements were carried out at 15 kV accelerating voltage, 40 nA beam current intensity and 5 μm electron-beam diameter, with a JEOL XA 8600 (Salzburg University). The FT-Raman spectra were collected at room temperature from the rough surface of the sample, using an Equinox 55 Bruker spectrometer with an integrated FRA 106 S Raman module optic fibre coupled to a Ramanscope II microscopy system (Babeş–Bolyai University of Cluj-Napoca).

The EMP results allowed the identification of the main mineral components of the chondrules and the matrix: forsterite – $(Mg_{1.63}Fe_{0.36}Mn_{0.01})_{\Sigma=2}SiO_4$; enstatite – $(Mg_{0.82}Fe_{0.16}Ca_{0.01}Mn_{0.01})SiO_3$; albite – $(Na_{0.83}Ca_{0.12}K_{0.05})Al(Si_{2.90}Al_{0.10})_{\Sigma=3}O_8$; and Fe-rich chromite – $(Fe^{2+}_{0.85}Mg_{0.15})_{\Sigma=1}(Cr_{1.62}Al_{0.30}Ti_{0.04}Mn_{0.03}Fe^{3+}_{0.01})_{\Sigma=2}O_4$. FT-Raman spectra confirmed some crystal chemical peculiarities of the main minerals. New phases for SM, *e.g.* the disordered macromolecular carbonaceous matter (a broad band at ~1600 cm^{-1} with a shoulder at ~1645 cm^{-1} and a band centred at ~1267 cm^{-1} with a shoulder at ~1350 cm^{-1}) were also evidenced. The relatively high degree of disorder in the carbonaceous matter is consistent with the moderate shock degree (S3) of the metamorphic event, which has been previously inferred from olivine and plagioclase (IANCU et al., 2004).

The combined EMP and FT-Raman analyses resulted in a more detailed knowledge on the SM composition, in particular the accurate identification of the carbon species. These show the advantages of using Raman spectroscopy for chondrites detailed studies.

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PRE- AND POST-FIRING MINERALS IN ANCIENT CERAMICS

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Accurate determination of mineralogical composition is a pre-requisite for reconstructing the ceramic raw materials and firing technology. In this respect, the electron microprobe analyses (EMPA) are a useful tool, routinely applied in petrology but rarely in archaeometry. We will show here the advantages and limitations of this method, exemplified with Late Bronze Age ceramics from Ilişua (N Transylvania, Romania). The studied tableware fragments have a brownish colour and a semifine to coarse granulometry.

One of the characteristic features of the EMPA is their often observed low sum. This can be explained by fine porosity as well as by hydration and hydroxylation processes. Another problem is the extremely fine matrix, which varies in composition on a scale of less than 1-2 μm, which is below the beam resolution. Despite some analytical problems, good results can be achieved with clasts exceeding 10 μm in diameter.

In the Ilişua potshards the clasts include quartz, plagioclase, K-feldspar and micas, rarely amphibole. Plagioclase grains are not zoned, but rather homogeneous or with patchy appearance, and show a wide range of compositions, from oligoclase to bytownite. They cannot be derived from a single rock source. The textural relation with the matrix suggests a firing origin of the more basic plagioclases, whereas the intermediate compositions can be related to the Neogene volcanics cropping out towards north and east of the site. The K-feldspars are partly clastic grains and partly formed upon firing, the latter showing frequently a low K_2O content. Muscovites occur mainly as form relicts, their composition is only exceptionally preserved. Mostly, they are altered by loosing K and Al and gaining Fe.

The majority of the clayish matrix displays low K, low Mg but high Fe contents and is clearly distinguishable from the composition of the micas. Another peculiarity is the variable P content, which can vary within few micrometers distance. The P content is positively correlated with the CaO, suggesting the presence of extremely fine-grained calcium phosphate. However, the P-free matrix has also a high Ca content. The peculiar chemistry of the matrix neither meets the composition of illite nor of montmorillonite or an according mixed layer. The high Fe content could be due to small Fe-oxides particles adsorbed in the clayish matrix, whereas the high Ca content could be related to admixture of extremely fine grained calcite in the raw material.

Summarizing, the EMPA revealed that the matrix is much more complex than is generally thought and consists of a mixture of various clay minerals, newly formed phases and additionally high Fe content. The clasts show partly, e.g. plagioclases, a wide variability and can be interpreted by compositional and textural evidence, either as being derived from some rock sources or having formed during the firing. The latter indicate high temperatures of firing, around 950°C. The precise determination of matrix and clast composition constrains much better the search for raw materials used for producing the pots.

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LOWER CRETACEOUS CONTINENTAL RIFT-TYPE BLACK SMOKER SYSTEM IN THE EAST MECSEK MTS.

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Modern continental rift-type vent hydrothermal activities have been reported from Lake Baikal, Russia (CRANE, 1991), and from Lake Baringo, Kenya (RENAUT et al., 2002), but we know only one ancient hydrothermal vent system, which can be related to continental rifting from North China (JIANGHAI et al., 2007).

Due to the Early Cretaceous crustal thinning in the European platform, alkaline magmatic rocks appeared in several fault zones in the form of volcanic and subvolcanic bodies in the Mecsek region, Moravian-Silesian Beskidy, North Pirenées, Western Carpathian nappe and in the Alpine region (Eastern Rhenodanubian flysch) (HARANGI et al., 2003). The volcanic sequence of the Mecsek Mts. was formed along a 250 km long and 50 km wide rift zone having a SW–NE direction, located in the Tisza megaunit (BILIK, 1983; KUBOVICS et al. cited by HARANGI, 1993). In connection with these submarine volcanics, there is a goethite ore occurrence (known in the Hungarian literature as the Zengővárkony iron ore deposit, mined between 1952–54) in the Mészégető-erdők area between Zengővárkony, Pusztakisfalu and Apátvarasd. A recent discovery may give clues to clear up the doubtful genesis of this deposit. A 1 m long and 80 cm wide chimney system and some smaller smoker chimneys have been found here, among strongly vesicular and hydrothermally altered pillow lavas with some metasomatised sediments. The extreme vesicularity of the pillows indicates a shallow sea level (maximum 200-300 m on the basis of the vesicularity index). The metasomatised sediments contain quartz- and calcite-filled vugs, and Crustacean coproliths. The chimneys are made of mainly goethite, pyrite, marcasite, fibrous opal (lussatite), calcite, and quartz. The diameter of the individual chimneys is between 0.1–1.5 cm. The first precipitation is opal-CT and pyrite, which is partly of framboidal texture, the diameter of the framboidal aggregates is 40–50 μm. Sulphur isotope study of the pyrite samples revealed extremely negative values ($\delta^{34}S$ between –35.9 and –28.0 per mil), which points to bacterial origin. Sulphide precipitations alternate with lussatite and form a multi-layered concentric structure. Homogenisation temperature distribution curve of primary fluid inclusions from zoned rhombohedral calcite crystals shows two maxima at 145°C and at 115°C.

This unique fossil smoker occurrence is the third one discovered in Europe and, having been formed in shallow marine continental rift environment, it is an even more special occurrence. Recognition of such submarine hydrothermal vents helps the reconstruction of the palaeoenvironment and the larger-scale tectonic setting.

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AN INSIGHT IN THE DEPTH: PETROGENESIS OF THE BASALT OF THE FÜZES-TÓ SCORIA CONE

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The Füzes-tó scoria cone is one of the youngest volcanic edifices in the Bakony-Balaton Highland Volcanic Field, which is one of the Neogene-Quaternary alkaline basaltic fields in the Carpathian-Pannonian Region. The scoria cone was built up by a Strombolian-type eruption at 2.6 Ma based on Ar-Ar dating (WIJBRANS et al., 2007) and it is well preserved.
We have found a lot of basaltic bombs with different shapes (for example spindle, rotational and scoriaceous bombs), which frequently contain dense ultramafic xenoliths. The peridotites have various composition and some of them have amphiboles, too. The host alkaline basalt is fairly uniform in petrographic point of view: it is very crystal-rich and most of the crystals derived from the subcontinental lithospheric mantle. During rapid magma ascent numerous olivine, clinopyroxene, orthopyroxene and spinel xenocrysts got into the melt, which resorbed in the melt. The chemical composition of these xenocrysts implies that they were incorporated from different depths of the lower lithosphere. The mantle-derived olivines have a very thin Mg-poor margin, which crystallized on the resorbed olivine xenocrysts from the basaltic magma. There is a remarkable reaction rim around the orthopyroxenes, which is the product of interaction between the basaltic melt and the mantle-derived orthopyroxene. The strongly resorbed clinopyroxene xenocrysts acted as a nucleation site for subsequent clinopyroxene crystallization, which took place during continuously decreasing pressure. The colourless, Mg-rich clinopyroxene xenocrysts have a lithospheric mantle origin, the rare green, Fe-rich ones, however, can be derived from the lower crustal mafic granulites. Near-liquidus olivine phenocrysts crystallized in crustal depths, most of them have Cr-spinel inclusions. These spinels show a similar composition to the MORB spinels, which have high Al-content. The crystallization of the magma took place at high fO_2.
The alkaline basalt of the Füzes-tó scoria cone gives a special opportunity for the genetic evolution of the basaltic magmas: through its mineral phases we can establish the different degree of depletion and the metasomatised character of the lower lithosphere, in addition we can recognize the melt-mineral reaction and the conditions of the magma evolution/crystallization.

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MINERALOGICAL INVESTIGATIONS OF AIRBORNE DUST IN TYROL

Kaindl, R., Botta, C., Hiden, S., Holzmann, J., Kozlik, M., Mayr, A., Perfler, L., Sagl, R., Schneider, P., Steidl, M., Stöbich, E., Ungerank, D., Viertler, J. & Weissenbacher, M.

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Airborne dust or particulate matter (PM) is a complex, heterogeneous mixture of solid and liquid particles. Especially the fine-grained fraction within visible dust < 10 µm (PM10, PM2.5) is able to diffuse deeply into the lung and causing serious health problems like cardiovascular diseases. In the framework of a graduate lecture, phase content and composition of PM in Innsbruck and its broader environs was investigated. The samples were collected close to heavy traffic crossroads as well as in low polluted rural environments. PM was impacted on a glass sample holder in a glass vessel by a battery-operated vacuum cleaner. The impacted particles were investigated by transmitted and reflected light microscopy, micro-Raman spectroscopy, Point-Counter and Electron microprobe analysis (EMPA).

The collected particles are transparent and opaque, quadrangular, globular, needle-like, fibrous, platy and irregular. Individual particles range in diameter from < 1 to several tenth of µm. In samples collected close to heavy traffic, frequently opaque carbon aggregates could be observed. One sample contained elongated, metallic chips, probably an abrasion product from railway tracks nearby. Reddish, laminated aggregates suggest the presence of iron oxides and hydroxides. Transparent flakes indicate mica minerals but also organic contaminants.

Raman spectroscopy allowed the identification of some organic and inorganic particles as dandruff, celluloses, nylon and $NaNO_3$. The spectral parameter of the D1 and G Raman bands of carbon particles suggest diesel engines, tyre abrasion and combustion residues of heating systems as possible sources (GUEDES et al., 2008).

Point-Counter analysis showed the dominance of soot particles in the heavy traffic samples and NaCl in rural environments. This can be attributed to diesel engines and salt dispersion to prevent ice formation.

By qualitative micro-chemical EMPA mineral particles were identified as NaCl, carbonates, gypsum, pyroxene, amphibole, mica, quartz, K-feldspar and hematite. This can be explained by aerial transport from nearby construction sites and/or the surrounding rocks (carbonates, sediments, metamorphic rocks). Furthermore, Cr±Ni±Cu±Zn and Fe-Ti metals and alloys from abraded railway tracks or brake discs of automobiles could be detected.

In conclusions, our investigations showed that the dominantly soot in the urban Innsbruck area is mainly caused by road traffic and heating systems. Inorganic matter is released by construction sites, metallic particles stem from individual and public transport whereas rural areas are influenced by intense salt dispersion and organic components.

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GEOCHRONOLOGY AND ISOTOPE GEOCHEMISTRY OF THE OPHIOLITES AND GRANITOIDS ALONG THE SOUTHEAST ANATOLIAN OROGENIC BELT

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The Southeast Anatolian Orogenic Belt is a result of closure of the Neotethyan Ocean, located between the Toride platform to the north and Arabian platform to the south, and continent-continent collision during Cretaceous-Miocene time. The tectono-magmatic units cropping out along the orogenic belt are located in Hatay-Kahramanmaras-Malatya-Elazig regions. These units are, structurally from top to bottom, a) metamorphic massifs, b) ophiolites, c) metamorphic rocks related to ophiolites and d) granitoids. The temporal-spatial and genetic relations between these units are very important to understand the evolution of the Southeast Anatolian Orogenic Belt.

The initial (calculated on the basis of relative U-Pb zircon ages) $^{87}Sr/^{86}Sr$ ratios of the ophiolitic units vary from 0.70314 to 0.70541, whereas the initial $^{143}Nd/^{144}Nd$ ratios vary between 0.513033 and 0.513093, corresponding to εNd_T values of +7.7 to +8.9. These results indicate that the ophiolitic units have a composition of depleted mantle. The initial $^{87}Sr/^{86}Sr$ ratios of the ophiolite related metamorphic rocks vary between 0.70286 and 0.70321, whereas the initial $^{143}Nd/^{144}Nd$ ratios vary between 0.51297 and 0.51299 corresponding to εNd_T values of +7.7 to +8.1 The initial $^{87}Sr/^{86}Sr$ ratios of the granitoids vary from 0.70389 to 0.70652, whereas the initial $^{143}Nd/^{144}Nd$ ratios vary between 0.512684 and 0.513016 corresponding to εNd_T values vary between +0.9 and +7.4. This situation can be explained by contamination via continental crust components during the forming of the granitoid units which primarily had a mantle composition.

LA-ICP-MS U-Pb analysis of the zircons separated from plagiogranites belonging to Kizildag ophiolite yields a crystallization age of 90.3±2.4 Ma and mineral Sm-Nd age of gabbro yields 95.3±6.9 Ma. These ages are concordant with the age of the Troodos (Cyprus) ophiolite to the west and Semail (Oman) ophiolite to the east, which have also similar origins. The mineral Sm-Nd age of the gabbros belong to Ispendere (Malatya) locality yields 85.1±7.1 Ma. All these ages can be interpretated there was two different subduction time (place) in the south branch of the Neotethyan ocean. The LA-ICP-MS U-Pb zircon ages of the granitoids yielded an age of 81.1±2.2 Ma for Esence (Kahramanmaras) and 82.0±1.2 - 84.6±1.1 Ma for the Baskil (Elazig) locality. These crystallization ages show that these granitoid bodies formed soon after the ophiolitic suites. Four zircon ages measured from Dogansehir (Malatya) by LA-ICP-MS U-Pb vary from 47.90±0.68 to 48.85±0.77 Ma. These crystallization ages indicate that the subduction, which also led to the formation of the granitoids, was still progressing during Eocene time.

STABLE ISOTOPES AND HYDROGEOCHEMICAL PARAMETERS IN A RIVERBANK FILTRATION SYSTEM (SZENTENDRE ISLAND, HUNGARY)

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Hungary's capital, Budapest, and a number of surrounding settlements are supplied by drinking water largely from the bank filtered aquifer at Szentendre Island of the Danube River lying to the north of the city. Precise knowledge of regional hydrogeological processes in riverbank filtrated aquifers are indispensable for aquifer protection and adequate quality water supply. To reach this goal, the origin and velocity/transit time of filtrating water was studied by stable isotopic, e.g. ^{18}O tracing measurements. The basis of these studies was the fact that $\delta^{18}O$ of Danube water (–10.9‰ as a mean) differs from the locally infiltrated precipitation (shallow groundwater, –9,5‰) as a consequence of the ”altitude effect”. Additionally, conductivity, temperature and various hydrochemical parameters were measured.

Water samples were taken on a daily basis from the Vác arm of the Danube, as well as from the water producing Kisoroszi-2 horizontal collector well, lying at the bank of Danube on the Szentendre Island. Collectors of this well are aligned to two horizons at the depth of ca. 12 m in the Pleistocene gravels. Electric conductivity and temperature were measured daily from the Vác Danube and weekly from the Szentendre arm. This was supplemented by daily $\delta^{18}O$ measurements for characterizing the region between the Danube and the well, and also by hydrochemical sampling every week.

Monitored parameters in the Vác and Szentendre arms of the Danube showed no significant difference, thus, the composition of water in both arms can be regarded as equal. Positive peaks in hydrochemical parameters correlated with episodic highs of the water level. Conductivity of the Kisoroszi-2 well did not exceed values measured in the Vác Danube. This might be explained by inhomogeneities of subsurface media. Combining the hydrodynamic model of Budapest Waterworks PLC with $\delta^{18}O$ data, a robust forecasting equation for $\delta^{18}O$ values of the Kisoroszi-2 well has been constructed. Longer data series would be needed to also include dispersion in this equation. The temperature of monitoring wells close to the shoreline is determined by Danube temperatures shifted with a few months. No seasonal variations exist, however, in the central zone of the island. Shallow sieving and the immediate vicinity of cover formations above in one of the monitoring wells resulted in the anomalously high precipitation percentage of the groundwater. The sulphate anomaly observed here could be attributed to agriculture in the vicinity.

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A COMPARATIVE ARCHAEOMETRIC STUDY ON THE BUILDING MATERIAL OF CHURCHES FROM THE ÁRPÁD AND MIDDLE AGES OF THE SOUTHERN GREAT HUNGARIAN PLAIN (ALFÖLD)

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Relatively low number of monuments built in the Árpád and Middle Ages survived on the southern Great Hungarian Plain (Alföld). Besides artefacts, many pieces of building and ornament material were recovered due to archaeological surveys. A wide variety of geological studies on the manufacturing and origin of building materials make archaeological data complete, providing useful information on historical building and economy.

The building and ornament materials used on the poorly supplied Great Hungarian Plain originated from Transylvania or north Hungary and were transported on the Maros and Tisza rivers. In the case of more scarce and valuable stones such as the red and Jurassic lime stones, sculptured stone material was transported from Transdanubia.

Most of the Árpád and Middle Ages settlements of Békés and Csongrád Counties were in ruins after the Tatar invasion and recovered only due to archaeological studies.

Macroscopic and microscopic studies of the building material of up to twenty-five churches were carried out. The macroscopic character, the source quarries, the period routes of transport and distribution of the rich building stones were identified as well as the economical potential of local builders.

Besides natural building and ornament materials artificial building materials also represent valuable information source.

Analyses of mortars and the hydraulic parameters of the mortar samples can make the absolute dating of the building materials and bricks binding to them possible. Based on previous reference studies carried out in Hungary, we conclude that comparative analyses of the $CaCO_3$ content, the insoluble residuals and the hydraulic factors introduced by JEDRZEJEWSKA (1960) may be an important tool for the relative dating of historical plaster samples.

JEDRZEJEWSKA, H. (1960): Stud. Conserv., 5, 132–138.

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MAGMA CHAMBER PROCESSES AND MAGMA ASCENT RATE BENEATH THE CIOMADUL MIC (KIS-CSOMÁD) LAVA DOME

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In the Carpathian-Pannonian region, the last volcanic eruption occurred in the Ciomadul (Csomád) at about 28 ka. The previous lava dome building phase, took place at about 500–600 ka. Considering the long repose time of the volcanic activity SZAKÁCS et al. (2002) suggested that the volcanic eruptions might continue in the future. Thus, it is crucial to obtain detailed information about the behaviour of this volcano. In this work, we carried out a detailed investigation of the older lava-dome building phase, particularly the evolution of the Ciomadul Mic (Kis-Csomád) lava dome. The main object of this study is to reconstruct the deep magma chamber processes, which ultimately lead the volcanic eruption. Understanding these processes is important to evaluate the possible future volcanic activity of the Ciomadul (Csomád) volcano.

Hornblende is the most frequent mafic mineral in the Ciomadul Mic (Kis-Csomád) dacite, which shows various zoning pattern and composition even in single samples. Based on their major and trace elements, they can be divided into two groups: a low-alumina and high-alumina group. The former one shows only little chemical variation and is classified as antecrysts. They occur often with quartz and potassic feldspar and could have been derived from a former crystal mush zone. The amphiboles were incorporated into the fresh dacitic magma and form the core of the reversely zoned crystals. In the outer rim of this kind of minerals, we can observe a drastic change of Al and Mg, which can be interpreted as the changing temperature and pressure condition. In the oscillatory zoned minerals the Al, Mg, Fe and Si show a cyclic variation, it is mainly controlled by the Al-tschermakitic substitution. The pressure difference of the crystallization of single crystals could exceed the 100 MPa, which suggest a vertically elongated magma chamber in the depth. Occurrence of Mg-rich minerals such as olivine and clinopyroxene implies repeated intrusion of mafic magmas in the dacitic magma chamber. The volcanic eruption could have been caused the last such intrusion event. Based on the applied geobarometry and geothermometry calculations the amphiboles could have crystallized in a pressure range from about 3.7 and 13 km and at a temperature of 850^{o}C. The reaction rim around the amphibole was formed during the ascent of the magma. The decompression-driven reaction between the amphibole and the degassed magma resulted in formation of clinopyroxene, plagioclase and oxide minerals at the contact zone. Based on the thickness of these reaction zones, we estimated an ascent rate of 0.3–0.6 cm/s, which means that the magma reached the surface within 6–12 days from the magma chamber.

SZAKÁCS, A., SEGHEDI, I. & PÉCSKAY, Z. (2002): Geol. Carpath. Spec. Issue, Proc. XVIIth Congr. Carpathian-Balkan Geol. Assoc. 53, 193-194

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NEOTETHYAN ADVANCED RIFTING STAGE PEPERITIC BASALTIC VOLCANISM IN THE DINARIDES AND HELLENIDES

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Comparative volcanological, mineralogical, petrological and geochemical studies of peperitic basaltic volcanic occurrences in the Dinarides (Kalnik Mts., Croatia and Vareš-Smreka, Bosnia and Herzegovina) and displaced parts of the Dinarides (Darnó Unit, NE Hungary), as well as in the Hellenides (Stragopetra, Greece) have been carried out. Lithostratigraphical and sedimentological studies suggested Triassic advanced rifting-type origin to these formations (PAMIĆ, 1997; HAAS & KOVÁCS, 2001; PALINKAŠ et al., 2008). The Hruškovec quarry in the Kalnik Mts. exposes a complete subaqueous basaltic volcanic centre with six different volcanological facies as coherent pillow, closely packed pillow, in situ hyaloclastite, isolated pillow breccia, pillow fragmented breccia and peperitic hyaloclastite (PALINKAŠ et al., 2008). In the other studied localities only distal facies in relation to the submarine basaltic eruption centre, such as closely packed pillow, carbonate peperite and pillow fragment hyaloclastite breccia facies were found. Role of the carbonate peperitic facies – which forms when lava arrives into the water-soaked carbonate sediment, obviously above the CCD – is clear, because it occurs at every studied locality and therefore bears correlation importance. However it also provides the evidence that these pillow basalt-bearing sequences could not be formed in deep water oceanic ridge settings as part of ophiolites. The seawater-rock interaction resulted in similar low temperature (200–70°C) hydrothermal alteration in each studied localities (plagioclase is more albitic in composition; chloritization; quartz, calcite and chlorite infillings in amygdales, jig-saw veins, former feeding channels and in the mineral band of the "pyjamas-type" pillow), and the role of seawater was dominant (3.2–7.8 NaCl eq. wt% salinity was proved). The hydrothermal processes were characterized by rapid cooling due to the lack of sufficient heat source for maintaining large scale hydrothermal fluid circulation (e.g. absence of ridge type magmatism). Fluid inclusion and mineral-chemistry data also support that the carbonate-peperite was formed in a relatively shallow marine setting in about 1-2 km deep water. On the ground of the extended geochemical study, the rocks show mainly within-plate basalt characteristics, while MORB-like features are subordinate. However the REE-spider diagrams suggest strong genetic similarities among the different Dinaridic and Hellenidic locations and distinct differences in relation to the ophiolite-related basalts of the studied regions.

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PALINKAŠ, A. L., BERMANEC, V., BOROJEVIĆ ŠOŠTARIĆ, S., KOLAR JURKOVŠEK, T., STRMIĆ PALINKAŠ, S., MOLNÁR, F., & KNIEWALD, G. (2008): J. Volcanol. Geotherm. Res., 178, 644-656.
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HYDROTHERMAL ALTERATION, FLUID INCLUSION CHARACTERISTICS AND K/Ar AGES FOR THE INTRUSIVE VOLCANIC-HYDROTHERMAL SYSTEM OF THE ZLATÁ BAŇA VOLCANIC EDIFICE (SLANSKÉ VRCHY MTS., EASTERN SLOVAKIA)

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In the Western Carpathians, one example of the intrusive-volcanic hydrothermal systems located in the Neogene intermediate-acidic calc-alkaline volcanic units is the mineralized zone in the vicinity of Zlatá Baňa village, Slanské vrchy Mts., Slovakia. The Slanské vrchy Mts. consist of several well defined andesitic stratovolcanoes (KALIČIAK, 1980) and the volcanic structure at Zlatá Baňa hosts low-sulphidation type epithermal gold-base metal veins and deeper seated Cu-Mo porphyry type ore mineralization which connected to a diorite stock intruding the mature stratovolcano (LEXA, 1999). The hydrothermal alteration in the system is characterized by illite and kaolinite in the shallow (until 300 m below the present surface) zones, whereas the predominant alteration assemblage contains sericite-chlorite to 800 m depth and the deepest known part of the system (below ~800 m) is characterized by high temperature propylitic alteration assemblage containing sericite-chlorite-actinolite±carbonate-epidote. This zonation is in well agreement with a generally observed pattern of an intrusion-related alteration zoning in an intermediate volcanic edifice at many places in terrestrial volcanic fields. The surrounding rocks of the veins in different depth have the alteration analogous with the zonation above. Radiometric age data for the fresh volcanic rocks extend from Late Badenian to Late Sarmatian (13.47–10.83 Ma), while the mineralization has Middle Sarmatian (11.87±0.43 Ma) age according to our K/Ar studies. Fluid inclusion data suggest that the intrusion-related hydrothermal system is characterized by boiling of a hot (around 350°C) intermediate salinity (10 NaCl eq. wt%) magmatic fluid. Boiling resulted in development of fluids with very high salinities reaching halite saturation during evolution of the magmatic-hydrothermal system. Mixing of magmatic fluids with a relatively cold (150°C) low salinity (0–1.5 NaCl eq. wt%) fluid of upheated meteoric water origin has been detected and the diluted fluids were responsible for the formation of the epithermal vein system. Due to boiling of fluids, the palaeohydrology of the hydrothermal system could be reconstructed. Results indicate that the mineralization located in the apical part of the diorite intrusion is recently in bigger depth (with ~300m) than was during the formation (based on the calculation of its depth below the paleogroundwater table). This suggests that during and after the hydrothermal activity the still active volcanic system produced sufficient cover on the recently exposed surface which is now eroded. This is confirmed by our K-Ar age dating: the last volcanic product in the region is younger than the age of the hydrothermal activity.

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LEXA, J. (1999): In: MOLNÁR, F., LEXA, J., HEDENQUIST, J. W. (eds): Epithermal mineralization of the Western Carpathians. Guidebook for the SEG Field Conference, 4–13 September, 63-108.

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PETROLOGICAL INVESTIGATIONS OF CONTACT METAMORPHIC MONTICELLITE- AND CLINTONITE-BEARING SKARNS FROM THE CIMA DI MINIERA (SOUTH-TYROL, ITALY)

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The contact aureole of this investigation is located at the Cima di Miniera in the Ortler Massif (South-Tyrol, Italy). In this area, a sequence of Tertiary (ca. 32 Ma) plutons intruded into dolomitic sequences (Hauptdolomite, Thurwieser member) of the Ortler nappe, which led to a massive skarn formation as well as to high-grade dolomite-marble formation. The mineral assemblage of the granodiorite is: amphibole + plagioclase + diopside + Fe-oxides + quartz ± K-feldspar ± titanite. The contact metamorphic dolomitic marbles contain the mineral assemblage forsterite + spinel + dolomite ± monticellite ± diopside.

Within the contact a mineralogical zonation occurs. In zone I, adjacent to the granodiorite, garnet, rich in the grossular-andratite-hydroandradite component, vesuvianite and diopside-fassaite-bearing clinopyroxenes are formed. In zone II, clinopyroxene (diopside), zoisite, olivine, monticellite and spinel, form. Textural investigations reveal that monticellite is thought to occur in the skarn via the reaction: forsterite + diopside +calcite = monticellite + CO_2.

The late magmatic high fluid activity also led to a massive alteration of the skarn. Alteration products are prehnite, pumpellyite, chlorite, serpentine, zoisite, clintonite; and calcite. Some samples of the skarn show 2 generations of clintonite, most likely attributed to prograde and retrograde growth.

Calculated *P-T* conditions of the granodioritic intrusive bodies, based upon the Al-in-hornblende barometer and the hornblende-plagioclase thermometer, yielded crystallization *P-T* conditions of 0.15 – 0.3 GPa and 720 - 830°C. Peak-temperatures of the skarn formation of 850-915°C were calculated with the zirconium-in-titanite thermometer. The solubility of forsterite in coexisting monticellite in the contact metamorphic marble allows calculation of a maximium temperature of 850°C. In terms of their stability with mixed fluids, monticellite, clintonite and vesuvianite are good mineralogical indicators for low X_{CO2} conditions during contact metamorphism.

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COMPARISON OF THE HUNGARIAN ULTRAPOTASSIC ROCKS BASED ON MINERAL CHEMISTRY AND TEXTURAL CHARACTERISTICS

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The ultrapotassic rocks are rare worldwide and this is the case also in the Carpathian-Pannonian region. Only two outcrops are known, the Middle Miocene Balatonmária trachyandesite and the 2,1 Ma years old Bár leucitite (HARANGI et al., 1995).

The Bár leucitite contains olivine, phlogopite and clinopyroxene. The olivines show often skeletal appearance and are forsterite-rich (Fo = 70–90 mol%). The margins of the crystals are variously resorbed and suffered iddingsitic alteration. The mg-number of the phlogopites is also high (0,79–0,90), they are usually strongly resorbed. The groundmass consists of olivine, clinopyroxene and phlogopite microphenocrysts, Ti-magnetite and ilmenite phases, whereas the interstitial spaces are filled by leucite, anorthoclase and Ba-rich alkali feldspar.

The Balatonmária trachyandesite contains clinopyroxene and phlogopite phenocrysts (mg = 0,64–0,81), but olivine appears only as microphenocryst, and shows much evolved character (Fo = 56–60 mol%). The groundmass consists of clinopyroxene, orthopyroxene, sanidine, plagioclase and Ti-magnetite F-rich apatite occurs in both rocks as inclusion in other minerals, microphenocrysts and groundmass mineral.

The ubiquitous clinopyroxenes in both case have various zoning patterns and show a wide compositional range, therefore they can be used to reconstruct the magma chamber processes. In case of Balatonmária the most important magma chamber processes are the following: fractional crystallization of clinopyroxene and mica from a relatively evolved magma at high pressure in the chamber, followed by the intrusion of a primitive magma, which indicated convection and formation of a strongly inhomogeneous zone of mixed melts. A subsequent intrusion of a more mafic magma caused further mixing.

The textural and geochemical characteristics of the minerals in case of Bár leucitite shows a different evolutionary history. In a shallow level magma chamber a potassium-rich magma underwent in-situ crystallization, which resulted in formation of a differentiated melt, which migrated upwards and accumulated at the upper zone of the magma chamber. Then, a potassium-rich mafic magma intruded into this stratified magma chamber, which induced strong convection and the two melts mixed thoroughly. Temperature of the magma before the eruption could have been around 850°C based on the composition of the coexisting Ti-magnetite and ilmenite pairs.

Comparison of the mineral composition data with other ultrapotassic occurrences suggests that the transitional character of Bár leucitite between the lamproites and the Group III ultrapotassic rocks, inferred from the major and trace element composition is reflected also by the composition of the mineral phases, whereas the Balatonmária volcanites has typical Group III characteristics.

HARANGI, Sz., WILSON, M., TONARINI, S. (1995): Acta Vulcanol., 7, 125-134.

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SECONDARY Sb AND Fe MINERAL PHASES AS PRODUCTS OF SULPHIDE OXIDATION OF TAILINGS MATERIAL AT ANTIMONY DEPOSITS DÚBRAVA AND POPROČ (SLOVAKIA)

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Abandoned Sb deposits Dúbrava and Poproč were in the past (second half of 20th century) important producers of stibnite ore in Central Europe. At both of the localities, Sb ore was mined and flotated. The flotation waste was stored in tailings.

Tailings studied contain a big amount of sulphide minerals (pyrite, arsenopyrite and stibnite). Secondary minerals formed through their oxidation contain Fe, Sb and As. Tailings at Dúbrava contain Fe up to 1.95 wt%, As up to 0.69 g/kg and Sb up to 3.5 g/kg. At Poproč content of Fe in the tailings is up to 4.82 wt%, As up to 4.70 g/kg and Sb up to 15.83 g/kg.

Crystals of stibnite, as the main source of antimony in tailings, are often broken and cracked. The crystals are slowly falling apart from border toward core. Secondary minerals neither fill the little cracks nor replace the stibnite crystals. The content of stibnite in the oxidation zone of tailings is low, probably due to the fast dissolution process of stibnite and the following migration of Sb into the surrounding environment.

Based on the present results we assume that there are two possible mechanisms of dropping of Sb from a solution. In the first case, Sb bonds on Fe oxides/oxihydroxides that were observed at both localities. In the second case, there occur probably a crystallization of "pure" Sb and Sb/Fe minerals in the environment of the tailings. These mineral phases are similar to stibiconite and tripuhyite by their chemical composition, further they are the dominant products of sulphides oxidation at the Poproč locality.

At Dúbrava, the most frequent secondary minerals are Fe-, Sb- and As-containing oxidation rims, which formed around pyrite and arsenopyrite grains. Oxidation rims on pyrite contain up to 62.72 wt% Fe, up to 2.66 wt% As and up to 4.84 wt% Sb. Samples of secondary rims on pyrite from tailings at Poproč had similar content of these elements. At Dúbrava, oxidation rims formed on arsenopyrite contain up to 49.77 wt% Fe, up to 25.69 wt% As and up to 7.01 wt% Sb. At Poproč, secondary rims around arsenopyrite crystals have not been observed.

The next products of sulphide oxidation of tailings material at both localities are Fe and Sb/Fe oxides and oxyhydroxides.

Furthermore, pseudomorphs of goethite after pyrite with perfect and almost idiomorphic crystal forms are very frequent (mainly at Dúbrava). At both localities, Fe oxides contain up to 54.60 wt% Fe, in some parts have high content of Sb up to 5.07 wt% and of As up to 3.37 wt%. Sb/Fe-oxides from Dúbrava that are not pseudomorphs after sulphides and do not contain relics of sulphides, contain up to 42.94 wt% Fe, up to 64.29 wt% Sb, up to 1.50 wt% As and 6.39 wt% Ca on average. Finally, Sb and Sb/Fe-oxides from Poproč contain high amount of Sb (up to 69.39 wt%).

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DEPICTING TIME SCALES IN THE FORMATION OF THE LOWER CONTINENTAL CRUST OF THE IVREA-VERBANO ZONE (N ITALY)

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Timing the inset and relaxation of the thermal perturbance induced by mafic intrusions in the lower crust is a crucial issue to understanding the evolution through time of continental magmatism and crustal formation. Some constraints may be derived from the case studies of the deep crustal Mafic Complex of the Ivrea-Verbano Zone of NW Italy.

