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## ACTA MINERALOGICA-PETROGRAPHICA

Tomus XLI.

## **SUPPLEMENTUM**



MINERALS OF THE CARPATHIANS INTERNATIONAL CONFERENCE Miskolc, March 9–10, 2000

## ABSTRACTS

SZEGED, HUNGARIA

2000

#### NOTE TO CONTRIBUTORS

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Name(s) of author(s) and their affiliations, in foot-note the address of the author to whom the correspondence should be sent.

Abstract

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Methods, techniques, material studied, description of the area investigated, etc. Results

Results

Discussion or conclusions

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Edited by B. Fehér, F. Mádai, S. Szakáll and T. Váczi

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NOTE

Abstracts were revised and if it was needed, sent back for corrections to the authors. Additional minor grammatical corrections were also made on the revised abstracts.

## **BIODEGRADATION OF GOLD-BEARING SULPHIDE MINERALS OF THE TATRIKUM UNIT (WESTERN CARPATHIANS, SLOVAKIA)**

<u>ANDRÁŠ, P.</u>, KRIŽÁNI, I. (Slovak Academy of Sciences, Banská Bystrica, Slovakia) & KUŠNIEROVÁ, M. (Slovak Academy of Sciences, Košice, Slovakia) E-mail: andras@bb.sanet.sk

The gold-bearing disseminated sulphidic ores from the Sb-Au deposits of Pezinok, Trojárová (Malé Karpaty Mts), Dúbrava and Vyšná Boca (Nízke Tatry Mts) forms impregnations of fine grained euhedral arsenopyrite and arsenian pyrite. The gold content in arsenopyrites range from zero up to 0.6 wt% in some crystals from the Trojárová deposit. Gold content in pyrite is lower (0–100 ppm). Most of the invisible gold incorporated in sulphide minerals is chemically bound (ANDRÁŠ *et al.*, 1995).

Arsenopyrite and arsenian pyrite exhibit strong zonation patterns. Generally two extreme types of growth zones can be distinguished, both with different compositional trends. The first one has high Sb and low As content and the second one high As and low Sb content. Progressive enrichment in As is generally in correlation with a decrease in S and Sb content. As and S are strongly negatively correlated. The As rich zone is considered to be the carrier of the substantial majority of chemically bound gold. At the deposits of Pezinok and Trojárová the rims of the gold-bearing crystals are rich in Au-As and at Dúbrava and Vyšná Boca the situation is the opposite: the crystal cores are rich in Au-As.

From environmental aspects it is very difficult to find convenient technology for gold production from ores with invisible gold. The most often used biochemical oxidation of these ores is satisfactory from an environmental viewpoint but very tedious. Sty of polished surfaces of investigated sulphides submitted to biological chemical oxydation by the culture *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* give the following results:

- The process of bacterial oxidation is a selective one, with preferential oxydation of arsenopyrite in As (Au) enriched zones.

- Process of biodegradation is followed by dissolution of As (Au) enriched zones of pyrite crystals preferentially along cracks, veins and growth zones of crystals.

- Biochemical leaching of investigated sulphides is also influenced by the galvanic interaction of parts with different As content.

- In the process various tunnels and depressions are formed. Their space orientation are directly related to the orientation of different crystal faces.

- The preferential biochemical solving of arsenopyrites, which contain about 80 wt% of the gold, and the preferential oxydation of arsenopyrite and pyrite As rich zones, which contain about 90 wt% of the gold in each grain, substantially speed up the technological process of gold leaching and enable the use of the tedious biological-chemical technology for gold production from arsenopyrite-pyrite ores containing refractory gold, convenient from an environmental point of view.

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## COMPARISON OF SELECTED ORE DEPOSITS OF WESTERN CARPATHIANS AND THE EASTERN ALPS

<u>ANDRÁŠ, P.</u> (Slovak Academy of Sciences, Banská Bystrica, Slovak Republic), SCHROLL E. (University of Vienna, Vienna, Austria), CHOVAN, M. (Comenius University, Bratislava, Slovak Republic). E-mail: andras@bb.sanet.sk

The oldest model ages are similar showing high  $\mu_2$ -values and age values around more than 600 Ma. They are typical of polymetallic massive sulphide mineralizations with exception of the ore district Stubai-Ötzal. The main difference is the frequency of radiogenic lead (J-type), causing distinct inhomogenities and anomalous negative model ages. The radiogenic leads are the mobilizates of Alpidic metamorphism (30 and 80 Ma) in the Eastern and Western Alps. The Hercynian granite intrusion of the W. Carpathians have not been seized by the "Tauern crystallization."The leads of the ore mineralizations connected with the young volcanism show relevant ages or are slightly radiogenic.

In the Eastern Alps, strata bound Pb-Zn mineralizations have a tendency to model ages which are stratigraphically too old (B-type). Such a isotope composition is also evident for the Devonian Pb-Zn-Ag-Ba mineralization of the Graz Paleozoic (540 - 570 Ma) and for most of the Triassic Pb-Zn- (F-Ba)-deposit there are age differences of 150 to 200 Ma. In the Eastern Alps, the lead isotope data of the carbonate-hosted Pb-Zn-ore mineralizations show model ages 160-400 Ma. In the Western Carpathians, the Pbisotope data are comparable with the Alpine data or analogous with mineralizations from the Slovak neovolcanics. The  $\mu_2$ -values vary from 8 to 10, corresponding to the average crust lead of the Hercynian granite complexes or to the thorogenic upper crust lead inherited from the pre-Cambrian clastic sedimentation.

The comparison is limited to the carbonate-hosted Pb-Zn deposits in respect to the problematic of biogenic and abiogenic sulphate reduction. The sulphide S-isotopes depend on the contemporaneous isotopic composition of the sea water sulphate. Differences in the S-isotope distribution are found between Anisian and Carnian Pb-Zn-mineralizations confirming different temporal origins. Biogenic reduction processes are more typical in the Eastern Alps. In the Western Carpathians, the acceptance of biogenic sulphide formation is conceivable only for the deposits of Poniky and of the vein range Vyšná Slaná. Ore mineralizations influenced by younger endogenic hydrothermal activities would be indicated by Pb-model ages around zero.

The C- and O-isotope study show that the Permian magnesites in W. Carpathians are in an adequate position. The Carboniferous-hosted magnesites are characterized by Oisotopes. In both cases, the sedimentary origin cannot be drawn in doubt considering the other facts too. The present state of the knowledge about the origin of siderites is not sufficient in all. Recent sedimentary siderites are distinguishable clearly from those of deep seated veins or of a higher metamorphic environment. The siderites of the Rudňany deposit show affinity to the siderites of Erzberg. But the thermical history of the Erzberg is more complex. Rožňava and "Penninic" (Tauern gold veins) seem to be genetically analogous. But, the siderites of the "Penninic" are formed at higher temperatures.

## ORE MINERALISATION HOSTED BY VOLCANIC ROCKS OF THE SLANSKE VRCHY MTS., SLOVAKIA

<u>BAČO, P.</u> (Geological Survey of the Slovak Republic, Košice, Slovakia), ĎUĎA, R. (Východoslovenské múzeum, Košice, Slovakia), JELEŇ, S. (Geological Institute Slovak Academy of Sciences, Banská Bystrica, Slovakia), KODĚRA, P. (Geological Survey of the Slovak Republic, Bratislava, Slovakia), KOTUĽÁK, P. (GSP, Spišská Nová Ves, Slovakia) & REPČIAK, M. (Geological Survey of the Slovak Republic, Košice, Slovakia) E-mail: baco@dodo.sk

Volcanic rocks of the Slánske Vrchy Mts are related to the Neogene to Quaternary volcanic activity of the Carpatho-Pannonian region and belong to the basalt–andesite volcanism of island arc type. Volcanic activity is represented by andesite stratovolcanoes. Mineralisation is spatially related predominantly to the central zones of these staratovolcanoes. Historically, Au-Ag, Sb and Hg ore mining activity is well-known essentially from the Zlatá Baňa district.

LEXA et al. (1999) distinguished 15 main types of volcanogenic mineralisation based on geotectonic setting, type of magmatic activity, relationship to the subvolcanic magmatic-intrusive systems and on the primary character of the ore bearing fluids. Applying these criteria ore mineralisations of the Slánske Vrchy Mts. could be assorted to the following types:

1. Fe skarn mineralization. Found in drill holes in the Zlatá Baňa deposit.

2. Cu-Mo stockwork (porphyry?) mineralisation. Found in drill holes in the central zones of the Zlatá Baňa and Makovica stratovocanoes.

3. Intrusion related base metal stockwork mineralisation. This is the most common type with economically interesting parameters, present at the Zlatá Baňa deposit and at occurrences, verified by drill holes in central zones of the following stratovolcanoes: Šťavica, Makovica, Strechový vrch and Bogota. Mineralisation has stockwork (veinveinlets) character and it is apparently of A–S (NW–SE) direction. The fillings of vein structures consist mainly of pyrite, sphalerite, galena, chalcopyrite and several other sulphide minerals. Au and Ag are characteristic and important components in the upper parts of the structures with base metal mineralisation. Stable isotope and thermobarogeochemic studies suggest that the cooling (from 300 to 150°C) and alkalization (from 3.5 to 7 pH) were the main ore forming factors, induced by the collapse of meteoric waters into the ore forming system.

4. Au-Ag + Sb low sulphidation epithermal, vein (vein-veinlets) mineralisation. It evolved predominantly in peripheral, lateral parts of the previous type of mineralisation. Stibnite is the main vein filling mineral. The proximate vicinity of veins are extensively pyritized and silicified. Au-Ag mineralisation is related just to this part of the structures.

5. Stockwork Hg mineralisation. This type of mineralisation is the most widespread in Slánske Vrchy Mts. The ore potential was checked at the locality Dubník (Červenica). Cinnabar is present in the space of the  $3^{rd}$  and  $4^{th}$  mineralisation types and forms numerous panning prospection anomalies in the whole mountains.

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## AN IGNIMBRITE DEPOSIT FROM THE HOLDVILÁG CREEK, VISEGRÁD MOUNTAINS, HUNGARY

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In the Visegrád Mountains, the westernmost part of the calc-alcaline volcanic arc of the Inner Carpathians, in a deep valley called Holdvilág Creek, there is a pyroclastic deposit which has not been described yet with the methods of modern volcanology.

The Visegrád Mountains are built up of Middle Miocene andesite and dacite lavas and pyroclastic deposits. Our research group has studied the deposits of the north-south striking valley of the Holdvilág Creek. Several volcanosedimentary units have been described on the basis of the main constituents of the deposits, their physical (grain size, roundness etc.), textural and structural characteristics, and considering the presence of the features in connection with the pyroclast flows and surges of magmatic eruptions (evidences of hot deposition, gas segregation pipes, etc.).

On the top of Miocene marine sediments, the basal layer is a fine-grained, weathered, thin-layered tuff, which could be the deposit of a pyroclast (ash) fall in marine conditions. It is overlain by a 0.5 m thick, medium sorted, cross-bedded unit containing coarse ash and fine lapilli size lithic elements and pumice, and accretional lapilli referring to a wet, turbulent deposition from ground surges. This is overlain by a 5 m thick, massive, unsorted unit made of graded lithics of garnet bearing dacite, pumice lapilli and ash. This is overlain by another, very thin tuff layer and a thick, massive, totally unsorted, structureless unit made up of angular, poorly vesiculated blocks of juvenile cognate lithics, sometimes showing the signs of oxidised surfaces and prismatic jointing (both are the main features of hot deposition and cooling). On the top of these, after an alternating series of fine and coarse-grained layers, a 7 m thick, massive, unsorted unit made of graded pumice lapilli and ash is deposited. This unit contains vertical channels filled with coarser material, which are gas segregation pipes. According to these characteristics the latter unit can be classified as a non-welded *ignimbrite*. The uppermost layers could are probably lost due to erosion.

Based on the lithological and volcanological characteristics of the deposits, the initial phases of the Miocene volcanic activity can be restored. It started with an ash fall in marine setting, followed by ground surges and a pumice rich pyroclast flow in a coastal environment, forming the crossbedded, coarse depleted basal layer and the coarser, pumiceous pyroclastic breccia respectively. On top of these a block and ash flow deposited its coarse blocks. At the end a pumice and ash flow created the ignimbrite unit.

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### EPITHERMAL Au-Ag MINERALIZATION IN PUKANEC (CENTRAL SLOVAKIAN NEOGENE VOLCANIC FIELD)

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The Pukanec ore district is situated in the SW part of Banská Štiavnica strato-volcano. The beginnings of mining activity date back in the 11th century. The maximum of exploitation was in the 15th and the 16th centuries and real end of mining was in the last century. Large ancient remnants after gold mining indicate the intensity of historical mining.

Four geological units are distinguished at Pukanec: prevolcanic sedimentary complex. complex of andesite porphyries. Tatiar intrusive complex (granodiorite, quartzdiorite and diorite porphyry) and intrusions of rhyolites and their porphyries. In this environment occur two genetic types of epithermal mineralizations; an older porphyry Cu mineralization and an overprinted, intrusion related base metal stockwork mineralization stage (high sulfidation) with a younger gold-silver vein stage (low sulfidation), which was the main object of mining in the past (STOHL et al., 1994).

Geological and mineralogical research in outcrops and old mines demonstrated that the main objects of exploitation were black coloured fillings of cataclased zones amidst altered (silicified) and esites. Auriferous zones (max. 1 m thick) are formed by clay minerals, fragments of vuggy quartz and fragments of silicified andesites. Black colour is due to Mn oxides and hydroxides. Sometimes quartz-carbonate veins are present without ore mineralization. Au-Ag content in mineralized zones is 5-25 ppm. In the black coloured clay zones occur gold (Ag 35-43 wt%), oxidized pyrite, Mn oxides and hydroxides, clay minerals and rare grains of stibnite. The size of gold grains (wire and skeletal form, flakes) is max, 0.2 mm. Black cataclased auriferous zones have a depth range of about 30 m. Wallrock alterations are sericitization, adularitization and silicification.

Primary gold mineralization was found at the depth 142–145 m (drill hole). Texture of mineralization is brecciated where argillitized (pyritized) andesites are cemented by quartz. Gold occurs in wire and flake forms (max. 1 mm) in the quartz druses. Their redbrown colour is due to Fe oxides. Wallrock alterations are argillitization and silicification.

Alluvial gold (Ag 32-50 wt%) occur in almost all brooks in the Pukanec area. Gold grains are very diverse in morphology (skeletal form, wire aggregates, slightly rounded aggregates of crystals, flakes). Surface of gold grains is smooth or spongy. Size of grains is variable (0.0x-2 mm). During a longer transport (about 3 km) in alluvium Ag is leached out from the Au-Ag alloy and an Au rich rim is formed.

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# SORPTION OF SELECTED HEAVY METALS (Cr(III), Cu(II), Pb(II)) ON SMECTITE-CLINOPTILOLITE SHALES OF THE OUTER FLYSCH CARPATHIANS (POLAND)

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Hazardous wastes contaminated with heavy metals often cause environmental pollution to surface waters, ground water and soils. Natural zeolites and bentonites are frequently used for remediation or as liner materials. The effectiveness of the treatment results from ion exchange properties of zeolites and adsorption properties of bentonites.

The aim of the work was comparison of sorption properties of raw clinoptilolitemontmorillonite claystone with the zeolite fraction separated from this rock. The claystone crops out near Rzeszów (SE Poland) as the Trójca Red Shale Member of the Variegated Shales Formation (Upper Paleocene-Lower Eocene) within the Skole Unit of the Outer Flysch Carpathians (RAJCHEL, 1990). The rock consists of 60–80 % Camontmorillonite, 15–30% clinoptilolite, and 15–30 % quartz, feldspars, illite, illitemontmorillonite, kaolinite and chlorite (WIESER, 1969).

Adsorption of aqueous Cr(III), Cu(II), and Pb(II) (0.05 to 270 mg/g of the adsorbent) was tested in 2 % suspensions. For desorption 1M NH<sub>4</sub>OAc at pH 7 was used. This experimental setup allows to determine the metal-to-solid range within which the adsorbent is the most effective. The samples after adsorption were examined with SEM/EDS.

The removability of heavy metals in question from their solutions is relatively high. At low initial concentrations of solutions the metals were completely removed. The maximum sorption of all the metals by both investigated sorption materials was higher than their CEC. The adsorption properties of raw clinoptilolite-montmorillonite claystone are better than of pure zeolite fraction. The desorption experiments revealed that a certain part of the sorbed metals did not desorb. The quantity of this unremovable portion depends on the metal and its concentration in the solution.

Scanning electron microscopy (SEM) did not reveal any morphological changes or new precipitates formed on the samples after adsorption. Energy dispersive spectroscopy (EDS) allowed for the detection of adsorbed metals in the samples.

Acknowledgement. The study was sponsored by the KBN (Warsaw), grant no. 6P04D 022 16.

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## ALTERATION, STABLE ISOTOPE AND FLUID INCLUSION CHARACTERISTICS OF THE CU-PORPHYRY TYPE AND RELATED HIGH SULPHIDATION TYPE MINERALIZATION IN THE TERTIARY ANDESITIC ROCKS OF THE VELENCE MOUNTAINS, HUNGARY

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In the eastern part of the Velence Mts. an andesitic volcanic structure of Upper Eocene-Oligocene age is exposed. A diorite intrusion beneath the caldera-like structure is known from the 1200 m deep Pázmánd-2 borehole. Subvolcanic andesite dykes and necks also intrude Variscan granitic rocks in the western part of the Velence Mts. Vertical and horizontal zonation of hydrothermal alteration in the epithermal zones consists of a central part with leached, silicified and brecciated quartz, rutile ± alunite rich rock surrounded by a transition zone with pyrophyllite, topaz, alunite  $\pm$  diaspore, zunyite, kaolinite and illite minerals. This is fringed by kaolinite-illite and chlorite-sericite-smectite zones. The alteration pattern indicates interaction of acidic fluids in the massive silica zone and decreasing acidity towards the margins and depth. The diorite intrusion beneath the epithermal zones shows Ksilicate (biotite and K-feldspar) and propylitic (chlorite, smectite) alteration and quartzcalcite-pyrite stockwork with pyrite, chalcopyrite, bornite and magnetite disseminations. \deltaD = -85 - -88‰ and  $\delta^{18}$ O = 8,1-8,8‰ data for hornblende and primary biotite from Tertiary unaltered andesite dikes and necks intruding the Variscan granite indicate that their parent magma degassed during solidification. Hydrothermal minerals (illite, pyrophyllite) from epithermal zones have much higher  $\delta D$  (-32 – -45‰) and lighter  $\delta^{18}O$  (-1.4 – +2.5‰) values suggesting that fluids responsible for alteration also had a meteoric component in addition to magmatic water. Coexistence of gas-rich and liquid-rich inclusions in quartz crystals from the brecciated silica bodies of epithermal zones indicates boiling of hydrothermal fluids. Homogenization temperatures of liquid-rich inclusions are between 220 and 380 °C. Coexisting pyrophyllite and diaspore suggest a temperature between 270 and 360 °C. Salinities of inclusion fluids are highly variable between 1 and 12 NaCl equiv. wt% and occurrences of elevated salinities indicate that a chlorine-rich, presumably magmatic fluid mixed with meteoric water. Quartz veinlets in the subvolcanic diorite intrusion contain aqueous and vapor phase rich liquid-vapor, and daughter mineral (halite, sylvite, hematite and other unknown solids) bearing polyphase fluid inclusions. This assemblage suggests that boiling of hydrothermal fluids also occurred at the subvolcanic level. Homogenization temperatures are from 270 to 520 °C and salinities are broadly varied from 13-20 to 31-47 NaCl equiv. wt%, and from 23-24 CaCl<sub>2</sub> equiv.wt% to 55-79 NaCl+KCl equiv.wt%. Occurrence of high salinity inclusions indicates presence of magmatic fluids in the hydrothermal system. Thus stable isotope and fluid inclusion data equivocally support that the diorite intrusion released a magmatic fluid phase, which played role not only in the formation of the Cu-porphyry type mineralization but also in the hydrothermal processes of the shallow epithermal zones.

This work was supported by the Japan–Hungary S&T Agreement and the OTKA (HNSF) No. F 007597 grant to F. Molnár and the SEG BHP Student Grant to B. Bajnóczi.

## HYDROTHERMAL Au-Ag MINERALIZATION OF THE PEZINOK–STARÉ MESTO DEPOSIT (MALÉ KARPATY MTS., SLOVAKIA)

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The most important type of ore mineralization in the Malé Karpaty Mts. is Sb-As-Au mineralization in the Pezinok area, hosted by Pezinok–Pernek crystalline formation of Silurian–Devonian age (amphibolites, actinolite schists, phyllites, black schists), mined until beginning of 1990's. In the vicinity of Sb-As-Au deposit, in distance less than 1 km, Au-Ag mineralization in several occurrences is hosted by a small massif of Variscan granitoids of Bratislava type (two-mica granodiorites, leucocratic granites and pegmatites). The largest occurrence, the Pezinok–Staré Mesto deposit, mined mainly in the Middle Ages until the end of 19th century, is formed by several parallel NW–SE and transversal E–W veins and veinlets bounded in mylonitized zones. The length of the mineralization, according to the area of old mining works, can reach more than 1 km, vertical extent is unknown. The power of veins varied from 0.0X to 0.X m, max. 1 m. From the gangue minerals quartz is dominating, carbonates are rare. The content of gold varied from 0.X to X0 ppm Au.

Mineralization occured in several stages. The oldest one is characterized by arsenopyrite, pyrite and gold. The grains of pyrite and arsenopyrite frequently form impregnations in silicified granitoid rocks and nests and strips in quartz. One of the latest minerals that crystallized in this mineral stage, was gold. It forms isolated grains, nests and rare veins of mm lenght. It is frequently concentrated in the margin of the thin veins. The size of gold grains varies from 0.01 to 5 mm, the largest amount of gold grains are concentrated in the fraction to 0.16 mm. Pyrite and arsenopyrite is often replaced by gold, it closes or cements their cataclased grains. Fineness of gold can have values from 792 to 909.

The minerals of the later mineral stage are rare in the deposit. They fill thin cracks and also create small nests and grains in quartz. The most frequent is the appearance of pyrite, Ag-tetrahedrite, chalcopyrite and electrum, and less frequent is galena, sphalerite, bournonite and polybasite. The fineness of electrum varies from 684 to 753. It was found that gold with high Ag content (fineness 584) has 0.0X mm grains in chalcopyrite and appears in the form of margins and thin veins in gold with higher fineness.

In the vicinity of the occurrences of Au-Ag mineralization in the alluvial sands and gravels there is an anomal content of gold grains. Gold placers were mined in Middle Ages, nowadays the content of gold in alluvial placers of Limbašský potok brook is max. 0.221 g/m<sup>3</sup>. Gold occurs mostly in the form of nuggets, less frequently in the form of flakes of size to 1 mm. Formation of nuggets and Au rich rims was not found.

One of the most frequent type of ore mineralization in Variscan basement is Sb-Au mineralization. The deposit Pezinok–Staré Mesto is a unique type of mineralization in the Western Carpathians, where Au mineralization develops on its own, without connection with Sb mineralization.

## CARBONATE BEARING VEINS AND MELT POCKETS IN UPPER MANTLE XENOLITHS FROM THE BAKONY–BALATON HIGHLANDS AND LITTLE HUNGARIAN PLAIN, HUNGARY

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Lithospheric upper mantle xenoliths hosted in Neogene alkali basalts from the Bakony-Balaton Highlands and Little Hungarian Plain Volcanic Fields of the Carpathian-Pannonian Region have been studied extensively (e.g. EMBEY-ISZTIN *et al.*, 1989, DOWNES *et al.*, 1992,). However, detailed study on silicate melt pockets and veins occurring in these xenoliths has not been carried out yet. Melt pockets and veins recognized recently worldwide in peridotite xenoliths can form by host magma infiltration, decompression melting of mantle minerals or mantle metasomatism.