The Ivrea-Verbano Zone (IVZ) is interpreted as a block of Variscan lower crust intruded/underplated by upper mantle magmas in the Permian. Rocks of the IVZ have been grouped in two major units: 1) a metamorphosed Carboniferous accretionary complex (Kinzigite Formation); and 2) the underplated or intraplated composite Mafic Complex (MC). Earlier models for this igneous event in the IVZ invoked a one-stage intrusion in the Permian and a subsequent slow cooling during the Mesozoic.

New in-situ U/Pb zircon age data provide the basis for a far more complex model:

In the Val Sessera and Val Sesia sections the 8-km thick upper Mafic Complex crystallized at 288±4 Ma while a large spread of ages between 295 and 285 Ma obtained from samples from lower levels supports the concept that at depth the mafic body remained as a partially molten crystal mush for a larger time lapse. Ages derived from regions N of the Val Sesia show a completely different age pattern: Magmatic ages of cumulitic pyroxene-gabbros and norites interlayered with the main lithologies of the MC at Campello Monti (Val Strona di Omegna) are 1600±34 Ma and 964±22 Ma. They thus constitute the oldest igneous rocks found so far in the IVZ and the Southern Alps. The Permian underplating event is documented only by a thermal impact on the rocks as evidenced by small metamorphic zircons and metamorphic overgrowths on the igneous crystals. A garnet-hornblende-gabbro intruding the 1600 Ma pyroxene-gabbro shows a magmatic formation age of 288±8 Ma thus testifying to the Permian underplating event. A later high-*T* overprinting event and subsequent slow cooling of this garnet-hornblende-gabbro is documented by distinct zircon rims and recrystallised domains with an age of ca. 273 Ma to 260 Ma. An alkaline dike crosscutting the pre-MC and the MC rocks at Campello Monti has a Triassic intrusion age of 229±4 Ma.

Magmatic formation ages of gabbros and alkaline dikes in the Finero section (northern IVZ) are also Triassic with ages ranging from 226 Ma to 204 Ma. Interestingly, no evidence for the aforementioned Lower Permian igneous activity is found.

Thus, the new ages witness a number of more or less discrete igneous events of a few Ma duration each leading to the formation of some amount of the lower continental crust now termed IVZ substantiating that magmatic events forming the lower crust of the IVZ have been active for ca. 1400 Ma and therefore are not restricted in time to the prominent and well documented Lower Permian underplating event.

The formation of lower continental crust thus seems to be a long-lasting process including strongly differing times scales (hundreds of Ma versus a few Ma) at least in the IVZ.

AN ORTHORHOMBIC DIMORPH OF BARSTOWITE, $Pb_4Cl_6(CO_3)\cdot H_2O$, FROM SLAGS AT MARIA WAITSCHACH, AUSTRIA, AND LAVRION, GREECE

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A systematic, ongoing study of slag minerals in the Pb-rich slag dumps of Maria Waitschach, Hüttenberg, Carinthia, Austria, has revealed a large number of Pb- and Pb-Cu-halogenide compounds which are partly known (diaboleite, fiedlerite, laurionite, matlockite, paralaurionite, phosgenite, pseudoboleite) and partly new to science. Among the latter is a previously unknown, orthorhombic dimorph of (monoclinic) barstowite, $Pb_4Cl_6(CO_3)\cdot H_2O$, a mineral originally reported from Cornwall where it formed due to interaction of a galena-bearing vein with seawater (STANLEY et al., 1991). The dimorph forms very elongate, colourless needles associated with phosgenite. It was subsequently also identified from the Vrissaki slag locality, Lavrion, Greece, where it is associated with fiedlerite.

The crystal structure was solved from single-crystal X-ray intensity data (CCD area detector) and refined in space group $Pmn2_1$ (a = 9.208(2), b = 16.654(3), c = 4.206(1) Å, V = 645.0(2) Å^3, Z = 2) to $R1(F)$ = 3.68% and w$R2_{all}$ = 8.37% from 2340 'observed' reflections with $F_o > 4\sigma(F_o)$. The crystal fragment used is racemically twinned (Flack parameter 0.471(17)). The topology and layer stacking are practically identical to that of barstowite, which has similar, but pseudo-orthorhombic cell metrics ($P2_1/m$): a = 4.2023(5), b = 9.2020(7), c = 16.6608(6) Å, β = 91.829(9)°, V = 643.94(9) Å^3, Z = 2 (STEELE et al., 1999; see also KUTZKE et al., 2000). The difference between both structures is very subtle: the number of atoms in the asymmetric unit is identical and the change to orthorhombic symmetry is achieved only by small changes of the orientation of two Pb3–Cl bonds (equivalent to a shift of the Pb3-based layer). Both structures are therefore assumed to have nearly identical Gibbs energies of formation, and the orthorhombic dimorph may occur as well in non-slag environments.

Single-crystal laser-Raman spectra of the orthorhombic dimorph will also be presented and discussed.

Fritz Schreiber, Roland Fink and Christian Auer are thanked for providing the studied samples.

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CONTRASTING MANTLE SECTION IN ALBANIAN OPHIOLITES: EVIDENCES FROM MINERAL AND BULK ROCK COMPOSITION

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The classical view on the Albanian Ophiolites was the division in an eastern SSZ and a western MORB belt, respectively. This genetic view should be also reflected in the mantle section by the occurrence of predominantly harzburgite in the eastern and lherzolite in the western belt. Recent investigations in the western belt revealed a quite different picture. The peridotitic massifs show regional a wide compositional variation. Voskopoja, Rehove and Morava in the south are indeed dominated by lherzolite and contain, if any, only minor harzburgite occurrences. By contrast the next two massif towards to the north, Devolli and Vallamara, are almost exclusively composed of highly depleted harzburgite. The following massifs towards north, Shpati, Kuterman and Skenderbeu are made up of comparable proportions of harzburgite and lherzolite. In all three massifs the more western part is dominated by harzburgite and only in the eastern part of the three massifs occur dominantly lherzolite. In contrast, further to the north, the next two massifs Puka and Gomsique are again dominated by lherzolites only. The next following massif in the north, with a more intermediate position between the western and the eastern belt, is named Krabi and is formed by both harzburgite and lherzolite. According to our first results the Tropoja massif at the Albanian-Kosovo border is build up by harzburgite, fitting into the eastern belt. In general the eastern belt of Albanian ophiolites is more uniform and contain mainly harzburgite, as shown by the examples of Shebenik and Bitincka.

Using bulk geochemistry the Al values of the investigated peridotites show a high variability from 0.3-3.8 wt% Al_2O_3 ranging from a fertile to a rather extreme depleted peridotite. Also the composition of olivine, chromian spinels and the pyroxene minerals varies in all of the ultramafics and reflects the lithological variability. X_{Mg} values of olivine range from 0.895 in lherzolite to 0.915 in depleted harzburgite. This is combined with a Cr# of spinels ranging from lherzolite to depleted harzburgite from 10-73. A similar wide variation can be found in the Cr# of both Cpx and Opx.

In the Albanian western ophiolite belt striking for more than 140 km in N-S direction the mantle composition varies alternately from a lherzolite close to primitive mantle composition to a highly depleted harzburgite. In contrast the Albanian eastern belt seem to be formed by more homogeneous mantle formed by harzburgite.

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PETROLOGIC AND GEOCHEMICAL STUDY ON SULFIDE MELT INCLUSIONS HOSTED BY UPPER MANTLE XENOLITHS FROM ALKALI LAMPROPHYRES (TUVA, S SIBERIA, RUSSIA)

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In this paper we present a detailed petrographic and major element geochemical study on sulfide melt inclusions occurring in mantle xenoliths and their Late Ordovician lamprophyric host rock from Tuva Region (South Siberia, Russia).

The lamprophyres have panidiomorphic textures with large ocelli and also contain olivine (replaced by chlorite), euhedral, zoned clinopyroxene, amphibole and mica phenocrysts. In addition to these, high amount of xenomorphic, fresh olivine, orthopyroxene and clinopyroxene xenocrysts can also be observed. The groundmass consists of opaque minerals (ilmenite, magnetite), biotite, amphibole, clinopyroxene, carbonate minerals, glass and apatite. The Tuva lamprophyres also hosted large amounts of crustal rocks and upper mantle xenoliths.

The studied upper mantle xenoliths are orthopyroxene-rich lherzolites, harzburgites, olivine websterite and orthopyroxenites; their rock forming minerals have high mg# (~0.9). Based on petrographic and major element evidences, the orthopyroxene-rich character of the studied xenoliths can be the result of a subducted slab-derived SiO_2-rich melt/peridotitic wall rock reaction (after KELEMEN et al., 1998). This idea is also supported by the geodynamical evolution of Tuva Region (subduction ~500 Ma, VLADIMIROV et al., 2005).

The primary sulfide blebs occur either as inclusions enclosed mostly in orthopyroxenes or as interstitial phases. They consist of maximum four constituents, such as pentlandite, chalcopyrite, pyrite and millerite and show re-calculated bulk compositions of monosulfide solid solution (MSS) and MSS + $\text{liquid}_{\text{Ni,Cu}}$ (above 1000 °C, after e.g. KULLERUD et al., 1969).

Based on the results of petrographic observations, geochemical analyses and geothermobarometric calculations, the physico-chemical state of the upper mantle beneath Tuva Region can be outlined prior to the entrance of the lamprophyric melt. Besides, we reconstructed the evolution of the lamprophyric magma and the sulfide melt inclusions hosted in mantle xenoliths during their ascent to the surface.

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PETROLOGY AND GEOCHEMISTRY OF MANTLE XENOLITHS FROM LETHLAKANE, BOTSWANA AND FROM THE KIMBERLEY AREA, SOUTH AFRICA

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Mantle xenoliths are commonly found in kimberlite pipes along with crustal xenoliths and single mantle minerals such as garnet, olivine, pyroxene, ilmenite and sometimes diamonds. Several samples were recovered from the open pit Lethlakane diamond mine, Botswana, as well as from dump sites around Kimberley, South Africa.

The majority of the Lethlakane mantle xenoliths consist of phlogopite bearing harzburgites and some lherzolites. Garnets were only observed in few samples in retrograde reaction textures where garnet is consumed by a kelephitic rim. The typical mineral assemblage consists mainly of olivine and orthopyroxene with variable amounts of clinopyroxene, garnet, spinel, phlogopite, and Fe-Ti oxides. Reaction textures involving calcite, phlogopite and spinel around orthopyroxene are commonly seen. The X_{Mg} of olivine, orthopyroxene, clinopyroxene, phlogopite and garnet are 0.83–0.89, 0.27–0.89, 0.77–0.92, 0.82–0.91, and 0.77–0.86, respectively. Cpx has an unusual high jadeite content of X_{Na} of around 0.30.

We applied the Opx-Cpx geothermobarometers of BREY & KÖHLER (1990) in garnet bearing lherzolites. Preliminary results indicate temperatures between 920 and 1020°C and pressures in the range of 4.5 to 6 GPa.

The Kimberly samples were collected on three different dump sites, where the tailings of the Big Hole, Kimberley, Bultfontein and Dutoitspan mines were deposited. These are the Boshoff road dump, the Old Dutoitspan Treatment Plant (ODTP) and the Kenilworth dump. The Kimberley samples consists predominately of phlogopite-/garnet- lherzolites and harzburgites as well as highly deformed and sheared xenoliths of lherzolitic and harzburgitic compositions and subordinate MARIDS (phlogopite, amphibole, rutile, ilmenite, diopside, orthopyroxene), also called “glimmerite”. The mineral assemblage of lherzolites comprises olivine, orthopyroxene, clinopyroxene, garnet, phlogopite, and oxides. The X_{Mg} of olivine, orthopyroxene, clinopyroxene, phlogopite and garnet are 0.86–0.87, 0.87–0.89, 0.87–0.89, 0.81–0.91, and 0.74–0.75, respectively. Opx–Cpx geothermobarometry (BREY & KÖHLER, 1990) in garnet-bearing lherzolites yielded temperatures between 1200 and 1220°C and pressures in the range of 5.8 to 6 GPa.

Furthermore we will investigate the water contents in nominally water free minerals (NAMS) such as olivine, pyroxene and garnet. Unusual high OH contents in these minerals indicate mantle metasomatism which is probably also seen in elevated concentrations of large ion lithophile elements.

This study is a contribution to IGCP 557.

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NEW CAVITY-FILLING ZEOLITES FROM THE BASALTS OF THE BAKONY–BALATON HIGHLAND VOLCANIC FIELD (WESTERN HUNGARY)

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Cavity-filling zeolites found in young (8-3 Ma) alkaline basalts of the Balaton Highland were described from several localities in the last century (e.g. MAURITZ, 1948; KOCH, 1985). However, a systematic mineralogical survey of these zeolites has not been performed yet. Based on WDS EMPA studies several zeolite species were identified here for the first time: chabazite-K - chabazite-Na - gmelinite-Ca - gonnardite-Na - phillipsite-K and phillipsite-Na (Fig. 1).

Chabazite-K: zoned crystal with chabazite-Ca; Badacsony Hill (Badacsonytördemic)

Chabazite-Na: zoned crystal with chabazite-Ca; Haláp Hill (Zalahaláp)

Gmelinite-Ca: Na/(Na+Ca) = 0.08–0.32; Haláp Hill (Zalahaláp).

Gonnardite-Na: common, Na/(Na+Ca) = 0.65–0.95; Farkas Hill (Bazsi), Gulács Hill (Nemesgulács), Hajagos Hill (Tapolca), Haláp Hill (Zalahaláp), Hermántó Hill (Zalaszántó), Kovácsi Hill (Vindornyaszőlős) and Láz Hill (Uzsa).

Phillipsite-K: common, K/(K+Ca) = 0.51–0.67; Badacsony Hill (Badacsonytomaj), Csehi Hill (Sümegcsehi), Gulács Hill (Nemesgulács), Hajagos Hill (Tapolca), Haláp Hill (Zalahaláp), Kovácsi Hill (Nagygörbő and Vindornyaszőlős), Prága Hill (Bazsi) and Szebike Hill (Uzsa).

Phillipsite-Na: rare, Na/(Na+Ca) = 0.60–0.62; Haláp Hill (Zalahaláp) and Prága Hill (Bazsi).

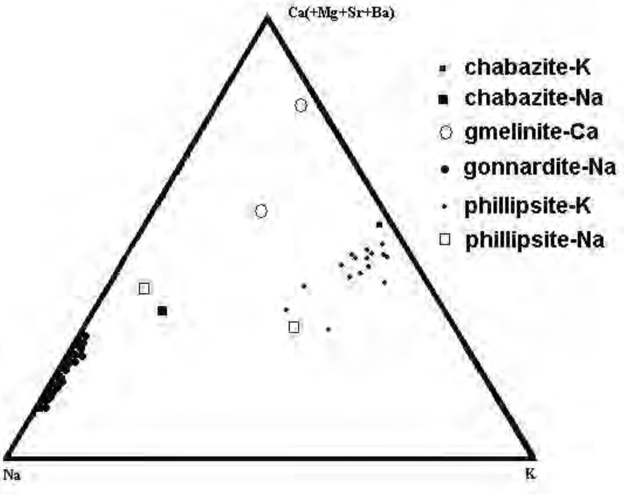

Figure 1. Distribution of exchangeable cations in new zeolites from Balaton Highland.

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RE-EXAMINATION OF "MONSMEDITE" FROM THE TYPE LOCALITY, BAIA SPRIE, BAIA MARE DISTRICT (ROMANIA)

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Monsmedite was discovered by one of the authors (József Muske) in 1963 in the oxidation zone of the epithermal gold-polymetallic ore deposit at Baia Sprie (Romania). The mineral grown on quartz and marcasite.

The chemical formula of mineral, according to the wet chemical analysis in the first description by MANILICI et al. (1965), is $K_2O{\cdot}Tl_2O_3{\cdot}8SO_3{\cdot}15H_2O$. A separate paper by GÖTZ et al. (1968) presented the full mineralogical description. The International Mineralogical Association Commission on New Minerals and Mineral Names (IMA CNMMN, 1971: 103) approved the mineral as new species.

Due to the problems of the interpretation of the chemical formula and based on the X-ray results obtained from topotype specimens, ZEMANN (1993) considered his samples voltaite with "at most minor contents of thallium". He urged the chemical analysis of type material. The IMA CNMMN discredited monsmedite (IMA Case 98–D: discreditation) in 2002 as voltaite (GRICE & FERRARIS, 2003: 1624).

The results of the recent investigations are as follows:

1) Based on the PGAA, LA-ICP-MS and XRMF data the Tl_2O_3 content of the mineral varies between 1.69–3.12 wt% (much less than the 28.7 wt% reported by GÖTZ et al., 1968).

2) X-ray diffraction, thermoanalytical and infrared spectroscopy data are very similar to those of voltaite and to the published original data of monsmedite.

3) According to the Mössbauer data the whole iron content of the mineral is in trivalent form.

4) Based on the chemical data the empirical formula of "monsmedite" is about: $K_{2.2}Mn_{0.82}Zn_{0.72}Fe^{3+}_{5.72}Al_{0.34}Tl^{3+}_{0.27}(SO_4)_{12}{\cdot}18H_2O$.

5) Compared with voltaite $[K_2Fe^{2+}_5Fe^{3+}_3Al(SO_4)_{12}{\cdot}18H_2O]$ the main difference is the dominance of the trivalent cations in "monsmedite".

Our results suggest that "monsmedite" is a Tl-bearing and oxidised variety of voltaite.

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TITANITE ZONING AS A RECORDER OF THE METAMORPHIC EVOLUTION OF METACARBONATES FROM THE CENTRAL OETZTAL COMPLEX (NORTH TYROL, AUSTRIA)

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Within the central parts of the Oetztal-Stubai Complex (OSC) metacarbonates are intercalated between various metamorphic rocks such as amphibolites, eclogites, and ortho- gneisses. These metacarbonates have undergone a complex history of metamorphism, which is also evident in the occurrence of rare accessory minerals such as baddeleyite, zirconolite, and chrome spinel (PURTSCHELLER et al., 1985; MOGESSIE et al., 1988). Petrography, textures and electron microprobe analysis (EMPA) reveal two different mineral assemblages in the metacarbonates: (1) olivine + diopside + wollastonite + phlogopite + calcite + dolomite ± spinel which is interpreted as a pre-Variscan contact-metamorphic assemblage and (2) omphacite + Ca-rich garnet + clinozoisite + calcite ± dolomite ± Al-rich pargasite which is interpreted to represent the Variscan eclogite-facies paragenesis. Noticeable are the occurrence of eclogite boudins within the metacarbonates. For mineral assemblage (2) pressures of 2.0 ± 0.16 GPa and temperatures of 709 ± 37°C were calculated with the program THERMOCALC v. 3.21 and the data set of HOLLAND & POWELL (1998).

Chemically zoned titanites occur in samples with the eclogite-facies mineral assemblage. The chemical zoning between rim and core is mainly manifested in the Ti, REE, and Nb contents. Titanites which do not show a significant difference in the Ti-values between rim and core show a strong zoning in the REE and Nb. The dominant substitution mechanism is $Ti^{4+} + O^{2-} <> (Al^{3+} + Fe^{3+}) + (F^- + OH^-)$. The cores of the titanites show higher REE and Nb contents and are thought to represent possible relicts of a pre-Variscan contact-metamorphic event while the rims have grown during the high-pressure stage of the Variscan metamorphic event and show highly enriched F and Al contents. Also Zr-in-rutile and Zr-in-titanite thermobarometers (FERRY et. al., 2007; HAYDEN et. al., 2008) were applied for samples with the eclogite-facies mineral assemblage. The Zr-in-rutile thermometer provides temperatures from 675°C to 715°C with an assumed SiO_2 activity of 1, which correlates with the results calculated with THERMOCALC v. 3.21.

Estimations with the Zr-in-titanite thermobarometer yield temperatures for the cores between 850°C and 1000°C and for the rims between 650°C and 800°C with an assumed activity for SiO_2 and TiO_2 of 1 at a pressure of 0.5 GPa for the cores and 2.0 GPa for the rims.

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HP-FLUID INCLUSIONS IN TOURMALINE, APATITE AND QUARTZ FROM ECLOGITES OF THE AUSTROALPINE POLINIK COMPLEX (KREUZECK MOUNTAINS, EASTERN ALPS)

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High-pressure primary fluid inclusions in the system H_2O-CH_4-N_2-NaCl-CO_2 from metasomatic tourmaline as well as H_2O-NaCl-$CaCl_2$ from apatite and quartz were examined from an eclogite boudin of the Austroalpine HP-belt in the Eastern Alps (Polinik Complex). All three minerals appear texturally in equilibrium and as mineral pockets surrounded by plagioclase. The eclogite host rock consists of the mineral assemblage grt + omp (jad_{33-48}) + phengite + qtz + zoi/czoi + calcic amphibole I + tourmaline + rutile + titanite + apatite + zircon + allanite. Retrogression has led to the formation of plagioclase + diopsidic clinopyroxene + K-feldspar + chlorite + calcic amphibole II. Metamorphic conditions of about 1.6±0.1GPa and 650±30°C correspond to the peak of Eoalpine eclogite facies in the Austroalpine at 90±9 Ma (SIMS U-Pb age dating on zircons).

Fluid density isochores of non-polar/aqueous and aqueous inclusions were linked with geothermobarometry and indicate that fluid infiltration, which led to formation of metasomatic tourmaline, was present at high pressure conditions above 10 kbar. Fluid densities from tourmaline correlate with fluid densities from apatite and quartz and are therefore indicative for the eclogite facies mineral assemblage. Primary fluid inclusions from tourmaline which lie in the system H_2O-CH_4-N_2-NaCl-CO_2 give estimates of salinity of about 5 equivalent wt% NaCl. Higher salinities of 29 wt% were derived by the depression of the melting point of ice from additional high-saline aqueous inclusions (H_2O-NaCl-$CaCl_2$) along cracks in tourmaline. Saline aqueous inclusions in apatite and quartz in the system H_2O-NaCl-$CaCl_2$ contain salinities between 8 and 22 wt%. Salinity calculations for non-polar and aqueous inclusions were derived from salt solution by clathrates and from the melting point of hydrohalite (antarcticite), respectively. The amount of gas composition of the studied fluid inclusions in tourmaline was semi-quantitatively estimated by Raman spectroscopy using respective band parameters.

The studied fluid inclusions in tourmaline are typical for inclusions that dominate in metasomatic tourmaline of granitic pegmatites. The occurrence of high- to low saline aqueous inclusions is typical for HP rocks. On basis of mineral textures, textural occurrence of fluid inclusions and comparable densities, it is concluded that both formation stages, the formation of the eclogite facies mineral assemblage and the crystallization of tourmaline due to external fluid infiltration, occurred at comparable PT conditions and timing. The occurrence of tourmaline as a metasomatic phase in eclogites of the Eastern Alps is documented for the first time and indicates external fluid flow at deep crustal level during formation of the Austroalpine HP-belt.

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FLUIDS IN SULPHIDE-BEARING SKARNS, CARLES (NW SPAIN)

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The Carles gold-copper-molybdenum skarn mineralizitation is located in Asturias, NW Spain (external zone Hercynian Iberian massif). The Carles stock consists of monzogranite and is placed in a syncline formed by carbonate rocks (Devonian) at their contact with quartzites (Silurian). The Carboniferous aged Carles intrusion is related to strong contact metamorphism and metasomatism. The skarn occurs at the contact between the monzogranite and the calcitic and dolomitic rocks as an irregular envelope (e.g. MARTIN-IZARD et al., 2000). Several samples from different positions in the skarn and monzogranite are available for mineralogical, petrological and fluid inclusion (fi) research, by using optical microscopy, Raman spectroscopy, Electron-Microprobe methods, microthermometry and computer modelling of fluids (BAKKER, 2003). In the skarn, a large number of calc-silicate minerals are discovered, ranging from plagioclase, grossular-andradite series, various Zo to zoned-Ep, vesuvianite, prehnite, diopside-hedenbergite series, amphiboles, and forsterite. In addition, a variety of native elements (Sb, Bi, stibarsen), several oxides (Mag, Hem, Ilm, Rt-Ant-Brk, uraninite, Gt), sulfides, and sulfosalts with widespread chemical constituents, sometimes with significant Au and Ag-contents, were explored. The sulfides include: arsenopyrite, löllingite (sometimes Sb-bearing), chalcopyrite, pyrite, marcasite, pyrhotite, various fahlore, stibnite, chalcostibite, bismuthinite, bournonite, stannite, sphalerite, galenite, pääkkönenite, fülöppite, and clausthalite. The ore generating processes and T-P formation conditions of the skarn are investigated with fi´s in quartz, calcite, garnet and Cpx. Quartz veins in the granite contain two types of equant-regular shaped fi's (up to 36 μm in length): a) low salinity H_2O-rich; b) CO_2-N_2-CH_4-H_2S-rich vapour bubbles with variable volume fractions (5 to 100%). The vapour composition is highly variable. Quartz veins in the skarn contain similar types of fi's, however, CO_2 is the major component in the vapour phase. The aqueous fi's homogenize at 120 to 150°C into the liquid phase, whereas gas-rich fi's homogenize at higher temperatures (up to 180-190°C). The Cpx in a sulphide-rich matrix contains fi's up to 50 μm diameter, with a variable sized vapour bubble (low density CH_4) and a highly saline aqueous solution (± 38 eq. mass% NaCl). Calcite is accidentally trapped in some inclusions. T_h (LV→L) in cpx is 480-540°C. Calcite in the skarn contains negative-shaped fi's (up to 30 μm diameter), with about 8 ± 2 vol.% vapour bubble. The aqueous solution is highly saline, and the melting of gas-hydrates indicates the presence of a gas component (probably CH_4, also in coexisting garnet). T_h (total) is either 60-80°C or 120-160°C. In conclusion, the fluids that were present during the skarn mineralization are highly variable in gas-component composition and salinity. Fluids that were transported through a vein system contain a gas-rich mixture or a low saline aqueous solution, whereas inside the skarn highly saline solutions are predominant.

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THE INTRUSION RELATED CU-FE-ZN-PB-AG DEPOSITS OF THE PFUNDERER BERG (SOUTH TYROL, ITALY): FAHLORE COMPOSITION AND T-fS_2 CONDITIONS OF FORMATION

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The mining district Pfunderer Berg to the west of Klausen in South Tyrol (Italy) is located in the contact area between Permian magmatic bodies, associated with the Brixen granodiorite, and the Southalpine basement of the Brixen Quarzphyllite.

During the Permian extensional event several dioritic dykes and small plutons intruded into the Variscan metamorphic basement near Klausen. This Permian magmatic event led to a strong (ca. 650°C and 0.2 – 0.3 GPa) contact metamorphic overprint of the surrounding quartzphyllites as well as the contemporaneous formation of Cu-ore deposits in the contact zone and hence ore mineralization occurs in the magmatic rocks as well as the contact metamorphic basement rocks. Due to the fact that the geological position of the mining area is in the south of the SAM (southern limit of Alpine metamorphism) these rocks were not affected by the Alpine metamorphic overprint and thus allow to provide *P-T* constraints on the pre-Alpine metamorphic evolution of this area. The Alpine orogeny only resulted in brittle faulting and occasional remobilization of the ore mineralization.

The ore mineral assemblage consists mainly of sphalerite, chalcopyrite, galena and fahlore. Most of the galena grains show abundant inclusions of fahlore and acanthite (Ag_2S).

Fahlore occurs texturally in two generations, as inclusions in galena and as well as in the matrix. The matrix fahlores are almost pure tetrahedrite with Sb contents ranging from 3.64 to 4.00 a.p.f.u. The Zn content in the fahlores ranges from X_{Zn} = 0.43 to 1. The Ag substitution for Cu is also strongly variable and ranges from 0.22 to 1.94 a.p.f.u. The composition of fahlore inclusions in galena differs from the fahlore composition in the matrix. Although they are almost pure tetrahedrite in composition, the Ag content is much higher (X_{Ag} = 0.57–0.86) and the Zn content is lower (X_{Zn} = 0.18–0.25).

The Cd-exchange thermometer (GELETII et al., 1979; BETHKE & BARTON, 1971) between galena and sphalerite inclusions yields temperatures of approximately 700°C which is consistent with the phase relations in the Cu-Fe-(Zn)-S system in the T-fS_2 space at high T (LUSK & CALDER, 2004).

In the context of the SFB HiMAT project (historical mining activities in Tyrol and adjacent regions) this mining area is important to understand historical mining and smelting activities

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MITT.ÖSTERR.MINER.GES. 155 (2009)

MINERAL CHEMISTRY AND BREAKDOWN REACTION OF FAHLORE FROM SCHWAZ-BRIXLEGG (TYROL, AUSTRIA)

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The copper deposits from Schwaz and Brixlegg are characterized by more or less monomineralic fahlore. Despite the same conditions and geological times of formation, fahlore from Schwaz and Brixlegg can be chemically distinguished. For this purpose we conducted a comprehensive electron microprobe investigation involving analysis of 21 elements. While fahlore from Schwaz is a strongly zoned iron-zinc tetrahedrite-tennantite solid solution with high Hg and low Ag concentrations, fahlore from Brixlegg encloses, beside strong zoning, small fahlore breakdown reaction textures containing the mineral assemblage enargite-famatinite + fahlore (third generation) + pyrite + sphalerite + stibnite + chalcostibite.

The major elements discriminate the fahlores as Zn-Fe tetrahedrite-tennantite solid solutions with a wide range in the Zn/Fe and the As/Sb ratio. Hg and Ag are the most important trace elements. In some samples from Schwaz, Hg can be considered as major element with concentrations up to 4.5 wt%. In Brixlegg Hg never exceeds 2 wt% with a mean value of 0.9 wt%. The Ag content of the fahlores ranges between 0.15 and 0.80 wt% in both localities. Compared to Schwaz, fahlore from Brixlegg is Zn richer and Hg poorer with comparable low Ag concentrations.

The thermodynamic modelling of fahlore breakdown reaction textures was not completely successfully due to lack of thermodynamic parameters for sulfosalts. As a result of rising sulphur fugacity and/or sinking temperature the fahlore breaks down forming the new mineral assemblage. Due to the presence of pyrite, the sulphur fugacity during reaction has to be above the pyrrhotite-pyrite transition ($\log fS_2 = -11.88$ at 300°C, calc. with data from ROBIE & HEMINGWAY, 1995). The upper boundary of sulphur fugacity is marked by the sulphur condensation reaction ($\log fS_2 = -3.72$ at 300°C, CRAIG & BARTON, 1973). Using fahlore-enargite transition equations from CRAIG & BARTON (1973), with simple fahlore composition (12 a.p.f.u. Cu), reaction took place at $\log fS_2 = -8.23$ at 300°C for As end-member and $\log fS_2 = -7.15$ at 300°C for Sb end-member respectively. Calculation with complex sulfosalts (Fe and Zn fahlore end-members) and CRAIG & BARTON (1973) approximations for thermodynamic data, yield $\log fS_2$ values ranging from –4.20 to –7.70 at 300°C for various end-member reactions. Calculations, combined with thermodynamic data for fahlore and SEAL et al. (1990), yield $\log fS_2$ values above sulphur condensation. This is a result of lack of thermodynamic data for enargite and famatinite.

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REGIONAL DISTRIBUTION OF As MINERALS IN THE NEOGENE VOLCANIC ARC – CRETACEOUS FLYSCH BOUNDARY IN THE ROMANIAN EAST CARPATHIANS

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The Neogene volcanic arc of the East Carpathians is in direct contact with the Cretaceous flysch deposits in several places. A number of arsenic sulphide occurrences are found at these boundaries. The occurrences are shown in Fig 1.

I. The oldest known occurrence is the historic one from Hankó Valley, Covasna (HAUER, 1860). This one is far out of the volcanic area, deep inside the flysch zone. We include it in this review due to its similarities with the other discussed parageneses.

II. South to the Bixad shoshonites one can found an As mineral assemblage at Bodoc. Since its discovery (by a shallow drilling) in the 1980's, it was only recently investigated (KRISTÁLY et al., 2006).

III. The occurrence at Lăzăreşti was also studied recently (KRISTÁLY et al., 2006).

IV. The fourth locality is at Şaru Dornei, southwards from the Vatra Dornei zone, on the east side of the Călimani caldera (GHERGARI et al., 1992).

Realgar is common for all the occurrences, mostly with calcite. Claudetite (monoclinic As_2O_3) and arsenolite (cubic As_2O_3) are characteristic at Bodoc. Alacranite (As_8S_9) and uzonite (As_4S_5) were found at Lăzăreşti. At Şaru Dornei para-alumohydrocalcite [$CaAl_2(CO_3)_2(OH)_4 \cdot 6(H_2O)$] is a common member of the mineral assemblage. Orpiment, although frequently reported by the earlier literature, has not been found as primary mineral.

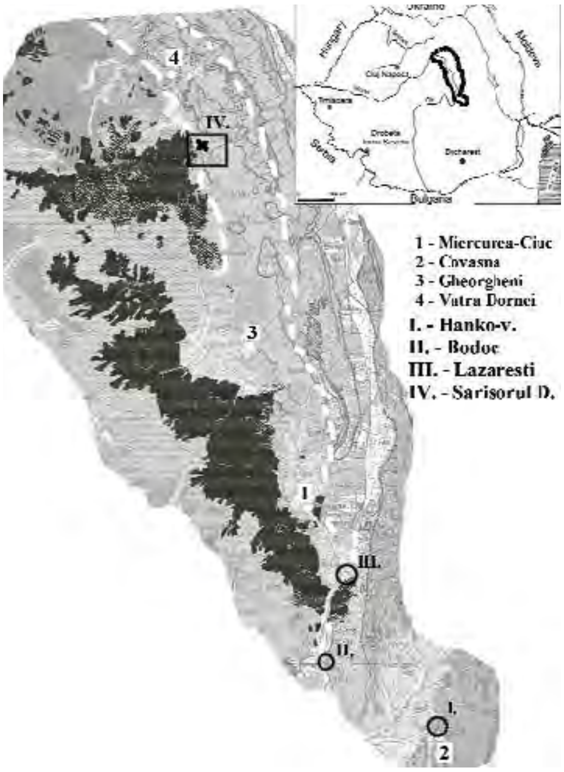

Figure 1. Sketch map of the discussed part of the East Carpathians. The dark-dashed regions represent volcanic massifs. White dashed lines are approximate limits of tectonic units (from the right: Cretaceous flysch deposits, Paleozoic metamorphic series). Based on the Geological Map of Romania 1: 1 000 000.

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PETROGENESIS OF THE ÜÇKAPILI GRANITOID AND ITS MAFIC ENCLAVES IN ELMALI AREA (NIGDE, CENTRAL ANATOLIA)

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Upper Cretaceous Üçkapılı Granitoid including mafic microgranular enclaves intruded into metapelitic and metabasic rocks, and overlain unconformably by Neogene ignimbrites in Nigde area. The Üçkapılı Granitoid is mostly granite and minor granodiorite in composition, whereas enclaves are dominantly gabbro with a few diorites in composition. The Üçkapılı Granitoid is composed mainly quartz, K-feldspar, plagioclase, biotite, muscovite, minor amphibole while enclaves contain mostly plagioclase, amphibole, minor pyroxene and biotite. The Üçkapılı Granitoid has H-type, calcalkaline and peraluminous (A/CNK = 1.0–1.3) geochemical characteristics while its enclaves are tholeiitic and metaluminous. The Üçkapılı Granitoid is characterized by high LILE/HFSE and LREE/HREE ratios ($(La/Lu)_N = 3–33$), and has negative Ba, Ta, Nb and Eu anomalies, resembling those of collision granitoid. In contrast, the enclaves are slightly enriched in LILEs (K, Rb and Th) and have negative Ta, Nb and Ti anomalies; propose that they were derived from subduction-modified mantle source. Based on mineral and whole rock chemistry, the enclaves are suggested to be formed by mixing/mingling of mafic and felsic magmas during their ascent. Chemical mixing is possibly restricted due to existence of high SiO_2, Na_2O and K_2O contents in the granitoids, and lack of samples with intermediate chemical composition in the field. The Üçkapılı Granitoid has relatively high $^{87}Sr/^{86}Sr$ (0.71148–0.71653) and low $^{143}Nd/^{144}Nd$ (0.512227–0.512346) ratios. Negative values of $\varepsilon_{Nd(t)}$ in the rocks, moderately range from (–5.24) to (–7.28), confirming crustal melting.

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CONTOURS OF A NEW THEORY ON CRYSTAL DISSOLUTION

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We discuss current progress in the theoretical and empirical treatment of crystal dissolution. Our approach abandons the limitations of closed-form equations and conventional "rate laws" and moves forward to a treatment of crystal reaction kinetics as a dynamic, many-body problem that must be solved stochastically. At the centre of our model is a fundamental understanding of the kinetics at kink sites that govern the overall processes of both crystal dissolution and growth (Fig. 1).

This change in treatment brings with it important consequences: it permits a more fundamental insight into the molecular surface processes and their cumulative result, including variation of rate within mineral systems, the effect of non-stoichiometric compositions, the relationship of ordering and temperature, and related phenomena. These insights potentially lead to a comprehensive theory of crystal dissolution and a unified dissolution-growth theory. However, they also require conceptual revisions in our approach to problems involving crystal-fluid interaction. First, we must re-examine our application of the concept of reactive surface area that has proven to be a largely unquantifiable parameter. Second, we must reconcile the lack of a single or "true" value for a so-called "rate constant". Instead, we suggest that a range of possible rates exists for any given mineral, with a certain probability for any given rate within this range. These insights have significant implications and consequences for our ability to predict long term behaviour in systems of environmental importance, such as nuclear waste, corrosion, and weathering of rocks and soils, with further implications for water quality and climate development.

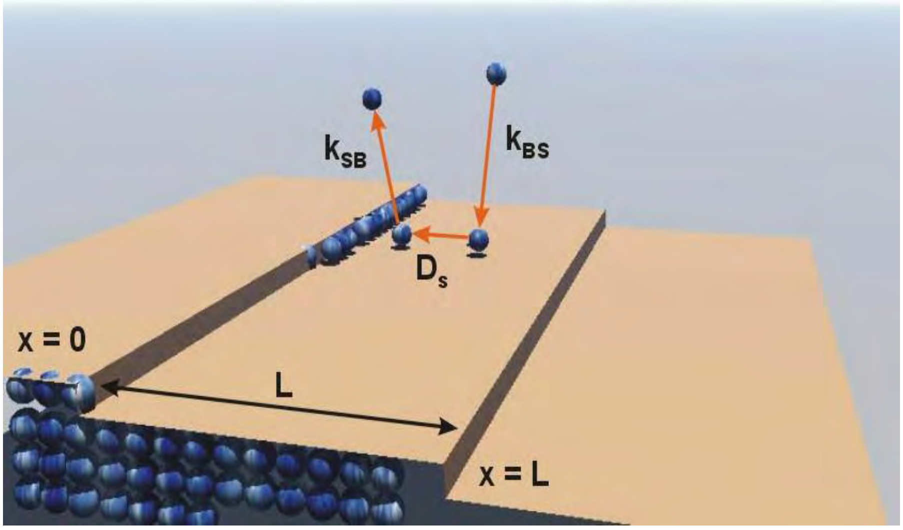

Figure 1. Schematic representation of fundamental processes of crystal dissolution.

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ARD-SCREENING OF SITE ROCKS FROM THE RUDABÁNYA BASE METAL MINERALIZATION (NE-HUNGARY)

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According to the current mine regulations, the ARD potential of a mining district – that can be developed to a future mine – should already evaluated already at the exploration. It can be derived also from the European "Mine Waste Directive" (21/2006/EC) or from other internationally accepted guidance documents (e.g. the currently finalized INAP's GARD Guide). This screening includes the evaluation of mineralogical abundance of the site rocks and ores as well as static ARD test methods.

The Rudabánya mine area is one of the oldest mining sites within the Carpathian region. Mining of different ore resources had taken place from the Neolithic Age (native copper), during the 14th-16th centuries (silver and copper) until the 1980s (carbonate iron ore). According to PANTÓ (1956), the Lower Triassic transgressive series of the Szilice Nappe (fine-grained Bódvaszilas Sandstone Fm., clay marl Szini Marl Fm., Szinpetri Limestone Fm., bituminous dolomite) were disintegrated by polyphase folding and thrusting. The overlaying carbonate rocks (dark gray Gutenstein Dolomite and Steinalm Limestone Fm.) are known in 10–100 m sized blocks embedded in the strongly folded gray clay marl. Most rock bodies are brecciated and fractured. Pantó developed a 4-stage ore formation model as: (1) siderite and hematite formation in the Bódvaszilas Sandstone, (2) metasomatic sideritization of the Gutenstein Dolomite, (3) formation of the baritic border zone with Cu- and Pb sulphides on the borders of the siderite bodies, (4) late epithermal formation of sulphosalts accompanied by pyrite.

New exploration works during the 1990s suggested an MVT massive sulphide mineralization of Pb and Zn. Recent explorations (FÖLDESSY et al., 2009) focus on base metal enrichments that occur not only in the baritic border zone but also on stratabound lenses in the clay marl, siltstone and fine-grained sandstone. Significant Zn-content was detected in cryptocrystalline sphalerite lenses and less common in smithsonite concretions.

Despite the prevailing part of host rocks are carbonates and the iron sulphides (mainly marcasite) do not have large abundance, it is worth to evaluate the site regarding to possible ML/ARD formation. An important factor is the high amount of siderite and other iron-rich carbonates among the potential waste rocks. Siderite does not give acid neutralizing effect, because the acid consumed during dissolution of the carbonate is re-released by the oxidation of Fe^{2+} to Fe^{3+} and its subsequent precipitation to iron oxyhydroxides (STEWART et al., 2006). If the siderite-content is more than 20% of the presenting carbonates, the acid neutralizing potential measured by the standard ANC test (SOBEK et al., 1978) will fall far behind the NP values predicted by carbonate-content.

To overcome the potential effect of siderite, the combination of the net acid generation (NAG) test with the modified H_2O_2 ANC method (SKOUSEN et al., 1997) is completed. The interpretation is based on detailed mineralogical data using XRD and EPMA.

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ORE MINERALIZATION AT THE RABENSTEIN OCCURRENCE NEAR BANSKÁ HODRUŠA, SLOVAKIA

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The Štiavnica–Hodruša ore field was one of the most productive medieval sources of silver and gold. Yet, the mineralogy of the ores that sustained the mining in this region for many centuries is not well known, mostly because the rich ores were exhausted a long time ago. Here I describe the minerals present at the occurrence Rabenstein, a system of old shallow mines where such rich ores were probably exploited. The mineralogical investigation was largely performed on heavy mineral concentrates because the available ore samples are relatively poor. The most common mineral is quartz; the ores are bound to a zone of silicified and altered rocks. The ores comprise disseminated pyrite with galena, sphalerite, and chalcopyrite. The composition of these minerals is simple; pyrite is devoid of any impurities, including As, galena contains no Ag. An interesting chemical feature of sphalerite from Rabenstein is a significant concentration of Cd, sometimes exceeding that of Fe. The identified Ag-Au minerals include acanthite, gold-silver alloys (electrum), freibergite, pyrargyrite, polybasite/pearceite, and uytenbogaardtite. They occur as tiny grains, either with the common sulfides or separately. The Ag/(Ag + Cu) (at/at%) ratio in freibergite varies from 0.25 to 0.46. The freibergite grains in contact with sphalerite have more Zn than those which associate with other minerals. The Sb/(Sb + As) (at/at%) ratio is more than 0.89 in freibergite and more than 0.87 in pyrargyrite. The Sb-dominant members of the polybasite–pearceite phases (polybasite) are sharply separated from the As-dominant members (pearceite) when they occur together. Pearceite is the only phase that accummulates a significant amount of As. The gold-silver alloys are always dominated by silver, with composition varying between ($Au_{24}Ag_{76}$) and ($Au_{46}Ag_{54}$). Acanthite and uytenbogaardtite replace galena and electrum, respectively, and seem to be a product of late hydrothermal or supergene stage of the ore formation. Perhaps these minerals, notably acanthite, were responsible for the significant enrichment of the ores that attracted the attention of the old miners.

STRUCTURAL STATE AND GENESIS OF ADULARIA FROM IGNIMBRITES OF SOKYRNITSYA DEPOSIT (TRANSCARPATHIANS, UKRAINE).

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Ignimbrites of Sokyrnitsya zeolite deposit are composed of two varieties of volcanic glass and fragments of magmatic minerals (quartz, plagioclase, potassium feldspar and biotite). Acid and basic glass (glass-1 and glass-2, respectively) prevails. Glass-2 is strongly devitrified and recrystallized. Fine-grained glass-2 forms felsitic material, which cements glass-1 and crystals. Monoclinic feldspar was represented by rare crystals of sanidine and dominant adularia. Three morphological types of adularia are observed: 1) Ad-1: crystals with typical "adularia" habit grown on glass-1/glass-2 boundary (Fig. 1); 2) Ad-2: crystals of the 1st type grown in microcavities of ignimbrite (Fig. 2); 3) Ad-3: fine-grained ball-shaped aggregates with green colour in felsitic matrix. The colour is due to the close association with a Fe-rich mica (celadonite).

Al/Si ordering in each adularia type is different. Ordering in Ad-1 is very low ($2t_1$ = 0.61–0.63), which is not typical for adularia. "Free-grown" crystals of Ad-2 have $2t_1$ = 0.69–0.71. This value of $2t_1$ is similar to those observed in hydrothermal adularia (SMITH, 1974). Very low Al/Si ordering was established in the fine-grained adularia ($2t_1$ = 0.55–0.57).

It is supposed that the very low Al/Si ordering in Ad-1 is due to the fact, that it grows in a disordered solid phase (glass-1). Adularia-3 may be a result of metasomatic transformation of the Fe-rich felsitic mass. We haven't found inclusions in adularia suitable for fluid inclusion studies, but according to KALYUZHNY & SAIKO (1999) adularia in rhyolitic tuffs (Kvasy, Transcarpathians) crystallized in the interval of 240–300°C.

Since adularia is always present in superincumbent clinoptilolite tuffs one can assume that hot ignimbrites have been as a source of heat and metasomatic solutions. It is possible that this is a variation of "autoclave effect" proposed by ALEKSIEV & DJOUROVA (1975).

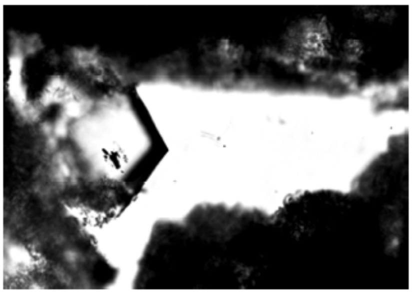

Fig. 1. Adularia-1 grown in glass-1

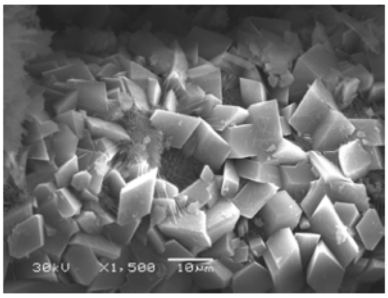

Fig. 2. Adularia-2 on the wall of microcavity

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IMMISCIBILITY IN RHYOLITE-DACITIC MAGMA FIXED IN IGNIMBRITES OF SOKYRNITSYA DEPOSIT (TRANSCARPATHIANS, UKRAINE).

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Ignimbrites are located under clinoptilolite tuffs of the Sokyrnitsya deposit. They are composed mostly of volcanic glass and crystal fragments of quartz, plagioclase and biotite (MELNIKOV et al., 2006). Two varieties of glass (observed) exist: 1) the glass-1 is a fraction of gas bubbles, they are colorless and SiO_2-rich (>75 %); 2) the glass-2 is brown and enriched in FeO and CaO. The glass-2 is devitrified and forms two texture types: a) globular one represents drops of glass-2 in glass-1; b) laminar one represents interlayering of these glasses. Thin glass-2 creates felsitic cement for the fractions of the glass-1. The coexisting of two glass types in ignimbrite allows suggesting that melt immiscibility in the magma chamber took place. Three types of melt inclusions in quartz and plagioclase confirm this thesis. They are: 1) melt inclusions with microheterogeneity structure which has been included before melt immiscibility; 2) glassy melt inclusions with or without gas bubble (Fig. 1a); 3) inclusions of glass-2 globules with thin colorless margin (Fig. 1b). The brown material of the 1st and 3rd type inclusions is partially or wholly recrystallized. The inclusions of the 2d type are similar to the same ones described by LUKÁCS et al. (2002). On heating the inclusions of the 1st type up to 1000ºC a gas phase filled about 30-40% of the inclusions volume. Homogenization of these type inclusions occurred higher than 1200ºC. Heating of the melt inclusions of the 2nd type results a homogenization of the two-phase system (silica melt + gas) at 1180–1190ºC. The 3rd type of the inclusions did not homogenize up to 1200ºC. Thus, immiscibility of silica melt was in the range of 1200–1300ºC.

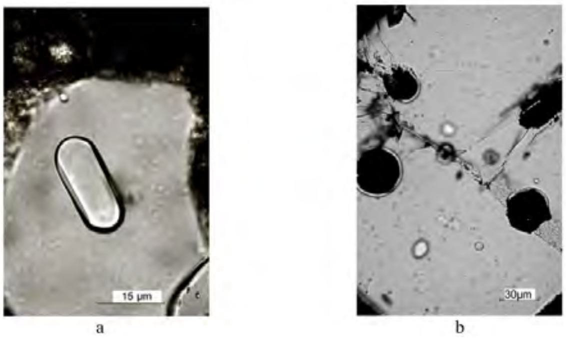

Figure 1. Melt inclusions in host quartz: a) glassy melt inclusion with negative crystal shape (2nd type); b) globular inclusions (3rd type).

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STUDY OF HYDROTHERMAL SiO_2 MINERALIZATION ON THE LOCALITY ĽUBIETOVÁ – JAMEŠNÁ (SLOVAKIA)

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Since the 17th century a vein system has been known at Jamešná and Tri Vody localities. The vein system consists of iron-bearing opal and Fe oxide ores, which were a major object of mining in these areas. The vein system is formed along a mylonitic zone on the contact of Badenian volcanic rocks (andesites) with Lower Triassic dolomites, Proterozoic and Paleozoic metamorphic rocks. Until now only a few studies were dedicated to this type of mineralization. ZIPSER (1817) and KODĚRA et al. (1986-1990) described the following minerals: siderite, ankerite–dolomite, chalcopyrite, quartz, opal, goethite, hematite, tetrahedrite. Unclear genesis and problematic mineral composition inconsistent with typical Alpine siderite – quartz – sulfide veins in neovulcanic rocks were the main reasons to study this locality.

Veins are formed by hydrothermal quartz, which is penetrated by Fe oxides. Fe carbonates (siderite, ankerite–dolomite) and limonite were weathered and Fe was incorporated into younger hydrothermal quartz. The breccia texture of the quartz vein system is composed of primary hydrothermal quartz (from the Fe carbonates – quartz – sulfide vein), newly formed hydrothermal quartz and clastic quartz from surrounding volcanic and metamorphic rocks.

EMPA and XRD methods were used for a mineralogical study of the quartz veins. The infilling of the mylonitic dislocation zone is formed by grey to brown quartz with up to 0.25 at% iron content and Fe oxides with up to 19.91 at% silicon content. Content of Mn and the other cations is distinctly lower. The brecciated texture is composed by different quartz varieties. Cavities of quartz are filled by different oxides in the following succession: goethite -> quartz (crystalline) -> chalcedony -> milky opal -> hyalite. Opal can be classified as opal-CT based on XRD results. Primary hydrothermal minerals (siderite, chalcopyrite, pyrite) reported by historic sources have not been identified. Most part of the vein system was affected by late hydrothermal solutions, and this caused the disintegration and decomposition of these minerals.

The study was financed by the projects VEGA 1/0287/08 and SOLIPHA VVCE-0033-07.

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HEAVY-ION IRRADIATION AND ITS CONSEQUENCE ON THE ELASTIC PROPERTIES OF CORDIERITE

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In many materials relativistic heavy ions create lattice defects of various types and on different length scales, such as e.g. zero-dimensional point defects or cylindrical nano-structures of a few nm in diameter and tens of μm in length. This study concentrates on ion-induced defects in cordierite, which exhibits extraordinary mechanical and thermodynamic properties and has been in the focus as a material sustainable to extreme ambient conditions including pressure, temperature and the exposure to high-energy corpuscular radiation.

Swift heavy-ion irradiations were performed at the UNILAC linear accelerator at the GSI using ^{208}Pb, ^{124}Xe, ^{197}Au and ^{96}Ru of 11.1 MeV per nucleon energy and fluences between 2×10^{11} and 1×10^{13} ions/cm^2. Irradiated and non-irradiated single crystals were investigated by means of Raman spectroscopy, optical absorption spectroscopy, Mössbauer spectroscopy, and single-crystal X-ray diffraction. High-pressure investigations were carried out using diamond-anvil cell techniques within the hydrostatic limits of the pressure-transmitting media.

In contrast to many other solids, swift-heavy ion irradiation does not lead to amorphisation of the cordierite lattice along the ion trajectories (WEIKUSAT et al., 2008). The most significant beam-induced modification concerns the molecular channel constituents, which includes the speciation change from CO_2 to CO (WEIKUSAT et al., 2009). This observation is in analogy to findings on natural radiohaloes (NASDALA et al., 2006) and α-particle irradiation experiments (KRICKL et al., 2008). Irradiation-induced structural changes involve a remarkable colour change, which can be attributed to electron centres at vacancies in the oxygen sublattice. The decrease of H_2O channel constituents correlates with a significant decrease in both the molar volume and the individual lattice dimensions. Static compressibility measurements reveal smaller compressibilities in both the axial directions and the molar volume for irradiated samples following the indirect bulk modulus-volume relationship. Structural stiffening through penetration of argon into the channels of the porous framework structure appears to play a significant role comparing the static lattice elasticities of non-irradiated cordierites in various pressure media. The results of high-precision isothermal equation-of-state measurements will be discussed based on the subtle crystalchemical differences, which result from irradiation with relativistic heavy ions.

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ZEOLITE MINERALIZATION IN THE JURASSIC ISLAND ARC VOLCANICS FROM SOUTH APUSENI MOUNTAINS

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The current paper presents the results of a study made on the zeolite association and other secondary minerals from the volcanic rocks in the area of the localities Balşa–Techereu–Poieniţa located in the eastern part of the Căpîlnaş–Techereu nappe (Mureş Zone, Southern Apuseni Mountains).

The rocks here belong to the Island Arc Volcanic complex of the calcalkaline series that were formed in a subductional setting at the end of Jurassic (NICOLAE & SACCANI, 2003). Basaltic andesites, prophyric andesites, andesites with augite phenocrysts, andesites with feldspar phenocrysts and pyroclastites, are the main type of rocks present in the area. The earliest alteration of the rocks involves albitization of the plagioclase feldspar, formation of mafic phyllosilicates, zeolites and silica minerals.

The mafic phyllosilicates were formed by alteration of the volcanic glass and consist of mixed dioctahedral-trioctahedral smectites and mixed layer chlorite-smectite (C/S) to discrete chlorite (>90% chlorite). The percent of chlorite was calculated using the method of SCHIFFMANN & FRIDLEIFSSON (1991). The transition between these minerals occurs as a continuous variation and not as a series of jumps. This transition can be related to an increase in metamorphic conditions (SCHIFFMANN & FRIDLEIFSSON, 1991).

To identify the zeolites electron microprobe and X-ray powder diffraction studies were used. The following zeolite minerals were identified: analcime, stilbite ± stellerite, heulandite, laumontite and epistilbite (only by XPD).

Other low-metamorphic minerals present in the rocks are prehnite and pumpellyite, which could indicate the highest metamorphic conditions that were reached in the area.

All these secondary minerals fill the amygdales and veins present in the rock. Different type of mineral association could be observed in these spaces: albite + mafic phyllosilicates + laumontite, albite + analcime + stilbite ± stellerite, C/S + heulandite + stilbite and albite + C/S + prehnite ± pumpellyite + laumontite. In some samples late calcite veins are present.

The presence of these minerals and their relations suggest that these rocks were affected by progressive low-grade metamorphism. The infilling of the amygdales with mixed dioctahedral-trioctahedral smectites and the replacement of Ca-rich plagioclase with smectites are characteristic to the lowest conditions, followed by mixed layer C/S, different type of zeolites and characteristic to the highest conditions being the presence of laumontite and prehnite ± pumpellyite.

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SCHIFFMANN, P., FRIDLEIFSSON, G.O. (1991): J. Metamorph. Geol., 9, 679–696.

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COMPARISON OF THE THERMAL EXPANSION BEHAVIOUR OF ICE AND THE RELATED HIGH PRESSURE PHASE TOPOLOGY OF H_2O

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The thermal expansion at one atmosphere conditions of a compound allows important conclusions with respect to the phase topologies at high-pressure. This holds also for ice, which at one atmosphere occurs in a hexagonal (Ih) and a low temperature cubic phase (Ic; irreversible transition Ic/Ih at 200 K). Unfortunately, investigations, which cover the entire temperature range between 273 and 0 K, are scarce. While a second density maximum of H_2O was discovered already in 1929 by JAKOB & ERK, only recently a diffraction study has provided coherent data of the temperature range from 9 to 269 K (RÖTTGER et al., 1994).
Fig.1a shows the thermal expansion of ice (dV/dT) as proposed by RÖTTGER et al.. Characteristics of this expansion curve are: i) the slight anomalous depression in the temperature range of 200 K causing an upper and lower hump in the expansion curve at 150 and 250 K; ii) the second expansion minimum of H_2O around 70 K. Fig.1b summarizes the P–T diagram of H_2O up to 600 MPa pressure accentuating its temperature dependent features, such as the temperature of homogenization (Th, the temperature of supercooled freezing) and the crystallisation temperature of the low temperature amorphous phases (Tx) at heating.
A comparison of a) and b) shows that the lower hump of the expansion curve matches with Tx, while the upper one seems to relate to Th, and maybe to the irreversible transition of iceII/III. The slight depression in between may be related to the so-called "no man's land" separating the amorphous "ice"-field from liquid water. In addition, the irreversible transition of Ic/Ih occurs in that temperature range. The second major characteristic of the low temperature behaviour of ice, the negative thermal expansion and the resulting density maximum, has not been investigated at high pressure yet.

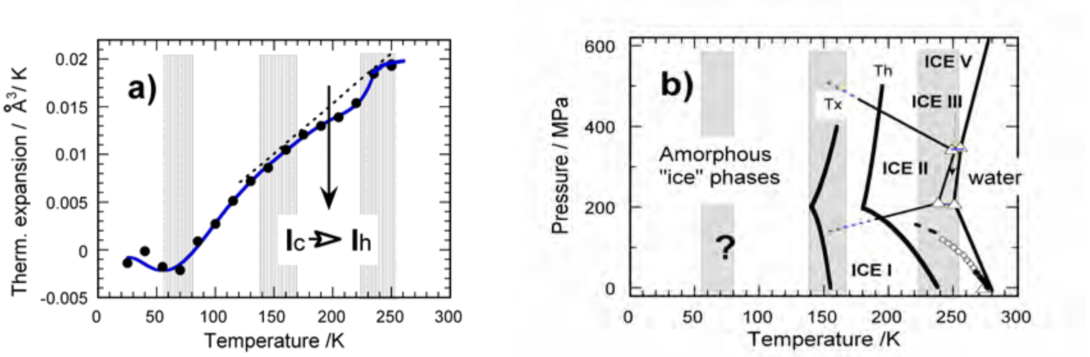

Figure 1. a) The thermal volume expansion of hexagonal ice between 10–265K (RÖTTGER et al.1994). b) Simplified P–T diagram of H_2O at low temperature up to 600 MPa (compiled from literature)

JAKOB, M. & ERK, S. (1929): Wiss. Abh. Phys. Techn. Reichsanst. 12, 302-316.
RÖTTGER, K., ENDRISS, A., IHRINGER, J., DOYLE, S., KUHS, W.F. (1994): Acta Cryst., B50, 644-648.

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P-T-STABILITY OF SILVER OXALATE AND THE MELTING CURVE OF CO_2

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Stability studies on otavite ($CdCO_3$) up to 2.3 GPa as well as on silver oxalate ($Ag_2C_2O_4$), and the melting line of CO_2 up to 1.2 GPa revealed that these boundaries are characterised by a number of inflections, which are interpreted as effect by anomalous PVT behaviour of CO_2 (MIRWALD, 2004, 2005). For a further substantiation of these observations, the stability study of silver oxalate ($Ag_2C_2O_4$) and the re-examination of the melting curve of CO_2 were extended up to 3 GPa. In addition, piloting compression experiments on silver oxalate were undertaken. The experiments were performed with a piston cylinder apparatus; the reactions were monitored by differential pressure analysis (DPA) technique.

Fig.1 shows the decarbonation boundary of $Ag_2C_2O_4$ exhibiting four inflections at 0.5, 1.1, 1.5 and 2.6 GPa. Preliminary results on its compressibility at –40 and 20°C indicate discontinuities at 0.55, 1.1 and 1.55 GPa and seem to be correlated with the inflections of the stability boundary. These findings were cross-checked by re-examining the CO_2 melting curve. The melting curve shows four kinks at 0.5. 1.1, 1.55 and 2.6 GPa, which interconnect four almost linear melting branches. The inflections of the decomposition boundary as well as the kinks of the melting line suggest a triple point topology assuming that each PVT anomaly of the liquid–fluid CO_2 phase is a (higher order) transition. However, if the observation of anomalous compression behaviour of solid silver oxalate should be confirmed by further experiments on solid CO_2 and other carbonates, the hypothesis of anomalous PVT-behaviour of CO_2 had to be extended on CO_2 incorporated in solids. This might imply that these CO_2 anomalies are related rather to intra- than to inter-molecular effects.

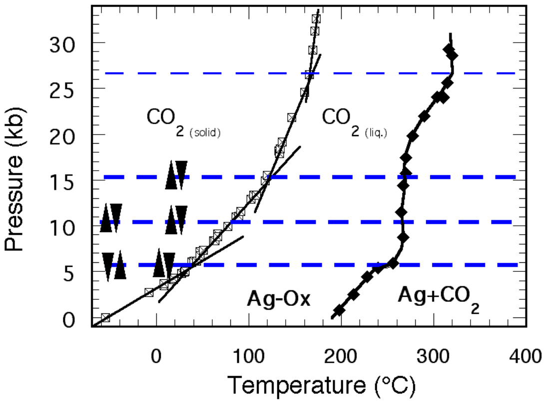

Figure 1. P-T stability diagram of silver oxalate (diamonds) and the melting line of CO_2 (squares). The compression experiments are indicated by small triangles (tips in run direction). The dashed lines indicate the tentatively proposed anomaly lines of CO_2.

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CONCRETE DAMAGING PROCESSES FROM SULPHATE ATTACK

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Concrete degradation by various processes as the Thaumasite Form of Sulphate Attack (TSA) and Alkali-Aggregate Reactions (AAR) has repeatedly been discussed in the literature (BELLMANN & STARK, 2007). Especially tunnel sites provide a great potential for studying concrete damaging processes since different ground water conditions and temperatures may occur. To gain new insight in the complex degradation reactions and to decipher the origin of compounds of newly formed damaging minerals as thaumasite, investigations including a chemical characterisation of ground water , concrete and natural in situ rock samples were carried out. Petrological, hydrochemical and stable isotope ($^{34}S/^{32}S$, $^{13}C/^{12}C$ and $^{18}O/^{16}O$) analysis were performed.

As objects of the study a highly frequented Austrian railroad and highway tunnel as well as a foundation, a hydropower head race tunnel and drainage systems were selected. They all have in common that respective concretes have suffered the TSA and additionally show dissolution of dolomite aggregates. Petrological analysis has shown intensively degraded material mainly consisting of thaumasite and to a lower extent of quartz sand aggregates and secondary calcite. The former cement matrix and dolomite aggregates have been completely altered or dissolved. In some parts sulphate-resisting Portland cements (SRPC) did not show any effect on lowering the degree of damage. The interacting ground water is characterized by high (14-120 mM) SO_4^{2-} and Ca^{2+} contents. The solutions are mostly saturated with respect to gypsum, exhibit high HCO_3^- content and slightly alkaline pH values.

Application of stable isotopes strongly suggests dissolved ions from the ground water to be the origin of the TSA. The DIC in the local SO_4^{2-}-bearing ground water and thaumasite yield $\delta^{13}C_{VPDB}$ values in the same range. In case of the Tauern highway tunnel $\delta^{13}C_{VPDB}$ values range from –6 to –9‰. At the Bosruck railroad tunnel the suspected sulphur source for the concrete damage was soot. Shotcrete was conveyed as a renovation measurement after a 50 year period of fossil fuel powered trains on the sooty tunnel wall. Nevertheless the damaged shotcrete at the boarder of the old tunnel wall is a result of the ground water. The sulphate minerals of the damaged horizons, local ground waters and local evaporites comprise $\delta^{34}S_{VCDT}$ of 20 ± 5‰. Soot relicts as a potential source of sulphur can be ruled out as the respective analysed $\delta^{34}S_{VCDT}$ values are in the range of 4‰.

Modelling approaches by PhreeqC (PARKHURST & APPELO, 1999) have shown a thermodynamically possibility in the alkaline range when additional Ca^{2+} in solution causes dolomite to become more and more undersaturated as calcite gets supersaturated. At pH > 10 the process of dedolomitization is further accelerated by the removal of Mg^{2+} as brucite ($Mg(OH)_2$) precipitates. Brucite and calcite were detected by microprobe and micro Raman spectroscopy surrounding relicts of dolomite aggregates.

BELLMANN, F., STARK, J., (2007): Cement Concrete Res. 37, 1215-1222.

PARKHURST, D. L., APPELO, C. A. J., (1999): User's guide to PHREEQC (version 2) U.S. Geol. Surv. Water-Res. Inv. Rep. 99-4259, 312 p.

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MINERALOGY AND GEOCHEMISTRY OF METABASIC ROCKS FROM THE KHOY AREA, NW IRAN

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Metabasic rocks investigated here are associated with ophiolitic rocks in NW Iran and are located between the Caucasus suture in the north and the Zagros suture in the south. These ophiolites mark the remnants of the Neo-Tethyan oceanic crust. Non-metamorphic ophiolites are similar to ophiolites in western Iran and Turkey in age. The metabasic rocks are mainly amphibolites. On the basis of bulk rock geochemistry, the studied amphibolites are produced from different original magma types. However, the main protolith for the amphibolites was tholeiitic basalt formed at a mid-oceanic ridge. Few samples showing OIB nature are attributed to formation of the protoliths as seamounts. Most of the studied amphibolite samples exhibit MORB nature. Mineral chemistry of garnet, plagioclase, amphibole and opaque minerals were studied in the samples. Also the mineral chemistry of relict igneous clinopyroxenes was used to place constraints on the nature of the original protolith rocks. Garnet exhibits a slight reverse zoning probably reflecting garnet growth during exhumation of the amphibolites. The garnet core shows the peak metamorphic condition. Since there is no abrupt changes in the zoning profile, amphibolites are more likely formed during a single metamorphic event. Semi-quantitative thermobarometry of amphiboles, hornblende-plagioclase thermometry, garnet-amphibole thermometry and Al in hornblende barometry along with THERMOCALC results indicate a pressure range of 10-12 kbar and a temperature range of ~700 to 800ºC for peak of metamorphism. *P-T* results for peak and post-peak metamorphism indicate a clockwise *P-T* path for the studied amphibolites. This path rules out the sole metamorphic nature for the studied amphibolites and confirms a collision-related metamorphism. Therefore the amphibolite protoliths formed at the mid-oceanic ridge of the Neo-Tethys oceanic crust and were metamorphosed due to collision followed by the closure of the subducting oceanic crust.

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MINERAL CHEMISTRY OF PLATINUM ALLOYS FROM THE HISTORICAL PLACER DEPOSITS OF YUBDO COMPLEX, ETHIOPIA

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The Yubdo mafic-ultramafic complex, located in western Ethiopia, hosts historical platinum and gold placer deposits known since ancient times. An extensive exploration activity started in 1926 and, although about 2700 kg of platinum have been extracted between 1929 and 1941, it still has an estimated reserve of 12 tons of platinum (MOGESSIE & BELETE, 2000). We have investigated, using reflected light microscopy and the electron microprobe more than100 nuggets collected in the Yubdo placers. The platinum group minerals (PGM) discovered are predominately Pt-Fe-Cu-Ni alloys, varying in size from 100 µm up to 3mm, accompanied by minor osmium (Figure 1A), erlichmanite and several platinum group elements (PGE) and base metals (BM) sulfides, arsenides and anthimonides. These minor phases generally occur as small inclusion included in the Pt alloys. Several nuggets of gold have been also observed. About 800 analyses of the Yubdo Pt alloys have been plotted as atomic proportion in the ternary diagram of figure 1B. Four main groups of Pt alloys have been identified: 1) isoferroplatinum, ideally Pt_3Fe, 2) tetraferroplatinum, ideally PtFe, that always contains appreciable amount of Cu and minor Ni, 3) tulameenite, ideally Pt_2FeCu, and 4) an unknown phase that fits the composition Pt_2Fe. On the basis of the mineral chemistry of the Yubdo Pt alloys, the following conclusions can be drawn: a possible new mineral corresponding to the formula Pt_2Fe occur among the analyzed Yubdo nuggets, and the continuous substitution Cu-Fe at constant content of Pt suggests the existence of a possible solid solution between tetraferroplatinum and tulameenite, as postulated by BOWLES (1990).

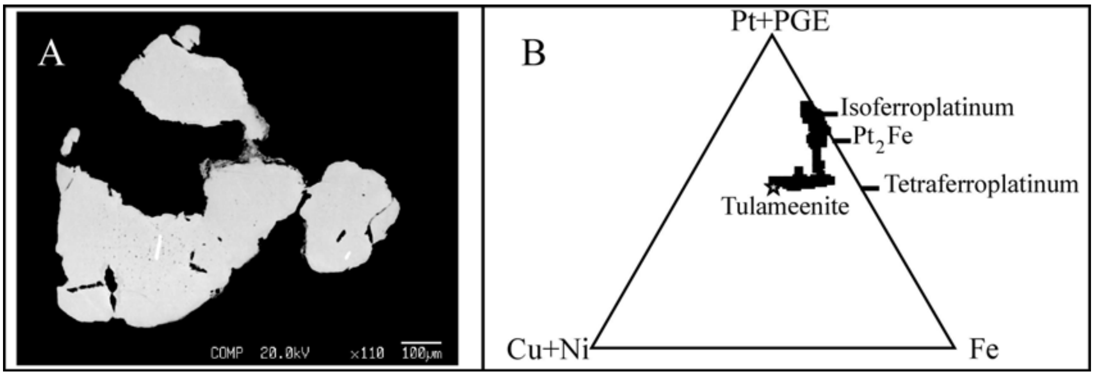

Figure 1. A = Back-scattered electron image of Pt alloy with osmium inclusions (white mineral). B = Triangular diagram showing the composition of the Yubdo Pt alloys.

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SOURCE STUDY OF AN EXTREMELY HIGH RADON-ANOMALY AREA (S-HUNGARY)

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In some houses of the village of Kővágószőlős, where the Hungarian uranium mining lasted for 40 years, the annual average indoor radon activity concentration exceeds 1000 Bq/m^3, this value is much higher than the EU recommendation for existing buildings (400 Bq/m^3). Our goal was to define the source of the high indoor radon activity concentration on the example of one of these houses.