About 5 % of the Hungarian xenoliths contain carbonate bearing silicate melt veins and pockets. Silicate melt veins, occurring as thin parallel veins crosscutting the whole xenolith, contain immiscible andesitic silicate glass and calcite with various amounts of MgO (up to 2.29 m/m%), FeO (up to 0.46 m/m%), MnO (up to 0.63 m/m%) and SrO (up to 0.50 m/m%). Small amounts of idiomorphic spinel and clinopyroxene can also be found in these veins. Silicate melt pockets, sometimes showing shapes after clinopyroxenes and/or amphiboles, differ in composition from those of veins. Glasses in the pockets are basaltic to andesitic and the carbonates have elevated MgO (up to 3.15 m/m%), FeO (up to 0.54 m/m%), MnO (up to 1.51 m/m%) and lower SrO (0.00–0.13 m/m%) content compared to carbonate in veins. These carbonate compositions are consistent with those recorded in peridotite xenoliths in Mongolia and Spitsbergen (IONOV, 1998).

Based on the modal composition of melt pockets and the chemical composition of mineral phases, we calculated the bulk composition of silicate melts that filled up the melt pockets. The calculated bulk compositions are strongly different from the compositions of primary mantle minerals (amphibole and clinopyroxene) which can melt and those of the host alkali basalt. We suggest that these mantle minerals reacted with a carbonatitic melt migrating in the upper mantle. This percolating melt could have caused mantle metasomatism and reaction melting in the mantle prior to the basaltic volcanic activity. Based on our estimation this percolating silicate melt which metasomatised the upper mantle contained carbonate up to 44 %.

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## IDENTIFICATION OF PROVENANCE OF ANCIENT AMBER BEADS FROM ROMANIA BY <sup>13</sup>C NMR AND FTIR SPECTROSCOPY

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Amber occurs in Romania along the length of the Carpathian Mountains. Chemical properties of Romanian amber was described by GHIURCA & VAVRA (1990). Until now many archaeological beads have been found in different parts of Romania, but their exact sources have not yet been investigated by modern spectroscopic methods.

Fragments of two archaeological beads, one (R14) found in the cave of Cioclovina and the other (R15) found in Piatra Cetii in Romania were studied by solid-state <sup>13</sup>C NMR and FTIR spectroscopy together with thirteen authentic samples of Romanian amber.

Solid-state <sup>13</sup>C NMR spectra of the samples were obtained using a Bruker MSL 300 spectrometer and the FTIR spectra were measured using a Perkin-Elmer 1760 FTIR spectrometer applying the KBr pellet method.

As far as the FTIR spectra of Romanian amber are concerned, the absorption bands in the region from 4000 to 1456 cm<sup>-1</sup> are almost identical in all specimens and the main differences are observed in the region from 1374 to 870 cm<sup>-1</sup>. It was noted that, in some cases, specimen of the same source, e.g. from Colti, can be recognised according to the pattern of their FTIR spectra in the region from 1347 to 870 cm<sup>-1</sup>. This is also true for the specimen from Motoca.

The most significant results of the present investigation are the following. The solidstate <sup>13</sup>C NMR spectra of the samples R14 and R15 match the spectrum of Baltic amber (LAMBERT & FREY, 1982) and differ from those of the samples of Romanian origin. Similarly the FTIR spectra of R14 and R15 differ completely from those of Romanian amber and are the spectra of Baltic amber = succinite (Beck, 1986).

The present investigation proves for the first time that not all archaeological beads found in Romania are of Romanian origin but some of them, e.g. the beads R14 and R15 are of Baltic origin. According to BACHOFEN-ECHT (1949) an ancient trade route existed on the North and East side of the Carpathian Mountain range along which amber used to be transported to Southern Europe via Romania. Hence it may be assumed that the beads R14 and R15 were once brought to Romania either as finished products or as raw materials out of which they were made.

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## INVESTIGATION OF FLUID INCLUSIONS IN "MARAMUREŞ DIAMONDS" BY FTIR SPECTROSCOPY

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Due to their sparkling appearance, limpid quartz crystals from Romania are called "Maramures Diamonds." GHIURCA & VALACZKAI (1996) described the host rocks, origin of  $SiO_2$ , shapes and dimensions of these crystals and compared them with other similar occurrences.

PINTEA (1995) identified several fluid inclusions, e.g. water, hydrocarbons and  $CO_2$  in these crystals by microthermometry. But the different types of hydrocarbons could not be differentiated by this method. Due to this reason FTIR spectroscopy was used in the present investigation.

An overview of bigger (>1mm) inclusions were obtained by a FTIR spectrometer (Perkin-Elmer 1760), equipped with a diffuse reflection accessory. The smaller inclusions (ca. 10  $\mu$ m) were investigated by direct transmission using a FTIR microscope (Perkin-Elmer, Auto-image).

It was possible by the present investigation to distinguish between inclusions of  $CH_2$ ,  $CH_3$  and  $CH_4$ . In addition to that inclusion of  $H_2S$  was identified in some samples as follows.

Band (cm <sup>-1</sup> )	<u>Vibration</u>	Inclusion
1604	H-O	Water
1640	C=O	Carbonyl
1787	C=O	Carbonyl
2361	C-0	Carbon dioxide
2598	H-S	Hydrogen sulphide
2663	H-S	"
2930	C-H	$CH_2$
2960	C-H	CH <sub>3</sub>
3013	C-H	$CH_4$
3200	=CH-	CH <sub>aromat</sub>

Results: Fluid inclusions identified in Maramures Diamonds:

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## HIGH-TITANIUM BIOTITE FROM GRANULITIC ROCKS – WHAT IS IT?

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High-titanium biotite is undoubtedly a typomorphic mineral of granulitic rocks (Ramberg, 1952; Snelling, 1957; Engel & Engel, 1957; Miyashiro 1958; Drugova, 1960; Wilikoslawinsky, 1960; 1965; Korikowsky, 1960; 1967; Phinney, 1960; Marakushev, 1961; Oki, 1963; Nikitina & Khiltova, 1964; Nikitina, 1965; Drugova & Glebovizky, 1965; Siroshtan, 1965; Sherbakov, 1965; Kizul, 1966; Zakrutkin, 1966; Ushakova, 1971; Duk & Baikova, 1975; Lennykh, Pankov & Petrov, 1978; Korovko, 1985). The general opinion on this question has not been shared only by scientists who supposed that Ticontent in biotite does not depend on temperature and, consequently on stage of metamorphism (Saxena, 1966). It was also mentioned that the lowest Al-content is associated with high-titanium content in biotites (Korikovsky, 1967).

Analysis of original samples and literature analytic data on trioctahedral micas has proved that high-titanium biotite is a common mineral of phenites (Bussen, 1972; Krivdik & Tkachuk, 1990), sienites (Perchuk & Pavlenko, 1967), miaskites and miaskitic pegmatites (Ronenson & Levin, 1974; Kaumov, 1971), carbonatites (Eskova, 1964; Belkovsky & Loktina, 1998), ditroites (Tichonenkova, Nechaeva & Osokin, 1971), shoshonites of island arcs (Zvetkov, 1982). These data indicate that high-titanium biotite is not a unique feature of granulitic rocks. High-titanium biotite is a common mineral of phenitisied gabbroides and granites (Zimin & Starkov, 1971; Panov, 1979; Belkovsky & Loktina, 1997; Borodina, 1987) as well as alcaline metasomatites formed on ultramafic rocks (Polkanov, Eliseev & Eliseev, 1967; Avakyn, 1992).

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## Ti-Zr- AND REE-MINERALIZATION ASSOCIATED WITH DOLOMITE-CALCITE CARBONATITES (THE MIDDLE URAL, RUSSIA)

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The high-pressure zone of the Ufaley metamorphic block (the Central Urals Rise, Middle Urals) is represented by mantle-crust eclogite-schistic melange. In the melange, mantle productions – "green" garnet clinopyroxenites and ore olivinites – have been altered into antigorite serpentinites. In the latter, bodies of magnetite-titanclinohumite-clinochlore rocks have been observed. From periphery to centre, the following zones were established: antigorite-titanclinohumite-chlorite. Central parts of the bodies are represented by Mn-picroilmenite-magnetite ore. In titanclinohumite, xenomorphic (10-150  $\mu$ m) inclusions of baddeleyite, favas-baddeleyite, apobaddeleyitic zircon and perovskite were detected.

Baddeleyite, calzirtite, zirkelite, perovskite, zircon and previously unknown in carbonanites monazite-(Ce) and xenotime-(Y) have been found in the Mn-picroilmenitemagnetite ores. Superimposed on ultramafites, an exotic REE-mineralization was developed due to carbonatite-forming processes of dolomite-calcite facies. Titanclinohumite and Mn-picroilmenite-magnetitic rocks with zircon and rare-earth mineralization should be considered as mantle apoultrabasite fenites. The chemical composition of calzirtite, zirkelite and perovskite is closed to the stochiometric; this feature distinguishes the investigated association from Nb-Ti-Zr-oxides camaforites of central type alcaline-ultrabasitic intrusions.

## CLAY MINERALS OF SAPROLITE AND RED CLAYS FORMED ON ANDESITE IN THE MÁTRA MOUNTAINS

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Red clays and andesite saprolite occur near the surface around Mátraháza and in the valley of Somor Creek. They unconformably overlie the grey pyroxene andesite indicating that they were reworked by mass transport. The aim of the present work is to find connection between the saprolite and red clays in the mountains and paleosols located on the southern pediment of the Mátra Mountains. Stratigraphy, mineralogy and pedology of paleosol profiles were studied by MICHÉLI *et al.* 1997, HORVÁTH 1999 and NÉMETH *et al.* 1999 on the southern where greyish and red paleosols were identified between the Pannonian sediments and the topsoil. The morphology of the studied red paleosol indicates that the parent material of the paleosol was not formed in situ.

Petrographic and mineralogical studies (XRD, DTA) were carried out on samples from around Mátraháza and the valley of Somor Creek from the fresh rock, weathered rock fragments and the weathering product (red clay). The texture of the weathered shows the original structure but it became rcd with some white and yellowish green grains. It consists of dioctahedral smectite, cristobalite, feldspars and some pyroxene. The predominating mineral in the red clay is a dioctahedral smectite having beidellitic character as the layer charge originates from the tetrahedral sheet and low layer charge. Besides smectite, they contain cristobalite, hematite and quartz in minor amounts and kaolinite interstratified with smectite in plagioclase remnants. The yellowish green grains are nontronite, based on the 060 reflection at 1.51-1.52 Å.

The feldspars of the massground have changed completely to smectite and in the meantime some  $SiO_2$  precipitated. The feldspar phenocrysts have only partially altered to smectite with some interstratified kaolinite. These data suggest that the red clay may have been the parent material of the red paleosols on the pediment.

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## CLAYEY MINERALS OF PRE-CARPATHIAN EVAPORITE DEPOSITS, UKRAINE

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Pre-Carpathian evaporite deposits characterise with exceptionally high content of the clayey minerals. Their main quantity had been supplied into Miocene salt-origin basin from Carpathian mountains during flysch series denudation with a help of water steams.

Illite terrigenous origin confirms by its age determined with K/Ar-method (154-278 mln. years).

Terrigenous clayey minerals had been altered considerably during progressive salinization of the Miocene basin. It's confirmed by presence in Carpathian flysch series of the illite, smectite, chlorite, kaolinite and mixed-layered phases, while in salinizated sandy-clayey deposits of Pre-Carpathian Foredeep one can see illite and chlorite with some admixture of kaolinite and disordered mixed-layered phase (illite-smectite) and in evaporites - only illite and chlorite. Such simplification of the clayey minerals is resulted by unstability of the terrigenous smectite and kaolinite under influence of the high magnesium and potassium ions concentrations and its transformational alteration into illite and chlorite.

Terrigenous illite in salt - origin basin had been altered too. These changes are connected with potassium content increase and decrease of the low-temperature water and swelled smectite layers.

Illite had been altered actually into dioctahedral aluminium mica as chemical and Xray analyses testify. Illite alteration into mica as it's known takes place on katagenesis stage under comparatively high temperature. In accordance with our investigations this process can also take place and under quite low temperature in presence of the high potassium ions concentrations in salt-origin basins on the potassium salts crystallization stage. At the same time alterations of chemical composition and structural peculiarities of the magnesium-ferruginous chlorite had took place by increase of magnesium content and crystallinity degree.

Close connection between chemical composition, structural peculiarities, clayey minerals paragenetic associations and its origin can be used for ascertaining of the salt-accumulation geological conditions in sedimentation basins.

## ILMENITE PSEUDOMORPHS AFTER TITANITE FROM THE GRANITE ROCKS IN THE TRIBEČ MOUNTAINS (WESTERN CARPATHIANS)

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A new type of the titanite alteration, not described up to now, has been observed in the granitoids of the Tribeč Mts., which belong to one of the core mountains of the Western Carpathian region. Euhedral wedge shaped titanites in these granites were substituted by ilmenite whereas their characteristic shapes were preserved and these grains became black. The newly formed ilmenite in the high level alteration products contain not less then 95% of the ilmenite modal composition of the former titanite. Such strong mineral exchange were observed only in the highly deformed (mylonitized) granitoids with sericite-epidote and chlorite matrix after rock forming minerals. However, the initial stage of the titanite breakdown process is a very widespread phenomenon in the granites of the south-west part of the Tribeč Mountains. The titanite host rocks represent mainly the granodiorite-tonalites which belong to the granites with I-type tendencies (PETRIK & KOHUT, 1997). The Upper Carboniferous age of these granitoides is known from U/Pb dating of zircons (306  $\pm$  10 Ma, BROSKA *et al.*, 1990).

Titanite breakdown products in the initial stage of alteration are firstly concentrated near rims inside titanite, then replacement continues irregularly in other parts within titanites. The final stage is represented by the replacement of the whole titanite grain by the newly formed ilmenite mineral phase. The ilmenite is rich in manganese that indicates its relatively low temperature origin (LYACHOVITCH, 1973). Except for ilmenite, mainly quartz but also epidote and allanite appear as further alteration products. The formation of numerous pores accompanies this breakdown process and the titanite obtains a more or less porous structure. The allanite and REE epidote inclusions in titanite originated by leaching of REE's from titanite (PAN *et al.*, 1993). In comparison with primary allanite (approx. 10 wt % Al<sub>2</sub>O<sub>3</sub> and 6 wt % total FeO), the secondary one is richer in aluminum and iron (approx. 20 wt% Al<sub>2</sub>O<sub>3</sub> and 10 wt % total FeO).

It is highly probable that the origin of secondary ilmenite and other mineral phases inside titanite would be the process which is connected with subsolidus alteration of rock that indicates the chemistry of alteration products and the porosity of the altered titanite.

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## EXCHANGE TRANSFORMATION BETWEEN ALLANITE AND MONAZITE MINERAL PHASES ON THE EXAMPLE OF THE WEST CARPATHIAN ORTHOGNEISSES

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Accessory monazite and allanite are two the most frequent primary magmatic LREE accessory mineral phases in the granites and orthogneisses in the Western Carpathians (PETRIK, 1999). Total breakdown of monazite was observed in metagranites of the Veporic Superunit in the Western Carpathians, while only slight alteration of monazite occurs in non-metamorphosed Tatric granites (BROSKA & SIMAN, 1998).

Monazite breakdown reactions have been observed in granites from a wide region of Central Europe including the Western Carpathians, the Tauern Window and the southern Bohemian Massif (FINGER *et al.*, 1998). The process always results in the mantling of monazite crystals by concentric coronas of apatite, allanite and REE bearing epidote. In extreme cases monazite cores are fully consumed by apatite which occupies the place of the former monazite. Upto this date, such total breakdown of monazite was described in the world only in the Veporic Superunit. However, it appears that the reaction kinetics is so sluggish that monazite relicts usually remain in the center of the grains. It was proven that no significant disturbing of the the U–Pb system in the breakdown monazite grains is recorded (FINGER *et al.*, 1998). Monazite alteration to apatite, allanite and REE bearing epidote was always observed in amphibolite facies.

The orthogneisses on the southern slope of the Low Tatra Mountains contain metamorphic monazite, evident from their U-Th microprobe monazite dating. These indicate an age coincident with the main Variscan collision stage between Europe and Gondwana (paper in preparation). Metamorphic monazite in these orthogneisses contain allanite inclusions that show their possible origin from allanite by transformation reactions during Variscan metamorphic events. The formation of monazite by breakdown of allanite was described already from the Swedish–Norwegian province (BINGEN *et al.*, 1996).

Both of the above described transformations (monazite-to-allanite and allanite-tomonazite) clearly indicate the mobility of the rare earth elements during metamorphic processes and that this mobility increases between amphibolite facies conditions.

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## FOITITE AND SODIUM DEFICIENT SCHORL IN THE SPIŠ-GEMER AND KLENOVEC GRANITE, EASTERN SLOVAKIA

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Recently, it has become apparent that vacancy tourmalines are more common than was hitherto realised, and it now seems reasonable to subdivide the tourmaline group into three subgroups: (1) calcic, (2) alkali (Na and K), (3) vacancy tourmalines (HAWTHORNE & HENRY, 1999). Fe-bearing vacancy tourmaline or alkali deficient tourmaline is named foitite (MACDONALD *et al.*, 1993), Li rich rossmanit (SELWAY *et al.*, 1998) and the Mg-bearing variant is still only predicted as Mg-foitite. Foitite was found in the Zlata Idka granite body and especially in their magmatic derivatives (BROSKA *et al.*, 1999).

Tiny crystals (0.3–0.4 mm) of disseminated accessory foitite with zones of schorl were found in biotite-muscovite leucogranite of Permian age near Zlatá Idka village, Spiš–Gemer Ore Mts., Gemer superunit (eastern Slovakia). Blue foitite forms irregular patchy zones (<0.2 mm in size) which replaces the primary brown schorl. EPMA analyses of foitite reveal a high Fe/(Fe+Mg) ratio (0.85–0.95); the ratio is higher than that of schorl (0.69–0.91). Low Na (1.2–1.5 wt% Na<sub>2</sub>O) and trace K and Ca resulted in an alkali deficient stoichiometry of foitite:  $^{X}\square$  = 0.51–0.61, whereas schorl reveals  $^{X}\square$  = 0.16–0.49. Replacement textures as well as gradual transitions of colour and composition from schorl to foitite indicate a secondary, probably hydrothermal origin of foitite by partial leaching of Na from primary magmatic schorl, along with the substitution:  $^{X}\square$  +  $^{Y}Al$  =  $^{X}Na$  +  $^{Y}Mg$ . The late aplitic dykes of the Zlata Idka granite body contain large aggregates (1 cm crystals) of the blue foitite with  $^{X}\square$  up to 0.7.

Late magmatic and probably post-magmatic hydrothermal alkali deficient blue schorl forms overgrowths around primary brown schorl in the Hnilec granite, ca. 50 km to the west from Zlatá Idka (BROSKA *et al.*, 1998). Replacement textures as well as gradual transitions of colour and composition from schorl to foitite from the Zlatá Idka granite indicate their secondary, probably hydrothermal origin by partial leaching of Na from primary magmatic schorl, along with the substitution:  ${}^{X}\Box + {}^{Y}Al = {}^{X}Na + {}^{Y}Mg$ . Ca, Ti and partly Mg could also be removed from primary schorl.

The foitite was discovered also in the Klenovec granites of the Vepor superunit which probably represent an analogue of the Spiš–Gemer granites.

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## ORGANIC MATTER MIGRATION IN THE TECTONIC ZONES OF THE POLISH WESTERN TATRA MOUNTAINS

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The crystalline basement of the Polish part of the Western Tatra Mts. is cut by shatter zones and faults running SW–NE. Some of these tectonic zones cut the Mesozoic sedimentary cover, trending further to NE. In the mylonitized rocks in the tectonic zones the presence of dispersed extractable bituminous organic matter was shown using Oxyreactive Thermal Analysis.

The oxyreaction patterns are characterised by the endothermic peaks in the range of 240–290 °C, while the exothermic (oxidation) reactions took place in the range of 300–320 °C. Such oxyreaction patterns suggest the susceptibility of parent organic matter to high temperature pyrobitumen formation.

Dry powdered samples were extracted in dichloromethane and fractionated into aliphatic, aromatic and polar organic fractions using thin-layer chromatography. GC-MS analyses of aromatic and aliphatic fractions show that all samples are on much the same level of maturity. In the saturated gas chromatogram  $n-C_{17}$  and  $n-C_{18}$  n-alkanes predominate. The pristane (Pr) to phytane (Ph) ratio is about 1. The m/z 191 mass fragmentograms of the aliphatic hydrocarbon fraction of all analysed samples show the high abundance of pentacyclic triterpanes and tricyclic terpanes ( $C_{23}$  is dominant) with lower amount of tetracyclic terpanes. The m/z 217 mass fragmentograms display high abundance of diasteranes and low molecular weight steranes (pregnanes) in relation to regular steranes. The biomarker analysis showed no evidence of higher plant material occurrence and this, together with a very low ratio of dibenzothiophene to phenanthrene (HUGHES *et al.*, 1995), suggests marine, oxic shale environments of the source rocks formation.

The theoretical value of vitrinite reflectance, based on metyldibenzothiophene ratio (RADKE *et al.*, 1986, RADKE & WILLSCH, 1994) are in the range of  $R_{cs} = 0.75-0.82$  %, which indicates the oil window thermal conditions for hydrocarbons generation.

The investigated hydrocarbons are allochthonous in character, probably migrated through the shatter zone and faults from an unknown source.

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## ORE MINERALIZATION OF THE TATRIC UNIT, WESTERN CARPATHIANS, SLOVAKIA

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The Tatric basement is built of large Variscan granitoid plutons emplaced within medium to high grade metamorphic rocks like gneisses, anatectic migmatites and amphibolites. Low to medium grade shales and basic rocks of the Devonian to Early Carboniferous are less abundant. Crystalline sequences are exposed in the central, most elevated parts of core mountains. The Tatric cover comprises characteristic lithological members: Upper Carboniferous and Permian molasse sediments, bimodal volcanics and Lower Triassic-mid-Cretaceous sedimentary rocks. A few Mesozoic nappes were thrust from the S and overlie the Tatric basement and cover complexes.

Formation of the most important ore mineralizations is believed to be linked either to Variscan granitoids or metamorphism. Scheelite, molybdenite and pyrite-arsenopyrite mineralization were formed at highest temperatures. The arsenopyrite, less frequenty pyrite, are usually rich in gold (invisible gold). Au bearing quartz mineralization is often associated with stibnite mineralization, the most important and most abundant in the Tatry and Male Karpaty Mts. The stibnite mineralization is accompanied by Pb, Zn sulphides and Pb-Sb(-Bi) sulphosalts, Ag bearing tetrahedrite and barite mineralization. Barite mineralization with galena is thought to have formed during Variscan tectonometamorphic event, although Alpine remobilization cannot be ruled out. Sideritesulphide mineralization of the Tatric unit may be analogous to the vein type of siderite mineralization of the Gemeric unit. Most frequently its Alpine age is cited, although there of Variscan age, and/or Alpine remobilization. Permian exist indiations volcanic/sedimentary complexes of the nothern Tatric unit carry minor occurrences of primary U (Mo, Cu) mineralization. Negligible concentrations of barite and Cu minerals are connected with the Permian melaphyre volcanism. Small occurrences of base metal and hematite mineralizations in Mesozoic sequences probably formed during the Alpine epoch.

Fluid inclusion and sulphur and oxygen isotope studies indicate metamorphic and/or magmatic origin of the  $CO_2$  rich fluids from the high temperature scheelite, molybdenite and arsenopyrite mineralizations. Wide range of salinities (3–24wt% NaCl), CaCl<sub>2</sub> rich composition of barite associated fluids, dilution trends and C, O isotope fluid signatures suggest an important role of interactions between formation and meteoric waters during crystallisation of low-T minerals, including the economically most important stibnite.

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## GEOCHEMISTRY OF THE BREZOVÁ POD BRADLOM BAUXITE, SLOVAKIA

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#### Geological setting

The bauxite from Brezová pod Bradlom represents the last bauxite deposit found in Slovakia (ČINČURA, 1998) and is restricted to the northern part of the Malé Karpaty Mts. near the city Brezová pod Bradlom. It represents a further link in the chain of the north Slovakian and Austrian bauxites. All Western Carpathian bauxites, including the Brezová pod Bradlom occurrence, belong to the group of karst bauxites and are closely connected with the longest and most important paleokarst period in the Western Carpathians, the Paleoalpine karst period (ČINČURA & KOEHLER, 1995). The bauxite fills up the basal parts of Pre-Gosau canyon-like depressions in the Upper Triassic Hauptdolomite, occurs in irregular, most probably small lens shaped bodies and is relatively rare. The covering formation of the bauxite forms the coarse and medium grained, basal Valchov conglomerate of the Upper Cretaceous Gosau group.

#### Mineralogical and chemical composition

The presence of individual mineral phases (boehmite, kaolinite and chlorite) was determined by X-ray diffraction. The results of semiquantitative analysis show that boehmite is the main alumina mineral of the bauxite. Its average content ranges between 53–68 %. Kaolinite content varies from 12–15 %. The relatively high average content of chlorite (19 to 37 %) is striking (ČINČURA, 1998).

The content of Al<sub>2</sub>O<sub>3</sub> in individual bauxite samples varies from 38.90 to 41.48 %. The range of total Fe<sub>2</sub>O<sub>3</sub> content varies in individual bauxite samples from 15.53 to 16.58 %. The content of Al<sub>2</sub>O<sub>3</sub> in individual bauxite clays varies from 17.47 to 37.61 %. The range of total Fe<sub>2</sub>O<sub>3</sub> content varies in individual bauxite clays from 7.04 to 21.18 %. The trace elements of bauxites/bauxite clays, which may reflect the source area (V: 261–630 ppm, Ni: 198–494 ppm, Cr: 101–316 ppm, Zr: 101–954 ppm), indicate that the geology of the source area was complex, and marked by a significant proportion of alkaline eruptive rocks or crystalline shale. A significant part of the parent rocks of the bauxite originates probably from paleovolcanites of the Hronic, occurring at present especially in the Malé Karpaty Mts.

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## INDEX MINERALS FOR THE ALPINE METAMORPHISM OF VOLCANIC-VOLCANICLASTIC ROCKS FROM THE DANUBIAN WINDOW, SOUTH CARPATHIANS, ROMANIA

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Mesozoic volcanic-volcaniclastic sequences from the Danubian Window (South Carpathians) show index minerals for an Alpine metamorphism in prehnite-pumpellyite to pumpellyite-actinolite facies. Microprobe analyses of index minerals from Late Cretaceous volcaniclastic turbidites (Cosustea Nappe) and Late Jurassic basalts (Severin Nappe) are presented.

The chemical analyses indicate that **prehnite** from volcaniclastic rocks of the Cosustea Nappe shows relatively high Fe contents.

For **pumpellyite**, widespread in rocks from both nappes, microprobe analyses show that compositional variation of Fe contents occur only in the prehnite-pumpellyite facies, whereas in pumpellyite-actinolite facies only low Fe pumpellyites occur.

Actinolite occurs in basalts of the Severin Nappe. The chemistry of actinolites varies between  $Mg/(Mg+Fe^{2+}) = 0.69$  and 0.81.

**Chlorite** is present both in prehnite-pumpellyite and in pumpellyite-actinolite facies. On a non-interlayer cation vs. Al plot the chlorite analyses scatter close to clinochlore; on the diagram  $Si-Fe^{2^+}$ -Al the analyses are situated between chamosite and clinochlore.

The white mica is ubiquitous in all samples analysed. On a Si vs. Al(total) plot, the results of the chemical analyses plot on the Tschermak exchange vector between celadonite and muscovite. Some analyses fall a little below this solid solution line, indicating a small ferri-muscovite component.

Illite crystallinity values, determined on metapelites associated to the volcanicvolcaniclastic rocks, indicate similar metamorphic grades, i.e. anchizone (which corresponds to the prehnite-pumpellyite facies) and epizone (which corresponds to the pumpellyite-actinolite facies).

## BISMUTH SULPHOSALTS IN THE NEOGENE HYDROTHERMAL VEIN ORES FROM THE BAIA MARE ORE DISTRICT

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Bismuth minerals are mainly represented by Bi-Cu-Pb phases. Bi-Pb with Ag and Bi-Ag have been identified only in two vein ore deposits, i.e. at Nistru and Băiuț, in the western and eastern part of the area, respectively.

The presence of bismuth sulphosalts in several occurrences of the Baia Mare area has recently been documented by COOK & DAMIAN (1997) and DAMIAN (1999).

The Bi sulphosalts from Nistru and Băiuț are present within the cupriferous sequences with gold and silver content which are connected with the Pannonian calc-alkaline igneous rocks of subvolcanic character (porphyry quartz-monzodiorites, porphyry microdiorites).

The Bi sulphosalts from Nistru and some of the Bi minerals from Baiut represent the first chemically documented occurrences. In both occurrences the Bi sulphosalts are mainly represented by the members of the lillianite homologous series. The compositional homogenity is emphasized by microprobe analyses yielding the general formula  $Pb_{1.47-1.97}Ag_{0.39-0.66}Fe_{0.03-0.19}Cu_{0.07-0.032}Bi_{2.40-2.53}Se_{0.02}S_{5.48-5.79}$ ), as well as by a small deviation from the theoretical line N = 4 of the members of the lillianite–gustavite series. Some mineral phases reminiscent of vikingite (N = 5.08) and heyrovskite are present mainly at Băiut.

The Bi minerals of the lillianite–gustavite series occur as inclusions in chalcopyrite or quartz and contain minute gold grains. In the Nistru ores the Cu-Pb-Bi sulphosalts are represented by compositions varying from pekoite  $(Cu_{0.55-0.70}Fe_{0.06-0.33}Pb_{0.20-0.90}Bi_{7.14-7.48}Se_{0.03-0.35}S_{11.50-12.26})$  to krupkaite  $(Cu_{1.88-2.17}Fe_{0.08-0.27}Pb_{1.85-1.97}Bi_{5.78-6.04}S_{11.98-12.19})$ , with subordinate participation of gladite  $(Cu_{1.30}Fe_{0.13}Pb_{1.2.1}Bi_{6.66}S_{11.58})$ . They are subordinately associated with matildite  $(Ag_{0.87-0.94}Cu_{0.08}Bi_{0.94-1}S_{1.87})$ . Cosalite has been identified in a few cases as a result of Bi enrichment and Pb depletion  $(Pb_{1.53-1.57}Ag_{0.013-0.014}Fe_{0.07-0.1}Cu_{0.26-0.33}Bi_{1.85-1.93}S_{4.58-4.76})$ .

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## TETRAHEDRITES FROM THE BAIA MARE NEOGENE ORE DISTRICT, ROMANIA

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The tetrahedrites are the most frequent sulphosalts in the base metal and gold ores of the Baia Mare ore district. EPMA allowed several types of tetrahedrites to identify. The Sb rich members are dominant. The contents in Zn and Fe are up to 7–8 % and are characteristic for all the investigated tetrahedrites. An exception is a sample which contains 21.33 % Fe and is rich in As, too. All the tetrahedrites contain up to 2 % Ag. A group has been separated which contains 10–29 % Ag including argentian tetrahedrites and freibergites. The coefficient of Ag in the formula of these tetrahedrites is between 1.5-5.7.

In all the examined samples As and Sb are present together and only in a small part of them is either As or Sb dominant. Bi and Te take one of the positions of As and Sb, Se substitutes for sulphur. The positions of  $Cu^{2+}$  are taken by Fe or Zn and only in the intermediate members they substitute for Cu in almost equal quantities. Zn substitutes for Cu in great amounts in the Sb rich tetrahedrites but Fe is a substitute of Cu in the As rich ones and in some Ag rich members, Ag substitutes only monovalent Cu. The substitution of the monovalent Cu with Ag takes place at the same time with the substitution of the bivalent Cu with Fe. These substitutions usually take place in the Sb rich tetrahedrites and are demonstrated by the good correlation of Fe/Ag. The argentian tetrahedrites show a limited substitution of Sb for As.

The cell parameter, calculated after CHARLAT & LEVY (1975), is between a = 10.172-10.578 Å. For tennantite, the *a* parameter varies between 10.172-10.240 Å, which is close to that of pure tennantite (a = 10.18 Å). The tetrahedrites have values between a = 10.358 and 10.383 Å and correspond to the value of pure tetrahedrite (10.33). The presence of silver in tetrahedrites increases the cell parameter (CHARLAT & LEVY, 1975), which is of 10.412-10.578 Å for the argentian tetrahedrites and 10.706 Å for freibergite. According to RILEY (1974), the highest value of the cell parameter is 10.59 Å when the Ag content is of about 20 wt%.

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## MINERALOGICAL CHARACTERISATION OF THE META-MORPHIC ROCKS FROM ȚICĂU HILL (NW TRANSYLVANIA, ROMANIA) AND THEIR CONTRIBUTION TO A RECONSTRUC-TION OF THE REGIONAL METAMORPHIC EVOLUTION

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The Țicău Massif appears like a crystalline island in the northwest of the Transylvanian Basin, surrounded by Tertiary sedimentary formations. From the tectonical point of view, most of the authors assign this massif to the northern structures of the Apuseni Mountains. From the petrographical point of view it is formed of metamorphic rocks belonging to the amphibolite facies: plagioclase bearing gneisses, mica schists, K-feldspar bearing gneisses, quartzites, amphibolites.

For the mineralogical characterisation microscopical observations on oriented thin sections and microprobe electron analyses were made. Thus, four mineral assemblages could be observed: (1)  $qtz + pl + ms + bt \pm grt$ , chl, kfs, ep; (2)  $qtz + ms + bt + grt \pm chl$ , cld, pl; (3)  $qtz + pl + kfs + ms + bt \pm chl$ , grt; (4)  $qtz + pl + amph + bt \pm chl$ , grt.

Quartz – the most common mineral, it is present in all these four assemblages.

Plagioclase -- anorthite content between 25-30 %, typical for the oligoclase species.

K-feldspar – microcline is the principal K-feldspar of the third assemblage.

**Muscovite** – the chemical analysis shows the following:  $Ms_{62-70}Pg_{11-23}Ce_{7-17}$  $Mrg_{0-2}Prl_{0-6}PhlAnn_{0-4}Ti-Ms_{1-5}$ .

**Biotite** – can be attributed to the phlogopite–annite series with the following end member composition:  $PhlAnn_{36-64}EasSid_{6-34}Won_{6-13}Ti-Bt_{8-15}TlcMin_{1-13}Ms_{0-10}$ .

Chlorite - belongs to the clinochlore-chamosite group (BAILEY, 1991).

**Garnet** – the microprobe analyses show the garnet close to the almandine species, having the following composition:  $Alm_{63-82}Prp_{6-12}Sps_{0-4}Grs_{4-21}Adr_{2-5}$  (DENUT & FLAUT, 1999).

**Amphibole** – we can point out the presence of two mineral species belonging to calcium amphibole group (LEAKE *et al.*, 1997): pargasite and magnesiohornblende.

On the basis of microscopic observations combined with microprobe chemical analyses, three regional metamorphic events of medium p/T type were pointed out (after MIYASHIRO, 1994): M1 – transient facies, garnet zone; M2 – amphibolite facies, staurolite zone; M3 – greenschist facies, chlorite zone.

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## COMPARATIVE ANALYSIS OF GEOCHEMICAL PECULIARITIES OF GOLD BEARING DEPOSITS

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Geochemical features of major associated elements of gold deposits as well as their role in gold mineralization were studied. Within Ukrainian territory the following most typical gold ore formations are known: a) the pre-Quaternary (Carpathians and Precarpathians); b) the pre-Cretaceous (Crimea); c) the pre-Jurassic (Dobrudzha); d) the pre-Mesozoic (Ukrainian Shield, Volin–Podolia). Among them the Carpathian region is worth particular attention, being the most perspective one. Such gold ore objects as gold-quartz, gold-adular-quartz, gold-quartz-beresite and gold-silver-argillitized formations are found to have formed as individual segregations. Complex gold- and gold-silver-polymetallic, barite-quartz and gold-quartz-sulphide objects may be combined to a special group. Laser mass spectrometry (LMS) and secondary ion mass spectrometry (SIMS), both of high sensitivity, locality and precision, were used for a determination of accompanying elements within the ore zones.

Three groups of deposits have been distinguished in this way. They are related to greenstone (the Ukrainian Shield), metamorphic (Donbass), terrigenous and volcanic rocks (Carpathian region), all characterized by quite definite geological and geochemical parameters. The characteristic elements for the first group are Pt, Ni, Co, V, Fe, Se and Te, for the second one W, Mo, Zn, Pb and Hg, whereas ore zones in the Carpathian deposits have the following characteristic element associations: Zn-Pb-Sb-Ag-Se, Cu-Bi-Hg-Te and Ba-Sr-As. The Ag/Au ratio varies from 0.4 to 20. Silver is a typical typomorphic element of the Carpathian gold ore deposits.

An indicative role of the  $10^9$ Ag/ $10^7$ Ag isotope ratio is also defined. It is found to be regularly changing in vertical direction within ore zones. Thermal conditions of crystallization, which promote formation of sulfide bearing inclusions, influence the ratio considerably. When temperature of ore formation increases, the enrichment of native silver in the light isotope  $10^7$ Ag takes place, whereas sulfide bearing inclusions are enriched in heavier isotope  $10^9$ Ag. This process is more intense at elevated temperatures. Due to the prevailing bonding of sulphur atoms to one of the Ag isotopes, there are differences in  $10^7$ Ag takes in samples with different sulphur contents. An increase of the  $10^9$ Ag/ $10^7$ Ag ratio is typical for upper ore zones. This factor can be a search indication for the mineralization prognosis on the depth and for the assessment of an ore body and to separate them by the degree of erosional truncation, and in the search for blind ore bodies. Zones with the stable and high Au/Ag ratio are typical for objects with a small vertical range of mineralization. Maximum Ag(total) and  $10^9$ Ag isotope concentrations are determinated in horizons making fluids.

According to our data the Muzhievske, Beganske, Berehivske, Sauljak, Kvasivske, and Kupljanske deposits are the most long range objects in the Carpathians.

## SOME PEGMATOPHILE AND SIDEROPHILE ELEMENT ENRICHMENTS IN MAFIC AND ULTRAMAFIC ROCKS IN HUNGARY

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We have studied the enrichments of some pegmatophile (Zr, Nb), transitional (Cr) and siderophile (Ni, Co) elements in more than 700 igneous and meta-igneous rocks in Hungary. Our aim was to delineate positive geochemical anomalies using optical emission spectroscopy and, as far as possible, to identify the mineral species bearing the above elements using electron microprobe analysis and optical microscopy.

The above pegmatophile elements were found to be enriched in the Mesozoic alkaline rocks from the Mecsek Mountains. The highest Zr enrichment (1119  $\mu$ g/g) was found in the phonolite of Dunaszekcső-2 core sample (248.4 m), where abundant eudialyte (with around 14 % ZrO<sub>2</sub> content) was identified in the groundmass by both the microprobe and under the microscope. The eudialyte appears to be stuffed with groundmass mineral inclusions (alkaline feldspars and foids) pointing to its late-stage crystallization from the silicate liquid. The highest Nb enrichment (190  $\mu$ g/g) was also found in the same rock. The Nb bearing phases, however, are far less abundant, and could only be identified by the microprobe as minute mineral grains of epistolite (Nb<sub>2</sub>O<sub>5</sub> content of around 45 %) and loparite (Nb<sub>2</sub>O<sub>5</sub> content of around 78 %). Significant Nb enrichment (171  $\mu$ g/g) was found in the alkaline trachyte sample of Somberek-1 core sample (1305 m), too. The Nb containing minerals here were TiO<sub>2</sub> phases (Nb containing rutile or nioboanatase) with Nb<sub>2</sub>O<sub>5</sub> content of around 4–8 %. Their varied textural appearance may point to both primary and secondary origin of the phases.

The transitional Cr with siderophile character as well as the siderophile Ni and Co are mostly enriched in metamorphosed Mg-rich ultramafic rocks (serpentinites). Cr. Ni and Co was found to attain highest enrichments in serpentinites of Felsőcsatár, Gyód (Gyód-2, 108 m) and Helesfa (Helesfa-1, 156 m). The element contents are around 0.3 %, 0.22-0.25 % and 80–100 µg/g, respectively. The principal Cr bearing phases in the Gyód and Helesfa core samples were Cr-magnetite with Cr<sub>2</sub>O<sub>3</sub> content of around 7-14%. In the serpentine itself, Cr<sub>2</sub>O<sub>3</sub> content of around 0.5 % and 0.8 % could also be found in the Felsőcsatár and Helesfa samples, respectively. In Felsőcsatár, Ni and Co enrichments were found in different phases, namely in gersdorffite-cobaltite intergrowths (with Ni content of around 14-18 % and Co content of around 12-16 %) and in linneite (with Ni and Co content of around 21 % and 7 %, respectively). Ni was rarely found also in ullmannite (with Ni content of around 34 %). The origin of these sulfide phases can most probably be linked to fluid remobilisation processes during metamorphism. Unlike the Felsőcsatár serpentinite, the Ni bearing phase in Gyód is the secondary Ni silicate, garnierite (with Ni content 31-39 %). In the Helesfa serpentinite the only Ni containing mineral found was the serpentine itself with around 1.3 % NiO.

### SILVER MINERALS IN THE SLOVAK REPUBLIC

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Slovak deposits belonged to the most important producers of silver in Europe. From the presently known approx. 130 Ag mineral species, 48 were described on the territory of Slovakia. Only those were considered as silver minerals by us which contain Ag firmly bound in the lattice. Minerals in which is Ag present in inclusions or as small isomorphic admixtures were not considered as Ag minerals (e.g. jamesonit, galena etc.).

Silver ores were mined in Slovakia together with gold ores in a few regions. The most important region was that of the Central Slovak neovolcanites. According to the archive documents, Ag ores were mined as early as 1217 in the area of Banská Štiavnica (annual production about 600 kg Ag). The production reached its maximum in the 1740s – 600 kg Au and 23 metric tons of Ag per annum. Up to the end of the 18th century the output was 14 to 15 metric tons. In 1869 depression followed. Hodruša, Pukanec, Nová Baňa and Rudno nad Hronom also belonged to the important Ag ore producers during the 14<sup>th</sup> to 16<sup>th</sup> centuries. Ag ore mining in the Nová Baňa area started in 1337 and finished in 1887, according to the archives. Smaller Ag production came in 15<sup>th</sup> to 16<sup>th</sup> centuries also from the Čavoj deposit in Malá Magura Mts., from the Poniky region in the 16<sup>th</sup> century and from Zlatá Baňa (Slánske vrch Mts.) in the 14<sup>th</sup> to 16<sup>th</sup> century. According to archive documents Au and Ag ore mining in Kremnica was already quite intensive in 1385. The youth of mining in this territory reaches back to the 10th century. In the time from 1801 to 1852 the output was 118 kg Au and 4 metric tons of Ag annually, however, the boom here was in the 14th to 15th centuries.

The second most important area of Ag mining in Slovakia was the Slovak Ore Mts. Silver was obtained here mostly as a by-product together with gold and it was bound on Cu and Sb ores. Zlatá Idka was an important deposit, where Ag was mined from the 15<sup>th</sup> century. Between 1863 to 1873 2.8 metric tons of Ag was obtained here annually. Ag was obtained as a by-product also at the deposits of Rožňava, Gelnica, Smolník and partially in Rudňany.

In the area of Špania Dolina and Ľubietová Ag production was bound to Cu ores. In the time of the highest boom of these deposits the Fugger family produced about 115 metric tons of Ag. Small scale Ag ore production also came from deposits in the Low Tatras area, where deposits in the surroundings of Nižná and Vyšná Boca were known. Ag ore mining started here in 1267 with a maximum in the 14<sup>th</sup> to 15<sup>th</sup> centuries. Smaller Ag production came also from the Sb deposits of Dúbrava and Magurka. From the 13th century Au and Ag were obtained also from the Drienok deposit in Malé Karpaty Mts. From the 17th century underground mining was active here and the depression fell at the beginning of the 19<sup>th</sup> century.

During explorations in the Mária mine in Rožňava, in 1981 a silver vein was caught, where Ag was bound in tetrahedrite. Despite the fact that the Ag content is relatively high, the production up to now has not started.

### FIRST DESCRIPTIONS OF NEW MINERALS FROM SLOVAKIA

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Slovakia is a relatively small but, from mineralogical point of view, a very rich region. We can-name 16 new minerals described from 10 occurrences. 15 minerals of them are accepted and confirmed by the International Mineralogical Association (IMA) as new minerals. The approval of the latest one is not finished yet.

Rutile was the first described mineral found in the neighbourhood of Muráň (formerly Murány, Hungary) by Born in 1772 as basaltes ruber. The type locality is most probably Revúca (formerly Nagyrőce). The name rutile (from the Latin rutilus "reddish") was established by Werner in 1800, and published by Ludwig in 1803. Libethenite, originally named according to Leonard (1812) as "phosphorsaure Kupfer" was later (in 1823) renamed by Breithaupt as a "libethenite" after the German name of the village where it was found (Lubietová/Libethen). Breithaupt (1823) determined at this deposit (Svätodušná locality) another new Cu-arsenate, euchroite. It was named after the Greek word euchroes, "having a beautiful colour". Tetradymite (original name: "prismatischer Wismuthglanz") was first described as a new mineral from Župkov (formerly Zsubkó/Schubkau) by Wehrle in 1830. Its detailed mineralogical research was done in 1831 by W. Haidinger. It was named after its four-fold twins. K. Adler mining engineer found a new mineral in the sulphur mine of Vígľašská Huta-Kalinka (formerly Kalinka) in 1846, which was described by W. Haidinger (1847) as hauerite. It was named in honour of geologists Joseph and Franz von Hauer from Vienna, Austria. Evansite was first described as a new mineral from Železník, near Sirk (Zseleznik, later Vashegy) by Forbes in 1864. It was named after Brooke Evans (1797-1862), mining geologist and nickel trade in Birmingham (England), who had brought the specimen from Hungary. Two minerals of extraterrestrial origin, schreibersite (Haidinger, 1847) and cohenite (Weinschenk, 1889) were determined in the "Magura" meteorite, found in 1840 at Slanická Osada, near Námestovo. The following new minerals were described by Krenner from the Smolník (Szomolnok) deposit: kornelite (1888), rhomboclase (1891) and szomolnokite (1891). Vashegyite was described from Železník (formerly Zselezník. later Vashegy) by Zimányi in 1909. It was named after the Hungarian name of the locality. Schafarzikite was at first described as a new mineral from Pernek by Krenner in 1915. It was named in honour of F. Schafarzik (1854-1927), professor of mineralogy and geology in Budapest. Hodrushite was discovered in Banská Hodruša (now part of Hodruša-Hámre) by professor M. Koděra with colleagues (Koděra et al., 1970). Mrázekite was named in honour of Zdeněk Mrázek (1952-1984) and described from Ľubietová (Podlipa locality) by Řídkošil et al. (1992). The last new mineral from the area of Slovakia is telluronevskite (Bi sulphotelluride), described from the Poruba pod Vihorlatom occurrence (Řídkošil et al., 1998).