In the study area (14,000 m^2) (1) gamma dose rate on the ground and 1 m above the soil surface at 578 places, (2) soil gas radon concentration and free-air radon concentration at 47 places and (3) radon exhalation of the soil at 21 places have been measured. From the results of these measurements and EOV (Uniform National Projection) coordinates of the places of measurements different isoline maps were constructed. In each isoline map an approximately 5 m in diameter anomaly can be observed at the same place.

We drilled in the middle of the anomaly to measure the dose rate in situ in the function of depth and to collect samples for the laboratory analyses. In the drill hole the ^{226}Ra equivalent activities for different depths were measured by drill hole probe. The results measured in drill hole are commensurable to specific ^{226}Ra-activity concentration of the samples measured by gamma spectroscopy. Both measurements found a horizon with significantly high activity (over 6000 Bq/kg) at the depth of 2.5 m. Some fragments of the Kővágótöttös Sandstone Member, which is the U-rich member of the Kővágószőlős Sandstone Formation, could be responsible for the high concentrations measured. However, until now no U-bearing minerals have been found by scanning electron microscopic analyses in the samples collected.

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PROVENANCE STUDIES OF THE BUILDING STONES USED FOR THE CALVARY CHURCH (CLUJ-NAPOCA, ROMANIA)

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[2]Romanian Academy, Institute of Geodynamics, Jean Louis Calderon Str. 29-31, RO-020032, Bucharest, Romania
[3]Sapientia University, Dept. of Environmental Sciences, Matei Corvin Str. 4, RO-400112, Cluj-Napoca, Romania
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The present work focuses on the texture, microfacies and mineralogical characteristics of limestones used for the XIIIth century Calvary Church – a Benedictine Abbey from Cluj-Napoca, Romania. It is also well-known as Cluj-Mănăştur Church (Kolozsmonostor in Hungarian, Abtsdorf in German). Large areas of the monument surface show various degrees of decay. The thickness of the degraded layer ranges from a few millimetres to a centimetre. Several forms of degradation have been identified: black crust (gypsum patina) formation, biofilm overgrowths (Chlorella sp., Xanthoria parietina and Rhizocarpon geographicum), and physical disintegration including scaling. The microfacies analysis provided information on the texture, amount and composition of abiogenic and biogenic particles and micrite matrix, as well as the type and spatial distribution of cement. The limestone blocks show a wide range of facies types, mostly highly porous oolitic packstone-grainstone and grainstone. Some wackestone and wackestone-packstone were also found.

To identify the geological source(s) of the Calvary church building stones, similar limestone deposits cropping out in the surroundings of the Cluj-Napoca city were sampled, e.g the Eocene limestones from Viştea, Mera, Izvorul lui Sfântul Ion, Gura Baciului, and Cluj-Mănăştur Quarry and the Oligocene sandstones from Cetăţuia-Cluj. Among these, the packstone-grainstone and grainstone from Mera and the Cluj-Mănăştur Quarry, respectively, show the highest petrographical and microfacial similarity with the examined monument rocks. Regarding the wackestone and wackestone-packstone ashlars, they could have the same origin as packstone-grainstone and grainstone, but were exploited in different part of the same Mera or Cluj-Mănăştur quarries.

Based on the comparison of the petrographical features, we may assume that the Calvaria Church was most likely built of limestone blocks exploited in the old quarry of Cluj-Mănăştur. This is also supported by a) historical records, which state that in the period of construction, the Cluj-Mănăştur quarry belonged to the Benedictine Abbey and was highly active, and b) the close location of the quarry, at less of 1 km southwest of the church.

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PETROGRAPHY AND MINERAL CHEMISTRY OF THE THAB SILA GNEISS, KANCHANABURI PROVINCE, WESTERN THAILAND

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Metamorphic basement rocks are mainly exposed in a north-south trending mountain chain in western Thailand. It extends from Chiang Mai through Tak, Uthai Thani, Kanchanburi and Nakorn Srithammarat Provinces. The only remaining basement rocks outside this belt crop out in Chonburi and Rayong Provinces in eastern Thailand. Theses basement rocks are mainly composed of gneisses with subordinate calcsilicates, marbles, schists and phyllites. According to stratigraphic field relations, these basement rocks have been regarded as inferred Precambrian age. Although several complexes of these metamorphic rocks were studied in recent years, most of the basement rocks are still poorly investigated, especially in Kanchanaburi Province, western Thailand.

Metamorphic rocks in Kanchanaburi Province that are named Thab Sila Gneiss are composed of mainly ortho- and paragneisses with intercalated calcsilicates, schists, phyllites, quartzites and marbles. The Thab Sila Gneiss contacts with Paleozoic sedimentary rocks by either conformal or fault contacts and is characterized by subvertical NE and SW dipping foliation planes. Strike of these metamorphic rocks are NNW–SSE trend concordant with the major fault zones in western Thailand, namely the Tree Pagoda and Sri Sawat fault zones.

The garnet-free calcsilicate shows a fine-grained equigranular texture and is composed of clinopyroxene – plagioclase – alkali feldspar – calcite – quartz – amphibole – biotite – titanite. Clinopyroxene is diopside-rich and amphibole occurs as 0.3–1 mm large crystals with X_{Mg} of 0.7–0.9 and low contents of F and Cl. Plagioclase has an anorthite content of 0.6–0.8. Biotite shows a X_{Mg} between 0.51–0.54. The second main rock type is a biotite – plagioclase - alkali feldspar – quartz – muscovite ± garnet ± sillimanite gneiss. Garnets do not show a zonation pattern and have a high X_{Alm} content of 0.8, while X_{Grs} and X_{Sps} are extremely low (<0.05). Plagioclase is typically albite-rich with an X_{Ab} content of 0.7–0.8. Biotite occurs as 0.2–1 mm flakes with X_{Mg} of 0.3–0.4. The intercalated schists usually consist of muscovite – biotite – quartz – alkali feldspar – tourmaline – garnet. *P–T* condition of metamorphism of metamorphic rocks was calculated by the garnet-biotite thermometer. The GRAIL barometer was used in favour of the GASP, Grt-Bt-Pl and Grt-Bt-Ms-Qtz barometers because of the extremely low grossular content of the garnets.

As a preliminary result, the Thab Sila Gneiss might be metamorphosed at the condition of ~650°C and 8 kbar. The shape of the *PT*-path has not been determined yet but first evidences suggest an isothermal decompression path after the peak of metamorphism.

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PHOTOLUMINESCENCE EMISSION OF RARE EARTH ELEMENTS IN NATURAL MONAZITE AND SYNTHETIC ORTHOPHOSPHATES

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Monazite-(Ce) ($CePO_4$; $P2_1/n$) commonly incorporates several wt% of non-formula elements, such as the actinides U and Th, and REE (rare earth elements). The alpha decay of U and Th, and their instable daughter nuclei, may cause severe radiation damage. The accumulated damage can be estimated, e.g., from the broadening of internal PO_4 Raman bands (SEYDOUX-GUILLAUME et al., 2002) and PL (photoluminescence) bands related to REE centres (PANCZER et al., 2005). We report results of a systematic PL study of REE emissions of radiation-damaged monazite samples, and their non-damaged analogues which were produced by dry annealing (1200°C; 96 h). Radiation damage results in loss of short-range order and hence affects the crystal-field splitting of electronic transitions. The widths of the emission bands at ~607 nm (Pr^{3+}) and ~871 nm wavelength (Nd^{3+}) were found to reflect sensitively the radiation damage, with additional minor effects of the sample's chemical composition (mainly the Th content).

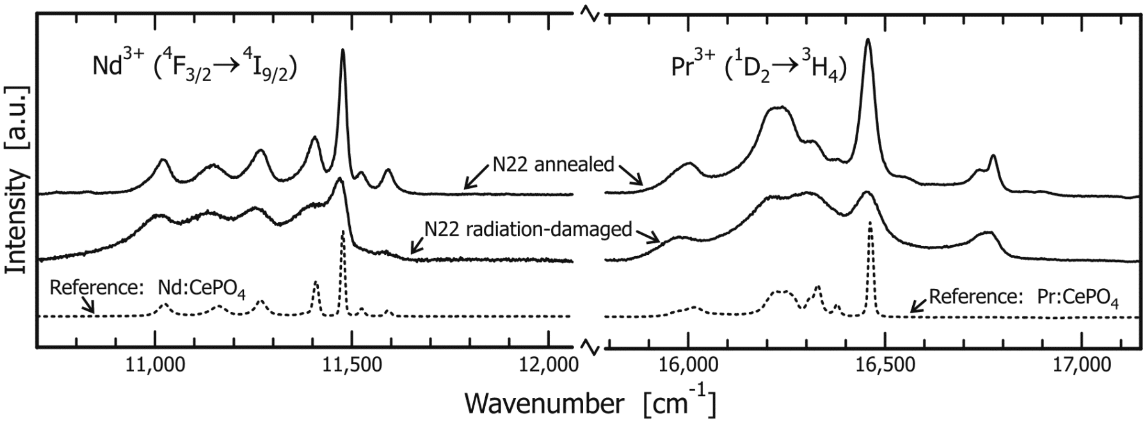

Figure 1. The PL spectrum of a moderately radiation-damaged monazite (#N22; Madagascar) shows broadened emission bands, compared to the spectrum of its annealed analogue. Spectra (stacked) are shown in comparison with those of REE-doped $CePO_4$ crystals grown using the Li-Mo flux technique (HANCHAR et al., 2001).

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TYPOMORPHIC PECULIARITIES OF FLUID INCLUSIONS OF GOLD-BEARING PARAGENESES OF ORE STOCKWORK BODIES OF BEREGOVO ORE FIELD (TRANSCARPATHIA)

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Data collected from the literature and obtained by the authors during thermobarometric and geochemical investigations of fluid inclusions in minerals from typical stockwork ore bodies of the Beregovo ore field in the Ukrainian Transcarpathians are analysed and generalised. They are supplemented by results of the geological-structural analysis. Results are summarised as follows. The solutions in the period of forming of the gold-bearing stockwork-type bodies were characterised by sulphate-bicarbonate salt composition with predominating calcium and magnesium cations, their gaseous phase was enriched by nitrogen at the expense of carbon dioxide (KALYUZHNYI et al., 1998). The optimal temperature interval of ore-(gold-) forming is determined as 250–170°C. The paragenesis of the ore bodies formed when gold-bearing hydrotherms intensively boiled and fluids of different (deep-seated and surface) origin were mixed in the zones of mineral forming. The migration of the deep-seated mineral-forming fluids from north-west to south-east is proved by the predominant increase of homogenization temperature of fluid inclusions in the same direction. A regional temperature zoning with predominantly lateral character over vertical was observed. These observations formed the basis of specific criteria for the estimation of the perspectives of the gold productivity of the stockwork-type ore bodies.

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EVOLUTION OF THE PRE-NEOGENE SUBCONTINENTAL LITHOSPHERIC MANTLE BENEATH THE POIANA RUSCĂ MTS. (W ROMANIA)

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Recently collected mantle xenoliths from Late Cretaceous–Paleogene alkali basic rocks from the Poiana Ruscă Mts. (W Romania) show new petrologic and thermobarometrical aspects of the pre-Neogene subcontinental lithospheric mantle. The mantle segment, represented by these xenoliths, now is situated beneath the southeastern periphery of the Carpathian-Pannonian Region. However, geodynamical reconstructions proved that the terranes, now composing this region, were amalgamated only during the Neogene basin formation and the southern Apuseni Mts (including the Poiana Rusca) were part of the Dacia block before. So these xenoliths can provide important information about the pre-Neogene physical-chemical conditions of the lithospheric root of the Dacia block.

The samples widely vary between wehrlitic, lherzolitic and olivine websteritic composition. The most distinctive feature of the modal composition is the high variability in orthopyroxene content (1–45 vol%). No OH-bearing minerals have been found in any xenoliths. Texturally, they are rather uniform, most are coarse-grained and contain notable amount of silicate mineral inclusions in other silicates, therefore, we classified them as poikilitic textured xenoliths. Some samples, however, seem to be sheared in texture.

Xenoliths are rather homogeneous in composition, but show distinct features from other mantle xenoliths from the region. Clinopyroxene has notably high Al_2O_3 (6–7 wt%) and Na_2O (1.5–2 wt%) content. Spinel is always Al-rich, cr# are low (0.08–0.18). Mg# of pyroxenes varies between 0.89–0.91. In fact, the major element chemical composition of minerals shows rather fertile composition and low degree of melt extraction (approx. 8–10%) from the mantle.

Clinopyroxene single crystal X-ray diffraction measurements show rather low cell (432.9–433.6 Å^3) and *M*1, *M*2 site volumes. Previous crystal chemistry studies on mantle xenolith clinopyroxenes have shown that cell and *M*1, *M*2 site volumes depends mainly on the different equilibrium pressures, and such low cell volumes are indicative of high equilibrium pressure. Their structural data are rather similar to data from garnet-bearing lherzolites worldwide, therefore, we suggest that the Poiana Rusca xenoliths can be equilibrated at high depths, near to garnet stability field, at pressure near to approx. 20–22 kbar. Thermometry, using several widely accepted thermometers, indicates a homogeneous equilibrium temperature for the xenolith series, between 950–1010°C.

The xenoliths suggest the existence of a rather homogeneous, fertile mantle segment, equilibrated at high pressure and temperature. Chemistry and textural evidences suggest that the mantle might have undergone interaction with an alkali silicic melt. Continuous increase in orthopyroxene content in the series indicates different degrees of interaction with the melt.

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MID-CRUSTAL FELSIC GRANULITE XENOLITHS FROM THE WESTERN PANNONIAN BASIN (BEISTEIN, AUSTRIA)

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The Pannonian Basin is famous of its xenolith localities hosted by late Tertiary alkaline basalts, where several kinds of ultramafic, mafic and other xenoliths from different depths of the lithosphere were found and studied. In this work we present the petrography, mineral chemistry, geothermobarometry and fluid inclusion study of mid-crustal felsic granulite xenoliths from Beistein (Styrian Basin) and compare them to other xenoliths of similar origin from the internal territories of the Pannonian Basin, namely from the Bakony–Balaton Highland Volcanic Field (BBHVF). We collected 17 crustal xenoliths, from the pyroclastics near Beistein, and one from Sabar Mt (BBHVF) and another one from Szigliget (BBHVF). The studies indicate that these xenoliths went through at least 3 evolutional stages. The relic microtextural features like characteristic poikilitic texture and exsolved antiperthitic feldspars refer to a silicic magmatic precursor rock, which intruded into the middle crust. Temperatures of 900–1100°C from reintegrated exsolved feldspars indicate the high temperature of the magmatic body. Cooling and crystallization gave rise to formation of a felsic rock with mineral assemblage of feldspar, pyroxenes, quartz, ± biotite ± garnet, opaque minerals, apatite and zircon. This mineral assemblage indicates 800–850°C at 500–700 MPa pressure. The second stage of the evolution was connected to partial melting of biotite-bearing assemblages occurred in association with the fluid invasion. The third step was the uplift of the xenoliths in the basalt to the surface, which generated a temperature increase and a pressure decrease, thus, limited melting of the xenoliths. All samples contain different amounts of melt patches. There is a light brown-yellow thin glass film along grain boundaries, which is sometimes gathered in small melt pockets. Based on the petrography of the samples, this type of melt is clearly originated from the host lava.

Fluid inclusion petrography shows that there were minimum two fluid events (fluid-rock interaction). The first event could be connected to the magmatic intrusion, whereas the second one is linked probably to the partial melting event. The very first fluid event was coeval with the emplacement and crystallization of the magmatic body at midcrustal levels as it is witnessed by primary inclusions in the relic magmatic minerals, like apatite and zircon. There are other primary fluid inclusions in the main rock-forming minerals, such as plagioclase, quartz and pyroxenes. The second fluid event happened still in the lower crust. This second event could be connected to melting of biotite-bearing assemblages in the granulite facies. A later generation of the secondary fluid inclusions is mostly in the felsic minerals and could be associated with the enclosing basalt. We could prove the presence of a difficult C-O-H-S-N fluid system dominated by CO_2 using Raman spectroscopy. The difference between the Tm values of the two generation fluid inclusions and the results of Raman spectroscopy shows us that the fluids in the crust slightly changed their chemical character during geological times.

MAGNESIUM AND STRONTIUM INCORPORATION AND CALCIUM ISOTOPIC FRACTIONATION DURING CALCIUM CARBONATE FORMATION AT LOW TEMPERATURES (5 TO 40°C)

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Trace element and calcium isotopic fractionation can provide fundamental insights into the growth mechanisms of calcium carbonates. These signatures may be used to reconstruct environmental conditions like precipitation rate, temperature and solution chemistry during calcium carbonate precipitation. Moreover, trace element and isotope distributions can also be used for monitoring aspects to evaluate ongoing sinter formation and inhibition effects in man made environments, e.g. in a tunnel drainage system.

In the present study, spontaneous calcium carbonate precipitation experiments without seeds were carried out using a CO_2-diffusion technique (TANG et al., 2008). Experiments were conducted (i) at various Mg/Ca ratios (up to 5), and/or (ii) in presence of polyaspartic acid. pH and concentration of aqueous Ca and Sr were adjusted close to modern seawater.

Calcite is preferentially formed at lower temperatures, at lower supersaturation degrees (Ω) and lower Mg/Ca ratios, while aragonite is preferentially formed at higher Mg/Ca ratios and/or at elevated temperatures (e.g. 40°C). Mg incorporation into calcite leads to rounded Mg-calcite crystals and smaller elementary cell sizes. Vaterite is formed at relatively high Ω values, e.g. in the presence of polyaspartic acid. Elevated temperatures tend to result in a higher Mg and a lower Sr incorporation in calcite as well as a lower Ca isotopic fractionation ($\Delta^{44/40}Ca_{CaCO3(s)-Ca(aq)}$ values). In general, $\Delta^{44/40}Ca_{CaCO3(s)-Ca(aq)}$ values are smaller for vaterite (≈ -4‰) compared to calcite (-0.9 to -2‰ from $\Omega \approx 7$ to 26) and aragonite (from -1 to -1.6‰). Sr incorporation during aragonite formation has an inverse dependency on the precipitation rate, which is in contrast to calcite and vaterite.

However, $\Delta^{44/40}Ca_{CaCO3(s)-Ca(aq)}$ values indicate an inverse correlation with the distribution coefficient of Sr into $CaCO_3$ (D_{Sr}) for all polymorphs. Individual $CaCO_3$ polymorphs display a distinct negative slope between Ca isotope fractionation and Sr/Ca discrimination. Notably, slope and intercept of individual regression lines are independent of temperature, precipitation rate and Mg incorporation. These findings may be used to decipher polymorph transformation, alteration processes and biogenic from inorganic induced $CaCO_3$ formation. Respective processes and proposed models are discussed.

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STRUCTURES AND COMPOSITIONS OF MAGHEMITE NANOPARTICLES

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Nanocrystalline magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) have special importance among the various iron oxides, both because of their widespread occurrence in soils and sediments and their nanotechnological applications. Concerning their structures, the two minerals are similar and thus difficult to distinguish using conventional transmission electron microscopy techniques. The structure of maghemite contains iron vacancies with respect to the magnetite structure. The cation vacancies may be randomly distributed with the conservation of the spinel structure (space group Fd3m) or may order in the octahedral sites, resulting in a reduction of symmetry. Although several models have been suggested (JORGENSEN et al., 2006; KELM & MADER, 2006), ambiguities remain over the vacancy ordering schemes that may occur in nanocrystalline maghemite. We used high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) and electron crystallography for the structural characterization of synthetic maghemite nanocrystals. The compositions of the particles were studied using electron energy-loss spectroscopy (EELS).

SAED patterns contained extra reflections with respect to the magnetite structure, and indicated the presence of several types of vacancy-ordered structures with cubic and tetragonal symmetries in the same sample. Under prolonged exposure to the electron beam, the vacancies disordered, and the SAED patterns became indistinguishable from those of magnetite. Nanocrystalline maghemite could therefore be overlooked in environmental samples if studied under a strong electron beam. In some grains, electron crystallographic image processing of HRTEM images indicated a highly variable, nanoscale domain structure, a consequence of different vacancy ordering schemes within the same particle. Consistent with the structural heterogeneity, Fe/O ratios obtained from EELS spectra were also variable. Further experiments and analyses are in progress in order to determine the possible structures of the maghemite varieties.

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SULFUR IN MONAZITE: A "CLINOANHYDRITE" SUBSTITUTION MECHANISM IN NATURAL OCCURRENCES AND THEIR GENETIC SIGNIFICANCE

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Sulfur could be incorporated into the monazite structure by the (1) "clinoanhydrite" substitution $(Ca,Sr)^{2+} + S^{6+} \leftrightarrow (REE,Y)^{3+} + P^{5+}$ (KUKHARENKO et al., 1961; CHAKMOURADIAN & MITCHELL, 1999; ONDREJKA et al., 2007; WILLIAMS, et al., 2007; KRENN et al., 2008), or (2) $S^{6+} + Si^{4+} \leftrightarrow 2P^{5+}$ substitution (WILLIAMS et al., 2007). The $(Sr,Ca)S(REE,Y)_{-1}P_{-1}$ seems to be the most important substitution mechanism incorporating sulfur in monazite. The highest S concentrations in natural monazite were determined recently from the Bacúch metamorphic magnetite deposit, Low Tatra Mountains, Slovakia, where S^{6+} contents attain up to 0.28 apfu or 10.7 wt% SO_3, in addition to ≤0.16 apfu Sr or ≤7.8 wt% SrO (PRŠEK et al., in prep.). S- ±Sr-rich monazite (≤8.5 wt% SO_3 and ≤8.3 wt% SrO) is known from a few other localities including Lesnaya Varaka apatite-dolomite carbonatite, Kola Peninsula (KUKHARENKO et al., 1961; CHAKHMOURADIAN & MITCHELL, 1998), Internatsional'naya calcite kimberlite, Yakutia (CHAKHMOURADIAN & MITCHELL, 1999), the Tisovec-Rejkovo A-type rhyolite, Slovakia (ONDREJKA et al., 2007), and ore-bearing mylonitic mica schists and aplitic rocks from the Schellgaden mining district, Austria (KRENN et al., 2008). These rare anomalous monazites are interpreted as products of secondary, mainly hydrothermal alteration of the primary magmatic or metamorphic rocks. However, an existence of monoclinic $CaSO_4$ end-member with monazite-type structure (named "clinoanhydrite" by ONDREJKA et al., 2007) was confirmed by their synthesis at 2–28 GPa and room temperature (BORG & SMITH, 1975; CRICHTON et al., 2005; BRADBURY & WILLIAMS, 2009).

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INDUSTRIAL MINERALS AND ROCKS OF ALBANIA

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Apart from the metallic minerals such as chromites, copper, iron – nickel, there are numerous of other industrial minerals and rocks of interest for the economy market. Commonly, those are known under the term "industrial minerals". The known industrial minerals in Albania are ~50. At least for some of them (asbestos, phosphorites, etc.) ore reserves have been calculated and technological studies have been accomplished.

Limestones and **dolomites** represent the raw materials, which belong to different geological times, from Triassic up to Eocene. They occur as massifs, in form of long belts up to some kilometres all over Albania. Limestone rocks of $CaCO_3$ higher than 50% are widely used in the cement and lime industry. **Dolomites** have been found together or close to the limestone deposits. In Ducati deposits (Vlora) the dolomites are 400 m thick of 18–21% MgO content.

Calcareous ornamental stones occur mainly in the Korabi zone, in the peripheral parts of Mirdita, in Albanian Alpet, Krasta–Cukali, Kruja and Jonian zones. The conglomerates of Munella (Puke), Pretusha (Pogradeci), Bitincka (Bilishti) show also good decorative features.

Phosphorites occur in the carbonate rocks of the Jonian zone at the areas of Gusmari and Nivica (Tepelena), Fushbardha (Gjirokastra), Galishti (Saranda).

Clay mineral deposits are among the most frequent ones and of a great importance for the market economy. Several clay deposits are known such as: bentonite clays for use in oil industry at Prrenjasi; ball clays for use in ceramics at Alarupi; potassic white clays (in Tamara) for porcelain; pigment clays for use in chemical industry at Dibra and clays for bricks, tiles that occur in the coastal plain from Shkodra to Lezha, Tirana, Durresi, Kavaja, and Vlora, Korça, Burreli, and Peshkopia.

Kaolin occurs in the western part of the Mirdita zone in the area of Puka, where the two main kaolin deposits Korthpula and Dedaj are found. Kaolin represents the alteration crust on gabbroic rocks. The kaolin crust is up to 50 m thick in the Dedaj deposit.

Quartz sands and quartzites occur mainly in the area of Tirana and Devolli. They extend for several hundred meters up to several kilometres and are of about 10 m thick. Two quartz deposits have been found in Kukesi and Tropoja (Kallabaku and Kernaja). The composition of the quartz sands is: > 80% SiO_2, 10% Al_2O_3 and up to 1.5% Fe_2O_3.

Gypsum and anhydrite represent minerals of interest not only because their huge reserves but also for their possible wide use for export. They occur in the Korabi zone (Peshkopia – Radomira), in the Preadriatic plain (Durresi, Kavaja, Fieri, Vlora), in Dumreja and in the Ionian zone along with the longitudinal and transversal faults. **Salt rocks** (halite) occur in the areas of Kavaja (Mengaj, Tilaj) and Saranda (Dhrovjani). The explored reserves are 300 million tones with NaCl up to 76–82%. From Dhrovjani mine halite was exploited between 1971–1991. The demand of the country is met by the salt production from seawater in the area of Vlora.

Alluvial deposits yield more than 242 million m^3 of reserves of sands and gravel.

Industrial minerals and rocks related to ophiolites are olivinites, volcanic glasses, basaltic rock, magnesite, and ornamental ophiolite rocks including plagiogranites.

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KAOLINITE POLYTYPES

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Common structural feature of layered silicates is polytypism, where polytype modifications differ from each other in the relative positions of adjacent structural layers. Few studies have been focused on possible one-layered kaolinite polytype modifications so far (ZVYAGIN, 1962; MERCIER & LE PAGE, 2008).

We characterised stacking of adjacent TO layers using the **R** vector and "+", "–" notation (introduced by DÓDONY, 1997 for trioctahedral TO sheet silicates); where **R** is the projection of the **c** axis onto the **ab** plane and "+" or "–" signs the slant of octahedral sheet. In addition, we adopted the "**s**" or "**o**" labels for kaolinite that are used for pyroxene structures (GRIFFEN, 1992) indicating tetrahedral rotations against the octahedral sheet.

All possible polytypes can be derived by combining **R** vectors, octahedral slants and orientations of the ditrigonal tetrahedral rings. When the **R** vector, the slant of the octahedral sheets and the orientation of the ditrigonal ring are the same between adjacent TO layers, the polytype is a one-layered type; in any other case when these variables alternate, it is a two- or multi-layered polytype.

As a result, we deduced and listed the possible 20, crystallographically different, one-layered kaolinite polytypes, including 8 enantiomorphic modifications. Each of them was characterized by simulated X-ray powder diffractogram, [001] SAED pattern and [001] projected charge density image. We measured one kaolinite sample (Mád, Tokaj Mts., Hungary) and found satisfactory match between the experimental and one of the 20 simulated one-layered polytype XRD patterns. Matching experimental and corresponding simulated electron diffraction patterns provides a good way to determine an actual polytype modification.

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AUTHENTIC (TYPE AND OTHER ORIGINAL) SPECIMENS OF MINERALS FIRST DESCRIBED FROM THE CARPATHIAN REGION IN THE COLLECTION OF THE NATURAL HISTORY MUSEUM, VIENNA – A SURVEY

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Type specimens of valid mineral species are irreplaceable reference materials. Their availability can be checked in the international Catalogue of Type Mineral Specimens (CTMS; http://www.agiweb.org/smmp/IMA-CM/ctms.htm). From among the minerals discovered in the Carpathian Region (PAPP, 2004), several invalid species have never been properly identified or characterised. The re-examination of these minerals also requires authentic specimens. For the discreditation of a species the type specimen must be used and this specimen remains type material after discreditation (DUNN, 1990). Nevertheless the (former) type specimens of discredited species are generally not included in the CTMS; therefore it is not easy to find them. Especially authentic specimens of species considered invalid long since are difficult to locate. The collection of the Department of Mineralogy and Petrography of the Natural History Museum in Vienna (NHMW) is the most abundant potential source of such specimens from the Carpathian region. In addition to the search of authentic specimens of invalid species, we collected data about type specimens of valid species for a planned web site about the minerals discovered in the region.

67 specimens of 11 valid (alloclasite, dietrichite, felsőbányaite, hauerite, hörnesite, krautite, ludwigite, pilsenite, szmikite, veszelyite, wollastonite (“*Tafelspat*”)) and 16 invalid species (biharite, dognácskaite, eukamptite, “*Flusserde*”, “*Gelberz*”, gelfischerite, herrengrundite, kapnicite, “*Kattunerz*”, kenngottite, partschinite, pettkoite, sommarugaite, szászkaite, szmikite, thrombolite) were located in the NHMW. Original acquisition catalogue data, the inspected specimens and their labels were documented. 15 specimens were sampled. Specimens of further 15 discredited species were searched but not found so far.

In addition to the type specimens included in the CTMS, we found and defined “authentic specimens” of different kinds (historic specimens whose type status cannot be established): “author’s specimens” (acquired from the author of the species, e.g. dietrichite, szmikite, tetradymite, wollastonite; biharite, eukamptite, kenngottite, pettkoite, szászkaite); “collector’s specimens” (acquired from the same collector / dealer who collected / sold etc. the type specimen); “early specimens” (acquired around or even earlier to the date of the publication of the species; or other “reference specimens” (labelled with a rare historic mineral name).

This research received support from the SYNTHESYS Project (http://www.synthesys.info/) which is financed by European Community Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme, Grant AT-TAF-5064 (for G. Papp).

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ZEPHAROVICH'S STUDIES AT THE ACADEMY OF MINING AND FORESTRY, BANSKÁ ŠTIAVNICA / SCHEMNITZ / SELMECBÁNYA

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Even the most detailed biographies of Victor Leopold Ritter von Zepharovich (1830–1890), prominent mineralogist of the Habsburg Monarchy, contain very limited information on his studies. Unpublished data can be found in the register of the Academy of Mining and Forestry, Banská Štiavnica / Schemnitz / Selmecbánya (in the Archives of the University of Miskolc). According to the "Vorstudien" (preliminary studies) entry he completed the two-year philosophy course but gave up his legal studies ("Philosophie, theilweise Jus"), then he attended the (last) geognosy course organised by Haidinger in the "k.k. montan[istisches]. Museum in Wien [1848–1]849". These data are in accordance with those published in his earlier biographies. Zepharovich matriculated to 6 semesters (1849/50–1851/52) at the Academy, but the academic year 1849/50 in fact began only in January, 1850 due to the Hungarian War of Independence, so he completed the 4-year academic course in less than 3 years. His subjects and grades are listed in Table 1. Remarkably, he had exemption from mineralogy, geology and palaeontology, obviously due to his studies in Haidinger's institute.

S	Subject (as in the register)	Subject (in English)	TC	PC	Grade
1	Mathematik	Mathematics	10	10	V
1	Situationszeichnen	Plotting	0	10	V
2	Physik und Mechanik	Physics and mechanics	10	10	V
2	Darstellende Geometrie	Descriptive geometry	5	5	V
3	Chemie	Chemistry	10	10	V
3–4	Geometrischen und Perspektivzeichnen	Geometrical and perspective design	0	10	V
4	Mineralogie	Mineralogy	5	10	–
4	Civilbaukunde	Civil architecture	5	0	A
5	Geognosie und Petrefaktenkunde	Geology and palaeontology	10	10	–
5	Grundriss der Forstkunde	Outlines of forestry	5	0	A
5	Bauzeichnen	Architectural design	0	10	A
6	Bergbaukunde	Mining	10	0	A
6	Pr. V. in Gruben- und Aufbereitungswesen	Pr. a. of mining art and ore dressing	0	10	A
6	Bergrecht	Mining law	3	0	V
6	Maschinenzeichnen	Machine design and drawing	0	10	V
7	a) Markscheidekunde, b) Bergmaschinenlehre	a) Mine surveying, b) Mining machinery	10	0	a) 1V, b) A
7	Pr. V. in Kunst- und Markscheidewesen	Pr. a. of engineering and mine surveying	0	10	A
7	Geschäftstiel und Kanzleiordnung	Official style and office management	3	0	A
7	Pr. V. in Grubenkartierung	Pr. a. of mine cartography	0	10	A
8	Probier- und Hüttenkunde	Assaying and metallurgy	10	0	V
8	Pr. V. in Probier- und Hüttenwesen	Pr. a. of assaying and metallurgy	0	20	E
8	Bergrechnungswissenschaft	Accounting in mining	3	0	V

Table 1. Zepharovich's subjects and grades at the Academy of Mining and Forestry, Banská Štiavnica / Schemnitz / Selmecbánya. S: semester (of the 4-year course); TC / PC: theoretical / practical classes per week (of the 4-year course); Grades: A: Ausgezeichnet (excellent), E: Entsprechend (satisfactory), V: Vorzug (passed with merit), 1V: Erste mit Vorzug (first with merit); Pr. a. = Practical aspects, Pr. V. = Practische Verwendung

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LIQUID MEMBRANE PERMEATION WITH SUPPORT LAYERS IN HEAVY METAL RECYCLING

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Generally Liquid Membrane Permeation is considered (KOCHERGINSKY & SEELAM, 2007) to be one of the most efficient membrane based separation technologies. It can be applied to a wide range of separation tasks including removal of various heavy metal ions from industrial wastewaters, extraction of pharmaceuticals or food additives such as lactic acid. Advantages of supported layers over comparable processes like solvent extraction are low consumption of organic solvent and extractant and the permanent maximum driving force. Extraction and re-extraction proceed in one step, which leads to continuous processes. Due to membrane instability and subsequent membrane breakthrough there are no industrial applications for this technology at present.

State of the art in heavy metal separation is precipitation. Afterwards the deposition is land filled. The main goal of the current research project is to establish a continuous process for the recycling of heavy metal ions from aqueous solutions. The three phase contact leads to an apparatus design similar to a filter press arrangement. As support layer microporous polyethylene membranes were used, which were impregnated with organic phase. All experiments were carried out using the EFCE test system for reactive extraction $Zn^{2+}|DEHPA|H^{+}$. For the interpretation of the results the mass transfer coefficient and the diffusion coefficient were calculated.

Based on the experimental data obtained from a small-scale unit (FRITZ, 2009) a pilot plant scale unit was constructed and commissioned. The mass transfer area, totally amounting to a value of 760 cm^2, was increased by a factor of 70. Membrane breakthrough was effectively avoided by continuous reimpregnation of the support layer with liquid membrane. The mass transfer coefficient of zinc was determined to a value of $6x10^{-5}$ m/s. The diffusion coefficient is in the range of 10^{-11} m^2/s.

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PARTIAL MELTING AND MELT SEGREGATION IN FOOTWALL UNITS WITHIN THE CONTACT AUREOLE OF THE SUDBURY IGNEOUS COMPLEX (NORTH AND EAST RANGES, SUDBURY STRUCTURE, ONTARIO, CANADA)

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Crystallization of the Sudbury Igneous Complex (SIC) from a superheated melt sheet within the 1.85 Ga Sudbury impact structure resulted in the development of an approximately 1-2 km wide contact aureole in which partial melting of footwall rocks also occurred (DRESSLER, 1984). Although a genetic association of such partial melting and hydrothermal Cu-Ni-PGE mineralization processes was proposed (MOLNÁR et al., 2001; PÉNTEK et al., 2008), so far no detailed study has focused on the melting process itself.