## ISOTOPIC COMPOSITION $\delta^{13}C$ AND $\delta^{18}O$ OF VEIN CALCITES IN FLYSCH DEPOSITS OF THE UKRAINIAN CARPATHIANS

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The structure of the Carpathian chain has a nappe pattern. Now the main outlook for the oil and gas fields is connected with thrust structures. The crack zones of allochthonous rocks were probably the way of migration of hydrocarbons and that is why the elaborate studying of the vein minerals can give us important information about the oil and gas content of the autochthon. Different hydrocarbons (as inclusions in main vein minerals such as calcite or quartz crystals called Marmarosh diamonds, hard bitumen, organic minerals and oil) are found almost in all rock complexes of the Ukrainian Carpathians.

With the purpose of investigation of the genesis of vein formations, the isotopic composition  $\delta^{13}$ C and  $\delta^{18}$ O of the main vein mineral (calcite) has been studied. The 52 specimens of the different aged complexes of different tectonic units of the Carpathians have been analysed.

The results of the analyses made it possible to draw the following conclusion. Values of  $\delta^{13}$ C of the vein calcite (-5.6 - +1.5 ‰) are close to the  $\delta^{13}$ C values of the enclosing rocks (-3.8 - -1.7‰).

In general, the isotopic composition of carbon becomes lighter in the direction from the Marmarosh massif to the Krosno zone. The reduction of weight of  $\delta^{13}C$  is connected with the presence of hydrocarbon inclusions. Vein calcite from Upper Cretaceous deposits has homogenous values of  $\delta^{13}C$  ranging between -2.6 ‰ and +1.5 ‰. The  $\delta^{13}C$  values of Lower Cretaceous and Paleogene deposits are similar one to another and a little lighter (-4.6 – +0.8 ‰ and -5.6 – +1.1 ‰). It can be explained in such a way. The main commercial reserves of gas and oil in the Carpathian region are connected with Paleogene deposits. The Lower Cretaceous deposits also have prospects of oil- and gas-bearing. Migration of hydrocarbon along the crack zones of these complexes caused the presence of the inclusions of gas condensate and "light oil" in vein minerals and the the reduction of weight of the isotopic composition of carbon. The similarity of average value of  $\delta^{13}C$  in calcite from Paleogene (-1.9 ‰) and Lower Cretaceous (-1.95 ‰) rocks confirm the idea about the possible oil and gas bearing of the Lower Cretaceous (-1.95 ‰) rocks confirm the idea about the possible oil and gas bearing of the Lower Cretaceous rocks.

Values of  $\delta^{18}$ O of vein calcite change from +19.4 ‰ to +27.7 ‰. Values of  $\delta^{18}$ O from Lower Cretaceous and Paleogene rocks show a wider range compared to Upper Cretaceous rocks. Average  $\delta^{18}$ O value of vein calcite is +21.3 ‰ for the Upper Cretaceous deposits and +22.4 ‰ for both Paleogene and Lower Cretaceous deposits.

Plotting these data in a  $\delta^{13}$ C- $\delta^{18}$ O coordinate system made it possible to single out the fields of different tectonic units of the Carpathians. One big field is formed by results of analyses of specimens from Rakhiv and Porculec nappes, which are located close to Marmarosh massif. Specimens from Chornogora nappe and Krosno zone forms the other field.

These results show that the studying of isotopic composition of carbon and oxygen of calcite from vein formations makes it possible to get an important information which can be used together with other geological and geochemical data for studying of the ways of migration of hydrocarbons and determination of prospects for oil- and gas-bearing of different sedimentary complexes of the Ukrainian Carpathians.

## Sb SULPHOSALT FORMATION IN THE BEREGOVO ORE FIELD (TRANS-CARPATHIANS, UKRAINE)

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In the Beregovo ore field there are the Muzhievo gold-silver-base metal and Beregovo gold-base metal deposits, where mainly sulphide (pyrite+sphalerite+galena), quartzsulphide and quartz ore bodies occur. In the Muzhievo deposit Ag-Sb-sulphosalts form rich Ag ores. Formation of Cu-Sb sulphosalts accompanied both of these ores and was completed before the formation of Au-Cu ores. All Sb sulphosalts are connected to galena bearing sulphide and quartz-sulphide aggregates. Only boulangerite was simultaneously formed with galena. In galena it forms thin grains. Their microaggregates. which often are observed as parallel "chains" (EMETZ & SKAKUN, 1999), formed as a result of fluctuation of Sb concentration in the solution forming Sb rich galena. Contact borders between galena and boulangerite bear the signs of concurrent growth. Along cavities and contacts of galena there are thin bands of Ag or Cu sulphosalts, which often form perfect pseudomorphs of boulangerite grains. The formation of all sulphosalts occurred through the way of Ag and Cu saturation of galena matrix during boulangerite dilution and galena recrystallisation. At the beginning they developed along the external boulangerite planes in galena crystals, then often recrystallised along zones of diffusion cleaning. Pyrargyrite and bournonite are contained only in galena. In sulphide aggregates around galena enriched by them the acanthite-polybasite veinlets and (or) tetrahedrite emulsion are observed. Sb removal from the silicified mineral forming system led to the destruction of sulphosalts and a shift to polybasite and tetrahedrite formation in galena. In silicified perfect massive blocks galena aggregates have no sulphosalts. The system was divided under oxidation process; in separated locations chalcopyrite, covellite or acanthite were formed.

The general succession of Sb sulphosalt formation in recrystallized galena is bournonite-pyrargyrite-polybasite-tetrahedrite. However, distribution of sulphosalt grains in the places of boulangerite occurrences is often similar for different sulphosalts. It reflects the independent replacement of boulangerite. Usually the grains of each following sulphosalt of this series have bigger grains then the previous, replaced sulphosalts. An exception is bournonite, which almost covered the field of pyrargyrite development. The amount of the sulphosalts depended on the velocity of the diffusion through galena matrix and Pb activity.

As a result of such forming conditions, all rich sulphosalts mineralizations occur only in the sulphide ores, the quartz-sulphide ores contain only rare polybasite and tetrahedrite grains. Sometimes relicts of primary galena with boulangerite are observed here.

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# MINERAL ASSEMBLAGES FROM BOBOLOS LOCALITY (EAST SERBIA)

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The studied locality lies in the Carpatho-Balkanian composite terrane e.g. its Stara planina – Porec terrane (KARAMATA & KRSTIĆ, 1996). It belongs to the Proterozoic Tekija crystalline complex composed mainly of gneisses, mica-schists (ERIĆ *et al.*, 1996) and amphibolites.

Three various type of mica-schist with exotic mineral assemblages occurs in Bobolos locality: kyanite-corundum, and alusite and muscovite-paragonite schists.

The importance is contributed to the unique occurrence of banded kyanite-corundum schist (5 x 4x 3 m in size) composed of kyanite (75 – 80 vol. %), corundum (15 – 20 vol. %), and rutile, paragonite, muscovite and chlorite (up to 5 vol. %). This banding characterised by exotic alternation of gray-bluish kyanite-rich (up to 10 cm thick) and dark-gray corundum-rich (0.5 - 1.3 cm thick) layers. The euhedral to subhedral kyanite crystals are up to 10 cm long. Corundum appears as pseudolamellar grain. Occasionally in the outer and inner marginal zones of both minerals appear tiny leafs of paragonite. Irregular rutile grains (up to 0.4 mm long) are mainly included in kyanite (rarely in corundum).

Kyanite-corundum schist alternate downward by grey-greenish porphyroblastic andalusite schists composed of muscovite and andalusite. Euhedral prismatic porphyroblasts of andalusite are 1 to 1.5 cm long. The section perpendicular to the c-axis characterised by two cleavages (90° and 102°). Muscovite (>  $2 \times 0.6$  mm) makes coarse-grained foliated matrix or lenticular accumulation among andalusite crystals. Fine follies of muscovite occasionally concentrated along andalusite cleavage. Radial aggregates of secondary chlorite developed around some andalusite crystals.

The lowermost part at the Bobolos locality is made up of grey-whitish porphyroblastic muscovite-paragonite schists with kyanite. The follies of muscovite and paragonite are up to  $1.5 \times 0.4$  mm and make foliated matrix. Kyanite as euhedral prismatic porphyroblasts (up to  $1 \times 3$  mm) or needles are scattered in mica-matrix.

The chemical compositions of all presented minerals were made as well as unite cell parameters and correlated.

According to all data it is quantified that above mentioned assemblages were formed by the metamorphism of kaolinite sediments in the temperature interval of 560 - 660 ° C  $\pm 60$  °C and pressure of 4 - 7 kbar.

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## A SYSTEMIC APPROACH FOR THE STUDY OF MIGMATITIC ENVIRONMENTS

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According to most of the researchers involved in studies on migmatitic fields, migmatites are complex petrographic environments consisting of at least two very distinctive rock types: the palaeosome and the neosome. This latter one, at its turn, is divided in leucosome and melanosome. Taking into account their very specific features, migmatitic rocks have to be considered complex petrologic systems, which can be assimilated with the theoretical model defined by the General Theory of Systems (GTS). Applying the main rules of GTS to a petrographic, namely, migmatitic environment, it becomes evident that the classical principles governing the GTS are valid also for the petrologic domain:

- the principle of **totality** allows to figure the migmatites as holding a plurality of petrografic subsystems, each of them representing a specific physical and chemical entity (i.e. palaeosome vs. neosome and leocosome vs. melanosome);
- the principle of **transformation** explains the mobility of the petrologic environment, the motion as a condition of the formation and evolution of the migmatic features;
- the principle of the **self-regulation** allows observing that the structural features, the mineralogical association and the chemical composition of the migmatitic rocks are the outcome of the feedback self-regulation mechanism where the main aims are the minimum energetic level and the entropic evolution.

The most profitable effect of applying a systemic approach on the migmatitic rocks is the mass-balance model, which can explain the mineralogy of the neosome, the specific microstructures of the leucosome and allows some genetical conclusions regarding an anatectic or metamorphic differentiation process.

The systemic approach is applied for the study of the migmatitic rocks from the Cibin area (South Carpathians, Romania). Genetically the most important component of a migmatitic rock, the leucosome, has nearly the same mineralogy as the granitic system. Usually, both potassium feldspar and plagioclase are present in the migmatitic leucosome, even if the participation ratio has different values. The results of the mass-balance studies prove a partially opened migmatitic system with an intensive fluid circulation. The results of the optical and the chemical investigation prove a relatively limited differentiation process of the crystallisation, the leucosomatic compositions corresponding almost to the **S-type** granites, except for the big pegmatitic bodies, which seem to be closer to the **I-type** granites.

37

## NATURE AND DISTRIBUTION OF SULPHIDE BLEBS IN UPPER MANTLE LHERZOLITE XENOLITHS OF ALKALI BASALTS IN THE CARPATHIAN–PANNONIAN REGION

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The main aim of this study is to give a comprehensive picture of the nature of sulphide blebs in petrologically and geochemically well described spinel lherzolite xenoliths hosted in the Plio-Pleistocene alkali basalts in the Carpathian-Pannonian Region. The petrologic and geochemical data of the xenoliths combined with new results obtained from the textural feature and phase chemistry of the sulphide blebs provide a better understanding of upper mantle processes and evolution of the mantle beneath the Carpathian-Pannonian Region (CPR).

Previous studies on upper mantle lherzolite xenoliths of the alkali basalts of the CPR (e.g. DOWNES *et al.*, 1992; VASELLI *et al.*, 1996) show that xenoliths represent the shallow sublithospheric mantle (40–60 km) of the region. Thereby, sulphide chemistry and distribution in the xenoliths are applicable for the whole mantle section represented by them.

More than 120 xenoliths were carefully examinated, searching for sulphide blebs coming from Graz Basin (GB) (Austria), Bakony–Balaton Highlands (BBH) (Hungary) and Persani Mts. (PM) (Transylvania, Romania). From the initial peridotite xenoliths only 20 xenoliths were found bearing sulphide.

The sulphide blebs are mostly spherical inclusions in primary mantle silicates (clinopyroxene >> orthopyroxene > olivine) but some occupy interstitial positions. The average size of the sulphides range from 10 to 100  $\mu$ m. The sulphide blebs generally consist of 2–3 phases. The most common phase is Ni rich monosulphide solid solution (MSS), which occupies more than 60 % of the blebs. Chalcopyrite, occurring generally at the edge of the blebs, is also common in the polyphase sulphide inclusions. Mineralogically pure pentlandite is rare and is only present in some PM and one GB xenoliths. The bulk composition of the blebs is quite alike, mostly plot in the MSS field (Fe 30–45 %, Ni 10–20 %, with up to 10–15 % Cu) ranging towards the pentlandite field in the S-Fe-Ni system. We compared our data with conclusions of a previous study dealing with sulphide inclusions in xenoliths from the Nógrád–Gemer area (SZABÓ & BODNAR, 1995). No real territorial distribution has been observed. Thus, it seems that sulphide inclusions have close genetics in the whole region which is believed to be a partial melting event of the mantle.

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## GEHLENITIC XENOLITHS FROM THE KLANÁC HILL, POMÁZ, VISEGRÁD MOUNTAINS, HUNGARY

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The Klanác Hill is situated north-west of Pomáz on the southern part of the Visegrád Mountains. An andesite tuff that belongs to the stratovolcanic sequence of the Miocene Badenian andesitic volcanism (Mátra Andesite Formation) occurs here in several outcrops. The andesite tuff is white due to a considerable argillization.

Xenoliths can be found in a large amount in the andesite tuff, which derive from the broken out rocks of the substratum. A considerable part of the rock inclusions have carbonate origin. These carbonatic protoliths underwent thermal metamorphism, resulting in contact marbles; however, where contact metasomatic processes took also place, Casilicate associations formed.

The most frequent minerals of the Ca-silicate xenoliths are: garnet with andraditegrossular composition, diopside, calcite, and the members of the spinel group (mainly magnetite). Gehlenite occurs very rare in these xenoliths, however, it is one of the main components where it occurs.

The gehlenite-bearing xenoliths consist of the following three phases in descending order of quantity: gehlenite, poorly crystallised silica (chalcedony) and garnet with  $Adr_{77}$  Grs<sub>21</sub> Prp<sub>2</sub> composition. The gehlenite has a honey yellow colour, resinous lustre and it forms sub-millimetric, equant crystals, which appear under polarising microscope as colourless, anhedral or subhedral grains. Its composition varies in a very limited range (Gh<sub>91</sub> Åk<sub>9</sub> to Gh<sub>92</sub> Åk<sub>8</sub>). The lattice constants of gehlenite calculated from the X-ray powder diffraction pattern are a = 7.706 Å and c = 5.008 Å.

The gehlenite formed from calcite of the protolith and metasomatically introduced silica and alumina as follows:

 $2CaCO_3 + SiO_2 + Al_2O_3 \rightarrow Ca_2Al_2SiO_7 + 2CO_2$ .

It is apparent, that the metasomatizing fluid should have to have a rather low Si/Al ratio to produce gehlenite. It could be formed rarely in  $SiO_2$  saturated magma (andesite). This fact can explain the much larger frequency of garnet xenoliths in the andesite tuff in Klanác Hill, because the garnet (grossular) is formed by a higher Si/Al ratio:

 $3CaCO_3 + 3SiO_2 + Al_2O_3 \rightarrow Ca_3Al_2Si_3O_{12} + 3CO_2$ .

Consequently, whether gehlenite or grossular was formed at this metamorphic stage probably would depend largely upon the local availability of alumina in the metasomatizing fluids.

The chalcedony is not in equilibrium with gehlenite and garnet, because it formed secondarily, perhaps simultaneously with argillization of the andesite tuff. In some places, the chalcedony appears as a pseudomorph after an undefined columnar mineral.

## OKENITE AND NEKOITE FROM THE SZÁR HILL, POLGÁRDI, HUNGARY

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Between Polgárdi and Szabadbattyán, on the Szár Hill, Middle Devonian crystalline limestone (Polgárdi Limestone Formation) outcrops to the surface, which can be studied in quarries. The limestone formation is cut by Triassic (?) andesite dykes, resulting in contact metamorphic and metasomatic effects on the limestone. The main types of these contact rocks are the followings: contact marble, vesuvianite-diopside skarn, diopside skarn and wollastonite skarn (HORVÁTH & ÓDOR, 1989).

In some places stubby columnar or dipyramidal, colourless apophyllite crystals cover the fissures in the wollastonite skarn. Okenite, nekoite, rhombohedral calcite crystals and white thaumasite masses consisting of minute, acicular crystals developed on the apophyllite coatings. Thaumasite is not always associated with apophyllite, it also appears alone in the fissures.

Okenite forms typical white "cottonball" like aggregates, the size of which are usually about 1 mm, but rarely can reach 4 mm in diameter. Nekoite appears as colourless, acicular crystals of 1-3 mm size, which form flat, fan-shaped crystal groups. The presence of both minerals was confirmed by X-ray diffraction investigations.

Deposition of this highly hydrous Ca-silicate association is the result of hydrothermal activity on the rock. The late crystallization of these relatively low-temperature minerals is indicative of the accumulation of water and volatiles in the final stage of mineralisation.

Okenite and nekoite are rather rare minerals. The Szár Hill is the first occurrence of nekoite and the second occurrence of okenite in the Carpathian region. Until now okenite has been known in the Carpathians only at Criscior, near Brad, Metaliferi Mts., Transylvania, Romania (ISTRATE, 1980).

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### APPEARANCE OF GOLD IN SOME DRILLHOLES OF THE LAHÓCA EPITHERMAL DEPOSIT, MÁTRA MTS., HUNGARY

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The Recsk mineralized complex lies in NE Hungary, 30 km west to the town of Eger. As an ancient mining district, it has been known, explored and mined from the 18th century. A wide range of ore mineralization is known in the complex. Porphyry copper and molybdenum, skarn copper are the most important formations in the central intrusive zone. Zinc skarns, lead-zinc metasomatic replacement mineralizations are found along the reactive horizons of the altered seimentary rocks. High sulphidation enargite-pyrite-gold mineralization was developed in relation to late volcanic centers. Low sulphidation gold-silver mineralization has become known in the peripheral southern parts of the volcanic–intrusive complex.

Gold is an important component in the epithermal part of the complex. Its distribution is known by systematic assaying of drift and drill-core samples. Several research studies have been carried out attempting to clear the details of mineralogical achemical relationships between the geological environment and the precious metal elements. In the present study the previous mass of information is completed by microscopic, microprobe and scanning electron microscope analyses of the main ore types.

The Lahóca epithermal ore is characterized by a complex sulphide and gangue mineralogical assemblage. The host rock is highly silicified. Both "vuggy silica" and strong silicification can be observed. Porphyric minerals are often substituted by quartz and pyrite. Pyrite is the most abundant opaque mineral. It is visible in euhedral, subhedral, framboidal and amorphous forms. Rutile needles are frequently associated with pyrite. Dawsonite was also determined. Enargite, luzonite and marcasite are present in minor quantities.

Gold assay results extend a few tenths to ten ppm. Gold is associated both with pyrite and quartz in native form. It does not contain measurable silver. It forms a few microns to few ten microns large aggregate-like structures. The largest native gold that was found in silica environment is 40  $\mu$ m. A few microns large native silver was also visible. Different minerals of Sn, Cu, Te, As and Sb were also identified as inclusions in enargite.

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41

## HEAVY MINERALS FROM THE VARIEGATED SHALES MEMBER OF THE SKOLE UNIT (POLISH FLYSCH CARPATHIANS)

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The aim of this work was to identify the heavy minerals assemblage of the Variegated Shales Member (Upper Palaeocene–Lower Eocene) sediments. The formation consists of argillaceous and clay–silty shales with some isolated sandy bodies. The upper Palaeocene part of the formation consists of the Zohatyn Variegated Shales Member, while the Lower Eocene part consists of the Trójca Red Shales Member, underlain and covered by variegated shales, not distinguished as members (RAJCHEL, 1990).

Heavy minerals from 10 samples of claystones were investigated. The samples were washed in order to remove clay minerals. Heavy minerals were separated by means of a magnetohydrostatic separator, with manganese chloride as a working fluid. The analyses were performed using transmitted light microscopy and electron scanning microscopy with EDS.

Detrital, transparent heavy minerals are represented by glauconite, zircon, tourmaline, rutile, staurolite, micas (biotite, muscovite) and apatite. Garnet, kyanite, sillimanite, chlorites and goethite were identified in small quantities. Ilmenite represents non-transparent minerals.

Zircon is present as colourless crystals with a wide range of shapes. Euhedral crystals are most common and they were classified according to Pupin's diagram (PUPIN, 1980). However, rounded and subrounded grains are also present. There are grains of zircon containing distinct inclusions and showing zonal structure.

Tourmalines occur in percentages comparable to zircon and their chiefly brown and green crystals are characterized by extremely strong pleochroism, coloured from almost colourless to nearly black.

Rutile occurs as euhedral and anhedral crystals, coloured from yellow to dark red. Sometimes elbow twins of rutile are present.

The ZTR factor is very high, indicating high mineralogical maturity of heavy minerals fraction.

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### **OCCURRENCE OF RANCIEITE IN THE POLISH FLYSCH CARPATHIANS**

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Four horizons with Mn oxide concretions were encountered in Nowa Wies near Rzeszów in the profile of the Variegated Shales Formation (RAJCHEL, 1990) of the Flysch Carpathians. These horizons occur in the upper part of the profile, in the so-called clinoptilolite-montmorillonite clays (WIESER, 1994; FRANUS & DUDEK, 1999). Up to now only diagenetic carbonate (rhodochrosite, Fe-rhodochrosite, and oligoniteankerite) macro- and microconcretions were reported from the Lower Eocene part of the Variegated Shales (MUSZYNSKI et al., 1978; WIESER, 1982). The predominating mineral of the examined concretion horizons is rancieite (Mn oxyhydroxide rich in  $Ca^{2+}$ ), as it was demonstrated by scanning microprobe analysis:

$$\begin{split} &I - (Na_{0.04}K_{0.07}Ca_{1.731}Mg_{0.133}Ba_{0.004}Al_{0.014}Fe^{2+}{}_{0.06})_{2.052}Mn^{4+}{}_{5.947}O_{13.93}(H_2O)_{5.67}; \\ &II - (Na_{0.03}K_{0.075}Ca_{1.755}Mg_{0.148}Ba_{0.001}Al_{0.014}Fe^{2+}{}_{0.052})_{2.048}Mn^{4+}{}_{5.98}O_{13.94}(H_2O)_{5.72}. \end{split}$$

Increasing activity of oxygene and  $Ca^{2+}$  ions upwards the profile is expressed by the increase of ratio:  $Ca^{2+}/cations < 4+ = 0.844$ ;  $Ca^{2+}/cations < 4+ = 0.857$ .

With this context in mind it should be pointed out that the Lower Eocene rancieites from Nowa Wies exhibit by far the greatest known content of calcium ions (ca. 85 %) in interstratal positions and completely oxygenated manganese in form of Mn<sup>4+</sup> ions.