We performed detailed mapping of partial melting features and felsic rocks (referred to as footwall granophyres) representing crystallized and segregated partial melts in stripped outcrops and drill core from the North (Windy Lake, Foy and Wisner areas) and East Ranges (Frost and Skynner areas) of the Sudbury structure. This revealed partial melting up to a distance of 500 m from the basal contact of the SIC in felsic footwall units of all occurrences and in gabbroic rocks from Frost, Windy Lake and Skynner. The intensity of partial melting does not gradually decrease with distance from the contact, but is localized especially in impact brecciated (Sudbury breccia) zones, probably due to the presence of fluids.

Footwall granophyres are dominantly composed of various quartz-feldspar intergrowths, with significant textural and mineralogical differences within and among the studied occurrences. Exsolution of a fluid phase during crystallization of these melts is evidenced by several observations including the abundance of up to cm-sized miarolitic cavities. From major and trace element compositions of these rocks we infer that they crystallized from melts derived dominantly from the partial melting of felsic Levack Gneiss and Cartier granitoids, with significant contribution of gabbroic rocks at Frost; this is in accordance with our observations on *in situ* partial melting features in both felsic and mafic rocks. Based on our field and analytical data we conclude that partial melting occurred at temperatures of up to 750°C in the Wisner area and up to 900° in the Frost and Windy Lake areas at a pressure of 1.5 ± 0.5 kbar.

Segregation of grain-scale partial melts to outcrop-scale veins and dikes may be observed in all localities and was promoted by high strain rates due to the ongoing Penokean orogeny. Footwall granophyre veins and dikes in gneissic and granitic rocks reflect brittle conditions of the host rocks during melt migration, whereas irregular, sheared melt pods with diffuse contacts in Sudbury breccia matrix indicate ductile conditions during crystallization.

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DEFECTS, COMPLEX LAYER STRUCTURES AND STRESS EFFECTS IN SYNTHETIC DIAMOND SINGLE CRYSTALS

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Synthetic carbon materials such as diamond have wide-ranging applications in many industrial fields e.g. electronics, gem industry or tool production due to their interesting physical and chemical properties. However, these properties strongly depend on the synthesis conditions. This contribution presents the results of a thorough characterization of synthetic carbon materials, which were studied in the course of a research project funded by an industrial company. Several carbon modifications namely amorphous carbon, poly- and nanocrystalline graphite as well as diamond single crystals have been investigated by Raman spectroscopy. The majority of the samples were diamond single crystals with a thickness greater than 1 mm and several mm in diameter grown by chemical vapor deposition (CVD). The photoluminescence spectra of some of these diamond samples revealed the presence of $[N\text{-}V]^0$ centers at 638 nm, $[N\text{-}V]^-$ centers at 575 nm as well as [Si-V] centers at 738 nm. The nitrogen related defects caused a yellow-green coloration due to absorption effects in the visible spectrum. The concentrations of the nitrogen impurities have been determined using a linear correlation function between the full width at half maximum (FWHM) of the characteristic F_{2g}-Raman mode of diamond at 1332 cm^{-1} (from 1.6 cm^{-1} in nitrogen-free samples up to 3 cm^{-1}) and the nitrogen content given by SUROVTSEV et al., 1999. The values varied from virtually nitrogen-free up to concentrations greater than 1000 ppm. Infrared spectra of various synthetic diamonds in turn showed dominating A defect centers (caused by a pair of substituted nitrogen atoms) at 1282 cm^{-1} and secondarily B- (1175 cm^{-1}) or C-centers (1135 cm^{-1}). By using a piezo-autofocus and a motorized x-y-table, Raman maps and depth profiles were collected, which showed in one sample a splitting and shifting of the F_{2g}-mode and an additional band at ca. 1328 cm^{-1}. The splitting was especially significant along grain boundaries. This may be related to the presence of hexagonal carbon polymorphs formed by a defect-induced symmetry modification of the diamond structure as well as anisotropic stress along grain boundaries (ROSSI et al., 1999). High-resolution transmission electron microscopy (HRTEM) images showed a grain boundary with a length of 10 µm and a width of 10 nm. The electron diffraction patterns of this grain boundary could be theoretically attributed to lonsdaleite or 6*H* polytype. Additionally, the surface topography of the diamond single crystals was investigated by atomic force microscopy. The average surface roughness varied from 0.4 nm to 1.2 nm. One of the samples showed several pyramid-shaped depressions with depths up to 1.5 µm and base area diagonals up to 15 µm. These depressions are probably growth defects created during the synthesis process.

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THE NOTATION “TSCHERMAK’S MOLECULE” IN A RETROSPECTIVE VIEW

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The modern lexicographical definition of the term “Tschermak molecule” is: A synthetic pyroxene $CaAlAlSiO_6$; a hypothetical component of natural pyroxenes.

The question now, by whom and in which paper was this nomenclature used for the first time? And further, transferred from one hypothetical molecule to a group of (also hypothetical) end-members of inosilicates, especially pyroxenes? Some answers in chronological order with authoritative citations:

A ratio for the two components (one real and one hypothetical compound) for pyroxenes (e. g. augites) was proposed by TSCHERMAK (1871):

$(n+o)\,MgO : n.CaO : o.Al_2O_3 : (2n+o)SiO_2.\quad [(n, o) \geq 0 \leq 1]$

Die einfachste Deutung, welche man dieser ***Mischungsregel*** *geben kann, ist, dass ausser dem Diopsid noch ein Thonerde-Magnesia-Silicat* [sic!] *beigemischt sei, die Formel also in zwei Glieder zerfällt:* $n[MgO\ CaO\ 2SiO_2]$ *Diopsid and* $o[MgO\ Al_2O_3\ SiO_2]$ *Magnesia-Thonerde-Silicat.*

Dabei wird als selbstverständlich vorausgesetzt, dass jeder Magnesiaverbindung eine Eisenoxydul- und Manganoxydulverbindung entspreche. Die beiden zuvor bezeichneten Silicate, welche als isomorph anzusehen wären, hätten auch in atomistischer Hinsicht eine Aehnlichkeit wie folgende Schreibweise zeigt: $MgCaSiSiO_6$ *und* $MgAlAlSiO_6$.

The first reference to a *“Tschermak’sches Tonerdesilikat* $Me(Al,Fe)_2SiO_6$*, Me = Ca,Fe,Mn”* we will find by MOROZEWICZ (1899).

GROTH (1908; 1921) defined in his textbooks the compound in which the hexavalent pair of Al-Al atoms, substituting the two atoms Ca-Si in pyroxenes, as *“Tschermaksches Silikat”* with the chemical formulas *“*$SiO_6Al_2(Mg,Fe)$ *bzw.* $SiO_6Fe_2(Mg,Fe)$*”.*

The definition “Ferri-Tschermak’s molecule” was created by HUCKENHOLZ et al. (1969): *The presence of a Ferri-Tschermak’s molecule* $CaFe^{3+}Fe^{3+}SiO_6$ *(abbreviated FTs) is inferred in which* $Fe^{3+}Fe^{3+}$ *occupies the sites of MgSi* [and not CaSi!] *in the diopside structure.*

In general terms: In substitutions the Al-Al-couple is often referred to as “Tschermak’s component”; $CaAlAlSiO_6$ in particular, is called “Calcium Tschermak’s component” (MORIMOTO, 1989).

In addition: The confused notation “Tschermakit“ (STRUNZ, 1966) in the booklet “Mineralogische Tabellen” (here the term Tschermak’s molecule was transferred to amphiboles): *Tschermakit (Winchell 1945), hypothetisches „Tschermaksches Molekül“* $Ca_2Mg_3Al_2\ [OH/AlSi_3O_{11}]_2$ *der Amphibole.*

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RARE PHOSPHATES FROM A Li-F-P GRANITE (GEMERIC UNIT, WESTERN CARPATHIANS, SLOVAKIA)

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A small pod of granite porphyry of Permian age occurring in the Hnilec area (Gemeric unit) shows a strongly peraluminous, Li-F chemistry with elevated P_2O_5 content (up to 0.67%) and an interesting assemblage of phosphate minerals. The texture is mostly porphyritic with matrix (0.02-0.15 mm) consisting of quartz, albite, topaz, phengitic mica and a variety of accessory oxides (cassiterite, columbite-tantalite, niobian rutile, uraninite), rarely wolframite and turmaline. Porphyroblasts (former phenocrysts, 0.2- 1.7 mm) are represented by sub- to euhedral alkali feldspars (perthitic microcline, albite An_{0-5}), topaz and large (0.2-0.7 mm) flakes of white mica. The mica, typically filled by small ores (niobian rutile, cassiterite), was identified as zinnwaldite (TISCHENDORF et al., 1997). Leucogranite (ab-qtz-Kfs-mus) fragments (0.5-2 mm in size) commonly occur with the phenocrystic minerals in the matrix.

The phosphate minerals occur as accessories and are represented by arrojadite [$KNa_5Ca(Fe,Mn)_{13}Al(PO_4)_{11}(PO_3OH)(OH,F)_2$], lacroixite [$NaAl(PO_4)F$], goyazite [$SrAl_3(PO_4)_2(OH)_5.H2O$], gorceixite [$BaAl_3(PO_4)_2(OH)_5.H_2O$] and viitaniemiite [$NaCaAl(PO_4)F_3$]. Small apatite grains were found filling cracks in arrojadite, but they also occur in small network-like domains enclosing albite and quartz. The mentioned Al-Fe-Mn-Sr-Ba phosphates are commonly referred from LCT pegmatites but not from granite porphyry. Their crystallization is interpreted in terms of changing P, F, H_2O and Ca activities. Phosphorus and F seem to be enriched in late stages of crystallization due to crystallization of quartz and feldspars while Li is buffered by early zinnwaldite precipitation. This makes stable topaz, viitaniemiite and lacroixite instead of Ab, Mu and amblygonite. Arrojadite is stable in Mn and Fe enriched F-rich domains instead of biotite. The P contents are 0- 0.8 % in K-feldspar, 0-0,5 in albite, reaching a maximum of 1.22 % in the rim of a Kfs. The bulk D P of crystallizing feldspars is < 1 enabling the build up of P (LONDON, 1992).

The apatite saturation temperature from apatite-bearing samples is 550-600°C (HARRISON & WATSON 1984; PICHAVANT et al., 1992) indicating depolymerising role of fluxes (water, F and B). Topaz muscovite thermometry (HALTER & WILLIAMS-JONES, 1999) gives very low T (ca. 250°C) probably indicating Alpine reworking characteristic of the Gemeric unit. The porhyritic texture may have originated due to pressure drop and following devolatilization of partially crystallized melt and brecciation of adjacent leucogranite.

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PETROGRAPHIC AND FLUID INCLUSION STUDY OF UPPER MANTLE XENOLITHS FROM THE CAMEROON VOLCANIC LINE

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We have studied upper mantle xenoliths from Nyos and Barombi maar lakes situated along the Cameroon Volcanic Line (CVL), an alignment of Tertiary to recent alkaline volcanoes, plutons and grabens extending over more than 1600 km (DÉRUELLE et al., 2007). Nyos and Barombi host alkaline basalts are from 1.5 to 0.2 My old (DÉRUELLE et al., 2007), their pyroclastic deposits contain large number of ultramafic xenoliths of which eight selected peridotites are presented here. All studied xenoliths are spinel lherzolites with protogranular texture in Barombi peridotites and porphyroclastic texture in the Nyos peridotites. Majority of the mantle minerals of Barombi and Nyos peridotites indicate a slightly variable major element composition with slight differences, and each xenoliths falls with a tight cluster of the mantle array (ARAI, 1994) in the olivine-spinel mantle array diagram, the peridotites show slight depletion. Expect one Nyos xenolith, clinopyroxenes show highly similar compositional range regardless of the texture type. Two generations of fluid inclusions can be distinguished in the xenoliths: an older and a younger generation fluid inclusions. The former one can be seen randomly in olivine and orthopyroxene of Nyos peridotite having negative crystal shape and 50 microns size. The large inclusions are often decrepitated and empty vugs now. The younger generations fluid inclusions occur in all the mantle silicates, including clinopyroxene, from both Barombi and Nyos xenoliths and they are accommodated along healed fractures showing various forms ranging from negative crystal to vermicular shape. Based on microthermometric results, on melting temperature and homogenization temperature, fluid inclusions in both peridotite series contain super dense CO_2-rich fluids with different proportion of apolar molecules, such as CH_4 and/or N_2, which were likely trapped as a miscible phase at lithospheric mantle condition in the constituent mantle silicates (VAN KERKHOF, 1990).

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A CONTRIBUTION TO THE REGULARITIES OF ALTERATIONS OF CHEMICAL SEDIMENTATION IN THE BADENIAN EVAPORITE BASIN OF PRECARPATHIA

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Lithological-geochemical studies of the Badenian deposits at the Shchirets, Verenchansk, Kudrynets, Gannusiv, Kryvsk gypsum quarries as well as core samples from the Zabolotsi, Korshiv, Silets-Stupnytsa areas allowed us to come to a conclusion about two stages of the development of the evaporite basin of Precarpathia of the Ukraine.

In conformity to the general rules of salt precipitation from seawater, reduce of mineralization from 30–35 to 360–370 g/l (at water evaporation), the beginning of the existence of the Badenian evaporite basin was characterised mainly by the precipitation of calcium sulphate with minor part of calcium carbonate. The accumulation rate was comparable with that of the analogous sediments in other regions of the Paratethys, a seam of 1-m thickness accumulated during 1000–1300 years. Chemical sedimentation was continuously accompanied by deposition of terrigenous material (illite, montmorillonite, chlorite, and quartz) in minor amount. Sedimentation of gypsum (after the accumulation of a sulphate unit up to 35-m thickness in some places) was gradually replaced by halite precipitation locally and in the most buried parts of the Badenian basin. Small (3-4 cm) thickness of annual layers of the rock salt, their interrupted and unrhythmic (irregular) nature, the availability of terrigenous material allow us to speak about a rather passive evaporation of the surface waters of the basin. Study of inclusions in sedimentary halite revealed that the chemical composition of water did not differ from the chemical composition of modern condensed seawater ($NaCl$ – 266; KCl – 14.1; $MgCl$ – 80.0; $MgSO_4$ – 23.3; $CaSO_4$ – less than 0.5 g/l). The first stage of the existence of the Badenian basin in the Carpathian Foredeep ended with halite precipitation. The existing point of view of coincidence to the given deposits of potassium salts does not agree with our data. The second stage started with distillation of solutions, change in their chemical composition in the direction of the decrease of the role of potassium and magnesium chlorides, replacement of halite, sedimentation for gypsum. The process outlined above is confirmed by the determination of the composition of mineral-forming solutions through the study of inclusions in the coarse-crystalline sedimentary gypsum, as well as by cryometric investigations. Common mineralization of water (solutions) in the basin decreased 2-5 times as regards waters of the halite stage and sometimes ranging from 150 to 65 g/l and less. This stage is characterised exclusively by the precipitation of gypsum from seawater saturated with calcium sulphate contained chlorides and sodium, potassium and magnesium sulphates. The ratio between cations sharply differed from that in the seawater. The existence of the evaporite basin ended by the precipitation of the carbonate formations of the Ratyn horizon covering the gypsum layers.

Two-stage development of the evaporite basin and succession of precipitation of chemical sediments, characteristic of evaporated waters of marine origin, is confirmed by the peculiarities of the distribution in the evaporite layers of the celestite mineralization.

MORPHOLOGICAL AND MINERALOGICAL BIOSIGNATURES FROM DIFFERENT PALEOENVIRONMENTS

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The aim of this study is representing morphological, textural and mineralogical features of fossilized products of biomineralization from different palaeoenvironments. Signs of biogenic-microbial activity were investigated on samples from a Jurassic cherty Mn-Fe oxide deposition, from a Toarcian chert/ironstone bed overlying the manganese deposit, Bakony Mts, and on cryptocrystalline silica cavity fillings from the Mátra Mts. The cherty Mn-Fe oxide blocks were formed in a structurally determined marine bacterially mediated hydrothermal vent system. Stromatolitic mounds were grown at the sediment/water interface around chimney-like micro channels. The chert/ironstone bed was formed in an organic matter-rich marine environment below the photic zone. Textures resembling bacterial cells are common with wavy, bulbous laminations composed of mounds with an underlying mesh-work stromatolite-like texture. The cavity fillings were resulted by complex interactions between the initial, in some cases supposed primary biogenic carbonate composition later replaced by silica, the weathering processes of the host rock with biogenic contribution, and the hydrothermal vent system. Rock varnish formations and stromatolites were raised on the surfaces of the fractures and cavities of the host rock entombed in silica matrix. Columnar non branching Conophyton-type stromatolites, bioherms, shell structures, and nodular-type biogenic forms appear in all studied environments under different conditions with biogenic contribution generating similar shapes (Fig. 1a-d).

Fig. 1a-d. Columnar non-branching morphotypes from the studied environments

XRD mineralogy of the Mn-Fe-oxide blocks is formed by hollandite, pyrolusite, todorokite, cryptomelane, goethite, manganite, phyllosilicates and quartz. The chert/ironstone bed consists of quartz, goethite, celadonite, pyrite and barite. The cavity fillings are composed by opal CT, quartz, goethite, hematite, nontronite, and celadonite.

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ELECTRON MICROPROBE DATA ON ROŞIA MONTANĂ (APUSENI MOUNTAINS) GOLD: TOWARDS A DATABASE FOR IDENTIFYING ANCIENT ARTEFACTS

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According to historical records, gold mining in the Apuseni Mountains spans over more than 3000 years; in the case of Roşia Montană (in antiquity known as *Alburnus Maior*), there is archaeological evidence of at least 2000 years of gold mining (*e.g.* CAUUET et al., 2003) by Dacians followed by Romans (106–273 AD). This gold ore deposit can be therefore considered as a major potential gold source for ancient populations. In order to achieve reliable correlations between archaeological gold artefacts and potential sources, detailed studies are needed for defining their mineralogical and chemical compositions.

This study represents a first step in the complex chemical characterization of the Roşia Montană gold, on samples from the valuable collection of the Museum of Mineralogy, Babeş–Bolyai University of Cluj-Napoca (POP et al., 2004). Electron Microprobe (EMP) analyses were carried out on ultrasonically-cleaned gold samples subsequently embedded in resin, at 25 kV accelerating voltage, 20 nA beam current intensity and 5 µm electron beam diameter, with a Jeol XA 8600 unit (Salzburg University). Based on the EMP results, two Au-Ag alloys could be identified in the Roşia Montană samples: gold, $Au_{0.67}Ag_{0.33}$ (dark yellow) and electrum, $Ag_{0.61}$ $Au_{0.39}$ (light yellow). Au and Ag show a strong inverse correlation ($r = –0.99$). Te concentrations are higher (between 0.15 and 0.35%) in electrum as compared to gold (< 0.13%). A similar relationship exists between Au and Cu, but at much lower Cu concentrations (< 0.06%).

As preliminary conclusions, we may state that the investigated gold samples from Roşia Montană show mineralogical and chemical variability at the ore deposit scale. Regarding the whole Apuseni Mountains area, an even more complex (geo)chemical heterogeneity is to be expected. The chemical correlation of Au-Ag may point to particular mineralogical-compositional relationships that may give a clue in further geochemical correlations. EMP proved to be more suitable for deciphering detailed genetic mechanisms at micrometer scale than other analytical methods (micro-PIXE or micro-SR-XRF) previously used in gold provenance studies. Consistent chemical information on gold ore deposits and archaeological gold artefacts from Romania would contribute to the establishment of a provenance database at regional and European scale.

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DEFECT DISTRIBUTION IN ORTHOPYROXENE AT ELEVATED PRESSURES

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The water content in the Earth's upper mantle influences many mantle processes such as mantle melting and physical properties such as rheology. It has been observed that pyroxenes contain generally much higher amounts of water than other nominally anhydrous mantle minerals and therefore are considered as major hosts for water in the Earth's upper mantle.

In the pure Mg-endmember $Mg_2Si_2O_6$ (enstatite) hydrogen incorporation is manly charge-balanced by Mg-vacancies (V_{M1}), $Mg^{2+}{}_{M1}\leftrightarrow V_{M1}+2\ H^{+}{}_{i}$, and a positive correlation between both pressure and water content (RAUCH & KEPPLER, 2002) and temperature and water content could be observed. Although the capacity of water-storage is additionally increased by the presence of trivalent cations ($2\ Mg^{2+}{}_{M1}\leftrightarrow M^{3+}{}_{M1}+V_{M1}+H^{+}{}_{I}$ and $Si^{4+}\leftrightarrow M^{3+}{}_{T}+H^{+}{}_{i}$), the presence of different cations may also reduce the water storage capacity due to the formation of anhydrous Tschermaks defects ($Mg^{2+}{}_{M1}+Si^{4+}{}_{T}\leftrightarrow Cr^{3+}{}_{M1}+Al^{3+}{}_{T}$, STALDER et al., 2005).

The aim of this study is the investigation of the spatial distribution and the interaction of hydrous defects in orthopyroxene in the system $MgO–SiO_2–H_2O\pm Al_2O_3\pm Cr_2O_3$. Single crystals are synthesised at different silica activities with varying amounts of Al and Cr at 6 GPa and different temperatures under water saturated conditions using a walker-type multi-anvil apparatus. Chemical characterisation of the synthetic crystals is performed using electron microprobe, Raman- and FT-IR-spectroscopy with a focal plane array detection system, which enables IR-imaging of our samples with a few µm spatial resolution.

Initial results on pure enstatite synthesized on the join En-H_2O at 6 GPa and 1300°C exhibit water contents around 500 wt. ppm. Interestingly, IR spectra taken from the center of the crystal show stronger absorbances around 3360 cm^{-1} compared to 3680 cm^{-1} (corresponding to V_{M1} and V_T, respectively), indicating a decrease of silica activity during crystal growth.

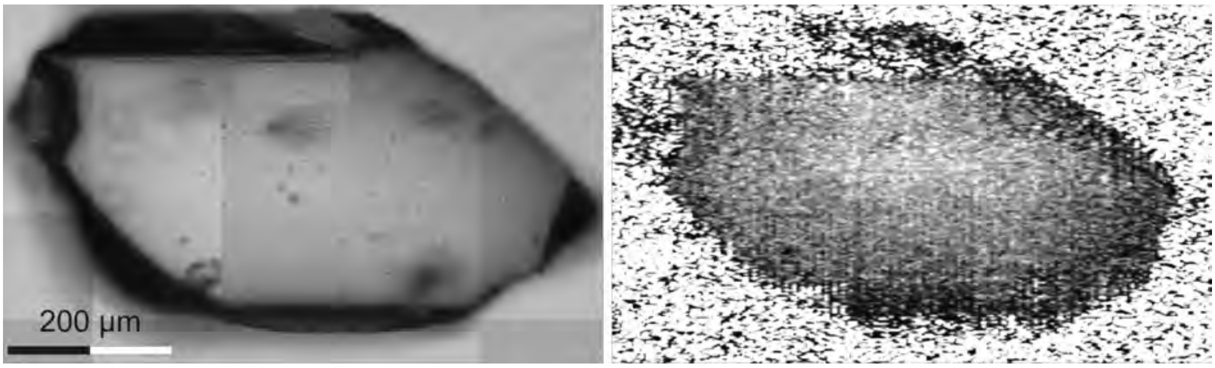

Figure 1. Visible image (left) and IR-image (right) recorded on a crystal synthesised at 6 GPa and 1300°C. Brighter areas in the IR-image represent a higher ratio of M-site vacancies to T-site vacancies.

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CRYSTAL STRUCTURE OF $CaSeO_4$ AND ITS RELATIONSHIP TO ANHYDRITE

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Anhydrous calcium selenate, the Se-analogue of the industrially important mineral anhydrite, has been synthesised under low-hydrothermal conditions. $Ca(NO_3)_2 \cdot 4H_2O$ and selenic acid in appropriate ratios were dissolved in minor amounts of H_2O. Subsequently, the reaction mixture was heated in a sealed teflon jar (3 cm^3 reaction chamber) to 220 °C and kept at these conditions for two weeks, followed by slow cooling to room temperature. The reaction product was predominantly gypsum-type $CaSeO_4 \cdot 2H_2O$, along with minor quantities of the anhydrous title compound.

Single-crystal X-ray data of a clear crystal with homogenous optical extinction were measured on a Nonius KappaCCD diffractometer and the structure was solved and refined in space group *Cmca* (a = 7.192(1), b = 14.404(2), c = 6.398(1) Å, V = 662.8 $Å^3$, Z = 8 to R1 = 2.0%, wR2 = 5.4%). The calculated powder diffraction pattern does not match any of the three different entries for $CaSeO_4$ currently listed in the ICDD database.

The investigated $CaSeO_4$ compound belongs to a new structure type, which bears close resemblance to that of anhydrite (space group *Amma*, a = 6.993, b = 6.995, c = 6.245 Å, V = 305.5 $Å^3$, Z = 4, HAWTHORNE & FERGUSON, 1975), but has a doubled b lattice parameter. Both structures consist of a framework of CaO_8 polyhedra and XO_4 tetrahedra. In each case, chains of alternating CaO_8 and XO_4 polyhedra with shared edges, running parallel to the respective c-axes, can be distinguished. Likewise, along the a-axes, the CaO_8 polyhedra share edges among each other. The main difference occurs along the b-direction, where common edges among CaO_8 polyhedra exist only in the title compound, but not in anhydrite.

The mean Ca–O distances are the same as in anhydrite, <Ca–O> = 2.470 Å, with individual distances varying between 2.36 and 2.68 Å in the title compound, versus 2.34–2.56 Å in anhydrite. The SeO_4 tetrahedron has a mean Se–O distance of 1.636 Å with practically no bond length variation and only moderate bond angle distortion.

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PETROLOGY OF METACARBONATE ROCKS OF THE AUSTROALPINE BASEMENT EAST OF THE TAUERN WINDOW (AUSTRIA)

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Marbles and calcsilicate rocks of the Austroalpine Basement east of the Tauern Window were investigated along a profile from the Wölzer Tauern (north-western Styria) to the Pohorje Mountains (northern Slovenia) regarding their metamorphic evolution. The profile is located within the Koralpe–Wölz nappe system, an eo-Alpine high-pressure unit comprising different tectonometamorphic complexes. Along this unit, the eo-Alpine metamorphic grade increases from north to south from greenschist- to eclogite facies conditions, which can also be recognized by the change of the index minerals in metacarbonate rocks:

Within the northernmost part of the profile in the Sölk valley, siliceous dolomitic marbles (CMSCH-system) consist of the mineral assemblage Dol + Cc + Qtz. These marbles belong to the low-grade Wölz Complex. *T* estimates were obtained with Cc-Dol-solvus thermometry which yields a *T* range between 437 to 465°C. About 20 km southwards the first occurrence of Tre can be recognized within the Greim Complex in the central Wölz Mountains (near Schoberspitz). Cc-Dol thermometry yields 540 to 562°C. Di starts to occur a few kilometres further south within the Rappold Complex (660–691°C) near Oberwölz and is further present towards the southward increasing grade in the Millstatt, Koralpe–Saualpe (680–740°C) and Pohorje Complexes. In the Rappold and Millstatt Complexes, Di may also occur as relics within Tre. Fo, usually indicating the highest metamorphic grade, is rare, reflecting the high P/T-gradient along the profile, and probably stabilized by high water activity. Along the profile Fo is restricted to the southern Koralpe–Saualpe Complex (Gupper quarry near Schwanberg) accompanied by Di and Ti-Chu. This assemblage is similar to marbles of the Strallegg Complex (Stubenberg quarry), where Fo occurs together with Ti-Chu and Chl. In the marbles of the Sieggraben Complex (Burgenland), however, Fo is accompanied by Spl (CMASCH-system) as a prior inclusion or as a separate mineral phase and may be stabilized in this case due to the higher temperatures which is recorded by Cc-Dol-solvus thermometry (ca. 760°C). Fo may be replaced by Di rims and both in turn are altered to serpentine.

Different types of calcsilicate rocks can be found dominantly within the Rappold and the Koralpe-Saualpe Complexes. Their mineral assemblage consists of Di + Grt + Amph + Czo + Qtz + Kfs + Pl in varying amounts. Carbonate phases are rare or even absent.

In general, the Rappold Complex is characterized by Di and minor amounts of Grs-rich Grt (X_{Ca} up to 0.68) whereas the Koralpe–Saualpe Complex shows higher amounts of Grt (X_{Ca} up to 0.65) and lower amounts of Di. Scp (X_{Mei} around 0.7 to 0.8) within the mineral assemblage Di + Amph + Scp + Czo + Cc ± Pl ± Kfs ± Qtz can be found in both complexes. Textural indicators for pre-Alpine metamorphism are rare and only present within the Rappold and Millstatt Complexes as Di relics in Alpine tremolite.

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REFRACTORY BRICKS OBTAINED FROM DUNITE ROCKS OF LESVOS ISLAND, GREECE.

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The range of application of olivine rocks in industry makes them a valuable raw material. Dunite is used mainly for the production of magnesia-silicate refractories (KISLOV, 1995).

This paper provides an assessment of the dunites rocks from the ophiolitic rocks of Lesvos Island, Greece, to be utilized as refractory raw material and especially for use as night storage bricks. This is reached by determining the chemical and mineralogical properties of the raw material and by making refractory bodies and study their phase compositions and microstructure. The data obtained has been compared with a number of published standards and specifications.

The mineralogy determined by X-ray powder diffraction. Polished and thin sections were examined using reflected and transmitted light microscopy. Selected areas of the thin sections were analyzed by microprobe analysis to determine the actual chemical composition of the different minerals present. Bulk chemistry analysis carried out by using fused discs for the determination of the major elements.

Refractory bodies were produced in laboratory conditions. The dunite samples were crushed and mixed together. An amount of 5% of Fuller's earth was used as bonding material. The dunite pellets then were fired gradually up to 1400°C, as this is the optimum firing temperature for sintering dunite-serpentinite rock (TABATCHIKOVA et al., 1990). Bulk density and apparent porosity of the fired pellets were determined. The various phases present identified by scanning electron microscopy and microprobe analysis and the average chemical composition of each of these phases have been compared with data of used bricks from British night storage heaters.

The bulk chemical analyses revealed that all dunite samples are similar with an average MgO 39.68%, SiO_2 43.34%, Fe_2O_3 8.59%, Al_2O_3 2.45%, CaO 2.65%, K_2O 0.004%, TiO_2 0.068%, MnO 0.134% and SO_3 0.08%.

The mineralogical study showed that the dunites consist of 82% olivine (with a mineralogical composition of 90.1% forsterite and 9.9% fayalite), 7% pyroxene, 8% serpentine, 1.5% spinel, 1% epidote and 0.5% sulphides.

Examination of the fired dunite pellets under SEM showed a good densification. Microprobe analyses showed that these pellets consist mainly of olivine with composition 95.1% forsterite and 4.7% fayalite. The olivine grains are bonded together with a thin film of cement which its chemical composition is classified as aluminous pyroxene and is quite similar to pyroxenes present in bricks which were used in British night storage heaters. The results of the mineralogical and chemical properties of the raw material as well as of those from the prepared refractory pellets compare favourably with published standards and specifications.

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THE PETROLOGY OF AN AMPHIBOLITE-METAGABBRO COMPLEX AND HORNFELSES FROM THE SOUTHALPINE BASEMENT IN THE NORTHERN EISACK VALLEY (GUFIDAUN, SOUTH TYROL, ITALY)

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This study area is part of the Southalpine basement unit and is situated in the Eisack Valley near Klausen. The area around the village Gufidaun is the focus of the geological mapping. The Villnöss Valley, situated north of Gufidaun, stretches eastwards and runs along a geological fault, the Villnöss Line. Questions about a possible Permian origin of the fault line and its Alpine reactivation still remain and are also part of this project. Within the rather uniform quartzphyllite (Brixen Quartzphyllites) basement, Permian contact metamorphic hornfelses and a large gabbro-amphibolite complex occurs near the village Gufidaun. These basement rocks have only been overprinted by the Variscan amphibolite-facies metamorphic event.

The amphibolites and gabbros contain the mineral assemblage amphibole + plagioclase + clinozoisite + chlorite + titanite ± ilmenite ± quartz ± calcite. Chemical zoning in idiomorphic amphiboles shows evidence for a prograde growth history. The core of the chemical zoned amphiboles show actinolite composition, the rim can be chemically classified as Mg-hornblende, edenite, Mg-hastingsite and pargasite. The chemical zoning shows increasing Na[B]-contents and decreasing Ca[B]-contents from core to rim. The increasing glaucophane substitution (Na[B]AlVI[C]⇔Ca[B]-1Mg[C]-1) and the increasing edenite- (Na[A]Al[T] ⇔ [B]-1Si[T]-1) and tschermakite- (Mg[C]Si[T] ⇔Al[C]-1Al[T]-1) substitutions towards the rims indicate increasing P and T conditions during the Variscan overprint. Matrix plagioclase is almost pure albite (ab95an5).

Application of multi-equilibrium thermobarometry to the matrix assemblage (amphibole + albite + chlorite), using THERMOCALC v.3.21 yields P-T conditions of ca. 550°C and ca. 0.4 GPa so far, but more investigations are currently in progress.

The hornfelses (contact-metamorphic-quartzphyllite) contain the mineral assemblage quartz + mica (muscovite, chlorite) + garnet ± calcite ± apatite ± ilmenite. These rocks are strongly retrogressed, but garnet porphyroblasts show discontinuous zoning with a presumably Variscan core and a Permian rim. Calculated Variscan P-T conditions, using THERMOCALC v.3.21 yield ca. 0.5 GPa and ca. 660°C.

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CLAY MINERALOGY OF CARNIAN (UPPER TRIASSIC) PELAGIC SUCCESSIONS FROM THE TRANSDANUBIAN RANGE (HUNGARY): PALAEOENVIRONMENTAL CONSEQUENCES

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During the Carnian (Upper Triassic), deep pelagic intraplatform basins (Veszprém Marl Formation) and prograding carbonate platforms developed at the western flank of the Tethys. This marine succession shows a significant change in sedimentation as the pelagic carbonate deposition was replaced by the formation of fine-grained marly sediments.

We determined the clay mineralogical composition of 240 samples from the Carnian marls and limestones from four boreholes in order to model the palaeoenvironment. The Carnian core sections display various clay mineral assemblages: the clay fraction of the samples includes variable proportions of illite, mixed layer illite-smectite, chlorite, and kaolinite. A high degree of expandability (50–70%) and a poorly ordered character (S = 0) of the mixed-layer phases results from a relatively low degree of diagenetic overprint. Therefore, the clay mineralogical composition seems to be an original signal. The relatively large amount of detrital illite (~40–60%) and chlorite (~10–30%) associated with kaolinite (~10–20%) reflect a strong erosion of high relief areas. Illite–smectite mixed layer minerals (up to ~60%) could be derived from altered volcanic material under a monsoon-like subtropical climate. In general, limestone intervals are enriched in mixed layer illite–smectite, whereas marl-dominated intervals are richer in illite reflecting fluctuations in either terrigenous input or sea-level. Relatively low values of the kaolinite/illite ratio (generally between 0 and 1) do not support unequivocally the idea of a constant humid and warm climate during the Carnian in the studied area. However, a slight fluctuation of this value in some sections could be related to changes in continental hydrolysis in the source area during the deposition. Consequently, the ultimate cause of the change in sedimentation style appears to be the diminished carbonate supply from the platform areas related to eustasy and tectonism, in addition to presumed change into a more humid climate.

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EFFECT OF FLUID-DRIVEN CHEMICAL ALTERATION ON RADIATION-DAMAGED FERGUSONITE

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We report first results of a study addressing heavy chemical alteration in a metamict fergusonite ($YNbO_4$) from Madagascar. The sample was found to be fully amorphised; it was initially identified based on its chemical composition only. Phase information supporting this assignment was obtained after structural reconstitution through dry thermal annealing; fergusonite was then identified from XRPD and Raman results (RUSCHEL et al., 2007).