Weakly cemented Mn rich, gel-like material was subjected in greater degree than Mn nodules included in turbidite type sediments to granulation and redeposition by oxygen rich bottom currents. The contact with bottom water was not long enough to allow a marked enrichment in heavy metal ions, as in typical recent, hydrogenous Mn nodules, called, not without reason, metal scavengers.

Rancieite seems to be a final stage of Mn nodule transformations relying on substitution, esp. of calcium in place of alkalies with simultaneous oxidation of  $Mn^{2+}$ , Mn<sup>3+</sup> to Mn<sup>4+</sup> stage.

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## QUARTZ CRYSTALS FROM THE VICINITY OF BRAD AND SACARÂMB, ROMANIA – MORPHOLOGICAL AND FLUID INCLUSION STUDIES

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The present work attempts to give additional information to the relationship between crystal morphology and physico-chemical circumstances of crystallization in the case of hydrothermal quartz.

The Neogene Brad–Sacarâmb Basin is situated in the southeastern part of the Carpathian–Pannonian region, genetically isolated from the western and eastern Carpathian volcanites. The studied crystals were obtained from low sulphidation veins, geodes and breccias from the following localities: Valea Morii Veche (Válemori, Altes Mühlental), Musariu (Muszári), Carpen (Kárpin), Sacarâmb (Nagyág, Großastdorf), Bocsa (Boksa), Hondol-Baiaga (Hondol-Bojága), Coranda (Koranda). The host rocks of the hydrothermal mineralization are dominantly Neogene andesites and dacites, subordinately Neogene sediments (sandstones and shales).

30 crystals from each locality were measured by a reflection goniometer. Two morphological types of quartz crystals were determined: "type D" where positive and negative rhombohedra were equally developed and "type B" where crystals are characterised by the dominancy of the positive rhombohedron.

Fluid inclusion studies were done on a Chaixmeca heating-cooling stage. The main results obtained by that method: homogenisation temperature is between 148–314 °C (Th); the last ice crystals disappear at 2.8–0.6 °C (Tm<sub>ice</sub>). Calculated salinity is 0.7–4.5 eq. wt% NaCl.

Two types of inclusions were found. Inclusions of "type L" (liquid rich) and "type V" (vapour rich) appear at the same frequency in "type D" crystals, which shows the boiling of the system (PINTEA, 1995). "Type B" crystals contain predominantly "type L" inclusions, supposedly as a result of dilution. These conclusions are derived from the Th/Tm<sub>ice</sub> diagram of HEDENQUIST & HENLEY (1985).

The results suggest a correlation between quartz crystal morphology and the circumstances of crystallization in the case of the crystals studied. A comparison with quartz crystals from Alpine occurrences (RYKART, 1989) is the subject of further study.

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## **GRAPHITE AS A PETROGENETIC INDICATOR OF METAMORPHIC CONDITIONS IN THE WESTERN TATRA MTS. (SOUTH POLAND, WESTERN CARPATHIANS)**

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Pre-Variscan metamorphic rocks with graphite content in the range of 0.1–6.0 wt% were found in the Upper Structural Unit (USU) of the Polish part of the Western Tatra Mts. Optical and scanning electron microscopical observations allowed us to distinguish two generations of graphite:

- Primary graphite (Gph1) in fact metamorphosed bituminous matter (ozokerite, asphalt or heavy fractions of crude oil), occurs mostly in quartzites or quartz rich gneisses as highly deformed crystals (GAWEDA & CEBULAK, 1999). Gph1 is characterised by oxyreaction in the temperature range 660–780 °C (sporadically to 840 °C, and R<sub>max</sub> = 10.20–18.78 %. In the graphitization process, apart from temperature, shear stress was an important factor.
- 2. Hydrothermal graphite (Gph2), syngenetic with post-magmatic muscovite + quartz + albite, precipitated from a  $CO_2$ -CH<sub>4</sub>-H<sub>2</sub>O fluid. Gph2 occurs as almost perfect, hexagonal, undeformed crystals with oxyreaction maxima in the range of 620–660 °C and R<sub>max</sub> = 5.84–11.41 %, that suggests the semigraphite stage of transformation. Samples with OTA maxima in the range 725–730 °C point out the differences in the properties of the graphite forming fluid.

The range of oxyreaction temperatures of Gph1 samples is much the same as the range of maximum temperatures of metamorphism (700–780 °C), obtained by different methods from the USU (GAWEDA *et al.*, 1998). The maximum temperatures of oxyreaction, comparable with geological ones (< 700 °C), were obtained for Gph2 as well.

For the set of samples from different localities of the world we compare the  $R_{max}$ -OT<sub>max</sub> and mean T<sub>geol</sub>-mean Ot<sub>max</sub> values. In the first case we have found the correlation with  $R_c = 0.867$  (MSWD = 0.751), in the second case  $R_c = 0.84$  (MSWD = 0.709).

Comparing the reflectance data from different cokes, anthracites, meta-anthracites, semigraphites and graphites we have found two trends on the  $R_{min}$ - $R_{max}$  diagram. These trends differentiated hydrothermal graphites as well as graphites influenced by stress (apart from temperature) as a significant factor during graphitization.

The presented data allow us to conclude that the oxyreactive thermal analysis with R measurements could be a new graphite geothermometer.

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## CARBONATE MINERALIZATION IN THE WESTERN TATRA CRYSTALLINE BASEMENT, POLAND

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In the Tatra Mts. crystalline complex the carbonate veins and nests are located in the shatter zones and fissures, cutting both metamorphic rocks and granites. The High Tatras (Eastern Tatra Mts.) and Western Tatra Mts. differ in mineralogical character of carbonate mineralization.

1. In the metamorphic complex of the Western Tatra Mts., the so-called "siderites" (in fact sideroplesite-metisite) and ankeritic dolomites predominate. The carbonates are the first minerals in the mineral sequence stated here: carbonate  $\Rightarrow$  quartz + sulphides  $\Rightarrow$  barite (PAULO, 1970). Cathodoluminescence investigations of carbonate veins show that a small amount of calcite is also present in brecciated carbonate veins as cement, binding the "sideritic" and dolomitic clasts.

2. In the High Tatra granitoid intrusion the rare ankeritic dolomites precipitated directly on the quartz crystals (sometimes automorphic). The abundant calcite mineralization is the youngest in the mineral sequence, forming both individual veins and cement in the brecciated rocks. Calcite locally forms pseudomorphs after ankeritic/dolomitic clasts but with preserved "ghost" structures.

The differences in the mineralogical character of carbonates in different locations could be influenced by the local changes in lithology and chemistry of host rocks. REE patterns of the ankeritic dolomites from the Western Tatra and the High Tatra Mts. show a pronounced LREE depletion with positive Eu and Tb anomalies. Such features suggest very low  $fO_2$  in the mineral forming fluid and REE mobilisation by F<sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> poor fluids at rather high temperatures, while precipitation from the fluid should occur in the low temperature regime (BAU & MÖLLER, 1992). Sideroplesite from the Western Tatra Mts. show steep REE patterns with LREE enrichment and no Eu and Tb anomaly, atypical for Fe-Mg carbonates (BAU & MÖLLER, 1992).

The investigations of C and O isotopes in carbonates show that  $\delta^{18}$ O and  $\delta^{13}$ C have relatively high values in the W. Tatra "siderites" and ankeritic dolomites (-14.82 ‰; 14.91 ‰ for  $\delta^{18}$ O and -5.32 ‰; -5.42 ‰ for  $\delta^{13}$ C).  $\delta^{18}$ O and  $\delta^{13}$ C for High Tatra carbonates have somewhat lower values (-16.62 ‰; -18.32 ‰ and -6.29 ‰; -7.33 ‰, respectively). In both cases the exogenic origin of mineral forming fluids is suggested. As an extreme case, in one calcite vein from the High Tatra Mts. the values of  $\delta^{18}$ O = -22.43 ‰ and  $\delta^{13}$ C = -12.33 ‰ are typical of biogenic origin, which has no plausible explanation as yet.

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### ORIGIN OF TOURMALINES FROM THE WESTERN TATRA MOUNTAINS, POLAND

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Black tourmalines, with composition of schorl-dravite, are present in vein and lenslike pegmatites of the Western Tatra Mts. (8–21 v% of tourmaline) and occasionally form the tourmalinite nests (~ 60 % vol.) coexisting with quartz, albite and microcline. They cut both metapelitic rocks and leucogranite intrusions. Unit cell parameters of tourmalines are:  $a_0 = 15.96$  Å,  $c_0 = 7.18$  Å. The zonation of individual crystals is poor, expressed in Z and Y cations substitution. Mössbauer spectra show the variable oxidation degree of Fe.

The field observations and geochemical data are consistent, showing the affinity of tourmalines to both metasedimentary Ca poor host rocks, saturated in Al, and anatectic, syn-collisional leucogranites, lacking magmatic Fe-Mg minerals. Comparing the p–T maximum conditions of anatexis (700–720 °C, 7.5–10 kbar; GAWEDA & KOZŁOWSKI, 1998), the mobilisation of (Mg, Fe) to melt/fluid phase could occur only when melting started in lower temperatures than in other parts of the complex. That process was catalysed by the presence of boron in the metamorphic fluid, lowering the melting point of so-called minimum granite composition. Such situations were very restricted, taking into account the water-undersaturated conditions of melting and the typical fluid composition:  $CH_4-CO_2-N_2-H_2O$  (JANAK *et al.*, 1996, GAWEDA *et al.*, 1996).

The enhanced admixture of buergerite-type suirnituflon in some tourmaline samples is interpreted as the result of re-heating to a temperature over 400 °C (possibly 600–650 °C) by the Main Tatra Granite intrusion. The multistage Main Tatra Granite is connected to the extensional stage of the Tatra crystalline basement development, which followed the compression (collision and nappe staking) stage which formed the anatectic melt and tourmaline forming fluid phase.

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### **EVOLUTION OF THE CARPATHIAN-PANNONIAN REGION**

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Surrounded by the mountain ranges of the Alps, Carpathians and Dinarides, the Pannonian Basin is a peculiar and complex geological object, which has attracted interest of many geologists for a long time. Based on geophysical measurements, great number of boreholes and geological mappings, however, concepts on the structural evolution of the basin have been significantly modified in the last decades. It turned out that the basement of the basin consists of structural units (Fig. 1) recording strikingly heterogenous development. They were situated relatively far from each other during the Paleozoic-Mesozoic times. The Tisza Unit was a part of the Hercynian Orogenic Belt in the Late Paleozoic, and a segment of the European margin of the Tethys in the Early Mesozoic. Dismembered from the European plate, it formed a microcontinental block from the Middle Jurassic. Blocks of the Pelso Unit belonged to the western and southern margins of the Tethys in the Triassic and were parts of the "Adriatic promontory" in the Late Mesozoic times. The two large composite blocks ("terranes") attained their present-day juxtaposed setting only by the Early Neogene as a result of multi-stage, large displacements. Characteristic features of the recent Pannonian Basin - such as thin, attenuated crust, thermal anomaly and extremely high subsidence rate - developed in the final stage of the evolution during the Neogene. A brief review of the whole history of evolution in the Carpathian–Pannonian region will be presented, showing paleoreconstructions of the major evolutionary stages and events from the Late Paleozoic to the Neogene.

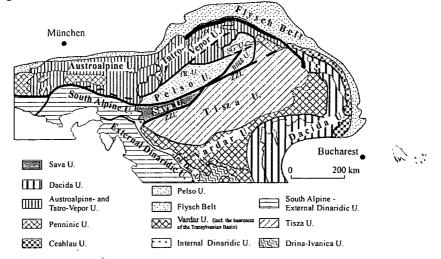


Fig. 1: Megatectonic units of the basement of the Pannonian Basin.

## NEOGENE VOLCANISM IN THE PANNONIAN BASIN -IMPLICATIONS FOR THE NATURE OF THE MANTLE AND FOR THE GEODYNAMIC RELATIONSHIPS

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In the last decade, considerable amount of new geochemical data (major and trace elements, radiogenic isotope ratios) has been obtained for each association of the Neogene volcanic assemblage of the Carpathian-Pannonian Region (CPR). These volcanic suites are strongly related to the main geodynamic events of the CPR, therefore their studies can contribute to our knowledge about the evolution of this area. In spite of the increasing amount of data, however, there are still major debates about the genesis and geodynamic implications of the volcanic series. Here, we attempt to summarize our present knowledge on these rocks and the different opinions about the origin of this volcanic assemblage.

In accordance with the main tectonic events of the CPR, the Neogene volcanism can be subdivided into pre-extensional, syn-extensional and post-extensional periods. The pre-extensional volcanism is characterized by voluminous explosive eruptions of silicic magmas roughly along the Mid-Hungarian Tectonic Zone (MHTZ). Melt generation could take place at the base of the hot, thick continental crust presumably due to the intrusion of mantle-derived magmas. Major lateral displacements along the MHTZ could enhance this process. The syn-extensional volcanism evolved continuously from this initial volcanic phase and resulted in widespread explosive volcanic eruptions of mafic to silicic magmas and minor potassic to ultrapotassic melts. Genesis of the Middle Miocene calc-alkaline volcanism in the Northern Pannonian Basin is a subject of dabate. We suggest that a series of geodynamic events resulted in the magmatic activity involving subduction-related metasomatism and subsequent extension-related melt generation in the lithospheric mantle. The calc-alkaline volcanic suites at the eastern segment of the Carpathian volcanic arc show some geochemical differences compared with those of the Northern Pannonian Basin and are commonly interpreted as the result of gradual slab break-off process. The post-extensional dominantly alkaline mafic volcanism might be a response of active upwelling of relatively hot asthenosphere beneath the thinned lithosphere of the Pannonian Basin. This mantle is akin to the common European Asthenosphere Reservoir. In addition, involvement of melts derived from variously metasomatised lithospheric mantle occurred beneath the central parts of the Pannonian Basin.



### RARE MINERALS IN THE CARPATHIAN METAMORPHOSED Mn-Fe DEPOSITS FROM ROMANIA

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The main metamorphosed Mn-Fe deposits from the Romanian Carpathians and their mineralogical composition are: (1) Răzoare Mn-Fe deposit, silicate-carbonate-oxide-sulphide (Preluca Mts.); (2) Bistrița Mn deposit, carbonate-silicate-oxide-sulphide (Bistrița Mts.); (3) Sebeş Mn deposit, silicate-carbonate (=queluzite) and gondite; Rascoala Fe-Mn deposit, silicate-carbonate-oxide (Sebeş Mts.) and (4) Delinești Mn-Fe deposit, silicate-carbonate and gondite (Semenic Mts.).

The rare minerals from the primary Carpathian metamorphosed ores belong to the following groups: (a) native elements: Au, Bi; (b) Mn-humites: sonolite, leucophoenicite, ribbeite, manganhumite, alleghanyte, jerrygibbsite; (c) pyroxenes: Mn-ferrosilite, donpeacorite (?); (d) garnets: noncubic spessartine garnets, spessartine-calderite; (e) pyroxenoids: pyroxferroite (?), nambulite, natronambulite, mangan-babingtonite (?); (f) amphiboles: winchite, kozulite, Li-amphibole of eckermannite type, Li-amphibole of ferroglaucophane type, Ti-richterite, Ni-ferroglaucophane; (g) epidote group: Mnallanite, piemontite, REE-piemontite; (h) micas: kinoshitalite, norrishite (?); (i) stilpnomelane: bannisterite, ganophyllite, parsettensite: pyrosmalite: (i) manganpyrosmalite, friedelite, mcgillite, schallerite, nelenite, caryopilite; (k) talc: minnesotaite; (I) chlorites: penanntite, brindleyite, nimite, kellyite, grovesite; (m) oxides: pyrophanite, iwakiite, galaxite, senaite, manganosite, Co-manganese spinel (?), ferrocolumbite, ulvospinel, neltnerite, ashanite, ixiolite, franklinite, gahnite, thorianite; (n) sulphides: alabandine, hauerite (?), cattierite; (o) phosphates: switzerite, gorceixite, xenotime; (p) wolframates: huebnerite, ferberite; (r) arsenates: sarkinite, johnbaumite, magnussonite, manganarsite, hedyphane: (s) borates: homilite, tusionite (?); (t) other silicates: helvite, genthelvite, thorite, bafertisite, hisingerite, fraipontite, anandite; (u) carbonate: holdawayite, smithsonite, takovite.

In the oxidised zone, where the main minerals are nsutite, pyrolusite, cryptomelane, manganite, etc., the following rare minerals were determined: khademite, groutite, lithiophorite, manjiroite, lennilenapeite, coalingite, groutellite, pyrochroite, ajoite, jusite.

The source of Li, Na, K, Be, B, F, REE etc., in the Bistrita manganese deposits was probably the alkaline Ditrău massive, while the source of Cl, S, As, OH etc., was probably the Neogene East Carpathian volcanic arc. The Ni, Co and Ti proceed from the submarine hydrothermal system that was associated with the deposition of the sediments in a rifting environment such as a back-arc basin or possibly a mid-ocean ridge. In the Delinesti Fe-Mn deposit many rare minerals with Ba, W, F, REE, Cl, Pb etc. were formed by metasomatism or hydrothermal phenomena, produced as a result of the vicinity of some granite.

### **'THE MINERALOGICAL SYSTEM OF SLOVAKIA' EXHIBITION**

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The Faculty of Natural Sciences at the Comenius University in Bratislava, Slovakia, was founded in 1940. Mineralogical collections of the Department of Mineralogy and Petrology have been formed through the history of the Faculty. Nowadays it contains some 9000 registered mineral samples (samples for research are not counted). The majority of specimens come from private contributions, either as gifts or through purchase. Most of the mineral samples are stored in the depository, approx. one quarter of them are displayed in cases and several hundred samples serve the study of students in geology.

There are several collections of exhibited minerals. The major one is the mineralogical system, built of ca. 1000 mineral samples from deposits and occurrences all over the world. Smaller collections are devoted to genetic and regional mineralogy.

The most attractive collection is the Mineralogical System of Slovakia, the only one of its kind exhibited in the Slovak Republic. The exposition is composed of minerals only from Slovak sites. Samples of minerals are systematically organised into nine groups, from elements to organoliths. The collection was made up of mineral samples from the Department of Mineralogy and Petrology as well as of loaned samples from several private mineral collections. The exhibition will be flexibly completed and changed in the future, mainly by contributions from private mineral collectors.

Presently the collection consists of samples of approx. 250 mineral species (counted without their varieties). Rare minerals that can not be seen macroscopically are presented by photographs made by either optical or scanning electron microscopes.

The worth of minerals increases with time in the sense that mining has declined rapidly in the past years and almost all mineral deposits are closed in Slovakia. Very valuable are the old mineral samples coming from occurrences that do not exist any more, i.e. kermesite from Pezinok, pharmacosiderite from Nová Baňa, or celestine from the Špania Dolina (Herrengrund) locality. Perhaps the most unique ones are minerals that were described for the first time in the area of the Slovak Republic, such as euchroite, evansite, hodrushite, libethenite, mrázekite, tetradymite, vashegyite, as well as other minerals rare in the Slovak Republic, Europe or in the world.

The Mineralogical System of Slovakia exhibition has been built over the last several months. It is currently in the final changes and will be opened in March 2000.

## COMPOSITION OF BIOTITE IN GRANITOIDS FROM THE PAPUK AND PSUNJ POLYMETAMORPHIC COMPLEXES IN EAST SLAVONIA, CROATIA

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Biotites from granitoid rocks of the Papuk and Psunj Polymetamorphic Complexes in East Slavonia (Croatia) were examined by optical and microprobe methods. The aim of the investigations was to determine the type(s) of magma by means of chemical composition of biotites.

Biotite is the main mafic mineral. It shows strong pleochroism from reddish brown to yellowish brown or yellow. Reddish colour is the result of  $TiO_2$  content. Biotite very often contains zircons with pleochroic halo. Besides zircon, epidote and acicular rutile occur as frequent inclusions.

The composition of biotites was analysed in six rock samples: two granodiorites, three monzogranites and one syenogranite. The samples were measured with EDAX and with WDS. Calculation of formulae was based on 22 oxygens. Six major chemical components (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MnO and MgO) were taken into consideration.

The Mg-rich biotite (FeO\*/MgO = 2.0) in granodiorite (Papuk polymetamorphic complex) plots in the central part of the phlogopite-eastonite-siderophyllite-annite compositional diagram and indicates a calc-alkaline character of rock which probably crystallized from a mixed melt (basic, acidic).

The Fe and Al rich biotites (FeO\*/MgO ratio varies between 2.81–3.65) are showing peraluminous character (ABDEL-FATTAH, 1994). They occur in S-type granites. These biotites coexist with muscovite, have  $SiO_2$  content between 34.68 wt% and 35.54 wt%,  $Al_2O_3$  from 17.01 wt% to 18.63 wt% and contain high FeO (21.71 wt%–23.61 wt%) and low MgO (6.31 wt%–7.71 wt%). These rocks originated most probably from partially melted continental crust.

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## APPLICATION OF CATHODOLUMINESCENCE MICROSCOPY TO THE STUDY OF METAMORPHIC REACTIONS IN MARBLES; EXAMPLES FROM THE MORAVIAN ZONE

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Only little attention has been paid to cathodoluminescence (CL) observations of metamorphosed carbonates related to the extensive works on sedimentary carbonates (MARSHALL 1988, YARDLEY & LLOYD, 1989). The studied marbles occur in the Moravian Zone of the Bohemian Massif, consisting of metapelites, metavolcanics and marbles ranging from amphibolite (Olešnice group) to greenschist facies (Lukov group). Tremolite marbles from the Olešnice Group exhibit polyphase metamorphism and several mineral reactions were found using transmitted light and CL. The mineral assemblage involving early tremolite (Tr I) is product of the reaction: 5 Tlc + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + 6 Cal + 4 Qtz = 3 Tr + 6 Cal + $5 \text{ CO}_2 + 2 \text{ H}_2\text{O}$ . It is supported by the textural relations of early calcite I (Cal I), with characteristic deep orange colour in CL image, associated with relics of quartz Qtz (blue CL) and grains of Tr I (black). Both Cal I and Tr I underwent brittle deformation. Their angular grains are rimmed and healed by younger Cal II with bright orange colour on CL. Formation of Cal II is very likely not related to the reaction producing Tr I, but represents the recrystallization of marble. Rare relics of dolomite (Dol) (dark red CL) and Qtz (blue CL) were found in large porphyroblasts of Tr I, indicating the mineral reaction: 8 Qtz + 5 Dol +  $H_2O$  = Tr + 3 Cal + 7 CO<sub>2</sub> (e.g. Olešnice and Jobova Lhota localities). Rare equilibrium assemblage Tr I + Dol (red CL) suggests the mineral reaction: 2 Tlc + 3 Cal =  $Tr + Dol + CO_2 + H_2O$ . Diopside (green CL) in rims around Tr I was observed in marbles near the contact with the higher grade Moldanubian Zone. It is formed by the reaction:  $Tr + 3 Cal + 2 Qtz = 5 Di + 3 CO_2 + H_2O$ . The latest Cal III (pale yellow CL) commonly fills cracks in some silicates, e.g. in retrograde Tlc. It may have originated during the latest metamorphic stage or in the zone of weathering.

Marbles with the mineral assemblage Cal + Qtz + Dol + Ab + Ms + Bt occur in the Lukov Group (Horni Dunajovice locality). The CL study revealed heteroblastic structure formed by angular grains of Fe-carbonates (Fe-calcite with FeO  $\geq 1$  wt% and Fe-dolomite; dull brown or without CL). These grains are located in the matrix consisting of Cal II (orange CL) grains. Minor micas and rare rutile appear black on CL, quartz and probably albite exhibit blue, apatite pale yellow CL. Late veins of Cal III (orange-yellow CL) cut early Fe-carbonates which were depleted in Fe and recrystallized on contact with Cal III, and exhibit orange CL.