The sample shows complex alteration textures overprinting the remnant primary zoning (Fig. 1). Alteration seems to be partly controlled by large fractures that may have served as "fast" pathways for alterating fluids. Sharp boundaries of altered patches indicate a fluid-driven replacement reaction whereas a rather gradual transition to surrounding areas should be expected for a diffusional process (PUTNIS, 2002). More detailed information on compositional changes in altered areas was obtained in extensive high-resolution element mapping. Altered areas show often inverse Nb and Ta variations. They are generally enriched in Si and Ca and depleted in Y (whereas centres of large fractures are filled with an yttrium phosphate phase). Lead, U and Th have rather irregular concentration patterns. The latter observation indicates a heterogeneous, perhaps multi-step alteration process. Results may add to our knowledge on the performance of fergusonite as a potential host phase for the disposal of actinides.

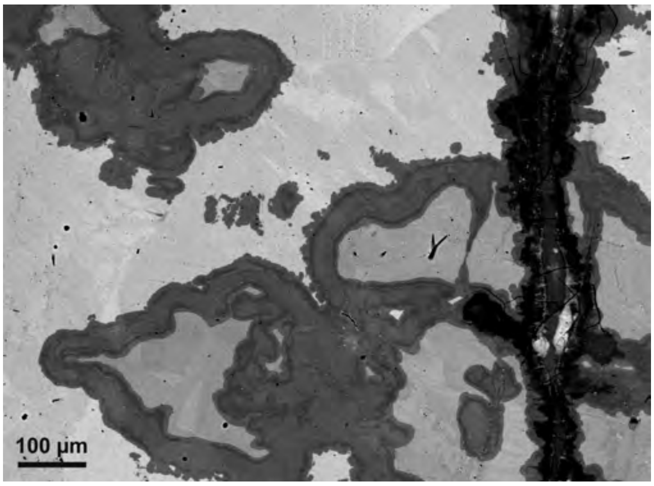

Figure 1. BSE image showing altered patches and zones (dark) in fergusonite from Madagascar

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PUTIKOV VŔŠOK, THE YOUNGEST BASALTIC VOLCANO OF THE CARPATHIAN-PANNONIAN REGION

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Putikov Vŕšok is an alkali basaltic volcano, situated on the left side of the Hron River between Brehy and Tekovská Breznica villages, in central Slovakia. The volcano consists of a cinder cone and associated lava flows north of the cone, which were forming a plateau on the alluvial flat of the river. Interaction of lava-groundwater caused explosions that prevent the formation of secondary cones.

According to K/Ar dating (0.53 ± 0.16 Ma), this volcanic eruption appears to be the last one in the Carpathian-Pannonian region (KONEČNÝ et al., 1995). However, the contact between basaltic flows and sediments by the Garam River indicates a slightly younger age ranging from 0.22 to 0.13 Ma (ŠIMON & HALOUZKA, 1996).

The studied scoriaceous and lava rocks are tephrites-basanites. Among them the highly vesicular ones have less silica and much less potassium and sodium content, and have an affinity to basalt-picrites, whereas all other rocks can be classified as basalt-hawaiite.

Petrographically they are also different. The lavas are olivine-phyric with little amount of clinopyroxene phenocrysts and microphenocrysts. The groundmass consists of plagioclase, clinopyroxene, olivine, Fe-Ti-oxides and glass. Scoriaceous rocks are olivine-phyric as well, but there are differences in the groundmass, where clinopyroxene crystals dominate, glass is more abundant than in lavas, and plagioclase is almost not present. In addition, olivine phenocrysts form the scoriaceous samples have inclusions of Fe-Ti oxide needles that are parallel to each other oriented and cover often the whole crystal. In both rock types olivine has spinel inclusions.

Electron microprobe analyses have shown that olivine from lava flows have Fo between 74-87, which is similar to olivines found elsewhere in the young Pannonian alkalibasalts. However olivin phenocrysts in the highly vesicular samples cover a wide range of composition (Fo74-96). The extremely high MgO contents (Fo96) could not be under normal condition in equilibrium with any melt. There must be another reason for such unusual forsteritic olivines. A possible explanation could be changes in the oxygen fugacity towards highly oxidized conditions, reducing in that way the amount of the available divalent Fe, which is necessary for the fayalitic components. On the other hand, other rock forming minerals like cpx and spinel do not show any evidence for high oxidized conditions.

Spinel compositions are similar to the Ság Hill, which are of OIB-like origin. Preliminary calculations of olivine-liquid thermometry show average mantle temperatures.

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HIGH-PRESSURE BEHAVIOUR OF REALGAR

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Realgar, As_4S_4, crystallizes in the monoclinic space group $P2_1/n$. The structure is characterized by cage-like molecules, oriented in rods parallel [100] and packed along [010] (BONAZZI & BINDI, 2008). Realgar is well known for its use as colour pigment in painting and art for many centuries.

A natural sample from Baia Sprie in Romania was compressed in a diamond anvil cell up to 5.4 GPa. Precise lattice parameters were measured as a function of pressure by X-ray diffraction using a Huber single-crystal diffractometer with point detector, and data collections were performed at selected pressures using an Oxford Diffraction single-crystal diffractometer. The lattice parameters show a smooth decrease with increasing pressure without any phase transition up to 5.4 GPa. Volume reduction occurs between the molecules, more precisely between the rods, whereas atomic distances within the molecules do not show a measurable shortening, comparable with Bi_2S_3 (LUNDEGAARD et.al., 2005).

Increasing pressure from ambient conditions up to 5.4 GPa involves a volume decrease of 18.14% from 800.54 A³ to 647.3 A³ (Table 1).

Pressure	*a*	*b*	*c*	*β*	*V*	Δ*V*
1 bar	9.3322 (9)	13.5698 (14)	6.5927 (7)	106.491 (8)	800.54 (14)	1.0
5.4 GPa	8.719 (4)	12.634 (6)	6.1490 (18)	107.13 (3)	647.3 (4)	0.81

Table 1. Lattice parameters of realgar at ambient conditions and 5.4 GPa.

Furthermore, a continuous colour change from very light red to intensive dark red and finally black was observed with increasing pressure (Fig. 1). The colour change is reversible on pressure decrease. Therefore chips of realgar, prepared of 50, 30, 20 and 18 µm thickness, show a faster colour change with increasing sample thickness.

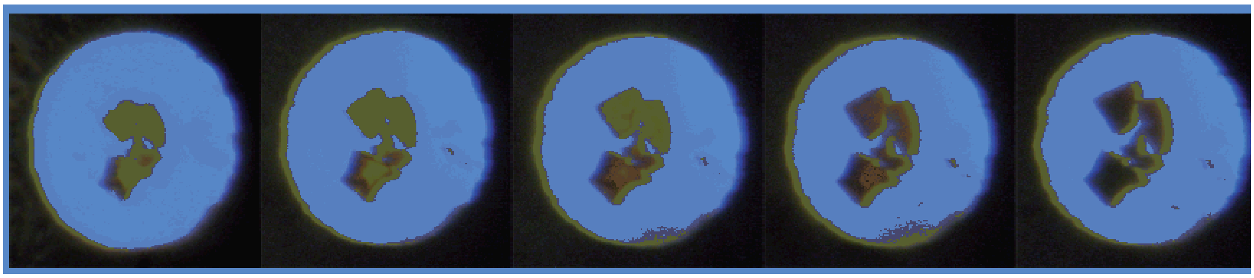

Figure 1. Images showing continuous colour change from very light red to darker red and finally black with increasing pressure from left to right.

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NEW GEOCHRONOLOGICAL DATA FROM ROCKS OF THE BULGARIAN RHODOPE

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New geochronological data were determined using zircons from amphibolites and orthogneisses of the Avren Complex (Southern Rhodope). Geochronological data were combined with zircon inclusion mineralogy to link ages with a magmatic and/or metamorphic history. The Avren Complex is considered as the northern continuation of the Greek Kimi Complex, which has been recently interpreted as a Suture Zone area containing UHP rocks (Rhodope Suture Zone after KRENN et al., 2008).

Zircons from amphibolites which are enclosed in pargasitic hornblende and feldspar were separated and investigated. They were found to be mostly homogeneous with minor patchy zoning. Zircons contain metamorphic minerals like pyroxene of X_{Jd}=0.17 that is higher than matrix pyroxenes (X_{Jd}=0.11). U/Pb age determinations of the zircon domains gave concordant metamorphic ages between 149.3 ± 6.6 Ma and 156.9 ± 4.2 Ma.

Zircon grains from the orthogneisses show a well developed magmatic zonation with a single- to multiphase inclusion character. Inclusions are feldspar, biotite and orthopyroxene. Compared to the matrix, feldspar and biotite inclusions show only slight variations in their chemistry. No pyroxene was found in the matrix. U/Pb age determinations of the zircon domains result in concordant metamorphic ages of 284 ± 15 Ma.

Age data can be compared with U/Pb ages from the Greek Kimi Complex. Zircons from the UHP paragneisses gave metamorphic ages between 170 and 160 Ma. Magmatic cores and metamorphic zircon rims from eclogites close to the paragneisses gave ages from 288 Ma and 160 – 80 Ma, respectively (BAUER et al., 2007).

It can therefore be concluded that age data from the orthogneisses of the Avren Complex suggest a common protolithic source during a Permian magmatic event of crustal extension and bimodal magmatism whereas metamorphic ages from the amphibolites support a coeval metamorphic history during Late/Jurassic Early/Cretaceous, where eclogites of the Kimi Complex have already reached post-eclogite facies metamorphic conditions (BAUER et al., 2007). On the basis of new age determinations from the Bulgarian Rhodope, a northern continuation of the already proposed Rhodope Suture Zone in the Kimi Complex is assumed to extend northwards to the Bulgarian Rhodope.

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THE MOST P-RICH OLIVINE ON EARTH SO FAR: THE FORMATION OF EXTREMELY PHOSPHOROUS OLIVINE IN PREHISTORIC BURNING SLAGS FROM THE GOLDBICHL, IGLS (TYROL, AUSTRIA)

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In this study, in the course of the special research project HiMAT (history of mining activities in the Tyrol and adjacent areas) at the University of Innsbruck, we report extremely P-rich olivines from partially molten quartzphyllites from the presumably La-Tène (450-15 B.C.) age sacrificial place at the Goldbichl, near Innsbruck, Northern Tyrol, Austria. During partial melting, foamy patches of dark glassy material formed at the surface of the rocks and also as layers within the rocks. Overall, the pyrometamorphic rocks contain the mineral assemblage olivine + orthopyroxene + plagioclase + spinel + glass. During the investigation of slag samples from this prehistoric sacrificial burning site, extremely P-rich microdomains were found, where P-rich olivine was found. The textures within these domains indicate strongly disequilibrium conditions. The phosphorus-rich olivine formed along reactions involving apatite, and coexists with graftonite $(Fe,Ca,Mg,Mn)_3(PO_4)_2$. In terms of its chemical composition, it shows a wide range in composition with P ranging from 0.3 to 0.55 apfu, which corresponds to up to 23 wt.% P_2O_5! This are the highest P-contents in olivine reported from rocks on the Earth surface so far! BOESENBERG et al. (2004) conducted experiments concerning the P-incorporation in olivine. They were able to synthesize P-rich rims around San Carlos olivine and predicted that olivine is capable to incorporate a maximum of 27 wt.% P_2O_5. This amounts to a substitution of 70% of the tetrahedral Si by P on the T-site in olivine. Besides high temperatures in excess of 1000 – 1100°C and strong disequilibrium conditions, an extreme low oxygen fugacity is necessary to form P-rich olivines (TROPPER et al., 2004). Micro-Raman spectroscopy measurements on the P-olivines indicate that P-bearing olivines can easily be identified with this method due to the strong signals of the SiO_4- and PO_4-vibration. The external vibrations at low wavenumbers are very distinctly developed. This might be due to the effect of P(V+) on the M_1(II+) and M_2(II+) positions. The substitution mechanism is $2P + \square M_{1,2} = 2Si + (Mg,Fe)M_{1,2}$ so phosphorous can only incorporated in combination with a vacancy on the $M_{1,2}$ position therefore it is expected that the substitution of P causes a decrease in symmetry.

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MONITORING THE HIGH-*T* BREAKDOWN BEHAVIOUR OF CHLORITE AND BIOTITE ± QUARTZ WITH HIGH-*T* XRD AND DTA/TG AND ITS APPLICATION TO SLAGS FROM PREHISTORIC SACRIFICIAL BURNING SITES

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Petrological investigations concerning slags and furnace samples provide information about the firing temperatures during the smelting process since abundant newly formed silicate (olivine, orthopyroxene) and oxide (spinel) phases are present and the breakdown of silicate precursor phases (e.g. biotite, chlorite, muscovite) as well as mixtures such as chlorite + quartz and biotite + quartz also provides limiting temperature estimates (TROPPER et al., 2004). In the course of these experimental investigations, the high-*T* behaviour of chlorites was examined. These investigations were conducted using high-temperature X-ray diffraction, differential thermal analysis (DTA) and thermogravimetry (TG). The DTA was calibrated with metal standards, so the change of enthalpy can actually be quantified. The investigated samples are chlorites with different iron content from $X_{Fe} = 0.11$ up to $X_{Fe} = 0.88$. In the experiments with samples with high X_{Fe} melt formed at high temperatures. The dehydroxylation of chlorite can thus be subdivided into two stages: A slow dehydroxylation of the brucite layers until 500-600°C and at higher temperatures a rapid dehydroxylation and subsequent breakdown of the talc layers (GUGGENHEIM & ZHAN, 1999). Only beyond this point SiO_2, MgO/FeO and Al_2O_3 are able to react and form new components. Depending on the iron content the dehydroxylation and the mineral reactions occur at different temperatures. With high-temperature X-ray diffraction the mineral reactions and thus growth of reaction products due to the breakdown of chlorite can be observed in-situ and also allows to investigate the change of lattice constants. Experiments with low-Fe chlorites show that the first product phase that occurs is olivine at around 800°C, spinel appears at 950 °C. These phases, especially the olivine, grow orientated along the schist planes (001). The last phase that formed was orthopyroxene at a temperature of 1000°C most likely due to the breakdown of olivine due to reaction olivine + silica = orthopyroxene (GRAPES, 2006).

The behaviour of biotite as well as a mixture of biotite + quartz (1:1) at high temperature was also investigated to obtain information about 1) phase transitions and the breakdown of biotite and 2) the changes of the lattice parameter due to a rising temperature. Biotite alone dehydroxylates constantly at a temperature of 560°C then at 1080°C, finally the structure of biotite breaks down completely to olivine and leucite. The behaviour of biotite + quartz is very similar but spinel, hematite, enstatite and melt also form. Fayalite was not observed because the oxygen partial pressure was most likely above the QFM buffer. Finally, these data provide important *T*-constraints on the firing history of sacrificial burning sites, which are investigated in the course of the Sonderforschungsbereich (SFB) HiMAT at the University of Innsbruck.

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BIOTITE AND APATITE COMPOSITIONS AS PETROGENETIC INDICATORS IN MAGMATIC ROCKS FROM THE ATHESIAN VOLCANIC GROUP (SOUTH TYROL, ITALY)

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The Permian age was marked by large-scale volcanic activity in the Southalpine domain. In the area of Bolzano and the surrounding area tremendous magmatic products were deposited (MORELLI et al., 2007; MAROCCHI et al., 2008). The composition of the volcanic and plutonic rocks ranges from acidic to basic. This project investigates different volcanic and plutonic horizons from the northwestern part of the Athesian Volcanic Group (AVD) based upon the investigations of MAROCCHI et al., (2008) with the aim to obtain comprehensive chemical analyses of biotite and apatite in order to investigate the nature of solid solutions in biotites and the interplay between late-stage magmatic fluids and the volcanics and provide thermometric estimates based upon F-Cl-OH partitioning between these phases.

The volcanic samples are mostly rhyolites and rhyodacites and contain the average mineral assemblage biotite + quartz + K-feldspar + plagioclase + apatite + ilmenite + zircon + allanite + rutile ± chlorite ± pyrite. The plutonic samples are granitoids (monzogranite and granodiorite) and contain the mineral assemblage quartz + biotite + K-feldspar + plagioclase + apatite + zircone + allanite ± chlorite ± rutile ± amphibole. EMPA analyses of biotites of rhyolites/rhyodacites from Terlan yielded an average mineral composition for biotite of: $(K_{0.817}Na_{0.069}Ba_{0.014}Sr_{0.007})(Fe_{0.834}Mg_{1.661}Mn_{0.003}Zn_{0.002}Ti_{0.243}Al_{0.091})(Al_{1.199}Si_{2.836}O_{10})(OH_{0.791}F_{1.168}Cl_{0.041})$. In contrast biotites from the Gargazzone Formation (IGG) contain more Fe and OH and less Mg and F. Furthermore rhyolitic tuffs from Monte Dian and from Grissian (ORA Formation: ORA1) have been investigated. The biotites from Monte Dian are even richer in Fe and more depleted in Mg and the biotites from Grissian are also very Fe-rich and contain slightly more Al. The sample from Sirmiano di Sopra (Andriano Formation: LAN), a rhyolitic lava, contains biotite showing compositional variations concerining Mg and F. Biotites from the plutonic rocks, the monzogranite and the granodiorite from the Ulten valley (GMR) are very similar in their compositional range to the rhyolitic tuff from the Monte Dian.

Apatite could only be measured from the granitoides so far, and is mostly F-apatite. For example the calculated average formula of apatite from the Ulten Valley monzogranite is: $Ca_{9.927}Na_{0.060}Sr_{0.001}Ba_{0.001}K_{0.008}Mn_{0.035}Ni_{0.001}Fe_{0.068}Mg_{0.003}Zn_{0.001}Cr_{0.002}Al_{0.002}Ti_{0.002}(P_{5.902}C_{0.055}Si_{0.064})(F_{1.699}Cl_{0.079}OH_{0.222})$, apatite compositions from the granodiorite are also very similar. Clearly more EMPA analysis are planned in order to improve the data from the different magmatic horizons.

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POST-COLLISIONAL CALC-ALKALINE TO SHOSHONITIC VOLCANISM IN NW OF IRAN: CONSTRAINTS FROM GEOCHEMISTRY AND PETROGENESIS

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Basalts, andesites, trachyandesites and pyroclastic rocks with calc-alkaline to shoshonitic affinities are the main volcanic pile of Paleocene to Eocene age in NW of Iran. Plagioclase, K-feldspar, Ti-rich biotite and amphibole (Ti-rich pargasite) associated with clinopyroxene (diopside to augite) are the main constituents of trachyandesites, andesites and basalts. The volcanic rocks show enrichment in LREE and characterized by enrichment in LILE and depletion in HFSE. Enrichment of incompatible elements increases towards shoshonitic suites. Petrographical observations along with geochemistry of rare earth and trace elements of these lavas suggest derivation from a subduction zone, although a metasomatized mantle is candidate for the genesis of shoshonites. The geochemical behaviour of the lavas reveals the role of the trench sediments in the source region and genesis of the volcanic rocks. These lavas exhibit low degree of partial melting from a garnet-spinel lherzolite mantle source. The comparison between shoshonitic volcanic rocks with calc-alkaline lavas from NW of Iran highlights the different mantle source and degree of partial melting/mantle enrichment degree for the genesis of the shoshonites. The formation of these lavas is linked to slab steepening and breakoff in Eastern Anatolian collision zone, proposed by KESKIN (2003).

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ASSOCIATION OF TRACE ELEMENTS WITH Fe-RICH NODULES IN AN ALLUVIAL SOIL

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Iron rich nodules are discrete bodies formed in the soil system under alternating reducing and oxidizing conditions. Their nature is of great interest from the viewpoints of both pedogenesis and environmental chemistry as they are sensitive diagnostic indicators of soil hydromorphism on the one hand, and exhibit high sorption capacity for many toxic metal pollutants on the other. The aim of this study was to investigate the association of 17 trace elements (Al, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Ni, Pb, Si, Sr, Ti, V and Zn) with Fe-rich nodules from an alluvial soil.

Total soil samples were subjected to sodium-dithionite and ammonium-oxalate dissolution to extract the total amount of Fe-oxides and the poorly crystalline fraction of Fe-oxides from the soil samples, respectively. Additionally, aqua regia digestion was performed on the total soil samples as well as on nodules separated from the sand fraction of the samples. Concentrations of the elements in the solutions were analyzed by ICP-OES method. The mineralogical characterization of the nodules was carried out by XRD analyses.

The Fe-rich nodules consist of amorphous phases, probably of ferrihydrite. Other phases in the nodules are corresponding to those forming the soil matrix. Additionally, disordered goethite was found in the pseudomorphs after amphiboles. These amphiboles may have been the source of iron (and other trace elements) in this soil.

Cobalt and Mn show 20-30 times higher concentration in the nodules when compared to their total soil concentrations. Other metals, such as Cd, Ba, Ni, V, Zn, Cu and Pb can be characterized by 3-6 fold enrichment similarly to Fe. According to the dithionite and oxalate extractions of the total soil samples, some of the other studied elements also show enrichment. However, they are probably associated with other phases which may be also dissolved due to the extractions used (such as poorly crystalline oxides and silicates, as well as carbonates).

These findings were also supported by statistical analysis which suggested the close association of Co and Mn, as well as that of Ni, Cd, Zn, Ba, Pb and Fe. Copper can be associated both with Mn and Fe. Additionally, Al, Mg, Si, Ti, K and Cr (e.g. elements bound to silicates and oxides), as well as Ca and Sr (e.g. elements bound to carbonates) also showed similar behavior during the extractions.

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HYDROUS DEFECTS IN PYROXENES

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Pyroxenes are amongst the most important rock-forming minerals in terrestrial planets and, next to olivine, the most abundant constituents of the Earth's upper mantle. Due to the ability of pyroxenes to incorporate significant trace amounts of hydrogen as point defects (i.e., distinctively higher amounts than other upper mantle minerals) they may be regarded as major hosts for hydrogen in the upper mantle. Since the incorporated hydrogen has major consequences for the physical properties and mantle processes such as melting, the exact knowledge of incorporation and dehydration behaviour is of general interest in geochemistry, petrology, mineral physics and geophysics.

In order to quantify the water content of nominally anhydrous upper mantle minerals, two main strategies have been followed: (1) direct analyses of samples derived from upper mantle rocks (mostly xenoliths from volcanic rocks from the Earth's mantle), which show water contents around 200 wt. ppm H_2O for orthopyroxene and around 400 wt. ppm H_2O for clinopyroxene (GRANT et al., 2007); (2) high-pressure – high-temperature experiments, investigating the effect of pressure, temperature, oxygen fugacity, silica activity and other chemical aspects on water incorporation. Water contents in the mineral phases observed by this strategy are generally much higher than observed in natural samples, and for pyroxenes contents up to several thousand wt. ppm H_2O have been observed (MIERDEL et al., 2007).

Several interpretations for the gap between analysis of natural material and experimental results have been put forward: (1) Partial hydrogen loss during ascent to the Earth's surface (MACKWELL & KOHLSTEDT, 1990), (2) interaction of different hydrous defects in complex composed systems (STALDER et al., 2005) and (3) reduced water fugacity in natural systems (STALDER et al., 2008).

In spite of steadily growing evidence for point defects in pyroxenes, indications for planar defects have hitherto not been found. However, some orthopyroxenes (both natural and synthetic ones, but all with high amounts of Al) show features similar to hydrous phases, such as chlorite. One possible interpretation is the survival of chlorite-like domains in orthopyroxene far beyond the stability field of chlorite, similar to OH-bearing humite-type lamellae, which survive in some mantle rocks well beyond the stability field of humite as planar defects in olivine (HERMANN et al., 2007).

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ANION RELATIONSHIPS OF BORATE ANIONS IN HYDROTALCITE STRUCTURE

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The triborate ($B_3O_3(OH)_4^-$) and tetraborate ($B_4O_5(OH)_4^{2-}$) anions have been incorporated in hydrotalcite structure ($Mg_{1-x}Al_x(OH)_2CO_3^{2-}{}_{x/2}.(1-3x/2)H_2O$, ($0.20 < x \leq 0.33$)) through coprecipitation of mixed acid solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ with alkali solution of NaOH. The synthesis was performed by dropping of the two solution to aqua solution of boric acid, which had been previously adjusted to pH = 8 (for $B_3O_3(OH)_4^-$) and pH = 9.5 (for $B_4O_5(OH)_4^{2-}$). The physico-chemical properties were investigated using X-ray powder diffraction and infrared spectroscopy. Competitive anion exchange between the $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and NO_3^-, SO_4^{2-} and CO_3^{2-} was performed by using various concentration (5:1, 2:1, 1:1, 1:2 and 1:5) of NO_3^-, $SO_4^{2-}$and CO_3^{2-} anions in aqueous solutions. The position of the two borates anions in the order of anion selectivity in hydrotalcite structure was found as follows: $CO_3^{2-} >> SO_4^{2-} \geq B_4O_5(OH)_4^{2-} > Cl^- > NO_3^- > B_3O_3(OH)_4^-$.

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PETROLOGY OF METAPELITES FROM THE MICHELBACH COMPLEX (DEFEREGGEN COMPLEX, EASTERN TYROL)

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The Michelbach Complex is a part of the polymetamorphic Austroalpine crystalline basement (Defereggen Complex) south of the Tauern Window and is situated in the eastern Defereggen Alps south of the Defereggen–Antholz–Vals Line. The dominant lithologies of this area are micaschists and paragneisses. Macroscopically, the complex can be subdivided into a sillimanite-bearing zone in the southern part and an andalusite-bearing zone in the northern part. Petrological, mineralchemical, and geochronological data indicate two metamorphic events: a Variscan event followed by a Permian high-temperature overprint (SCHUSTER et al., 2001).

The main mineral assemblage is garnet + biotite + muscovite + plagioclase + quartz + staurolite + andalusite in the andalusite zone and garnet (1+2) + biotite + muscovite + plagioclase + quartz + sillimanite in the sillimanite zone. Garnets show continuous as well as discontinuous zoning in their chemical composition. Differences in the discontinuous zoned garnets indicate two stages of mineral growth: garnet cores, which probably grew during the Variscan event and garnet rims, which most likely represent the subsequent Permian overprint. In sillimanite-bearing samples the Permian metamorphic event was verified with geochronological data of micas. Ar-Ar dating on muscovites gave ages of 190 to 206 Ma what is interpreted as a typical cooling age of the Permian metamorphic event (SCHUSTER et al., 2001). First own electron microprobe measurements of monazites in sillimanite-bearing metapelites yielded Permian ages between 240 and 260 Ma as well as older ages between 310 and 370 Ma which can be attributed to the Variscan event.

Thermobarometric calculations with THERMOCALC v. 3.21 (HOLLAND & POWELL, 1998) yielded *P-T* conditions of the andalusite-bearing metapelites of 450–550°C and 0.38–0.57 GPa. In the sillimanite-bearing metapelites the *P-T* conditions are slightly higher with temperatures around 600–650°C and pressures of 0.44–0.56 GPa. Thermometric results obtained with the Ti-in-biotite geothermometer (HENRY et al., 2005) confirm the already obtained temperatures.

The obtained *P-T* data are very similar to areas like the pre-Alpine Strieden Unit in the Kreuzeck area to the east (HOKE, 1990).

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THE SEARCH FOR EARLY VARISCAN HIGH-P METAMORPHISM IN THE MOLDANUBIAN: THERMOBAROMETRY OF GRANULITES FROM THE BAVARIAN FOREST, SOUTHERN BOHEMIAN MASSIF, BAVARIA

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The Bavarian Forest is located at the southern rim of the Bohemian Massif between the Danube and the Bohemian Forest in Bavaria, Germany, and belongs to the Moldanubian Unit. The Variscan evolution in the Moldanubian sector consists of two distinct tectonometamorphic phases called the Moravo-Moldanubian-Phase (345-330 Ma) and the Bavarian Phase (330-315 Ma). While the Moravo-Moldanubian-Phase is associated with high-*P-T* conditions, the Bavarian Phase is defined by a significant reheating which was triggered by a Late Variscan delamination of mantle lithosphere (FINGER et al., 2007). In order to look for possible Variscan high-*P* relicts, garnet-bearing metapelitic and metabasic samples from the localities Grögöd and Aubach, near Passau were sampled. The samples belong to the Kropfmühl Unit which is a part of the Variegated (Bunte) Series. Grögöd is situated in the Bavarian Terrane which was overprinted respectively reheated during the Bavarian Phase (*LP-HT* regional metamorphism) at around 325 Ma. The metapelitic rocks contain the mineral assemblage garnet + sillimanite + K-feldspar + plagioclase + quartz + biotite + graphite ± cordierite and no evidence for high-*P* relicts (e.g. kyanite) were found so far. Multi-equilibrium thermobarometric calculations, using THERMOCALC v. 3.21 and Ti-Bt-thermometry of the metapelites yielded pressures ranging from 5-6 kbar and temperatures of 700-800°C. The mineral assemblage of the metabasites is clinopyroxene + amphibole + biotite + plagioclase + K-feldspar + spinel + ilmenite + quartz, but we are still looking for garnet-bearing metabasic rocks, since these samples might provide more information about the earlier stage of Variscan metamorphism. Thermobarometry of these samples, using THERMOCALC v. 3.21 and Ti-in-biotite-thermometry yielded *P-T* conditions of 500-750°C and 4-7 kbar so far. Furthermore granulites, from the locality Aubach were taken. These granulites contain the mineral assemblage garnet + biotite + cordierite + spinel (hercynite) + sillimanite + K-feldspar + rutile + ilmenite± plagioclase. Thermobarometric data are not available at the moment. Although the so far obtained *P-T* data correlate well with the late-Variscan *P-T* estimates (FINGER et al., 2007), the search for possible early Variscan high-*P* relicts continues!

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OPHIOLITES OF THE UKRAINIAN CARPATHIANS – NEW INSIGHTS INTO THE PROBLEM

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Since the first description of ophiolites from the Ukrainian Carpathians there has been an ongoing debate on the origin of these ultrabasic rocks. Initially, they were considered as ophiolites, which were thought to be a manifestation of basic geosyncline magmatism, later "ophiolite complexes", the initial magmatism before folding. Even later ophiolites in the Ukrainian Carpathians were interpreted as the remnants of the oceanic lithosphere formed during seafloor spreading. In the Ukrainian Carpathians more than ten types of ophiolite occurrences are distinguished nowadays, which were formed in different geodynamic situations. However, it is not clear exactly, that which parts of the oceanic lithosphere are represented by these ophiolite associations. The occurrence of an entire section of the ophiolite complex is not typical for the Ukrainian Carpathians. They occur only as incomplete fragments of the whole sequence – ultramafics, gabbroids, basalts, diabases and associated marine sediments formed in various environments. Studies of magmatic rocks of ophiolite association of Triassic to Lower Cretaceous age are of great importance for the geodynamic reconstruction of the initial stage of the development of the Carpathians. In connection with allochtonous occurrence of the ophiolites it is necessary to investigate their mineralogical-geochemical features. Peridotites are represented by lherzolites, serpentinized lherzolites, serpentinites. The studies have revealed a number of peculiarities which are characteristic for them only. In particular, they differ by the low values of Na_2O, K_2O, SiO_2, TiO_2, moderate FeO* and increased MgO values, which corresponds to the chemistry of Alpine-type peridotites and ultramafic parts of the ocean floor. Also one can observe a low concentration of the compatible trace elements as Cr, Ni and Co in lherzolites and serpentinites, which have an order of magnitude lower concentrations than the standard values of this rock type (Cr – 246 g/t, Ni – 136 g/t, Co – 58 g/t). Exactly the opposite trend is valid for lithophile elements: the concentration of Ba is high – 80 g/t, that can be connected with a high degree of alteration. The concentration of Cu and Zr is low as compared to their crustal abundances (Cu – 10 g/t, Zr – 6 g/t). This picture can be explained by the intensive serpentinization of rocks, because, based on the composition of primary mafic minerals: the high mg-numbers of olivine and pyroxene $((Mg_{1,84}Fe_{0,19})_{2,03}(Si_{0,98}O_4)$, Fo 92%, Fa 6%, other 2%) the presence of the jadeite component in clinopyroxene $((Ca_{0,73}Na_{0,12}Fe_{0,08})_{0,93}(Mg_{0,82}Al_{0,20}Cr_{0,03}Ti_{0,01})_{1,06}$ $[(Si_{1,89}Al_{0,11})_2O_6]$, Di 73%, Jd 12%, other 15%), as well as the presence of accessory spinel, hyperbasites correspond to the typical lherzolite of the upper mantle. Basaltic rocks of the ophiolite complex show a low degree of differentiation, normal or slightly increased alkali contents, sodium seriality, increased alumina contents that corresponds to the oceanic type basaltic rocks. But decreased content of compatible trace elements (Cr, Ni, Co) and depletion in lithophile elements (Zr, Ba, Sr) suggest that they are not the products of the MOR, but they probably were formed by dispersed spreading from a non-depleted mantle source.

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RELATIONSHIP OF RADIOACTIVITY AND GEOLOGY IN THE CENTRAL HUNGARIAN REGION (PEST COUNTY)

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The major source of natural ionizing radiation is the Earth's crust because of the high concentration of such radioactive elements as uranium, thorium and potassium. A recent study revealed the average concentration of U, Th and K in Hungarian soils, which was found 2.8 ppm, 7.4 ppm and 1.3 wt%, respectively (UNSCEAR, 2000).

The main aim of this study is to determine the radioactivity of the widespread geological formations of central Hungary on the example of different soil profiles collected in the framework of a countywide soil survey from Pest County (VÁRALLYAY et al., 1995). Representative samples were collected at 43 localities in the area from several depths of maximum 150 cm depending on the soil profiles. The specific activity of uranium, thorium and potassium were measured using HPGe gamma-spectroscopy technique, which provided average concentrations of 2.5 ppm, 4.9 ppm and 0.8 wt% for the set of samples, respectively. Considering that the soil type is strongly related to the underlying rocks, the obtained activity values were assigned to geological formations to create U, Th and K distribution maps.

TIKHOMIROV (1966) compiled gamma dose rate maps of Hungary at specific energies corresponding to uranium, thorium and potassium obtained by airborne gamma spectroscopy. The comparison of these maps for Pest County to the results of this study in many cases revealed significant similarities, which provide an opportunity to link radioactivity to exact geological formations. In 70% of the cases the validity of uranium and thorium anomalies were supported by our in situ measurements. However, a possible explanation for the observed differences may indicate that the anomalies are not related to the geological structure.

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MINERALOGY AND ORIGIN OF THE PISKANJA BORATE DEPOSIT (JARANDOL BASIN, SERBIA)

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The Miocene lacustrine Jarandol Basin (located in the Vardar-zone, Serbia) hosts magnesite bodies, borate beds and coal seams that are interbedded with tuffaceous rocks, claystones and marls (OBRADOVIĆ et al., 1992). Two borate deposits are known in the basin; Piskanja (geological reserve: 7.5 Mt, 39% B_2O_3), which is known only from drillings, while Pobrdje (geological reserve: 250 000 t, 37% B_2O_3) is known from surface outcrops as well.

During this work a drillcore from Piskanja borate deposit was analyzed. Representative samples from the borate beds and the host rocks (sedimentary rocks e.g. dolomitic travertines, claystones, shales) were collected in order to make macroscopic and microscopic analysis and fluid inclusion study. Recognizing the borate minerals in thin sections was fairly difficult so XRD-method was needed to use to determine the different types of borate minerals.