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# POLYHALITE IN MIOCENE POTASH DEPOSITS OF THE CARPATHIAN FOREDEEP, UKRAINE

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Polyhalite is a widespread sulphate mineral of potash salt deposits of the Carpathian Foredeep. It occurs as an admixture in almost all salt rocks, in some cases it forms polyhalite rock. The three most widespread varieties of polyhalite rocks are described below.

Clay polyhalite rock occurs as thin (1-10 cm) layers in the potash strata. This rock is grey coloured, with laminated, thin bedded or crossbedded structure. The rock contains 0.09 % Sr.

Red polyhalite rock occurs as thin (1-3 cm) layers and packets of layers whose thickness reaches 1-2 m. The rock is laminated with small lenticular halite grains, which are encompasseds by polyhalite laminae. The rock contains 0.65 % Sr.

Polyhalite-anhydrite layers (0.3-30 cm) take place in salt bearing breccia next to the boundary of potash deposits. They are meandering, fickle along the strike and thickness. These layers consist of polyhalite (from potash deposit side) and anhydrite (from salt bearing breccia side) parts. Polyhalite is mainly parallel fibrous, the fibres are arranged across the layer. Strontium content is 0.41-2 %, average 0.74 %. At one of such layers of the Stebnik potash deposit in which polyhalite is replaced by gypsum, kalistrontite, a rare sulphate of K and Sr was found (HRYNIV *et al.*, 1986).

The concentration of brines needed for polyhalite precipitation is reached at the end of the halite stage. Although the possibility of polyhalite precipitation from brines is confirmed by experimental data (VALIASHKO & NECHAEVA, 1952), more likely is the formation of polyhalite through early diagenetic replacement of primary gypsum (VALIASHKO, 1962; BRAITSCH, 1971). Clay polyhalite rock was formed during early diagenetic origin (the signs of gypsum layers, red polyhalite rock perhaps also has a diagenetic origin (the signs of gypsum replacement are not seen). Polyhalite-anhydrite layers were formed during diagenesis at the geochemical barrier as the result of the reaction of sulphate brines from potash deposits and chlorine-calcium brines from salt bearing breccia. Besides, polyhalite replaces others salt minerals of potash deposits of the Carpathian Foredeep (JARZHEMSKIJ, 1954).

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## GOLD PLACERS IN THE WESTERN CARPATHIANS, SLOVAKIA

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Detailed mineralogical-geochemical exploration works for gold showed several large ancient gold placers in the Western Carpathian area. Some of them have been repeatedly exploited since Celtic times. The whole historic production of gold from old placers deposits may be estimated over 10 t. The gold placers were exploited in the Middle Ages. The typical placer relics are in the Tatric unit (Malé Karpaty Mts., Považský Inovec Mts., Malá Magura Mts., Tribeč Mts., Nízke Tatry Mts.), in the Veporic and the Gemeric units (Slovenské Rudohorie Mts.) (POLÁK, 1969, HVOŽĎARA, 1999, BAKOŠ & CHOVAN, 1999).

The spatial connection of gold occurrences with mafic and ultramafic rocks shows similarities between the greenstone belts and the superimposed granitisation ore hydrothermal processes, as are known from many gold bearing areas in the older geological formations. Gold is usually concentrated in the shear zones conducting the hydrothermal or metamorphogenous solutions.

Alluvial and deluvial-eluvial placers with typical morphology and fineness of gold are present in the crystalline areas. The size of gold particles in the alluvial placers is 0.1-2 mm. Gold finenesses are above 900.

Gold in the deluvial-eluvial placers (so-called "cementation" gold) has dendritic morphology and more variable finenesses and size of 0.1-5 mm. Recognised placer deposits are possible to use for prognosis of primary gold mineralization.

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## RARE EARTH MINERALS IN THE WESTERN CARPATHIANS, SLOVAKIA

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The REE minerals (mainly allanite, monazite and xenotime) in the Western Carpathians were studied by numerous authors. The distribution of these minerals were studied mainly in magmatic (various types of granites) and metamorphic rocks. The REE minerals are distributed in the form of accessory minerals in these rocks (MIŠÍK, 1955; HOVORKA & HVOŽĎARA, 1965; BROSKA & UHER, 1991; BROSKA & SIMAN, 1998).

The regional mineralogical and geochemical research works oriented on exploration of ore minerals showed that REE minerals (mainly monazite and xenotime) are associated with the distribution of ore minerals (HVOŽĎARA, 1980; HOLOCSY *et al.*, 1999; TRÉGER, 1973; DONÁT, 1998).

The contrast aureoles with high contents of monazite and xenotime are connected with ore structures. Gold, scheelite, maghemite, cinnabar, cassiterite, wolframite, xenotime, tourmaline and sulphides are associated with monazite.

The crystals of monazite have typical forms in these localities, the crystal grains are of the size 1–5 mm. The most frequent morphological types are isometric and isometric-tabular crystals (60–90 %). Isometric-prismatic (0.5–10 %) and tabular (1–5.5 %) morphological types are less abundant; tabular-prismatic (1–3 %) and prismatic ones (0.5–2 %) are rare. Typical colour varieties are yellowish brown, brown, grey. This type of the monazite is frequent with gold in the Veporic unit (localities: Podrečany, Lovinobaňa, České Brezovo, Čierny Balog).

Monazite is also associated with cassiterite, wolframite, scheelite mineralization near the locality of Kociha in the south part of the Veporic unit, where xenotime is frequent as well.

Xenotime is a typical mineral in some hydrothermal (siderite, Mg-Fe carbonates) veins, as well as in hydrothermal apatite veins with U and REE near Čučma in the Gemeric unit.

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# THE VEIN CARBONATES IN THE VEPORICUM UNIT (WESTERN CARPATHIANS)

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The vein carbonates in the Veporicum crystalline complex belong to the typical accompany minerals of ore mineralizations. They occur mostly in metamorphic rocks of NW part of the Veporicum (so called Lubietovská, Krakľovská, Kráľovohoľská and Kohút zone) and they are typical for Cu deposits (Lubietová - Liebethen, Kolba), Fe (Tri Vody - Háromvíz), Fe (Čierny Balog - Fekete Balog), in the SW part predominantly in the deposits Uderiná, Lovinobaňa, Cinobaňa, together with Au mineralization. Carbonates are part of quartz-sulphide mineralization. We found out that they have Mg-Fe composition (Fe-magnesite, ankerite, named in previous reports only as siderite). The results (HVOŽĎARA & IRÓ, 1999; IRÓ, 1996) of vein carbonates in the Veporicum metamorphites (which are the typical part of quartz – sulphide  $\pm$  (Au) mineralizations) showed, that they are isomorphous mixtures of Mg-Fe carbonates (named as mesitite, breunnerite in previous reports).

Locality	1	2	3	4	5	6
CaO	0,67	28,90	1,52	1,04	0,52	27.60
MgO	21,63	17,90	34,15	32,78	27,72	11.39
Fe <sub>2</sub> O <sub>3</sub>	1,88			1,73	1,20	
FeO	29,15	5,48	16,24	15,18	21,92	13.13
MnO	1,22	0,42	0,38	1,37	1,19	1.6
CO <sub>2</sub>	42,02	45,30	47,46	46,51	45,94	43.16
IR	1,95	1,83		1,78	0,64	
Σ	99,46	99,83	99,75	100,39	99,13	96.92
Ca		49,08				51,25
Mg	55,57	43,56	78,91	77,74	68,25	30,00
Fe	44,43	7,36	21,09	22,26	31,74	18,75
Total	100	100	100	100	100	100

Table 1: Carbonates of Veporicum (oxide content in weight%, element content in mol%.)

1: Ľubietová - Svätodušná – mineral ferromagnesite (mesitite); 2: Ľubietová – Fedolomite-ankerite 3-5: Čierny Balog – 3 - ferromagnesite (breunerite), 4 - Fe-dolomite ankerite, 5 - ferromagnesite (mesitite); 6: Uderiná (ankerite), IR - insoluble rest

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### APPLIED MINERALOGICAL STUDY ON THE HUDEȘTI QUARTZITIC SAND FOR GLASS INDUSTRY USES

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This study is aimed at establishing the chemical, granulometric, mineralogical and morphological specific features of the Hudeşti quartzitic sand from the view of its higher utilization in the glass industry. There were four samples analyzed: one consisting of raw sand and three sorts (pre-graded,  $S_0$ , and Special  $S_0$ ).

The chemical analyses revealed that the  $SiO_2$  content is about 94.12 % for the raw sand and it rises up to 97.40 % for the superior sorts (S<sub>0</sub> and Special S<sub>0</sub>). It also came out that, among the other compounds, CaO had the highest content (2.70 % for the raw sand and approx. 1.40 % for the superior sorts).

Thus, it can be concluded that all the four samples have a very high  $SiO_2$  content, and that the  $S_0$  and the Special  $S_0$  sorts have virtually identical compositions.

The grading analyses were performed through wet classification by using a vibrating installation. Their results show that the raw sand sample and the pre-graded sort have a greater ratio of material with sizes under 0.15 mm. Again, it is obvious that the  $S_0$  and Special  $S_0$  sorts are very similar.

Several analyses and determinations, such as separations in heavy liquids, magnetic grading, HCl treatments, and others were performed in order to establish the mineralogical composition, which showed that the main impurity was calcite (2.00-2.20%) in the superior sorts).

The mineralogical study pointed out two detrimental aspects:

1. Calcite occurs mainly as crusts on other grains' surface;

2. Quartz shows  $\mu$ m-sized inclusions, the most important of these being the metallic oxides that cannot be removed by mechanical preparation methods.

The morphoscopic analyses pointed out that the samples' sphericity is between very spherical and sub-sharpened, and their roundness is generally between sharp and very rounded. These characteristics indicate that the sand had a long evolution, with repeated shifts from sub-aquatic to sub-aerial environments, due to the vertical oscillations of the continental plateau.

The existence of the Fe, Ca, Ti and Zr inclusions in quartz was confirmed by electronic microprobe scanning. Iron is present both as concentrations in certain specific minerals and as molecular dissemination in the entire mass of the quartz grain.

In conclusion, the samples' iron content can be decreased by removing the free ferriferrous minerals, but, due to the inclusions and the dissemination found in the quartz grains, it cannot be totally taken out from the superior sand sorts.

## NEW RESULTS ON ORE MINERALIZATION IN THE ŠTIAVNICA–HODRUŠA ORE DISTRICT, SLOVAKIA

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Historically, the Štiavnica–Hodruša ore district, with a large number of precious metal and base metal hydrothermal veins, is famous about findings of several interesting minerals.

Galena, sphalerite, chalcopyrite, marcasite, pyrite and hematite are the dominant ore minerals, while bornite, chalcocite, covellite and scheelite are less pronounced. Locally, rare realgar, cinnabar, arsenopyrite, pyrrhotite, stibnite, digenite, famatinite, greenockite, wurtzite, boulangerite (var. plumosite), jamesonite, bournonite, heteromorphite, ferberite, hemimorphite, coffinite and uraninite were found.

Ag and Au minerals occur predominantly in southern subsurface parts of the veins. Already in the past, gold, electrum, küstelite, silver, argentite/acanthite, polybasite, pearceite, Ag-tetrahedrite/freibergite, pyrargyrite, proustite, stephanite, rare xanthoconite and pyrostilpnite were described. Recently stromeyerite, mckinstryite, diaphorite, miargyrite, freieslebenite and rare benleonardite were also found.

For deeper parts of the veins Bi sulphosalt assemblage is characteristic, whose minerals overgrow each other intimately together with galena solid solution (PbS<sub>ss</sub>). This assemblage consists of emplectite, matildite, hodrushite, aikinite, wittichenite, Agwittichenite, paděraite, vikingite, gladite, krupkaite, hammarite, lindströmite, friedrichite, new mineral phases similar to mummeite and ourayite (Kovalenker *et al.*, 1993). Apart of these minerals numerous new other mineral phases were discovered that belong to the system Ag-Cu-Pb-Bi-S (Ag<sub>4</sub>Pb<sub>4</sub>Bi<sub>6</sub>S<sub>15</sub>, (Cu,Ag)<sub>4</sub>PbBi<sub>2</sub>S<sub>6</sub>, Cu<sub>5</sub>AgPb<sub>2</sub>Bi<sub>4</sub>S<sub>11</sub>, Cu<sub>2</sub>AgPbBiS<sub>4</sub>, Ag<sub>5</sub>CuPbBi<sub>2</sub>S<sub>7</sub>, AgPb<sub>4</sub>BiS<sub>6</sub>, AgPb<sub>3</sub>BiS<sub>5</sub>, Ag<sub>6</sub>Pb<sub>5</sub>Bi<sub>6</sub>S<sub>17</sub>, Ag<sub>2</sub>PbBi<sub>2</sub>S<sub>5</sub>, Ag<sub>5</sub>PbBi<sub>5</sub>S<sub>12</sub>, AgPb<sub>2</sub>Bi<sub>3</sub>S<sub>7</sub> and (Cu,Ag)<sub>7,2</sub>Pb<sub>1,3</sub>(Bi,Fe)<sub>11,5</sub>S<sub>22</sub>), associated with gold of high purity (~ 860). Furthermore, naumannite and an Ag<sub>10</sub>Cu<sub>2</sub>Te<sub>3</sub>SeS<sub>4</sub> mineral phase are also present.

In the currently exploited Svetozár precious metal vein system in Hodruša, gold of three generations occurs with different fineness. The oldest gold has the highest fineness (910–960), younger gold has lower fineness 810–880 and the youngest electrum has fineness ranging 745 to 790 and it is the visible gold. Recently, hessite and altaite were described in this precious metal assemblage.

Quartz and carbonates of several generations and varieties represent the gangue vein filling. In upper parts rhodonite, barite are abundant, rare adularia, epidote, chlorites, stilbite, gypsum, kaolinite, fluorite, illite/smectite, and halloysite are also present. The supergene mineral assemblage is represented by cerussite, anglesite, wulfenite, gypsum, pyromorphite, malachite, chalcanthite, melanterite, goslarite, diadochite, jarosite, voltaite, copiapite, coquimbite, quenstedtite, halotrichite, alunogen and other minerals.

## ENVIRONMENTAL MINEROLOGICAL STUDY OF SOILS OF THE CSEPEL ISLAND (HUNGARY); TRACING THE TOXIC HEAVY METALS (V, Ni)

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The "Dunamenti" Thermal Power Plant (DTPP) has been working since 1959 at Százhalombatta, 20 kilometres south from Budapest. The power plant operates on extra heavy fuel oil containing 3,5% S (average) and small quantities of vanadium (50 ppm) and nickel (15 ppm). It emitted almost 1000 tons of heavy metal containing solid pollutants into the air in the last 40 years. 95 percent of the flying ash's metal content are vanadium and nickel compounds. The flying ash settled down on the ground according to its morphology, size and density. Considering the dominant direction of wind, the main area of dustfall pollution is the Csepel Island in the Danube.

During the last decade some, mainly chemical, examination were done on the metal content of the dust: 5% of vanadium and 1,5% of nickel were detected in the airborne particles ( $\dot{O}V\dot{A}RI \& Z\dot{A}RAY$ , 1996, MOLN $\dot{A}R$ , 1993).  $\dot{O}vari$  and Zaray (1996) demonstrated that V and Ni are present as NiS, NiSO<sub>4</sub>x6H<sub>2</sub>O and VOSO<sub>4</sub>x3H<sub>2</sub>O.

Up to now no extensive investigation has been carried out to discover the penetration of heavy metal pollution into the soil. We took 5 drill core soil samples (from surface down to 1 meter depth) from different location of the Csepel Island. Each of them are 5-10 km far from the DTPP (this might be the maximum spread of significant pollution). The soils are alluvial meadow soils and alluvial soils (Fluvisols, FAO classification). They contain almost 50 % of quartz, significant amount of feldspars and carbonates (calcite and dolomite, up to 15 %) and small quantities of clay minerals and other sheet silicates (illite, smectite, chlorite, kaolinite).

X-ray powder diffraction, ICP-MS, thermoanalythical and conventional chemical methods were used. The XPD results show a very similar composition for the soils samples. Only the distribution of minerals changes with depth (carbonates and clay minerals increase, quartz and feldspars decrease). The vanadium concentration of the samples are 10–30 ppm, while the nickel contents are 10–48 ppm as measured by ICP-MS. Correlation were found between V and Fe and V and Ni contents. It is supposed that the main absorbents of these metals are the organic matter, clay mineral and carbonate soil constituents, so we focus our future investigations on these minerals.

Our primary aim is to find correlation between vanadium and nickel content versus depth, mineral species, and the organic matter as well as the distance from the DTPP.

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## IDENTIFICATION OF Fe-BEARING DAUGHTER MINERALS FROM THE VYHNE-KLOKOČ SKARN DEPOSIT, SLOVAKIA

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Vyhne-Klokoč, the largest Ca-magnetite exoskarn in the Western Carpathians (KODĚRA & CHOVAN, 1994), is related to the emplacement of a granodiorite pluton in the central zone of the Banská Štiavnica Neogene stratovolcano. Fluid inclusion (FI) studies of granodiorite quartz from samples located close to the contact with altered Mesozoic carbonates revealed abundant FIs with variable vapour/liquid/solid ratios and often several solid phases at room temperature (KODĚRA *et al.*, 1998).

Fe-bearing daughter minerals (DM) are predominantly present in high salinity, liquid rich, probably secondary FIs, which are believed to represent evolved aqueous magmatic fluids. Only halite, hematite and sometimes sylvite were possible to identify based solely on the their optical properties. The other solids were identified using *in situ* analytical methods of individual solid phases: by scanning electron microscopy coupled to an energy dispersive X-ray spectrometer microanalyser (SEM-EDS) and by laser Raman spectroscopy (LRS). The optical and microthermometric properties of the different solid phases were integrated with analysis as an aid to identification.

SEM-EDS analyses showed the common presence of halite, a whole range of K-Fe-Cl solids, ranging from pure KCl (sylvite) up to pure Fe-Cl phases, hematite, magnetite and galena. The pure Fe-Cl phases are probably represented by ferropyrosmalite [Fe<sub>8</sub>Si<sub>6</sub>O<sub>15</sub>(OH,Cl)] and/or by some Fe chloride hydrates. The common K-Fe-Cl solids were identified as  $K_2$ FeCl<sub>5</sub>.H<sub>2</sub>O (erythrosiderite), an unnamed KFeCl<sub>3</sub>.nH<sub>2</sub>O mineral and/or ferropyrosmalite/Fe chloride crystals, contaminated by precipitation of small sylvite crystals on their surface after opening.

Confirmation of the identification of daughter minerals by LRS analyses was performed by comparison with known published Raman spectra of pure minerals and with the analyses of a pure quartz host. The following solids were identified: ferropyrosmalite (in several FIs), hematite, magnetite, biotite, siderite, molybdenite. All these phases except for ferropyrosmalite are probably captive phases, as they are relatively rare in FIs and they did not dissolve during heating. The LRS method is not suitable for identification of Raman inactive solid phases, such as halite, sylvite, erythrosiderite etc.

The presence of multiple Fe-Cl bearing DMs suggests very high Fe contents in the magmatic fluid (several wt% Fe), that could be explained by subsolidus fluid-rock equilibrium reactions. Reactions add Fe to the fluid, providing the potential source for magnetite in skarns (KODĚRA *et al.*, 1998).

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61

### PRESENT RESULTS OF GEOCHEMICAL PROSPECTING OF THE STRIEBORNA VEIN DEPOSIT, SLOVAKIA

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The Strieborna vein deposit is part of the Rožňava ore field, situated in the southern part of the Gemericum. It occurs NW and NE from the Rožňava town and forms a 12 km long and 4 km wide zone. The Rožňava ore field is characterised by the presence of hydrothermal vein deposits of siderite formation.

The Strieborna vein belongs to hydrothermal vein deposit of siderite formation. The vein structure is formed by older siderite and younger quartz – sulphide mineral associations. A prevailing mineral from the sulphide group is tetrahedrite. The chemical composition of tetrahedrit is various, depending on Ag, Hg, Cu, Bi contents. Economically significant elements for mining are silver and copper.

Detailed information on distribution of silver and copper is very important for the geological exploration and mine development in the future. The distribution of silver and copper is shown in 3D (block) diagrams constructed by means of izolines.

## RHÖNITE IN SILICATE MELT INCLUSIONS OF OLIVINE PHENOCRYSTS FROM THE ALKALI BASALT OF HEGYESTŰ, BALATON HIGHLANDS, HUNGARY

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The Bakony–Balaton Highlands are one of the major Late Tertiary alkali basalt volcanic fields within the Carpathian–Pannonian Region. We have studied rhönite bearing silicate melt inclusions occurring in olivine phenocrysts in porphyritic alkali basalt at the locality of Hegyestű, Bakony–Balaton Highlands. The olivine phenocrysts formed under mantle conditions and enclosed small droplets as silicate melt inclusions from the magma at great depth.

Besides rhönite, the silicate melt inclusions contain augite, Na and K rich glass, apatite, spinel, sulfide blebs and bubbles. Rhönite occurring in similar environments has not been studied yet extensively, although SHARYGIN (unpublished), KUZMIN *et al.* (1999) and SZABÓ (unpublished) have also recognized rhönite in silicate melt inclusions from mafic volcanic rocks.

Rhönite is a reddish brown Ti rich silicate mineral, a member of the aenigmatiterhönite group, based on the classification of KUNZMANN (1999). According to experimental data, the stability field of rhönite in alkali basalts is between temperatures of 840 to 1200 °C and below pressure of 600 bars. These conditions are true if the coexisting alkali basalts have ne/(ne+ab+or+lc) above 0.18 and Mg/(Mg+Fe) ratio greater than 0.46. In our case, the estimated bulk composition of the silicate melt inclusions are consistent with the experimental conditions. Based on experimental results for the stability of rhönite (KUNZMANN, 1999), crystallization of rhönite should happen near the surface; however, our observation is inconsistent with it. We propose that the partial crystallization of the silicate melt inclusions occurred at a greater depth than suggested by KUNZMANN (1999).

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63

## SERPENTINIZATION OF THE GYÓD ULTRAMAFIC BODY – A LOW TEMPERATURE PARTIAL HYDRATATION STORY

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Ultramafic bodies in South Transdanubia have long been known through aerial geophysical measurements as well as sporadic boring activity. For many reasons the most intensely studied serpentinite body is located in the realm of the Görcsöny metamorphic complex in the vicinity of the small village, Gyód.

The Gyód Serpentinite Formation extends over 5–7 km with a WNW–ESE strike and can be traced down to about 700 metres below Pannonian sediments. It most probably has a tectonic contact with the surrounding basement, which consists of high grade metamorphic rocks. The aim of this study is to sketch the post-magmatic evolution of the ultramafic rocks by petrological as well as geochemical examination of this rock mass.

Macroscopic as well as microscopic observations suggest a basically three-step postmagmatic evolution. The last deformation event had a strong effect on certain segments of the body, where relic orthopyroxene grains are sheared, while the serpentine mineral rich parts of the rock samples indicate plastic deformation. The other main type of serpentinite is a non-foliated rock. The two types occur alternately downwards. Microtextural observations suggest a pervasive carbonatization prior to the late deformation.

Based on the dominating ultramafic phases, the serpentinite can be divided into two distinct domains. The significant part of the rock exhibits a well-developed mesh structure. Mesh center is formed probably of brucite. Mesh rim is chrysotile, while the central parting unit is marked by magnetite grains mimicking an igneous texture of an olivin bearing rock with equigranular grain contact. Ortopyroxene dominated parts of the serpentinite appear separately, and contain talc and chlorite as significant secondary phases with only a low amount of serpentine.