The borate beds (thickness is about 3.5–4.5 m) mainly consist of Ca, Na-Ca and Sr borate minerals (such as colemanite, howlite, nobleite, jarandolite, ulexite, probetite, tuzlaite, hydroboracite, studenitsite, strontioginorite and veatchite). The borate formation and alteration process mainly depends on the ion concentration, ion activity, pH and temperature of the lake from which the minerals precipitated (CHRIST et al., 1967; HELVACI, 2005). These borate minerals could precipitate from a quite low temperature solution and also easily transform one into another. Field and textural evidences clearly indicated the following mineral forming sequence: Ca borate -> Ca-Na borate -> Sr borate, which caused a zonational appearance of the borate body. This zonation is proved also by the geochemical data.

Fluid inclusion study was carried out on colemanite crystals. According to the results the solution, from which borates precipitated, can be modelled in a $NaCl-CaCl_2-H_2O$ system with a very high, 6.56 to 12.89% bulk salinity. This suggests a playa-lake type environment during the formation of the borates, though this range of salinities is a quite high, but not impossible value for a simple evaporation process. However, an external factor might have influenced the increase of boron and other ion concentration of the lake.

All the observations suggest that Piskanja Borate Deposit was formed in a playa lake, where other important conditions like increased concentration of boron in the lake in relation to volcanic activity, thermal springs near the area of the volcanism, arid to semi-arid conditions and a lake water with pH between 8.8 and 11 were also essential. The process can be compared to the formation of evaporate deposits.

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COMPARISON OF TWO RADON AND THORON MAPPING METHODS

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Radon (^{222}Rn) and thoron (^{220}Rn) isotopes are responsible for 52% of the total annual effective (radioactive) dose of a man living in average environment (UNSCEAR, 2000). The inhalation of these radioactive isotopes and their short lived daughters may cause lung cancer (e.g. BOCHICCHIO, 2008). Main sources of indoor radon and thoron are (1) the uranium- (radium-) and thorium-bearing soil constituents below the basement of buildings and (2) the uranium- (radium-) and thorium-bearing raw (clay, sand, sandstone) and additive components (fly ash, coal slag) in building materials.

Radon and thoron potential is a good indicator of the presence of radioactive materials in geological environments, too. Generally, mapping of radon and thoron potential is based on soil gas concentration measurements (e.g. USA – GATES & GUNDERSEN, 1992; Germany – KEMSKI et al., 2001). Another method, based on measurements of exhalation rates of soil samples in laboratory, was already tested in Pest County, Hungary (SZABÓ et al., 2009). The comparison of these two different methods became available on the basis of measurements of in situ soil gas concentrations and that of exhalation rates of soil samples from the Zsámbék basin, western part of Pest County.

Radon and thoron concentrations in soil gas were measured using RAD7 radon detector and soil probe at 10 sites of a 40 km^2 area in the Zsámbék basin, at an average depth of 75 cm (according to GATES & GUNDERSEN, 1992). Parallel radon and thoron exhalation rates measurements were done by accumulation chamber technique on 36 soil samples. These samples were collected from the same 10 sites by drilling to maximum 4.5 m and were separated from each other, based on their physical properties (e.g. colour and consistence). Data of upper 2 m is considered to be responsible for indoor radon. Radon concentrations in the soil gas at the depth of 75 cm show a good correlation (0.77) with results of exhalation rates measurements. This suggests that both of these radon mapping methods give reasonable values and may be used with success in future radon mapping studies.

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METASOMATIC IMPRINTS BELOW THE EASTERN TRANSYLVANIAN BASIN – AMPHIBOLES IN THE UPPER MANTLE XENOLITHS

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In the Carpathian–Pannonian Region (CPR) there are many places where alkaline-basaltic volcanism was developed during the Neogene – Quaternary period but only five of these volcanic fields are of xenolith bearing. The Perşani Mountain is situated in the easternmost and youngest Plio-Pleistocene alkaline basaltic volcanic field of the CPR, in the Eastern Transylvanian Basin (ETB). This alkaline basalt contains a lot of peridotite, pyroxenite xenoliths and various megacrysts (clinopyroxene, amphibole). The presence of amphiboles as megacrysts, as well as vein forming phases or interstitial minerals between constituent phases of peridotites and pyroxenites is a very common feature in the ETB. They are indicative of a clear melt-mantle interactiom. Chemistry of the studied vein and interstitial amphiboles shows differences in the function of their textural position. The interstitial amphiboles are enriched in Mg and Cr, whereas the vein amphiboles show elevated K, Ti and Fe content. These characteristics might be related to the influence of the wall rock.

Behind amphiboles, rarely apatites and phlogopites can be found in pyroxenites hosting large amounts of fluid inclusions. These fluid inclusions are present as intergranular secondary inclusion trails crosscutting the constituent minerals. They show negative crystal shape ranging 5 to 30 microns in size and possess one, probably CO_2-rich liquid phase at ambient conditions. The presence of these fluids and the chemical variation of the texturally defined amphiboles indicate a complex metasomatic history at the shallow lithospheric mantle beneath the ETB as suggested previously be e.g. SZABÓ et al. (2004). The main aim of this study is to shed light on the details of the general evolution of the lithospheric mantle beneath the studied area by textural and major element geochemical data of amphibole and coexisting clinopyroxene, as well as reconstruction of retrograde and metasomatic reactions in the mantle.

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OCCURRENCE OF CHROME-KYANITE IN ECLOGITES FROM POHORJE, SLOVENIA

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The Pohorje Mountains (Slovenia) are part of the Austroalpine Basement (Eastern Alps) and show eo-Alpine eclogite to ultra-high-pressure facies metamorphic conditions (JANAK et al., 2006) with subsequent amphibolite facies retrogression. Some eclogites of this region show rare chromium-bearing turquoise coloured kyanites, which are focus of this study. The investigated kyanite-eclogites comprise the mineral assemblage Omph – Grt – Spl – Ky – Crn – Zo – retrograde Amph and Pl. Cr-bearing kyanite only occurs near Cr-spinel. With increasing distance to the Cr-spinel the content in chromium in kyanite decreases. Fig. 1 shows a back-scattered electron (left side) and a Cr distribution image (right side) where the content of Cr in kyanite is decreasing from the centre to the outer parts of the image. Cr_2O_3 in kyanite reaches up to 8 wt% in the immediate vicinity to the spinel. Surrounding pyroxenes and amphiboles are also showing increased Cr_2O_3 contents close to Cr-spinel.

Geochemically these eclogites are characterized by noticeable amounts of chromium (up to 4900 ppm) in bulk composition. Furthermore high concentrations of MgO (up to 15%) and Ni (up to 460 ppm) as well as high contents in Al_2O_3 (up to 23%) and low ones in SiO_2 (43%) are typical for these rocks. In addition CaO and Al_2O_3 increase with decreasing MgO. These facts suggest that the protolith was an olivine, plagioclase and spinel bearing cumulate. The association of eclogite facies cumulates with ultramafic rocks indicate that the south-eastern part of the Koralpe-Pohorje mountain range consists of basal parts of an ancient oceanic crust.

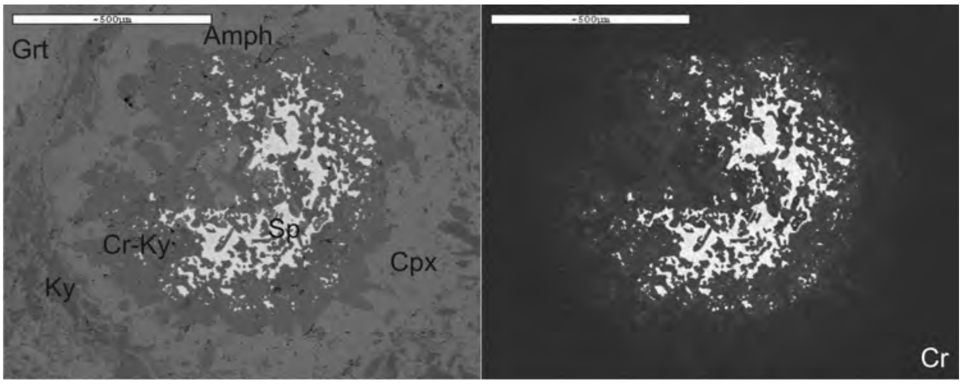

Figure 1. Reaction textures around chromium spinel with phases of ky, crn, amph and cpx (left: BSE image, right: Cr-distribution map)

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FLUID INCLUSION MICROTHERMOMETRY AT THE MIDUK PORPHYRY COPPER DEPOSIT, KERMAN PROVINCE, IRAN

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The Miduk porphyry copper deposit is located 85 km north-west of the Sarcheshmeh porphyry copper deposit in Kerman province. The deposit is hosted by Eocene volcanic rocks of andesite-basalt composition and the porphyry-type mineralization is associated with two calc-alkaline intrusive phases (P_1 and Miduk porphyry) of Miocene age. Five hypogene alteration zones at the Miduk deposit are distinguished including magnetite-rich potassic, potassic, potassic-phyllic, phyllic and propylitic. The high intensity of mineralization occurs as disseminated and stockwork in the Miduk porphyry intrusive phase. On the basis of shape and number of phases, five major fluid inclusion types have been identified in quartz crystals including multiphase brine, opaque-bearing brine, simple brine, vapour-rich and liquid-rich inclusions. Based on the petrography and crosscutting relationship, the multiphase brine inclusions (halite + multiple opaque and transparent solid phases) are formed in the early stage of deposit with potassic alteration zone. The highest homogenization temperature and salinity (450–500°C, 50–60 wt% NaCl) are present in this type of inclusions. The final homogenization temperature and salinity of opaque-bearing brine inclusions is 400–500°C and 40–60 wt% NaCl, respectively. Boiling identified at the Miduk porphyry copper deposit by coexisting opaque-bearing brine and vapour-rich inclusions that constrained copper deposition at a temperature range of 400–500°C and pressure of 200–400 bar. The final homogenization temperature of majority of brine inclusions is indicated by halite disappearance and displays a positive correlation between final homogenization temperature and salinity of these inclusion types at the Miduk deposit. On the basis of stratigraphy sequences and fluid inclusion data, the emplacement depth of the Miduk deposit is about 2.5 km.

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TRACES OF STRUCTURAL H_2O MOLECULES IN BARYTE

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It is now well established that hydrogen is a common trace constituent of many nominally anhydrous minerals. The major part of studies on this topic deals with silicate phases, especially those that constitute the Earth's mantle and could thus represent an important reservoir of hydrogen (BERAN & LIBOWITZKY, 2006). Comparatively few studies have been devoted to non-silicate mineral species.

In this work, the OH stretching vibrational region of baryte, a commonly occurring and industrially important mineral, has been subject to thorough IR spectroscopic investigations. Doubly polished thin slabs cut parallel to (001) and (100) have been made from a series of twelve samples from geographically and genetically different occurrences. These have been studied by means of polarized and unpolarized IR radiation.

Apart from a distinct peak group with a constant appearance at 3020 cm^{-1}, assigned to sulphate overtones and/or combination modes, four weaker bands can be distinguished in the 3100–3300 cm^{-1} spectral region. These can be divided into two pairs, one at 3115 and 3155 cm^{-1} and the other at 3220 and 3280 cm^{-1}. Within both pairs, the maximum absorption directions among the two bands are perpendicular to each other.

This type of pleochroic behaviour, as well as the wavenumber difference of about 50 cm^{-1} between the bands within each pair, corresponds perfectly to the ν_1 and ν_3 symmetric and antisymmetric stretching vibrations of H_2O molecules contained in the structure of minerals such as beryl and nepheline (WOOD & NASSAU, 1967; BERAN & ROSSMAN, 1989). Based on these findings, each of the two pairs of bands in baryte is interpreted as evidence of a structurally incorporated H_2O molecule residing on vacant Ba-sites. The lower-energetic band in each pair represents the symmetric, and the higher-energetic one the antisymmetric stretching vibration of H_2O.

Generally, the water contents do not exceed 4 wt.ppm, the usual values range from 1.7 to 3.5 wt.ppm. Samples of supergene baryte appear to have lower water contents than those of hydrothermal origin.

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Nd, Pb ISOTOPE RATIOS AND TRACE ELEMENT SIGNATURES OF THE ALBANIAN VOLCANIC ROCKS: MAGMA SOURCE IDENTIFICATION

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Based on the geochemical characteristics of the volcanic rocks, three phases of the Mesozoic geodynamic evolution in Albanides can be distinguished: 1) a rifting phase of the Early Triassic (Permo-Triassic?) to Middle Triassic, 2) spreading phase of the Middle Triassic to Middle Jurassic and 3) a new spreading phase of the Middle Jurassic.

During the Early Triassic in Albania volcanic rocks were formed, derived from an enriched mantle source (EMII) in the continental rifting phase. These volcanics are characterized by negative εNd values (–1.91), high Th, Zr and REE (20–100 times chondrites) content and marked negative Eu, Ti and Nb-Ta anomalies. Middle Triassic volcanism is characterized by low εNd values (+0.69 to +1.98), high Zr and REE (3–20 time chondrites) content, a very low Th content, but no marked Eu and Nb-Ta anomalies. The magma source is an enriched mantle of type EMI. For all these volcanics crust contamination component is evident from the low εNd values and the fractionation of REE, LREE being clearly enriched compared to HREE.

Subsequently, in the spreading phase, the oceanic crust evolved to the basalts of the volcano-sedimentary series (T_2–J_1), characterized by higher εNdi values, ranging from +6.5 to +7.7, a REE content about 10 times chondrites, flat REE patterns to LREE depleted, no Nb-Ta negative anomalies, low Th contents (0.2 ppm, on average) and a relatively high (1.3 %) TiO_2 content. These basalts were probably formed in an opening of a back-arc basin context (BABBs) from a depleted mantle magma source (DM). The same magma source produces the basalts of Jurassic western ophiolite type (J_2 basaltic series) that have the same geochemical characteristics as the basalts of the volcano-sedimentary series.

Jurassic volcanics of the eastern ophiolite type (J_2 basalt-andesitic series) show the same geodynamic conditions (i.e. BABBs) but have a distinctively different and more depleted magma source (DMM) as evidenced by the lower REE, Ti and Zr content, though, the εNdi values (+5.58 to +6.94) are quite similar. Significantly lower-than-chondrite Zr/Hf ratios may be explained by a previous zircon fractionation, as zircon mineral is the primary reservoir for both Zr and Hf and preferentially incorporates Zr.

The Pb isotope ratios of all rocks studied do not testify to the existence of an HIMU component in the magma source. The observed trend, from OIB volcanism in the southern part of the Eastern Mediterranean (Cyprus) to back-arc basin basalts associated with arc-related and with in-plate volcanism in the northern part (Greece), seems to evolve in Albania with a decreasing role or absence of oceanic within-plate volcanism (enrichment by HIMU source).

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OPTICALLY STIMULATED LUMINESCENCE DATING OF SEDIMENTS ON ARCHAEOLOGICAL SITES

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Luminescence dating method gives the time elapsed since mineral grains were last exposed to sufficient heat or sunlight. It has been applied in archaeological studies from the early 1960s to date fired pottery by thermoluminescence (TL). Since the 1980s optically stimulated luminescence (OSL) was also established to determine e.g. depositional age of sediments, and age of fired potteries, bricks, and burnt stones.

The aim of the OSL dating in the Geological Institute of Hungary is to give chronostratigraphic framework of Late Pleistocene and Holocene sedimentation and landscape evolution. First of all we study different fluvial and aeolian sediments. Among them there are some samples from historical periods, and archaeological sites too.

OSL-measurements were made by using a Risø TL/OSL DA-15C/D automatic reader with a calibrated 90Sr/90Y beta source on 100-200 µm quartz grains extracted from sediments. Blue light optical stimulation and Single-Aliquot Regenerative-dose (SAR) protocol was applied to estimate equivalent doses (WINTLE & MURRAY, 2006). Environmental dose rates were calculated based on laboratory high-resolution gamma spectrometry measurements of sediments surrounding the OSL samples in the Eötvös Loránd Geophysical Institute of Hungary.

Dated fluvial sediments of near past flood events at Tisza and Hármas-Körös rivers in south-east of Hungary deposited in the 19-20th centuries according to their minimum OSL ages (THAMÓNÉ BOZSÓ et al., 2007). Fluvial deposits at the Danube River study site near Vienna can be attributed to different periods ranging from Bronze Age to the 18th century. Fluvial sediments at the Ebro River are the deposits of Roman age and of the late 17th or early 18th century (FIEBIG et al., 2009). These OSL ages are internally as well as stratigraphically consistent and agreement with independent age control.

Sediments were dated from Nagytevel prehistoric quarry site (Bakony Mts.) where Upper Senonian flint was exploited and processed. Distribution data on archaeological sites indicate a Middle/Late Neolithic age for the bulk of the quarry operations (BIRÓ & REGENYE, 2007). There is a possibility for earlier use (Late Würm 3) of the material. The situation is very similar to the well known Sümeg flint mine. The new OSL ages seem to corroborate these observations.

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NEW DATA FOR THE ROMAN AGES SETTLEMENT HISTORY OF MISKOLC: ARCHAEOLOGICAL AND ARCHAEOMETRICAL INVESTIGATIONS

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During the spring and summer of 2007 excavations were carried out in Miskolc to investigate the Roman Age remains found there. The excavations, lead by András Gábor Szörényi (Herman Ottó Museum, Miskolc), were larger than the earlier exploration works carried out in the area. With the consent of the museum a part of the finds was investigated by mineralogical methods.

It was possible to classify the pottery finds into 12 groups based on the clay tempering techniques used. This indicates that the assemblage found was quite varied. Based on the type of rims, bases and substrate of the vessels a further classification is possible.

The first group according to this classification is of La Tène character. This indicates the survival of Celtic traditions in the region, such as the use of clay glaze, such as was found on more than one discovered vessel. A second group has finger tip impressions and flowerpot shaped pots, which indicate a Dacian component to the finds, or possibly a Carpathian Basin style. Germanic vessels make up the third group, they are characterized by the incised crossed lines, wavy line ware, and averted rim with raised shoulder found on the pottery. This style has been found to occur in South Poland, East Slovakia, Ukraine and Northeast Hungary. The fourth group of the finds is the Roman import pottery, which was also widespread in these regions. Its presence in the Miskolc area indicates the recovery of intensive trade after the Marcomannic wars. Terra sigillatas helped to date these objects between the end of the 2nd and the 3rd century AD.

On selected pottery and plaster samples mineralogical analyses were carried out. The investigations were made in the Institute of Mineralogy and Geology of the University of Miskolc. X-ray powder diffraction (XRPD) investigations and polarization optical microscopy (POM) analyses were performed. The aim was to determine the clay minerals of the vessels and the firing temperature at which they were prepared, by XRPD. Fabric of pottery was characterized by POM.

Based on the appearance of gehlenite–akermanite, a sample of plaster was deduced to be from the wall of a pottery kiln (~700–800ºC). In another case it was found that the interior of a storage vessel was made from clay of different composition than the clay from the external part. Another vessel was found to contain exclusively angular quartz grains, which are supposed to be of man-ground origin. Metamorphic lithic fragments, mainly of polycrystalline quartz, have also been found.

However, without reference materials, it was not possible to determine the origin of raw materials, or vessels. Based on the logical assumption that the closest raw material occurrences are likely to be the sources for the applied raw materials, in the future it will be possible to deduce the origin of ceramic materials and artifacts.

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APATITE AS A MONITOR OF TRACE ELEMENT VARIATIONS IN A CONTACT AUREOLE: COMBINING EXPERIMENTAL AND PETROLOGICAL INVESTIGATIONS FROM THE BRIXEN GRANITE CONTACT AUREOLE

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The distribution of trace elements can provide important information of the metamorphic evolution of samples. In the majority of magmatic and metamorphic rocks most of the REE, Y, Th, U and other HFSE are incorporated into accessory minerals such as apatite, monazite/xenotime and allanite. The analyses of trace element contents in accessory minerals from different geological settings (magmatic as well as metamorphic) as a function of pressure, temperature, mineral reactions, whole-rock and fluid composition have recently obtained a lot of research attention (e.g. CHERNIAK, 2000; CORRIE & KOHN, 2008; FINGER & KRENN, 2007; JANOTS et al., 2008).

The variation of the minor and trace element contents of accessory phases from the metapelitic contact aureole at the southern rim of the Brixen granite was described by THÖNY (2008). These investigations on the minor element variation in apatite from samples of the contact aureole show distinct trends in accordance with increasing metamorphic grade. The elements of interest were Cl, F, Mn, Y+REE, Si, and Na. Minor element variations in apatite do not vary consistently but a distinct increase towards the contact was observed in Mn, Cl and ΣREE + Y.

The aim of this investigation is to obtain complementary quantitative data on the modification of the chemical composition of apatite from previous experimental investigations using natural quartzphyllites from the Southalpine Basement, carried out by WYHLIDAL (2008). The experiments were conducted at 0.3 GPa and a temperature range between 580°C to 780°C. These experiments will provide additional data on the trace element distribution in metapelites as a function of progressive temperatures. Preliminary apatite data from the H_2O-bearing experiments indicate a slight increase in the REE with increasing temperature, which can be explained by the continuous breakdown of garnet. On the other hand the content of Y in apatite decreases as a consequence of new formed monazite. It is therefore planned in this investigation to correlate mineral reactions and the role of coexisting phases in a controlled *P-T* setting with natural observations in order to understand the nature of trace element incorporation in natural apatites (FINGER & KRENN, 2007; HUGHES & RAKOVAN, 2002; HARLOV & FÖRSTER, 2003).

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SOLUBILITY OF ACCESSORY MINERALS ($CePO_4$, YPO_4) IN H_2O, H_2O-NaCl AND H_2O-NaF AT 800°C AND 1 GPa: IMPLICATIONS FOR REE TRANSPORT DURING HIGH-GRADE METAMORPHISM

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Monazite ($CePO_4$) and xenotime (YPO_4) are important accessory minerals because they host REE and Y and are useful for geochronology. Although the distribution of REE during high-grade metamorphism has long been a subject of intense research (e.g. PAN and FLEET, 1996), experimental investigations on monazite solubility at high *P-T* are scarce (AYERS & WATSON, 1991). It is therefore essential to understand their behavior during high-grade metasomatic processes. To constrain solubilities at high *P* and *T*, we carried out weight-loss experiments on synthetic single crystals of each phosphate at 800°C, 1 GPa, with H_2O, H_2O-NaCl or H_2O-NaF (methods of MANNING & BOETTCHER, 1994, TROPPER & MANNING, 2005, 2007). Results indicate that the molality (*m*, mol/kg H_2O) of $CePO_4$ and YPO_4 dissolved in pure H_2O is very low ($CePO_4$: 0.0006 *m*, YPO_4: 0.0002 *m*) but that $CePO_4$ solubility increases strongly with increasing NaCl to 0.021 *m* at 40 mol% NaCl, similar to fluorite (TROPPER and MANNING, 2007) and calcite (NEWTON & MANNING, 2004). Solubility of YPO_4 increases only moderately, to 0.0037 *m* at the same NaCl content. Thus $CePO_4$ shows a stronger solubility enhancement by NaCl than YPO_4. Data from the NaF-H_2O system show an enormous increase in solubility of both phosphates: $CePO_4$ and YPO_4 solubility increase to 0.22 and 0.49 *m* in only 10 mol% NaF; YPO_4 shows stronger solubility enhancement. The REE solubility data therefore support the previous indications that REE and Y mobility are strongly promoted by complexing with Cl and especially F in the aqueous phase (PAN & FLEET, 1996). Because F is readily partitioned into high-grade fluids, even small amounts of this element in metasediments will yield at least local REE metasomatism during devolatilization reactions associated with high-grade metamorphism.

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SALT MATTERS: EXPERIMENTAL INVESTIGATIONS OF THE TRANSFORMATION OF HIGH-GRADE METAPELITES AND GRANITES TO ECLOGITES AND THE ROLE OF BRINES IN SUBDUCTION ZONE PROCESSES

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A common feature of HP and UHP terranes is the subduction of lower crustal rocks to great depths. Investigations in the Bergen Area in Norway have shown that this process is triggered by fluids present during eclogite-facies metamorphism (e.g. AUSTRHEIM, 1987). Fluid inclusions in eclogite-facies minerals range from dilute solutions to chloride-rich brines and previous studies have shown that highly saline fluids occur in subduction zones, where continental material is involved. Key examples of these processes is exposed in the metapelites at Val Savenca and the metagranites of Monte Mucrone, both in the Sesia-Lanzo Zone, Italy, where Eo-Alpine eclogite-facies metamorphism and fluid flow led to partial transformation of Variscan amphibolite-eclogite facies metapelites (garnet + biotite + sillimanite + K-feldspar + plagioclase + quartz) and metagranites (garnet + biotite + K-feldspar + plagioclase + quartz) to zoisite ± jadeite + kyanite + phengite + quartz with associated jadeite veins. Application of the K-feldspar – jadeite – quartz barometry to the plagioclase domains yields P-T conditions of 1.7 – 2.1 GPa at 600°C and low $a(H_2O)$ of 0.3-0.6 (TROPPER et al., 1999). In order to understand the role of brines in the mineralogical and textural transformation exposed at Val Savenca and Monte Mucrone, we carried out piston-cylinder experiments with a fresh, natural orthogneiss granulite from the Moldanubic Unit in upper Austria with the assemblage garnet + biotite + K-feldspar + plagioclase + quarz. The experiments were conducted in the presence of H_2O-NaCl fluids at 600°C and 2 GPa for 2-4 days. The fluids had the compositions $X(H_2O)$ = 1.0, 0.90, 0.80 and 0.70, and the fluid/rock ratio varied from 1:1 to 1:10. Oxygen fugacity was buffered at NNO and HM in most experiments. The data from the experiments clearly show increasing reaction progress with increasing salinity in the fluid. At $X(H_2O)$ = 1.0 experiments, no visible reaction occurred, whereas at $X(H_2O)$ = 0.7 experiment, the protolith assemblage is almost completely replaced by large (up to 100 m long), euhedral crystals of the assemblage jadeite + phengite + quartz thus biotite breaks down along the reaction: 3Anorthite + 2K-feldspar + Phlogopite + H_2O = 3Diopside + 3Muscovite. Clinopyroxene composition also changes as a function of NaCl content in the fluid. Omphacite forms in the experiments at $X(H_2O)$ = 1, in all other experiments, only jadeite occurs. Biotite, K-feldspar and quartz are the only relict phases. Although no mineralogical change with buffering occurred, the mineral assemblage in the HM experiments is Fe-richer. The experiments also show a strong indication of Na-Ca exchange: the anorthite component of plagioclase goes readily into solution, producing zoisite needles only upon quench. These experiments so far show that the biotite breakdown reaction is similar to the one observed in the natural samples and that brines highly effective promote reaction progress in subduction zone processes.

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CHARACTERIZATION OF HYDROTHERMAL ALTERATION ASSEMBLAGES OF 'LOW-SULPHIDE' Cu-Ni-PGE MINERALIZATION (WISNER AREA, SUDBURY STRUCTURE, CANADA)

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One type of Cu-Ni-PGE occurrences in the footwall of the 1.85 Ga Sudbury Igneous Complex (SIC) is referred to as 'low-sulphide' system, in which sulphides occur as disseminations and stringers (FARROW et al., 2005). Despite the much lower sulphide contents compared to 'sharp-walled' massive veins, this mineralization type is extremely enriched in Pt and Pd. The association of hydrothermal processes to footwall mineralization has long been recognized (e.g. FARROW & WATKINSON, 1992; MOLNÁR et al., 2001), and recent studies suggest that they were probably entirely responsible for the formation of 'low-sulphide' systems (PÉNTEK et al., 2009). However, the importance of hydrous-silicate veining associated to 'low-sulphide' occurrences as a field exploration tool has not been recognized so far, and no detailed studies have focused on the zonation and gangue mineralogy of their alteration assemblages. We performed mapping of hydrothermal alteration related to recently discovered 'low-sulphide' occurrences in the footwall of the Wisner area (South and Southwest Zones) to address these questions also important from an economic standpoint.

In both areas, NW–SE to NNW–SSE striking extensional veining represents the Cu-Ni-PGE-bearing hydrothermal system once driven by the heat of the SIC. As an effect of fluid-rock interaction, the mineral assemblage may be dominated by actinolite (in mafic host rocks), or by epidote and quartz (in granitoid rocks). The great chemical similarity (high Ni, low K, predominance of Fe^{2+} over Fe^{3+}) of the actinolitic rim of zoned vein-filling amphiboles to actinolites in ore-bearing assemblages, and the occasionally anomalous PGE contents in veins suggest that actinolite veining is basically the 'precursor' of the main sulphide precipitation. Fluid inclusion petrography of the extensional quartz-chalcopyrite and epidote-quartz±feldspar veins also indicate a genetic link to the ore-bearing system.

Sulphide mineralization, mainly composed of chalcopyrite and millerite, occurs in veins or disseminations, which have wide rims of hydrous-silicates. Most important is the 'spongy' epidote, a poikilitic intergrowth of epidote and chalcopyrite, containing inclusions of platinum-group minerals. The assemblage also includes euhedral actinolite and chlorite (both Ni-bearing). The identification of this silicate assemblage is possible in hand specimen, and is a key for pointing out PGE-bearing samples even when their sulphide content is low.

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ACCESSORY RARE-ELEMENT (REE, Y, Zr, Th, Nb, Ta) MINERALS OF THE TURČOK A-TYPE METAGRANITE, GEMERIC UNIT, SLOVAKIA: TRACERS OF MAGMATIC TO METAMORPHIC EVOLUTION

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Rare element (REE, Y, Zr, Th, Nb, Ta) accessory minerals revealed their wide compositional variations and primary magmatic, post-magmatic to metamorphic evolution in the Turčok metagranite, the Gemeric Unit, Western Carpathians (eastern Slovakia). The metagranite shows hypersolvus A-type character and strong post-magmatic albitization and metamorphic overprint. The SHRIMP dating of primary magmatic zircon displays their post-Hercynian, Permian age (ca. 260 Ma).

Prismatic transparent zircon I with fine oscillatory zoning contains low Hf (0.8–1.4 wt% HfO_2, up to 0.01 apfu) and low REE, U and Th (usually up to 0.2 wt% of oxide). Dipyramidal metamict zircon II reveals distinctly higher Hf concentrations (2.0 to 3.8 wt% HfO_2, 0.05–0.08 apfu) and usually increased Th and U contents (up to 0.8 wt% ThO_2 and UO_2). Y_2O_3 contents vary between 0.1 to 1 wt% (0.02 apfu Y) in both zircon populations. Allanite-(Ce) shows 22-25 wt% REE_2O_3 (0.8–0.9 apfu REE) and low Y (0.2–0.3 wt% Y_2O_3, ca. 0.01 apfu Y). Xenotime-(Y) forms overgrowths/intergrowths with zircon II. Thorite appears intermediate compositions enriched in Y (6–8 wt% Y_2O_3, 0.14–0.19 apfu Y), REE (7–8 wt% REE_2O_3, 0.10–0.12 apfu REE), Zr (4.6–13 wt% ZrO_2, 0.10–0.26 apfu Zr), Al (2.5–3.6 wt% Al_2O_3, 0.13–0.17 apfu Al), and P (10–11 wt% P_2O_5, 0.33–0.39 apfu P). Monazite-(Ce) shows usually anhedral grains with low proportions of cheralite and huttonite molecules (0.0–1.3 wt% SiO_2, up to 0.05 apfu Si; and 0.04-4.3 wt% ThO_2, up to 0.04 apfu Th). The monazite EMPA dating indicates their mainly Alpine metamorphic origin. Hingganite-(Y) is enriched in REE and Ca, and depleted in Y and Fe in comparison to the gadolinite-(Y). Fergusonite-(beta)/samarskite-(Y) and especially aeschynite/polycrase-(Y) show increased P, Si and Al content. Both minerals show strong predominancy of Nb over Ta and very low Ta/(Ta+Nb) atomic ratio: 0.02 in fergusonite-(beta)/samarskite-(Y) and 0.05–0.06 in aeschynite/polycrase-(Y). Titanium contents are high in aeschynite/polycrase (20–25 wt% TiO_2; 0.76–0.90 apfu Ti) but low in fergusonite-(beta)/samarskite (2.5–4 wt% TiO_2, 0.07 to 0.1 apfu Ti).

Zircon I and allanite-(Ce) belong to primary magmatic phases. However, the late-magmatic to early subsolidus processes led to the formation of a more complex assemblage: zircon II, xenotime-(Y), thorite, gadolinite-hingganite-(Y), Nb-Ta-Y-REE-bearing oxide phases (fergusonite-(beta) or samarskite-(Y), aeschynite or polycrase-(Y), and Nb-rich rutile?), and possibly also part of monazite-(Ce). Moreover, formation of monazite-(Ce), as well as partial alteration of xenotime-(Y) and the Nb-Ta-REE minerals are probably connected with a younger, Alpine metamorphic overprint of the Turčok granite.

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DECOMPOSITION TEXTURES AFTER DRY THERMAL ANNEALING OF ZIRCON

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Zircon behaviour during annealing is an exciting topic because zircon is used in several high-temperature applications such as refractory bricks, thermal barrier coatings and experiments aimed to recrystallise radiation damaged zircon for various reasons. Although zircon is predicted to be stable up to ca. 1676 °C (e.g. BUTTERMAN & FOSTER, 1967), it is very common to observe decomposition into ZrO_2 and SiO_2 at significantly lower temperatures (e.g. KAISER et al., 2008). In this study zircon samples from diverse sources without and with secondary chemical alteration were heat treated at 1400 °C in air for 4 days. The temperature was chosen because it is sufficient to anneal radiation damage but far below the accepted solid-state decomposition temperature.

Post-anneal phases and textures reveal thermal decomposition of zircon into component oxides. The advancing stages of surface corrosion (Fig. 1a) and later the build-up of porous ZrO_2 crusts are reconstructed from the images of annealed unaltered zircon samples. The post-anneal textures on secondary altered samples are considerably different from their unaltered counterparts (Fig. 1b). The crucible material (Al_2O_3 vs. Pt) was found to have a strong influence on the extent of zircon breakdown, especially in the case of altered starting materials.

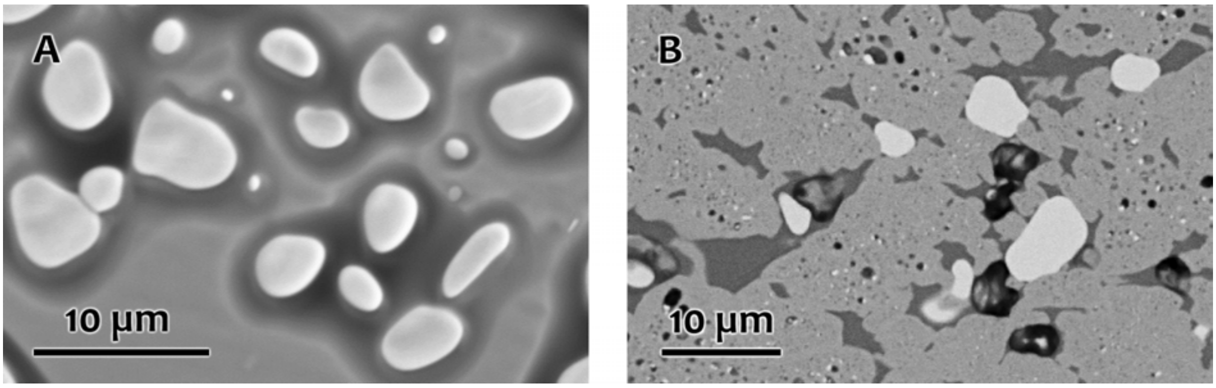

Figure 1. (A) surface corrosion on an annealed Sri Lankan gem zircon (M257). Rounded ZrO_2 grains (white) are seen in shallow pits, medium grey is zircon (BSE image). (B) Typical texture of an altered zircon (87165) annealed in a Pt crucible, showing coexisting zircon (mid-grey), ZrO_2 (white), amorphous silica (dark grey) and porosity (BSE image of a polished mount).

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PRE-ORE STAGE IN THE MADAN Pb-Zn DEPOSITS, SOUTH BULGARIA

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Pre-ore stage in the Pb-Zn deposits from Madan district, Central Rhodopes, is connected with formation of infiltration type reduced skarns consisting of highly manganoan clinopyroxenes and their subsequent alteration products. As a result of later hydrothermal activity associated with sulphide deposition, a retrograde postskarn paragenesis of silicate and carbonate minerals was formed. The composition and textures of the retrograde products are strongly influenced by the original skarns. Primary pyroxenes, affected by hydrothermal changes are the most suitable environment for localization of rich metasomatic Pb-Zn ores with economic importance. Madan deposits are among the largest Pb-Zn accumulations, associated with Mn skarns (EINAUDI et al., 1981). The skarn ore bodies are of variable morphology and size – stratiform, multilayered, irregular or mushroom shapes in cross section (BONEV, 2003).

The primary zoning of the manganoan skarns depends on the differing Mn/(Fe + Mg) ratio in the hedenbergite–johannsenite solid solution. Clinopyroxenes, proximal to the ore-conductive faults have higher Fe content, while those near the original marbles are mostly manganoan. Johannsenite prevails in the apical parts of the ledges and in the upper levels of the deposits as general. On the contrary, hedenbergite with different Mn-content occurs mainly in the deeper levels of the skarn-ore bodies (VASSILEVA, 2004). A thin outermost (Fe-free) rhodonite zone along the marble contact was formed as a late reaction product after johannsenite, as seen by the pyroxene-rhodonite mineral relationships and textures of replacement.

The overprinting of the retrograde paragenesis and subsequent ore deposition leads to a more complex secondary zoning in the replacement bodies. The lowering of temperature and pH of the fluids in the hydrothermal system leads to transformation of the primary clinopyroxenes and formation of highly manganoan association of pyroxenoids (rhodonite, bustamite and pyroxmangite), calcic and subcalcic amphiboles, manganilvaite and ilvaite, Mn-bearing chlorites and garnets as well as carbonate minerals. The Mn-dominant members of the johannsenite–hedenbergite solid solution are more stable in acid environment, as compared to the Fe-dominant ones. In the distal zones the johannsenite aggregates remain unaffected by the hydrothermal processes. On the contrary, the proximal Fe-enriched pyroxenes, typical for the inner parts, are easily and almost fully replaced by rich sulphide ores with massive texture. The degree of pyroxene replacement in the individual metasomatic ore bodies differs. Sometimes only relics of fresh and retrograde skarns are preserved.

The altered infiltration skarn bodies are a favorable environment for deposition of the high-grade Pb-Zn replacement ores. The extensive underground work and the detailed mining exploration showed that the metasomatic ores are fully enclosed within the contours of the primary skarn bodies, following their complex morphology.

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MADAN Pb-Zn SULPHIDE DEPOSITS AS PART OF THE ALPINE–BALKAN–CARPATHIAN–DINARIDE PROVINCE

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The Tertiary (~30Ma) hydrothermal Pb-Zn-(Ag) deposits in the Madan and Laki ore fields, Central Rhodopes comprise a part of the Alpine–Balkan–Carpathian–Dinaride province of the Alpine–Himalayan metallogenic belt. Known and exploited since ancient times these deposits are extensively mined during the last 50 years in more than 60 underground mines, producing over 100 Mt ores grading 2.54% Pb and 2.10% Zn (MILEV et al., 1996). The base-metal mineralization is hosted by the Rhodopian metamorphic core complex of the Madan Dome (various gneisses, amphibolites, mica schists and certain marble horizons).

The morphology of ore bodies comprises: (1) two types of steeply dipping zones – simple ore veins (1-3 m wide; to 7 km long) and mineralized stockwork zones; (2) gently sloping bed-like and irregular skarn-sulphide bodies in the intersections of ore veins with marble horizons. The deposits are structurally located along six subparallel NNW–SSE-striking (320-340°) faults. Fracture structures is controlling factor for the ways of movement of ascending fluids, and arising of open space favoring the ore deposition.

The stages of mineralization in the hydrothermal system include: (1) Pre-ore manganese clinopyroxene exoskarns; (2) Retrograde alteration of skarns by a Mn association of pyroxenoids, hydrous silicates and carbonate minerals; (3) Main quartz–sulphide stage T 260-350°C; (4) Carbonate–quartz assemblage with minor sulphides. Main ore minerals are galena, sphalerite, pyrite and chalcopyrite. Galena prevails over sphalerite in the veins, sphalerite is more abundant in the skarn ore bodies. Subordinate ore minerals are arsenopyrite, tennantite–tetrahedrite, pyrrhotite, sulphosalts of Ag, Bi and etc. The various ore textures characterize the mode and local conditions of deposition: open space filling (cutting veinlets, druses, crustifications, breccias) or replacement (impregnations, rhythmic-banded, radiate, massive).

Fluid chemistry determined from inclusions studies represents diluted, slightly acid (pH~6.5) Na-K aqueous solutions (4–5% wt.% salinity); mean Na:K:Ca ratio of 11:2:1; low CO_2-content in the vapour phase (BONEV et al., 2000). Stable isotope composition of the fluids (δD –40 to –80‰ and $\delta^{18}O$ 0 to -10‰) indicate predominantly meteoric origin of waters. $\delta^{34}S$ of sulphides (0–7‰) cannot discriminate between an igneous or crustal source. $^{87}Sr/^{86}Sr$ isotopes of barite (0.71126 to 0.70946) and Pb isotope ratios of galena ($^{206}Pb/^{204}Pb$ 18.68–18.75; $^{207}Pb/^{204}Pb$ 15.66–15.70; $^{208}Pb/^{204}Pb$ 38.86–39.05) reveal strong contribution from the host metamorphic rocks. Close spatial and temporal relationship of ores to silicic magmatism suggests a genetic connection. These deposits are among the largest Pb-Zn accumulations associated with manganoan skarns.

Acknowledgements: Part of this study was supported by The Bulgarian National Science Fund (DO1-904/MON)

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STUDY OF SILICATE MELT INCLUSIONS IN OLIVINE AND SPINEL PHENOCRYSTS IN ALKALINE BASALT FROM DALJEON-RI (POHANG, CENTRAL KOREA)

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Generally, silicate melt inclusions represent the melt composition at the time of entrapment. Therefore, silicate melt inclusions entrapped in different minerals that crystallized at different stages of magmatic evolution might preserve the composition of a continuously changing melt. The ~2 million years old alkaline basalt in Daljeon-ri (central South Korea) contains many hexagonal stone pillars, in which large amounts of silicate melt inclusions have been found enclosed in spinel and olivine phenocrysts. These silicate melt inclusions may provide unique opportunity to reconstruct the evolution path of the crystallizing mafic magma.

The studied alkaline basalt has porphyritic texture and contains euhedral and subhedral phenocrysts of olivine (0.5–5.0 mm in size) with forsteritic (Fo = 84–86) composition, clinopyroxene, Cr-rich spinel (cr# = 23–24) and plagioclase. The groundmass also consists of microphenocrysts of olivine, clinopyroxene, spinel, plagioclase and significant amount of glass.

A large amount of silicate melt inclusions have been found enclosed in the core and along healed fractures of olivine and spinel phenocrysts. These inclusions, usually, have negative crystal shape with sizes ranging from 5 to 100 µm in diameter. Both spinel-hosted and olivine-hosted silicate melt inclusions contain Ni-Cu-rich sulphide blebs, Al-Mg-rich spinel, zoned, Si-poor, Al-Ti-Mg-Na-rich clinopyroxene daughter phases, Si-Al-rich residual glass and fluid bubble(s) (Fig. 1). Based on the preliminary results, obtained from petrographic observations and geochemical analyses, we assume that the silicate melt inclusions of olivine and spinel phenocrysts were entrapped at the early stages of the crystallization process and their bulk compositions are representatives for the primary magma.

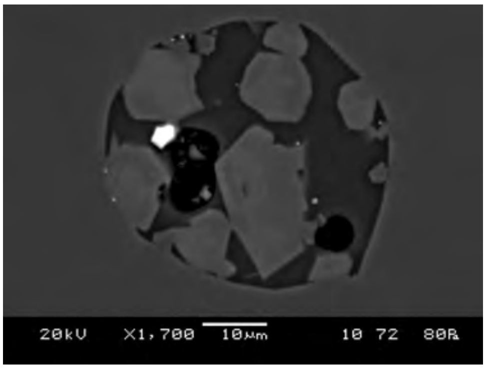

Figure 1. Olivine-hosted SMI consisting of sulphide blebs (white), spinel (middle gray), large, zoned clinopyroxene (dark and light gray), residual glass (dark gray) and fluid bubbles (black holes). BSE image

ASSOCIATION OF H_2S – ANKERITE – LATE PYRITE SUGGESTS ACTIVE THERMOCHEMICAL SULPHATE REDUCTION BELOW 5 KM IN THE PANNONIAN BASIN, SE HUNGARY

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Drilling revealed presence of natural gas unusually rich in H_2S and volatile organo-sulphur compounds (up to $n\times100$ and 2000 ppm, respectively) in the deep part of the Makó Trough (SE-Hungary). $\delta^{34}S$ of the H_2S is 32.5‰ in one gas sample.

Microscopical, chemical, isotopic, Rock-Eval and thermal investigations have been undertaken on oil well core samples for clarifying the origin of these unpleasant gases. Results show the dichotomy of the Pannonian sequence in respect of geochemistry and mineralogy of sulphur.

Above 4.5-5 km sulphur content is <0.1%, $\delta^{34}S$ ranges between –7.5 to 10.5‰, and pyrite occurs in framboidal and cubic forms, giving one peak on DTA curves at around 405°C. The low sulphur content suggests that the Pannon Lake was poor in sulphate during deposition of the corresponding strata. Pyrite is of early diagenetic, bacterial origin.

The deeper part of the sequence contains up to 2.1% isotopically heavier sulphur ($\delta^{34}S$ ranges between –4.7 to 34.9‰). While here pyrite, present again in framboidal and cubic forms and additionally as fine-grained matter and gives two peaks on DTA curves at around 405 and 465°C, is the dominant sulphur species, traces of native sulphur have been also observed. Presence of solid bitumen, traces of heavy oil and high amounts of ankerite below 4.5–5 km contrast with their absence above this depth. It is obvious that fine-grained pyrite gives the higher temperature DTA peak. Its higher stability suggests a slow, late crystallization. The two pyrite peaks on DTA curves commonly are of similar magnitude, hence the abundances of the early and late (?) forms are similar. The relatively high amount of bacterial pyrite suggests that the Pannon Lake was brackish during deposition of the corresponding strata.

Since the oil certainly entered the deep reservoirs at temperatures higher than 80°C, the upper limit of the bacterial activity, bacterial sulphate reduction coupled with oil degradation can not be envisaged as the H_2S producing mechanism. Thermochemical sulphate reduction (TSR), coupled with oxidation of oil above 140°C explains the high level of H_2S and volatile organo-sulphur compounds in the gas, and the late (?) pyrite / ankerite / solid bitumen association. Traces of native sulphur, an intermediate product of (ongoing?) TSR and powerful oxidizer of hydrocarbons, and the very positive $\delta^{34}S$ of the H_2S strongly support this assumption.

Sarmatian gypsum, developed in many points of the Pannonian Basin, and Triassic gypsum/anhydrite known in the basement are the possible sources of sulphate.

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TEACHING ENVIRONMENTAL CLAY MINERALOGY – OUTLINES OF A UNIVERSITY COURSE

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The course consists of 4 main chapters.

1. The first chapter is introduction to *mineralogy* of clays. The notion of clay and clay mineral follows the definitions of AIPEA (1996). The basic structural and crystal chemical properties of clay minerals are given. The classification scheme of AIPEA (2006) is accepted. Individual mineral species are mentioned in connection with special identification methods. The basic principles of identification by X-ray diffraction, electron microscopy, thermal analysis and IR spectroscopy are presented.

2. The second chapter deals with occurrence and formation in various *natural sedimentary environments.* Continental, marine and oceanic environments are discussed separately. In connection with climatic zones of weathering clay minerals of the main soil types are characterised. In evaporitic lacustrine environment the chemical neoformation of palygorskite and sepiolite, in the shallow marine environment the formation of green grains of berthierine and glauconite are mentioned. Mechanical modes of transport are important in regions off main deltas, in shallow marine conditions and in the oceanic currents. The importance of eolian transport is specially mentioned. Halmyrolitic and hydrothermal alteration of oceanic basalt are of primary importance. After the characterising of sedimentary conditions diagenetic and very low grade metamorphic transformation is mentioned.

3. *The interaction* of solid mineral particles *with water* is discussed in a separate chapter. Diagrams of solution equilibria are included here and the metastable nature of most natural clay minerals is emphasized. Dissolution – precipitation conditions serve as chemical explanation to the behaviour in various natural sedimentary environments. The anthropogenic environmental problems of acid rain and acid rock drainage of sulphide ores can be discussed here. Surface and colloid phenomena on clay minerals are included into this chapter. After introducing basic notions of ion exchange and adsorption special environmental problems are mentioned. Examples are the pollution by toxic heavy metals and arsenic waters of the Great Hungarian Plain. In both cases adsorption on iron oxy-hydroxides can play important role.

4. The last chapter deals with the *application of clay material* in the technical solution of *environmental problems*. One of the main fields of application is the sealing of communal waste depositories. Special attention is given to the depositories of nuclear waste, in particular to the Upper Permian Boda Claystone Formation. The role of clay minerals in landslides and other construction works such as motorways and barrages is mentioned in this chapter. Special fields of application are various medical problems, such as the beneficiary properties of healing mud, the difference between chrysotile and amphibole asbestos and the problem of fluorine emission during heating of clays in the concrete industry.

The course is offered both for B.Sc. and for M.Sc and postgraduate students. In the higher level course an additional (5th) chapter on *clay minerals* of the most important Hungarian *sedimentary formations* is included. The course runs since 1996 in the Debrecen University and since 2005 in the Eötvös University, Budapest.

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MINERALOGICAL AND CHEMICAL INVESTIGATIONS OF SLAGS FROM TWO PREHISTORIC SMELTING SIDES AT THE MITTERBERG AREA

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The determination of the mineralogical and chemical composition of the major components in slags, yields important information concerning the reconstruction of archaeometallurgical processes. The Mitterberg region near Salzburg (Austria) in the eastern Alps was one of the most important Bronze Age mining and smelting districts in the Old World (STÖLLNER et al., 2006). The geological basis of the prehistoric mining was a mesohydrothermal ore deposit containing copper primarily as chalcopyrite (RÜFFLER, 1996). This project is part of the special research program "The History of Mining Activities in the Tyrol and Adjacent Areas". From the locations Windrandegg and Wilder See near the Troyboden almost 30 samples (slag cakes) were sliced into polished sections and analysed by transmitted and reflected light microscopy. Few representative slag samples of each smelting place were selected for electron microprobe analysis (EMPA), micro-Raman spectroscopy, X-ray fluorescence spectrometry (XRF) and X-ray diffractometry (XRD).

The surfaces of these slag cakes are rough and highly irregular showing coarse porosity and the slags show unreacted quartz embedded in a fayalitic matrix with occasionally distributed Cu - Fe sulphide- or copper droplets. The slags are mainly constituted by silicates (olivine) and oxides (magnetite) in a glassy matrix. Olivine is highly zoned, with a Mg-Ca-enriched core and a Fe-enriched rim.

The copper prills show a large range of compositions from Cu_2S to almost pure FeS. In terms of additional sulphide minerals, chalkopyrite, bornite and pentlandite could be determined. XRF analyses indicate lower SiO_2, MgO, K_2O and CaO, levels at the Wilder See smelting site, compared to the Windrandegg site, which might be due to differences in the gangue of the ore horizons which were mined. The total amounts of Cu and S from both sites are in the range from 0.4 to 2.7wt.%.

Further analyses will have to be done also concerning ores from different sites at the Mitterberg region in order to make inferences about the prehistoric archaeometallurgical processes.

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RADIOMETRIC MEASUREMENTS ON FLY ASH- AND SLAG-BEARING BUILDING MATERIALS – A HUNGARIAN CASE STUDY

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By-products of industrial production processes are used ever more often in national and international construction technologies as building materials on their own or as additives to building materials. There are a considerable number of known examples, both from national and international results, revealing cases of building materials or tiles containing coal slag and fly ash, all potentially dangerous for human health due to their content of some natural and artificial components.

A statutory act put in place in 1960 by the Ministry of Construction of Hungary (which, however, has later been repealed) banned the use of coal slag containing high levels of Ra concentration as building materials. Even so, different types of coal slags have not ceased to be utilized as building materials at private and at public construction sites. In Hungary, currently a Government Order and Ministry for Health Order are set to regulate building materials related issues, none of which are setting threshold values for unacceptable levels of radioactive radiation. Nor does any statutory rule exist for setting the maximum level of radon concentration allowable in premises.

In Hungary, from a radiological point of view, one of the most important issues is the utilization of the different types of coal slag and fly ashes as building materials. Therefore, the main aim of this study is to analyse gas silicate and coal slag concrete samples from five different locations within the central part of Hungary, using radiometric and geochemical methods.

During laboratory analysis, the ^{232}Th, ^{40}K and ^{226}Ra content has been measured by HPGe gamma-spectrometry and the radon production was measured by Rad7 continuous radon detector. On the thin sections, made from the coal slag and gas silicate samples, microscopic description and observation, mineralogical/phase composition and porosity estimates have been performed. To identify the chemical composition of the building materials, scanning electron microscope measurements have been used. The results have indicated that, due to the nature of coal slag and fly ash production techniques, both natural and artificial components can be found in building materials. On the other hand, the most frequently identified mineralogical phases are quartz and calcite. It has also been ascertained that fly ashes, and the coal slag concretes contain carbon, iron, glass and metallic phases. Iron and the different carbon phases adsorb Ra, Th and U well. In the samples analysed, there is also a high probability of appearance of U- and Th-containing monazite ($(Ce,La,Nd,Th)PO_4$) and xenotime (YPO_4) minerals.

The obtained values of the radium equivalent index and the activity concentration index show that the investigated building materials do not expose people to harmful radioactive risk. However, the deficiency of the legal regulations makes the reuse of the secondary raw materials difficult and future actions are needed to minimize the radioactive risk of building materials.

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SYNTHETIC RUBY AND CUBIC ZIRCON DIOXIDE: SURFACE MODIFICATIONS DUE TO CUTTING, GRINDING AND POLISHING

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Synthetic zircon dioxide and ruby are materials with interesting physical properties. Therefore, they are employed in many industrial fields e.g. electronics, metal industry and tool production. This contribution presents the results of investigations aimed to study the influence of cutting, grinding and polishing on these important materials.

Cubic zirconia is usually stabilized at ambient temperatures by adding yttrium oxide. Electron-beam microprobe measurements of various samples showed that they were stabilized with 21–24 wt% Y_2O_3. In contrast, samples of tetragonal zirconia contained only 6–7 wt% Y_2O_3. Coloration effects can be easily obtained by the incorporation of REE oxides. A pink coloration, for example, is caused by 7–8 wt% Er_2O_3, whereas adding of 1–2 wt% Nd_2O_3 results in purple color (NASSAU, 1981).

X-ray powder diffraction proved the cubic symmetry of most of the analyzed samples. Tetragonal samples can be distinguished by clear splitting of the reflections at about 35° (110, 002), 50° (112, 200) and 60° 2θ (103, 211). Furthermore, several analyses of cubic-tetragonal ZrO_2 mixtures were performed. On the basis of the (102) line at $2\theta = 43°$ (which appears only in the powder pattern of the tetragonal modification) it could be shown that the lower detection limit of tetragonal ZrO_2 in a cubic-tetragonal mixture is about 10% (under the specific measurement conditions).

Moreover, the surface behavior of grinded and polished ZrO_2 single crystals was investigated. By using a piezo autofocus and a motorized x–y-table, confocal Raman-images were collected, which showed a dependency between surface roughness and the depth of the stress marks on one side and the size of the abrasive grains (1, 5, 20 and 40 µm) on the other side. These results have been approved by atomic force microscopy.

Verneuil-grown ruby surfaces were treated with variable abrasive grain sizes and grinding directions. Raman maps of spectral parameters of the R1 and R2 luminescence bands at 694 and 693 nm provided details on structural interferences. A negative wavelength shift and a simultaneous increase of the full width at half maximum (CHEN et al., 2000) indicates surface grain size reduction and structural disordering. Ruby samples, which were polished perpendicularly to their crystallographic *c* axis showed less surface destruction than ruby specimen polished parallel to the *c* axis. A decrease in surface roughness and depth of the stress marks by using smaller polishing grain size could be proofed by atomic force microscopy.

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FLUX GROWTH AND TOPOLOGIES OF THREE NEW COMPLEX SILICATES OF GADOLINIUM

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In continuation of a comprehensive study of the synthesis, crystal chemistry and topologies of new microporous mixed-framework silicates containing octahedrally coordinated M^{3+} cations (M = Sc, V, Cr, Fe, In, Y, Yb) (WIERZBICKA-WIECZOREK, 2007), additional syntheses were conducted using the three M^{3+} (REE^{3+}) cations Ho^{3+}, Er^{3+} and Gd^{3+}, in order to verify the assumed existence of potentially luminescent compounds isotypic with previously obtained M^{1+}(-M^{2+})-Sc, -Y and -Yb silicates.

Three new Gd silicates were grown as small colourless crystals using the high-temperature flux-growth technique (MoO_3–based flux mixtures in Pt crucibles in air; T_{max} = 1150°C, cooling rate 2 K/h, T_{min} = 900°C). The crystal structures have been determined from single-crystal X-ray intensity data.

$Ba_2Gd_2Si_4O_{13}$ crystallises in space group $C2/c$, with a = 12.896(3), b = 5.212(1), c = 17.549(4) Å, β = 104.08(3)°, V = 1144.1(4) Å^3 ($R(F)$ = 2.64%). $Ba_2Gd_2Si_4O_{13}$ represents a new structure type and is a rare example of a silicate with finite Si_4O_{13} chains. These chains are connected with GdO_7 polyhedra. Two such polyhedra share a common edge, thus creating isolated Gd_2O_{12} groups, which form the basis of a heteropolyhedral slab in the *ab* plane. The Ba atoms are located in channels running parallel to the *b* axis.

$Rb_3GdSi_8O_{19}$, with space group *Pnma* and a = 11.399(2), b = 7.025(1), c = 26.940(5) Å, V = 2157.3(6) Å^3 ($R(F)$ = 4.62%), is a new representative of the microporous mixed-framework structure type 'MCV-1' of $Cs_3ScSi_8O_{19}$ (KOLITSCH & TILLMANNS, 2004), also adopted by the isotypic silicates $Cs_3YSi_8O_{19}$, $Cs_3YbSi_8O_{19}$ and $Rb_3ErSi_8O_{19}$ (WIERZBICKA-WIECZOREK, 2007). Corner-sharing of SiO_4 tetrahedra and isolated MO_6 octahedra results in the formation of an open framework with four-, six- and eight-membered rings and large voids, which indicates a potential as application for immobilisation of radioactive ^{137}Cs waste, cationic conductivity or catalysis.

The last new gadolinium silicate, $BaKGdSi_2O_7$, has space-group symmetry $P2_1/n$, with a = 9.853(2), b = 5.741(1), c = 13.184(3) Å, β = 104.56(3)°, V = 721.8(3) Å^3 ($R(F)$ = 1.59%). $BaKGdSi_2O_7$ is isotypic with the disilicates $BaK\mathit{REE}Si_2O_7$ (REE = Y, Yb, Sc) (KOLITSCH et al., 2009) and $SrKScSi_2O_7$. The novel tetrahedral-octahedral framework structure type is based on isolated Si_2O_7 groups connected with isolated $\mathit{REE}O_6$ octahedra parallel to the *c* axis. The M^{1+} and M^{2+} cations are located in voids in the framework. The narrow Si–O–Si angle of the disilicate group in $BaKGdSi_2O_7$ (123.1°) is noteworthy.

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CRYSTAL STRUCTURE OF NANLINGITE – THE FIRST MINERAL WITH A [$Fe(AsO_3)_6$] CONFIGURATION

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Nanlingite was first described as a new mineral (GU, DING & XU, 1976) from a dolomitic limestone along a contact between greisenized granite and dolomitic limestone in Nanling area, Hunan Province, associated with fluoborite, fluorite, zinnwaldite, magnesian dolomite, asenopyrite, pyrrhotite, gahnite and nigerite. Nanlingite forms brownish-red tabular crystals up to 2 mm in size, it is optically uniaxial negative, with $\omega = 1.82$, $\varepsilon = 1.78$. The mineral was reported to be trigonal (space group *R3m* or *R-3m*, $a = 10.24(5)$, $c = 25.76(5)$ Å, or $a = 10.42(5)$ Å, $\alpha = 58.83°$). Chemical composition of nanlingite by wet chemical analysis gave the general formula written as $CaMg_3(AsO_3)_2F_2$. By recalculation the formula was also suggested by CHAO in FLEISCHER et al. (1977) as $CaMg_4(AsO_3)_2F_4$.

The present single crystal X-ray study on type material was performed on a Nonius KappaCCD diffractometer. The structure was solved and refined in space group *R-3m*, with $a = 10.211(1)$, $c = 25.689(3)$ Å, $V = 2319.8(4)$ Å^3, to R1 = 0.023, wR2 = 0.055. The idealized formula of nanlingite is $NaCa_6(Mg,Fe,Li)_{12}(AsO_3)_2[Fe(AsO_3)_6]F_{14}$ with $Z = 3$ according to the crystal structure refinement.

The complex framework is formed by edge- and corner-sharing of distorted NaF_8 and CaF_4O_4 cubes, MgF_2O_4 octahedra, and AsO_3 trigonal pyramids. In addition, one further atom (at 3*b*, site symmetry *-3m*) is surrounded by six As atoms of AsO_3 groups (with the lone-pair electrons pointing towards the central atom) at a distance of 2.4 Å. Based on its scattering power an occupation of this site by iron seems plausible. Among minerals, similar arrangements of arsenite groups coordinating cations have rarely been observed: in magnussonite, $Mn_{18}[Mn(AsO_3)_6]Cl_2$, formally monovalent Mn is bound to six As atoms with an average Mn–As distance of 2.65 Å (MOORE & ARAKI, 1979). Cu^{1+} is bound to four As atoms of arsenite groups in distorted tetrahedral coordination (ARAKI & MOORE, 1981) in dixenite, $CuMn_{14}Fe(OH)_6(AsO_3)_5(SiO_4)_2(AsO_4)$. In freedite, $Pb_8Cu(AsO_3)_2O_3Cl_5$ the Cu^{1+} atom is tetrahedrally coordinated to two Cl atoms and two As atoms belonging to (AsO_3) groups (PERTLIK, 1987). The project was supported by the National Natural Science Foundation of China (No. 40872044).

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FIRST DISCOVERY OF PLATINUM GROUP MINERALS IN COSTA RICA

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We report on the presence of platinum group minerals (PGM) that were discovered, for the first time, in Costa Rica. The PGM were found in small chromitite bodies of the Santa Elena ophiolite, located in the northern Pacific coast of Costa Rica, close to the border of Nicaragua. The PGM were previously investigated microscopically using reflected light at 250 to 500 times magification. Subsequently, they were analyzed by electron microprobe at the E.F. Stumpfl laboratory of the UZAG consortium, installed at the Leoben University. The following PGM have been identified: laurite (RuS_2), erlichmanite (OsS_2), irarsite (IrAsS) accompanied by these unknown phases: Ir-Rh-S, Ir-Ni-Fe-S and Ir-Ni-Fe-Cu-S. The PGM form very minute and polygonal grains (from 1 to 10 µm in size) forming single phase crystals or in polyphasic aggregates with Fe-Ni-Cu sulphides, clinopyroxene and chlorite (Fig. 1). Most of them occur enclosed in fresh chromite. Some grains are associated with chlorite forming the filling of cracks and the intergranular matrix, others are in contact with ferrian chromite. The presence of Ru-Ir-Os PGM in the Santa Elena chromitites is consistent with the typical assemblages of the chromitites hosted in the mantle section of ophiolite. Morphology and texture of the PGM inclusions indicate that most of them formed at high-temperature during the crystallization of the host chromite. The presence of abundant Ir and base metals sulfides, erlichmanite and laurite coupled with the absence of magmatic Os-Ir-Ru alloys, suggest that the PGM associated with the Santa Elena chromitites crystallized under high sulfur fugacity.

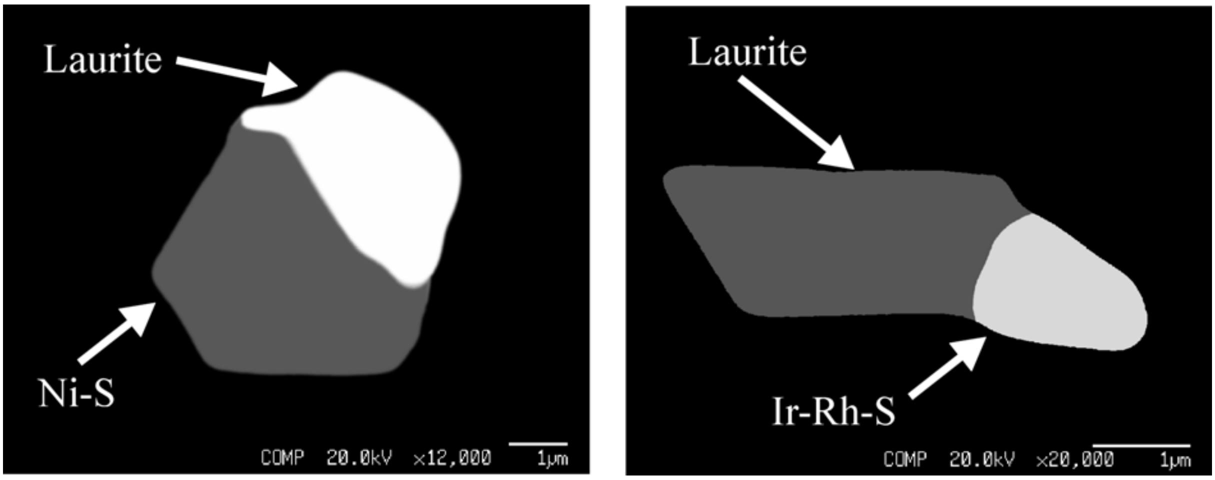

Figure 1. Back-scattered electron images of PGM enclosed in fresh chromite.

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GEOCHEMICAL CHARACTERISTICS OF IELOVA GNEISSES (SOUTH CARPATHIANS, ROMANIA)

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Ielova Metamorphic Sequence (IMS) is located in the south-western part of Romania, in the so-called Banat area. As part of the South Carpathians, the IMS was considered to represent the most western area of Danubian Realm in the region, although recently it was placed within the Getic Realm (*e.g.* KRÄUTNER & KRSTIĆ, 2002).

Lithologically, the main constituent rock type of IMS is represented by gneisses, with various subtypes (*e.g.* gneisses with garnet and biotite, micaceous gneisses, amphibolitic gneisses, granitic gneisses). Amphibolites, migmatites with various structures and lizardite-dominated serpentinite bodies also occur.

Geochemical studies in the area were performed only on basic and ultrabasic rocks (ZLARATOVA-ȚOP et al., 1971; MUREŞAN et al., 1974). It was showed that the mafic rocks, with a calcalkaline composition, are products of the initial magmatic phase, proceeding from a gabbroic magma.

The IMS gneisses are intermediate to felsic rocks, with 54.50–76.21 wt% SiO_2, and variable contents of K_2O (0.60–3.72 wt%), Na_2O (3.09–5.30 wt%), MgO (0.21–7.09 wt%) CaO (0.78–6.90 wt%), Al_2O_3 (11.15–19.54 wt%) and Fe_2O_3* (total Fe = 0.73–8.66 wt%). Low TiO_2 (0.10–1.30 wt%) and P_2O_5 (<0.31 wt%) contents were noticed.

Based on the incompatible element ratios, the IMS gneisses show mainly an andesitic affinity, with the majority plotting within the fields of andesites and basaltic andesites, few samples showing trachy-andesites or rhyolites characteristics.

Chondrite-normalized REE patterns of five intermediate and felsic rocks are fractionated, with LaN/YbN = 13.24–6.13 and CeN/YbN = 10.38–4.94, displaying LREE enrichment and flat HREE patterns. A slightly negative Eu anomaly is observed ((Eu/Eu*)N<0.8) indicating that plagioclase was probably a residual phase involved in the formation of the rocks. The ORG-normalized trace elements patterns of the studied rocks show close similarities to the granitoids of modern arc settings. Also, primitive mantle-normalized incompatible elements patterns show enrichment in LILE and exhibit significant negative Nb, P and Ti anomalies, resembling patterns of calc-alkaline melt from a continental margin setting.

The REE and trace elements data are in agreement with the tectonic discrimination diagrams for granitoids, using trace elements, which show that Ielova gneisses formed in a continental margin.

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ACTIVITY AND NATURE OF SKARN-BUILDING FLUIDS IN THE METAMORPHIC COMPLEX OF THE LYS-CAILLAOUAS MASSIF (CENTRAL PYRENEES)

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The axial zone of the Pyrenees (France-Spain) consists of a number of Hercynian massifs (e.g ZWART, 1979). The studied area is located in the Lys-Caillaouas massif, in the Central Pyrenees. The area has been affected by a several deformation phases, regional, and contact metamorphism (see KRIEGSMAN et al., 1989). The metamorphic rock consists mainly of micaschists, quartzites, and meta-conglomerates. This study is concerned with calc-silicate metamorphic rocks and skarn formation adjacent to the intrusive massif of different types of granites, aplites, and pegmatites.

Several samples of different locations in this area have been collected to reconstruct the formation history and formation conditions of the skarn by analysing fluid inclusions (fi) using Raman spectroscopy and microthermometry (homogenisation and melting temperatures). Fluid inclusions were studied in grossular, quartz and vesuvianite.

Most fi's in garnet are irregular shaped and elongated, and of a primary origin. Their sizes are up to 40 μm in diameter. The phase assemblage at room temperature consists of vapour (12 ± 2 vol%), liquid, and calcite and/or quartz. The vapour bubble contains a mixture of CH_4 and N_2. The liquid is a salt-rich aqueous solution. The homogenisation of the liquid and the vapour phase occurs at approximately 240 to 250°C (into the liquid phase), in the presence of quartz and calcite. Hydrohalite and methane-clathrate have been detected in frozen fi's.

The larger fi's in quartz are irregularly shaped (± 20 μm diameter), whereas smaller inclusions (< 7 μm diameter) are regular shaped. Fi's in quartz contain highly saline aqueous solutions but in contrast to the garnet, the vapour phases (8 ± 2 vol%) are only composed of steam. At room temperature, the inclusions contain a halite crystal, which melt at temperatures between 130 and 180°C. The homogenisation of the liquid and vapour phase occurs at similar temperatures, between 130 and 170°C into the liquid phase. The calculated salinity of these inclusions is about 29.0 ± 0.7 eq. mass% NaCl. From the same sampling site, vesuvianite contains regular, elongated fi's (maximally 20 μm in length). Fi's contain a vapour bubble (± 10 vol%, low density CH_4-N_2 mixture), a highly saline liquid (T_m about -25°C), and occasionally calcite and apatite. Homogenisation of vapour and liquid occurs in a relatively broad range between 160 and 220°C into the liquid phase.

The skarn mineralisations, especially grossular and vesuvianite, were generated in a reducing H_2O-salt-CH_4-N_2-rich fluid system. The minimum trapping conditions of the garnet are slightly higher (240-250°C) than vesuvianite (160-220°C). The large variety in T_h values in vesuvianite is probably caused by post-entrapment alterations due to well developed cleavages. Quartz in the skarn zone records a completely different fluid (H_2O-salt), which belongs to a different metamorphic event.

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