Application of the isocon method for differently altered sample pairs shows that the serpentinization of the one-time ultramafic rocks was close to isochemical for most major and trace elements. Important exceptions are Ti and Sr with decreasing and Cr with increasing concentration with the rate of the alteration. Immobile element distributions as well as classical discrimination methods show in good agreement with the mineralogical composition that the precursor of the Gyód serpentinite should have been harzburgite.

Independent thermobarometric modelling (Domino–Theriak) of the olivine and pyroxene rich domains of the rock, respectively, suggests that the characteristic metamorphic parageneses in both cases are stable at LT (< 250 °C) in the presence of a low  $f_{CO_2}$  fluid. The observed mineral sequences could form due to intensive hydratation without significant change in p or T.

In contrast to the previous models we conclude that the Gyód serpentinite body formed during a single LT hydratation event. No subsequent MT overprint was needed to grow talc and chlorite as it was suggested earlier.

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### WHAT DO WE CALL CHERT? A MINERALOGICAL CASE STUDY FROM ÖRDÖGOROM HILL, BUDAPEST, HUNGARY

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Chert can frequently be found in Hungarian Mesozoic formations. From the mineralogical point of view this material is traditionally considered to be microcrystalline quartz. This affirmation is generally based on data gained with polarized light microscopy (PLM) and X-ray powder diffractometry (XPD).

The investigation of the microstucture of chert is warranted by new pieces of information recently appeared in international literature. In 1992, MIEHE *et al.* determined the crystal structure of a new natural silica modification called moganite. In the same year a report in Science spoke about the widespread distribution of this silica polymorph in microcrystalline quartz varieties (HEANEY & POST, 1992). Since then several new data were publicated about moganite and the IMA is actually working on its approval as a valid mineral species.

The aim of our work was to examinate microcrystalline silica samples of different ages and genesis from Hungarian localities. In this poster we present the results of the measurements made on the chert nodules of the Upper Triassic cherty dolomite of the Ördögorom (Devil's Cliff).

The methods we mainly used were electron microscopy (SEM, TEM, SAED, HRTEM) and X-ray powder diffractometry (XPD). Morphological examinations were made with SEM on etched and natural fracture surfaces.

Structural properties were investigated with TEM. SAED patterns reveal the presence of an ordered quartz phase and a disordered phase with several streak systems and satellite reflections, which imply superstructures. The HRTEM images made of the quartz crystals show a cavernous surface and a strongly dislocated mosaic structure. The images made about the disordered crystals contain areas which are characterised by a lattice spacing periodicity of 6.6 Å. Probably the peak appearing on the XPD profiles at the same d-spacing (6.5-6.7 Å) is related with this periodicity, which is not consistent neither with the symmetry of quartz nor with that of the supposed moganite phase. All these observations motivate us to do XPD structure refinement which should provide further information.

Based on our investigations up to now, the chert from Ördögorom is not analogous with microcrystalline quartz, because it has its own structural properties, furthermore it probably consists of the close composition of two phases: quartz and moganite.

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### NEW DATA ABOUT THE CRYSTAL MORPHOLOGY OF "MARMAROSH DIAMONDS"

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We carried out electron microscopic and goniometric studies on quartz crystals from the area of the village Nyzhni Vorota in the Ukrainian Carpathians. Among the crystals one can distinguish a few morphological types:

- The prism type, in which the  $\{1 \ 0 \ \overline{1} \ 0\}$  prism predominate in their development over the main rhombohedra;
- The prism-rhombohedron type of nearly equal development of both the prism {1 0 1 0} and rhombohedra {1 0 1 1} and {0 1 1 1};
- The complicated prism-rhombohedron type, showing a good development of faces of the {1 1 2 1} dipyramid;
- The rhombohedron (pseudocube) type. The forms of the rhombohedrons {1 0 1 0} and {0 1 1 1}; prevail over those of the prism {1 0 1 0}, the faces of which are presented only by narrow strips.

Sometimes intergrowth of quartz, close to twins after Fridel's law ([0001] axes of the crystals are oriented at the angle of 90°), are also observed.

Investigation of surfaces of various simple forms of the crystals from the surroundings of Nyzhni Vorota by means of scanning electron microscopy has shown that the crystals display almost no signs of various visible forms of growth or dissolution. On the faces of prism there are noticeable narrow faces of different rhombohedra, polar coordinates of which differ from those of the main rhombohedra.

Such crystals of quartz, as well as ones showing a good development of the dipyramid faces, were an object of the goniometrical study. In many crystals, minor faces of the acute rhombohedra  $\{2 \ 0 \ \overline{2} \ 1\}$  and  $\{7 \ 0 \ \overline{7} \ 3\}$  are observed in the zone of the  $\{1 \ 0 \ \overline{1} \ 1\}$  rhombohedron. Sometimes minor faces of the  $\{0 \ 5 \ \overline{5} \ 1\}$  and  $\{0 \ .10, \ \overline{1} \ \overline{0}, \ 7\}$  rhombohedra appear in zone of the  $\{0 \ 1 \ \overline{1} \ 1\}$  rhombohedron. A combination of the above mentioned acute rhombohedra make faces of prism  $\{1 \ 0 \ \overline{1} \ 0\}$  complicated.

Two crystals of quartz, having an extraordinary scarce form of the  $\{0 \ 1 \ \overline{1} \ 2\}$  rhombohedron, are of unique finding not only among "Marmarosh diamonds" but also among crystals of quartz in general. The obtuse rhombohedron  $\{0 \ 1 \ \overline{1} \ 2\}$  is established for the first time not only for the crystals of "Marmarosh diamonds" but also for quartz crystals from various hydrothermal mineralizations of the Ukraine.

## KAERSUTITE MEGACRYSTS IN CAMPTONITES FROM THE SOUTHEAST CARPATHIANS, ROMANIA

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The Mesozoic intraplate magmatic activity in the Southeast Carpathians generated dikes of basalts, diorites, camptonites, syenites and rhyolites, intruded in the crystalline schists of the Getic and Supragetic Unit.

Megacrysts of kaersutite have been identified in camptonites occurring in this area. They appear as single crystals up to 5 cm long. The kaersutite crystals are cut by very fine calcite, quartz and chlorite veinlets.

The megacrysts have been investigated by optical microscopy, chemical methods (electron microprobe for major elements, ICP-MS for trace elements) and XRD.

The chemical composition is homogenous along and across the crystal. The calculated formula on the basis of 23 O is:

 $(K_{0.39}Na_{0.26})_{0.65}(Na_{0.32}Ca_{1.68})_2(Fe_{0.96}Mg_{3.01}Mn_{0.01}Ti_{0.53}Al_{0.36})_{4.87}(Si_{5.82}Al_{2.18})_8O_{23}(OH).$ 

The LREE are slightly depleted. The selected XRD data sorted by intensity  $(I/I_0)$  are 3.17(100), 8.75(93), 3.32(31), 2.92(22), 2.84(19), 2.73(19), 7.36(11), 2.78(10).

Kaersutite megacrysts represent samples from the mantle beneath the Southeast Carpathians at the time when the camptonites have been formed.

## STRAIN ESTIMATION FROM TWINNING IN CALCITE CRYSTALS OF CARBONATE ROCKS FROM THE BÜKK MOUNTAINS (NORTHEAST HUNGARY)

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Most of late Palaeozoic and Triassic stratigraphic units of the Bükk Mountains are composed of limestones, mainly of platform and pelagic facies. These rocks experienced very low- and low grade Alpine regional metamorphism (Austrian and Sub-Hercynian orogeny), resulting in most of cases in the complete recrystallization of the carbonate mass.

The recrystallized limestones are mainly composed of flattened, neomorphic calcite crystals of 10-30  $\mu$ m in diameter. Relics of the original texture are reduced to large (over 100  $\mu$ m) calcite crystals of Crinoidea fragments and intraclasts.

A characteristic feature of the large calcite crystals is that they are twinned. Since other textural parameters of these rocks are rather weak, the morphology of the twins was investigated in detail to obtain information about the metamorphic history. Four types of twins were distinguished by their thickness and deformation (MÁDAI, 1995):

 $\alpha$  - thin (1-2 µm in thickness), straight, undeformed twins that appear only in the very large (>250 µm) crystals. They definitely are of post-tectonic origin.

 $\beta$  - post- or syntectonic, thick (>4  $\mu$ m), straight, undeformed twins that enclose high angle with the schistosity.

 $\gamma$  - pre- or syntectonic, curved, bent twins inclined into the plane of schistosity.

 $\delta$  - pretectonic, intensively deformed, sheared twins transformed sometimes to chains of small, recrystallized calcite crystals.

The post- or syntectonic origin of the  $\beta$ -type twins can be appraised by calculation of the strain that caused the twinning. The method of calculation was contributed by GROSSHONG (1972, 1974). It requires to measure the total thickness of twin lamellas perpendicularly to the *e* plane as well as the co-ordinates of the *c* axis of the host crystal and the co-ordinates of the normal vector of the *e* plane. The co-ordinates were defined with universal stage and the thickness was measured by digital image analyser equipment.

The error of the calculated strain components was small for some samples and large for others indicating that the  $\beta$ -type twins had been formed by one or by multiplied tectonic events, respectively. Comparing the results with analogous measurements completed in the Northern Subalpine Belt (FERRILL, 1991), the  $\beta$ -type twins were formed after the metamorphism.

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### **BRUSHITE AND HYDROXYLAPATITE IN THE CIOCLOVINA CAVE (SUREANU MOUNTAINS, ROMANIA)**

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During the study of the minerals ardealite (SCHADLER, 1932) and crandallite (CONSTANTINESCU *et al.*, 1999), brushite and hydroxylapatite were abundantly found in the bat guano deposit from Cioclovina Cave, Sureanu Mountains, Romania.

Brushite generally occurs single or in irregular intergrowths with ardealite, in white earthy aggregates that overgrow hydroxylapatite or crandallite. Very thin veinlets of brushite were also recognized as infillings of some fissures that affects the hydroxylapatite mass. A wet chemical analysis of a carefully hand picked separate gave CaO = 32.06, MgO = 0.03,  $P_2O_5 = 40.78$  and  $H_2O = 26.43$  (all expressed in wt%). The corresponding chemical-structural formula is ( $Ca_{0.995}Mg_{0.001}$ ) $H_{1.008}(PO_4)$ ·2.049  $H_2O$ . The cell parameters, taken as the mean of least-squares refinements on 20 different sets of Xray powder reflections, are a = 5.810 Å, b = 15.176 Å, c = 6.239 Å and  $\beta = 116.37^{\circ}$ . The density of isolated grains, established by sink-float in toluene-methylene iodide solutions, is  $D_m = 2.325(1)$  g/cm<sup>3</sup> for a calculated value  $D_x = 2.328$  g/cm<sup>3</sup>. At about 200 °C (202 °C on the DTG curve and 196 °C on the DSC one, at a heating rate of 10 °C/min), the mineral breaks down into monetite [a = 6.900(3) Å, b = 6.637(3) Å, c = 6.991(4) Å,  $\alpha = 96.00(3)^{\circ}$ ,  $\beta = 103.00(3)^{\circ}$ ,  $\gamma = 88.00(3)^{\circ}$ ], by losing two molecules of water in a well-defined single step. By continuing heating, monetite turns into  $\beta$ - $Ca_2P_2O_7$  [a = 6.686(3) Å, c = 24.089(18) Å] at 426 °C (420 °C on the DSC curve).

*Hydroxylapatite* occurs as aggregates of acicular or fibrous crystals composing crusts or mounds that are generally overgrown on a carbonaceous support. These aggregates are commonly corroded and coated by brushite, which fills fractures and embayments in the hydroxylapatite mass. The physical constants of a selected sample  $[D_x = 3.151 \text{ g/cm}^3; D_m = 3.180(2) \text{ g/cm}^3; \varepsilon = 1.645(2); \omega = 1.653(1)]$ , as well as the cell parameters, taken as mean of least-squares refinements on 18 different sets of X-ray powder reflections (a = 9.433 Å, c = 6.872 Å), account for the presence of a nearly stoichiometric hydroxylapatite at Cioclovina. A wet chemical analysis gave  $CaO = 55.10, MnO = 0.19, MgO = 0.04, Na_2O = 0.30, K_2O = 0.05, P_2O_5 = 42.36$ and  $H_2O^+ = 1.80$  (all data expressed in wt%), which leads to the formula  $(Ca_{4.939}Mn_{0.013}Mg_{0.005}Na_{0.049}K_{0.005})(PO_4)_3(OH)_{0.968}$ , in which it is necessary to deduce a surplus of 0.018 molecules of H<sub>2</sub>O for consuming all H in the initial analysis.

The textural relationship between different phosphate species suggest that brushite formed late, replacing hydroxylapatite and crandallite, but it predated ardealite.

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### GEHLENITE IN HIGH TEMPERATURE SKARNS FROM THE ROMANIAN BANATITIC PROVINCE: A REVIEW

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Gehlenite is a common mineral in the high temperature calcic skarns from the Romanian Banatitic Province. The mineral was recognized in three such occurrences: at Magureaua Vatei (MV) and Cornet Hill (CH) in the Apuseni Mountains and at Oravita (Or) in Banat. The host skarns are typically zoned and are fairly similar in their internal structure. In all the three occurrences, a gehlenite zone occurs at the very contact between a monzodioritic body and carbonaceous sequences of Mesozoic age. The mineral was found in the following contexts and parageneses: (1) blocky gehlenite associated with wollastonite, perovskite and grandites (MV, CH), with monticellite, grandites and ellestadite (Or) or with wollastonite, perovskite and ellestadite (CH) in the inner skarn zone; (2) veins or clusters of gehlenite surrounded by spurrite and associated with perovskite and granet in a median skarn zone (CH).

Late stage metasomatic replacement of gehlenite by vesuvianite is common, as well as its replacement by hibschite, gismondine, 11 Å tobermorite and allophane as a result of late hydrothermal and weathering processes.

The solid solutions toward åkermanite vary from Ak 22.90 to Ak 36.28 (mean Ak 29.80) at CH, from Ak 33.64 to Ak 38.13 (mean Ak 36.22) at MV and from Ak 34.68 to Ak 50.25 (mean Ak 45.28) at Or respectively.

Both chemical and crystallographic parameters are influenced by the chemical variability. The physical parameters, as measured on representative samples approaching the mean composition, are as follows:

Occurrence	Magureaua Vaței	Cornet Hill	Oravița
ω	1.658(1)	1.660(2)	1.666(1)
3	1.656(1)	1.655(1)	1.662(1)
$D_{\rm m} ({\rm g/cm}^3)$	3.064(2)	3.065(2)	3.095(5)
n <sub>Gladstone-Dale</sub>	1.637	1.638	1.643
$D_{\rm x} ({\rm g/cm^3})^*$	3.062	3.069	3.081

\* as calculated for the mean composition and cell volume, for Z = 2 unit cells per formula.

Cell parameters are highly variable: a ranges from 7.679(3) to 7.734(3) Å at Or, from 7.684(3) to 7.733(1) Å at CH and from 7.687(3) to 7.718(3) Å at MV, whereas varies from 5.043(3) to 5.065(3) Å at Or, from 5.044(1) to 5.067(4) Å at CH and from 5.049(2) to 5.063(3) Å at MV.

The record in the infrared absorption spectra of a couple of bands located at ca. 855 cm<sup>-1</sup> and ca. 670 cm<sup>-1</sup> respectively, that may be tentatively assigned to Al-O-Al (antisymmetric and symmetric respectively) stretchings, is indicative for the presence of gehlenitic terms of the melilite group in all the three occurrences.

# MINERALOGICAL ZONATION OF THE UKRAINIAN CARPATHIANS

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One of the main tasks of topographic mineralogical investigations is the recognition of mineralogical zonation carried out with a help of geology-structural principle. In the course of such zonation, the mineralogical province as elementary regional mineralogical taxon may be used. Province margins according to N. Yushkin coincide as a rule with the boundaries of the large and middle sized structural elements.

The Ukrainian Carpathians belong to the united Carpathian mineralogical province with diverse development of precious metal, sulphide, carbonate and sulphate-chloride mineralization. Four mineralogical subprovinces can be distinguished within the bounds of the Carpathian province: Marmaroshska, Precarpathian, Carpathian and Transcarpathian.

The Marmaroshska mineralogical subprovince occupies marginal northwestern Marmaroshsky massif part with outflow of the most ancient (Upper Paleozoic) metamorphic and magmatic rocks and can be divided into Rakhivsky and Chyvchynsky mineralogical regions. The main mineralogical objects there are the deposits and ore manifestations of gold, subgraphite and manganese rhodonite-rhodochrosite ores, stratiformed iron pyrite, copper-pyrite, pyrite-polymetallic and veined polymetallic ores and marbles.

The Precarpathian mineralogical subprovince includes the territory of the Pre-Carpathian Foredeep filled with thick Miocene molasse series. Three main mineralogical regions can be distinguished here: Stebnyk–Truskavetsky with the deposits of potassiummagnesium and lead-zinc deposits in Miocene halogenous rocks; Kalushsky with potassium-magnesium salt deposits and insignificant copper (chalcopyrite) mineralization and Nadvirnyansky–Yablunivsky with widespread manifestation of the copper mineralization (chalcocite mainly), as well as with ancient placer (Slobodsky conglomerates) and contemporary alluvial gold mineralization.

The Carpathian mineralogical subprovince occupies most of the area of the Folded Carpathians composed of Cretaceous and Paleogene terrigenous flysch formations. The main mineralogical objects here are stratiformed copper (chalcopyrite and chalcocite) and post-sedimentation iron-manganese carbonate mineralization, mercury and antimony-mercury-arsenic ore manifestation and regional development of the Marmaroshsky "diamond":

The Transcarpathian mineralogical subprovince occupies the foredeep of the same name, formed with the thick series of molasse rocks and Neogene volcanites with intensive and diverse post-volcanic mineralization. Four mineralogical regions can be distinguished here: Beregivsky with the deposits of gold, gold-polymetallic, baritepolymetallic, alunite and kaolinite ores; Vyshkivsky with mercury deposits in the form of cinnabar, metacinnabar-cinnabar and sphalerite-galena-cinnabar mineral types; Solotvynsky with rock salt deposits; Vyhorlat–Gootynsky one with almandine mineralization in dacites, ungvarite and ferriferous (nontronite-goethite) mineralizations as well as quartz-topaz, quartz-tourmaline, quartz-kaolinite and other metasomatites accompanied with tellurium-bismuth mineralization.

# QUARTZ FROM THE BEREGOVE ORE FIELD OF TRANSCARPATHIA, UKRAINE

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Quartz, as a predominant vein mineral of the ore bodies and near-ore metasomatites of auriferous polimetallic mineralization, is the main rock forming mineral of the enclosed volcanic rocks and metasomatites of the secondary quartzite facies. Three genetic types of quartz can be distinguished: magmatic, metasomatic and hydrothermal.

Magmatic quartz in the form of phenocryst relics and fragments is characteristic for liparite tuffs. It is mainly transparent, pale pink to grey, strongly fissured. Metasomatic quartz is the main component of the secondary quartzites. It is present as cryptocrystalline and fine grained grey aggregates. Veined and streaky quartz segregations belong to the hydrothermal type, have thicknesses from 1–5 cm to 10–20 cm and more and are connected with auriferous polimetallic mineralization. This type of quartz is characterized with striped and porous texture. In leached cavities one can see fine-faced quartz crystals up to 5 cm in dimension and its drusy aggregates. These crystals are mainly colourless, transparent, sometimes amethyst-like milk white or grey in their basis.

Two morphological types can be distinguished amongst quartz crystals: early oblong prismatic and late short prismatic (the last is presented by amethyst in near-surface zones). The most characteristic first type crystals have zoned structure caused by the presence of zones with gaseous–liquid and solid inclusions. Quartz belonging to different genetic types has differences in thermoluminescence, X-ray luminescence, IR spectroscopic and EPR nature as well as oxygen and carbon isotope composition and cryometric data.

Hydrothermal quartz formed in two stages. The earlier one is the final component of the polymetallic stage, crystallized from heterogenetic carbon dioxide-water solutions under 260–230 °C. The late quartz (amethyst) is connected with the barite-alunite mineralization stage under 180–210 °C. In accordance with L. Z. Skakun's data, four quartz generations can be distinguished in the Muzhyievo gold-polymetallic deposit connected with four mineralization stages: sulphide, quartz-barite, carbonate-quartz and carbonate-goethite.

### SEPARATION OF THE 10 Å GREEN CLAY MINERAL FROM THE CARBONATIC MANGANESE ORE, ÚRKÚT, HUNGARY

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The green clay mineral(s), referred in the geological literature mainly as glauconite, of the banded carbonatic manganese ore in Úrkút, Hungary was studied by several authors. A comprehensive list of results is given by POLGÁRI (1993). In spite of the intensive studies in the past there is no consensus concerning the nature of the mineral. The main reason of that uncertainty is that the very fine grains of the mineral are always to be found in intimate mixture with other very fine grained phases, like rhodochrosite (RH), quartz (Q) and goethite (G). In all of the previous studies, part of these phases were omitted only by recalculation of data measured on mixtures, in other words there has been no full mineralogical data set measured on the pure green clay phase.

The aim of this study was to design a separation procedure applicable for the given mineral assemblage and the preliminary characterisation of the separated pure green mineral phase (and, as a by-product, the chemical characterisation of the other phases).

We investigated the reference samples studied in details by a team of Prof. Gyula Grasselly (GR) during the 1980s (for the list of these research reports see POLGÁRI (1993)). When selecting samples we took the earlier analyses into consideration for finding samples containing the less interstratified 10 Å phyllosilicate(s) (CM10A) and being available in appropriate quantity for further studies. Having tested several samples and having observed all the four expected phases (CM10A, RH, Q, G) by XPD and IR we selected two samples from the bottom of the "Main Ore Bed": MV1 (= #188a of GR = the green part of the #3 of GR) and MV2 (= #4a of GR = the green part of the #4 of GR), and one from the top of the same bed MV3 (URK-6 of Polgári = # 49 of GR).

The separation procedure consisted of three steps. In the first two RH and G were removed by traditional chemical separation. In the third step, Q was separated from CM10A by applying a new mechanical separation method. In the case of the carbonate removal both diluted hydrochloric and acetic acids were used in parallel control separations. In the third step we used the water soluble carboxymethylcellulose-Na salt (CMC) for preparing a separation medium. We found that a 2 % CMC solution was of viscosity high enough to be applicable for the separation of CM10A and Q (based on density and shape) in an ultracentrifuge. All steps of the separation were monitored by XPD and ICP measurements, reference materials from all steps were kept for control.

Detailed study of the separated phases available now will help the more exact reconstruction of the Toarcian anoxic basin in Úrkút. This work was supported by OTKA Grant # T25873.

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## GENETIC ASPECTS OF MINERALOGY IN SHALLOW LEVELS OF LOW SULPHIDATION TYPE EPITHERMAL SYSTEMS OF THE TOKAJ MTS., NE HUNGARY

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The Tokaj Mts. is located in the central-western part of the Tertiary-Quaternary volcanic arc of the Carpathians. They consist of a less differentiated, mostly andesitic-dacitic volcanic sequence of Badenian (15-13.5 Ma) age that is covered by a more differentiated series of medium- to highpotassic calc-alkaline andesitic-dacitic-rhyolitic volcanic rocks of Sarmatian-Pannonian (13-9 Ma) age in a north-south oriented graben-like structure. The Sarmatian-Pannonian, mostly subaerial and subordinately submarine andesitic-dacitic lava flows, extrusions and shallow intrusions are the most widespread and are related to small caldera-like structures, effusive cones and fissure volcanoes. The synchronous rhyolitic rocks form extrusions and various deposits in distal and proximal facies of dome-flow complexes as well as tuff units with large areal distribution. Locations of epithermal systems (12.5-10.8 Ma K/Ar age for adularia and alunite) in andesitic and rhyolitic rocks are controlled by the major faults of the graben. They also frequently occur in close spatial relationships to shallow subvolcanic andesite bodies in caldera-like structures. Exposures of low sulphidation type alteration and mineralization correspond to different levels of paleohydrothermal activity. The deepest levels, with about 200-500 m minimum paleodepth, are characterised by K-feldspar-sericite alteration surrounded by regional propylitisation along siliceous veins. Potassium feldspar replacing plagioclase of andesite and sanidine of rhyolite show sericitic alteration and Ba enrichment. Younger adularia in fractures and veins is fresh and has pure K-feldspar composition. Fluid inclusion data indicate 200-260 °C for boiling parent fluids. Degassing (CO<sub>2</sub> loss) generated by opening of veins explains the double appearance of K-feldspar. Boiling horizons are also marked by the presence of quartz pseudomorphs after bladed calcite and occurrences of euhedral scepter quartz in the cavities of host rocks. Textures of vein filling quartz correlate with crystallization temperature. These deepest levels are the predominant zones of Au-Ag enrichment with minor amount of Pb-Zn-Pb-Fe sulphides. The intermediate zone corresponds to about 100-200 m paleodepth where overprinting of acidic steam-heated alteration with alunite and kaolinite in funnel shaped bodies was generated by the drop of paleowater table during the hydrothermal activity. Neutralization of steam-heated fluids during lateral flow in permeable tuff units resulted illite-montmorillonite and montmorillonite zones around the acidic alteration funnels. The strongly silicified and brecciated bodies above this horizon consist of quartz, opal, barite, cinnabar and hematite with anomalies of As, Sb, Tl and erratic Au-Ag enrichments. Paleotemperatures for these zones are between 100 and 200 °C. The paleosurface of hydrothermal activity is marked by rarely preserved hot spring centers that consist of hydrothermal eruption breccias surrounded by sinter-like aprons of bedded-laminated silica deposits. Opal C, opal CT and chalcedony are associated with cinnabar, hematite and anomalies of Sb in this environment. Silica content of fluids outflowing from these hot spring centers deposited in local fresh water basins in forms of thick siliceous sediments. These silica layers are intercalated with bentonite and kaolinite beds and are characterised by Sb and As anomalies with erratic occurrence of realgar, orpiment and stibnite. Recognition of the position of an exploration field in the above described vertical zonation may also support the evaluation of potential for precious metals in other, less eroded low sulphidation type systems of the Carpathian volcanic belt.

## **NEWLY-FORMED PHYLLOSILICATES FROM** HYDROTHERMALLY ALTERED GRANITOID ROCKS IN THE PEZINOK-KOLÁRSKY VRCH SB-AU DEPOSIT, WESTERN **CARPATHIANS, SLOVAKIA**

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Granitoid rocks are often affected by different degrees of hydrotermal alteration in the surroundings of Sb-Au deposits. Many authors (e.g. BRIL & BEAUFORT, 1989 and others) have recognized three alteration zones: chlorite zone, muscovite zone and illitecarbonate zone. Our recent study has found analogous conclusions from altered granitoid rocks in the Pezinok-Kolársky vrch Sb-Au deposit. Newly-formed phyllosilicates are represented by chlorites and K-micas. Chlorites were formed from primary biotites of two-mica granitoid rocks. We have recognized trioctahedral chlorites ( $\Sigma R_{5,62-5,90}$ ,  $\Box_{0,09-1}$  $_{0.49}$ , isomorphous series clinochlore-chamosite) according to the classification of WIEWIÓRA & WEISS (1990) and WEISS (1991). They can be divided into two subgroups:  $Fe^{2+}$ -clinochlore (schematic formula Mg<sub>3439-3632</sub>Fe<sub>2831-3707</sub>X<sub>2402-3539</sub>) and  $Mg^{2+}$ -chamosite (schematic formula  $Mg_{34,34-37,90}$  Fe<sub>34,76-39,32</sub>X<sub>23,18-28,30</sub>). Chemical composition of these chlorites (originated from strongly and less altered rocks) is: (Mg195- $_{2.30}$ Fe<sub>1.56-2.18</sub>Mn<sub>0.01-0.02</sub>Ca<sub>0.01-0.03</sub>Al<sub>1.23-1.69</sub>Ti<sub>0.01-0.03</sub> $\Box_{0.12-0.49}$ ) (Si<sub>2.81-3.16</sub>Al<sub>0.84-1.19</sub>)O<sub>10</sub>(OH)<sub>8</sub> for dominant type of substitution, which is combined with low "dioctahedral" substitution Al<sub>2</sub>Mg<sub>-3</sub>. Chlorite-like material from weakly altered rocks is not in compliance with theoretically possible composition of chlorites according to WEISS (1991). It is caused by incomplete alteration of biotites into chlorites ( $\Sigma R_{6,12-6,25}$ ). K-micas were formed from plagioclases and can be divided into illites and "alumo-celadonites". Chemical composition of illites (originated from strongly altered rocks) is  $K_{0.77-0.965}$  (Al<sub>1.61</sub>-1.89Ti<sub>0.005-0.02</sub>Fe<sub>0.02-0.105</sub>Mg<sub>0.11-0.41</sub>D<sub>0.865-1.055</sub>) (Al<sub>0.77-0.95</sub>Si<sub>3.05-3.23</sub>) O<sub>10</sub> (OH)<sub>2</sub>. Main type of substitution is  $I_1(Si_{+1}AI_1)$  and it is combined with low celadonitic substitution. In the MR3-MR2-2R3 diagram (VELDE, 1977) these illites are grouped near and slightly below the muscovite end-member, along the muscovite-pyrophyllite tie-line. In "alumoceladonites" (originated from middle altered rocks), the dominant relation among chemical constituents is given by the celadonitic substitution  $(Si_{+1}Al_{-1})^{IV}(Al_{-1}R^{2+}_{+1})^{VI}$  and it is demonstrated by a strong positive correlation of Si<sup>IV</sup>/Al<sup>VI</sup>. This substitution is combined with the low  $K_{-1}(Si_{+1}Al_{-1})_{V}$  substitution of Al by Si together with a decrease of interlayer occupancy. Chemical composition is (K<sub>0.685-0.87</sub>Na<sub>0.02-0.24</sub>Ca<sub>0.015-0.035</sub>) (Al<sub>1.555-</sub>  $1_{685}$ Ti<sub>0.015-0.02</sub>Fe<sub>0.10-0.165</sub>Mg<sub>0.215-0.26</sub> $\Box_{0.957-1.005}$ )(Al<sub>0.567-0.68</sub>Si<sub>3.32-3.425</sub>)O<sub>10</sub>(OH)<sub>2</sub>. Analysed "alumoceladonites" are perfectly parallel to the tie-line muscovite-celadonite in the MR3-MR2-2R3 diagram.

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## THE MAGMATIC-HYDROTHERMAL TRANSITIONAL PROCESS EVOLUTION OF THE BAIA DE ARIEŞ NEOGENE BRECCIA PIPE ORE DEPOSIT (APUSENI MOUNTAINS, ROMANIA) VIA MINERAL MICROINCLUSIONS IN PYRITE

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Gold bearing and polymetallic mineralizations at Baia de Arieş are spatially and genetically closely related to breccia pipe structure developed on the top of some shallow subvolcanic bodies.

SEM-EDAX quantitative analyses, performed on pyrite crystals sampled from the Baia de Arieş ore deposit, reveal a large spectrum of mineral microinclusions, as follows: Fe sulphides, K and K-Fe chlorides, sericite, anhydrite, carbonates (Ca, Ca-Fe, Ca-Mn-Fe), apatite, hematite, titanite, marcasite, pyrrhotite, sphalerite, quartz, spinel. According to their origin and position in the host mineral these microinclusions are daughter phases, arborescent microstructures and captured minerals.

Based on these mineral microinclusions, the following paths of the magmatichydrothermal transitional process evolution of the Baia de Arieş breccia pipe ore deposit could be inferred:

1. Breccia column formation according to Burnham's model (BURNHAM, 1985).

2. Ascension of high temperature fluids with K and Fe rich composition, the potassic neomineral association requiring a pH 3-6 (CRERAR & BARNES, 1976).  $(PO_4)^{3-}$  in solution is supported by apatite presence in the mineral paragenesis. H<sub>2</sub>S increasing in solution leads to Fe sulphide deposition.

3. Zn, Pb sulphide deposition at the same physico-chemical constraints (T = 350-400 °C, pH = 3-6) favouring under lithological control (calcareous rocks) an abundant deposition of zinc and lead sulphides (HEMLEY & HUNT, 1992) at the Valea Lacului zone. Supplementary, the estimation of the process constraints is based on geothermometric determinations using both the distribution of Cd and Mn between coexisting sphalerite and galena (350-390 °C), and the sulphur isotope fractionation data (430 °C).

The presence of K, Fe chlorides in the magmatic and hydrothermal mineralization stages emphasizes the transitional process (NEDELCU *et al.*, 1998) occurred in the Baia de Arieş breccia pipe system.

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## VESUVIANITE WITH DIFFERENT SPACE GROUPS FROM SZÁR HILL, POLGÁRDI, HUNGARY

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Vesuvianite is a rock forming mineral of the Szár Hill skarn, formed during the Mesozoic when the Devonian Polgárdi Limestone was metamorphosed by volcanic intrusions.

On the basis of morphology there are two types of vesuvianite. One consists of brown, idiomorphic elongated prisms with dipyramid terminations. The other type consists of anhedral isometric grains, forming granular aggregates at the boundary of the andesite.

Petrographic microscopy showed brownish isotropic crystals (garnet and vesuvianite) in calcite and clay matrix in the sample from the transition zone, i.e. the boundary zone between the andesite and the skarn.

The  $c_0$  lattice constant and the 001 projection of the unit cell of vesuvianite is quite similar to that of garnets. The main difference between them is the presence of the channels in the vesuvianite structure with two fourfold axes. The fivefold and the eightfold coordinated cations (both of A and B positions) and oxygen anions (also A and B positions) are arranged along these axes and the ordering process between the A and B positions result the P4/n and P4nc space groups. The P4/nnc can be considered as the statistical arrangement of the P4/n and P4nc type ordering.

ALLAN & BURNHAM (1992) suggested 400 °C for the lower temperature limit of the presence of the P4/nnc vesuvianite. VEBLEN & WEICHMANN (1991) studied the cation ordering as a function of temperature. They found that the P4/nnc phase transforms into P4/n at slow cooling rate. They determined 780–800 °C as the transition temperature between the two symmetries (P4/n and P4/nnc) but there is no evidence for the stability conditions of the P4nc phase.

The samples from Polgárdi were studied by TEM. The SAED patterns revealed the high temperature P4/nnc and the ordered P4/n, P4nc phases besides garnet.

These observations confirmed that the isotropic crystals are garnet and P4/nnc vesuvianite. In the transition zone the mineralogically interesting P4nc space group vesuvianite was found.

According to these data, the skarn can be formed at high temperature by a volcanic body enriched in volatile materials. But the intruded body was not large and its temperature could not be higher than 500–600 °C. That is the reason why we suppose that a part of the intruding material saturated with volatiles parted from the main body and caused the metasomatosis the limestone. The coexistency of the ordered and the disordered vesuvianite phases suggests that the temperature of the metasomatism could reach 700 °C.

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## MINERALOGY AND GENESIS OF METACINNABAR FROM RÓKA HILL, BUDAPEST, HUNGARY

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The metacinnabar and cinnabar occurrence on Róka Hill was described and studied by NAGY & PELIKÁN (1976). The main mass of the area is built up of Dachstein Limestone and brecciated dolomite. Eocen sedimentary sequence overlie unconformably the Triassic carbonates. The deformed rocks are rich in hydrothermal occurrences. The dispersed pyritization of the Triassic limestone with high As bearing pyrite, marcasite, sphalerite, goethite and gypsum preceded the deposition of mercury.

The metacinnabar and cinnabar occur as veins and cavity fillings in the Eocene sandy limestone along a clayey-silicified zone. The minerals accompanying the metacinnabar are: calcite, cinnabar, barite, pyrite, galena (?), goethite, lepidocrocite, and quartz and well ordered kaolinite. The crystals are idiomorphic, the predominating crystal forms are tetrahedra, rarely hexahedra. Inhomogeneity of the grains and the zonation can be seen in microscope: black, inclusion free metacinnabar and red inclusion rich cinnabar zones alternate parallel to (111). Maybe this zonal pattern of texture represents the deposition of the two HgS phases following the oscillating physico-chemical parameters (e.g. pH,  $f_s$ ). Electron microprobe studies revealed that the cinnabar's composition is pure HgS, while the metacinnabar contains 1.5 at% of zinc. On the basis of XRD, the calculated  $a_0$  cell parameter proves also the presence of Zn in the structure.

The real crystal structure was studied with TEM. The SAED patterns reveal the presence of the disordered metacinnabar phase besides the presence of cinnabar, metacinnabar. Based on structural analogy between sphalerite and metacinnabar, disorder can be interpreted as the appearance of hexagonal close packed lamellae in the cubic close packed host. To define the degree of the disorder (PANDEY & LELE, 1986), fault concentration and growth probability were used as parameters. Intensity curves were plotted with a set of different input parameters. By comparing the measured intensities with the calculated curves, the metacinnabar can be characterised by low fault concentration and high growth probability. The hexagonality varies between 30–50 %.

According to the data of fluid inclusion of barite related to metacinnabar, it was deposited from boiling hydrothermal solution of medium salinity, at about 180 °C. The low Sr content of barite also supports the volcanic hydrothermal genesis.

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## ALMANDINE PHENOCRYSTS IN INTRUSIVE ANDESITES FROM THE RODNA MOUNTAINS (SUBVOLCANIC ZONE, EAST CARPATHIANS, ROMANIA)

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In the subvolcanic zone of the East Carpathians, calc-alkaline intrusive magmatism took place during Pannonian–Pontian time span. In this area (Rodna and Bărgău Mountains) many shallow intrusions penetrated either a Precambrian metamorphic basement or a Paleogene sedimentary one. Garnet phenocrysts occur in quartz andesites with hornblende and biotite, always containing normative corundum.

Garnets form subhedral to anhedral inclusion-free phenocrysts (0.5 to 2 mm in size). No significant compositional differences occur between various phenocrysts or between core and rim within the same phenocryst. They have an almandine content slightly above 50% (mole percent), pyrope more than 20%, grossular up to 14% and 7–8% spessartine. The physical parameters (i.e. the refraction index of 1.794 and cell edge of 11.552 + 0.007 Å) is consistent with the almandine rich composition. Garnet crystals are almost always enclosed in plagioclase phenocrysts.

The garnet bearing plagioclase crystals (3–4 mm in size) are identical in form and composition (An = 42–52%) with the garnet-free plagioclase. The chemical composition, the occurrence of the garnets only in a few quartz andesite and dacite bodies and their constant association with the plagioclase, indicate a genetic relationship between garnets and their host rocks. The garnets crystallized from intermediate calc-alkaline magmas in an early stage of their evolution. Garnet coexisted with the plagioclase but was resorbed during hornblende crystallization. The magmas were stored in intermediary crustal magmatic chambers, at depths of about 15–20 km (6.43–6.83 kbar), as indicated by AI in hornblende geobarometry.

## COMPOSITIONAL VARIATION IN TOURMALINE FROM ORBICULAR AGGREGATES IN LEUCOGRANITES, MOLDANUBIAN ZONE, CZECH REPUBLIC

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Felsic peraluminous leucogranites with accessory tourmaline are widespread in orogenic belts, e.g. the Hercynian belt in Europe (northwest Spain, Massif Central and Brittany in France). Tourmaline is randomly disseminated in rock but it also may form orbicular aggregates consisting of tourmaline + quartz  $\pm$  feldspar intergrowths.

Tourmaline bearing granites, both disseminated and orbicular types, are quite widespread in the Moldanubian Zone, Czech Republic. Orbicular granites, fine to medium grained rocks without apparent preferential orientation, occur in dikes and small intrusive bodies, up to several hundred m thick. Tourmaline poor matrix consists of quartz, K-feldspar, albite–oligoclase, minor muscovite, very rarely biotite and tourmaline. Typical accessory minerals include apatite, zircon, ilmenite and andalusite. Quartz-tourmaline orbicules, up to 10 cm in diameter, commonly with a narrow, leucocratic, biotite free halo are distributed randomly in granite or concentrated to linear zones, up to 10 m thick, with abundant orbicules. They also occur in border units of some granitic pegmatites.

Chemical composition of tournaline from orbicules, Al rich schorl to schorl-dravite, is similar to that of the tournalines from granites and Li poor granitic pegmatites and slightly overlaps the metapelite and metapsammite field (HENRY & GUIDOTTI, 1985). The Z site is fully occupied by Al; the Y site shows <sup>Y</sup>Al 0.96–0.24, Fe 1.89–1.18, Mg 1.10–0.36; low concentrations of Mn, Zn and Ti are typical. The X site exhibits Na 0.70–0.54, Ca 0.13–0.03 and <sup>X</sup> $\square$  0.44–0.16; F contents vary from 0.39–0.05 (all given values in *apfu*). Tournaline is slightly heterogeneous in the X site, but highly variable in the Y site, Fe/(Fe+Mg) = 0.84–0.52. Tournaline from single localities exhibit low to high variation in Fe/Fe+Mg.

The tourmaline-quartz orbicules seem to be a product of crystallization of evolved, B rich medium (melt and/or fluid) during late solidus to early subsolidus stage of the granite formation. The high Mg/Fe ratios at some localities examined suggest that the parent leucocratic and B rich melts exhibit rather low degree of geochemical fractionation. Consequently, the formation of granites with tourmaline + quartz orbicules is not limited only to highly fractionated melts with low Mg/Fe ratio (see SINCLAIR & RICHARDSON, 1992, NOVAK *et al.*, 1997).

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#### MINERALS AS MATRIX FOR IMMOBILIZATION OF TRITIUM

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Tritium is one of the most hazardous  $\beta$  emitters. Its large amounts are contained both in the cooling water of nuclear reactors and settling basins, and it can escape into the environment in case of leakages. The same can occur in subsurface radioactive waste repositories, which thus can become the sources of underground water contamination. In the sorption process, materials such as vermiculite, clay or diatomaceous earth can be used to adsorb measured quantities of tritiated liquid. Tritium absorption effect had been marked in palygorskite-alkaline type interaction. Ion exchange and molecular sorption effects prevail at tritium isotope absorption processes. Even though these materials are being used, some disposal sites no longer accept absorbent materials and require a free standing solid for disposal. Additional problems may result from breaching of the waste container and subsequent release of the absorbent material into the surrounding medium.

Solidification of tritiated water with cement or other materials that form a monolith provides a waste package of high integrity that is more acceptable for disposal. They provide no better retention of the tritium. It should be noted that, regardless of the treatment provided prior to packaging, tritium is capable of migrating out of the waste package and into the surrounding medium to some degree. Barriers can significantly reduce this migration and will be the subject for the development of a forming technique for blocks made of the matrix minerals with the entrapped tritium and the elaboration of protective self-packing layers (barriers) for these blocks and other purposes, which will self-pack in case of water leakages using hydration reactions for the conversion of relatively weakly fixed adsorbed T<sub>2</sub>O into the chemically bound one in mineral crystal matrix. Tritium quantities that exceed 1 TBq per package may require additional barriers, such as high density rigid polyethylene liners, asphalt barriers and multiple packagings. We examine the current knowledge of the phase equilibria, crystallography, thermochemistry and kinetics of reaction for calcium sulphate; the sorptive capacity of anhydrite for radionuclides; and effects of radiation on anhydrite and related phases; development of a method for tritium water adsorption by clay minerals, zeolites and other natural adsorbents and the following chemical binding of the adsorbed  $T_2O$  in the crystal structure matrices of minerals resulted from hydration of additional compounds (CaSO<sub>4</sub>. 0.5 H<sub>2</sub>O, CaO, etc.) mixed with the adsorbents; development of a forming technique for blocks made of the matrix materials with the entrapped tritium and elaboration of protective self-packing layers (barriers) for these blocks and other purposes, which will self-pack in case of water leakages using hydration reactions for the conversion of relatively weakly fixed adsorbed T<sub>2</sub>O into the chemically bound one in mineral crystal matrix. As a result, tritium water will be bound much more rigidly than the merely adsorbed one. Consequently, mineralogical and geochemical barriers containing clay minerals and adding sulphate or heat treatment should be more effective than ones using only clay minerals.

# SIDERITE MINERALIZATION IN THE NÍZKE TATRY MTS., WESTERN CARPATHIANS, SLOVAKIA

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Siderite deposits are the most abundant type of mineralization in the Western Carpathians. The Nízke Tatry Mts. is located in two basic geological units: the Tatric unit (Ďumbier part) and the Veporic unit (Kráľova hoľa part). These basic tectonic units are divided by the Čertovica line. The most frequent occurrence of siderite mineralization lies around this line. Hydrothermal carbonate-quartz-sulphide veins have small length, up to 3 km. Veins are hosted by the Mylonitic zone in gneisses and amphibolites of the Tatric unit, by phyllites of the Veporic unit and rarely by Lower Triassic quartzite. Prevalent direction of veins is ENE–WSW. Veins have an inclination to the south. Maximum thickness is around 4 m. Hydrothermal alteration, such as silicification and less prominently sericitization, are very typical around the veins. The thickness of the alteration zone is max. 25 cm.

Carbonate-quartz-(barite-)sulphide veins are formed in several stages. The alternation of carbonate and quartz-sulphide±barite phases is typical. Carbonate and quartz-sulphide stages precipitated as the main phases of the mineralization. Sometimes a barite-sulphide phase is also present. Ni-Co mineralization is also part of the siderite-quartz-sulphide mineralization. A hematite stage terminated the hydrothermal process in the siderite veins. Primary minerals identified in the siderite veins are ankerite, dolomite, calcite, kutnohorite(?), siderite, albite, apatite, barite, hematite, clinochlore, muscovite, schorl, aikinite, arsenopyrite, benjaminite, bismuth, bismuthinite, carrollite, cosalite, friedrichite, galena, gersdorffite, gustavite(?), hammarite, chalcopyrite, cobaltite, quartz, krupkaite, krutovite(?), cubanite(?), lindströmite, magnetite, marcasite, pekoite, pyrite, schirmerite(?), sphalerite, tennantite and tetrahedrite. Secondary minerals identified here are aragonite, azurite, cerussite, chalcocite, covelline, pharmacosiderite, ferrisymplesite, goethite, hematite, malachite and pyromorphite.

Occurrence of sulphosalts of the bismuthinite-aikinite series is a typical sign of siderite mineralization in the Nízke Tatry Mts. Brecciated textures dominate at the majority of localities in the Nízke Tatry Mts. Combed textures are also very abundant. Sulphides and sulphosalts occur disseminated. Massive, drusy and banded textures are also present at the several localities.

Fluid inclusions are also studied in these localities. Two-phase inclusions were observed in ankerite from the Jánov grúň locality. They consist of vapour and aqueous solution of NaCl. The size of inclusions is less than 7  $\mu$ m. Homogenization temperature (Th) ranges from 173 to 246 °C. Salinity of solution was calculated from melting temperature of ice, it ranges from 16.9 to 26.5 wt% NaCl equiv. The same two-phase inclusions were observed in quartz from the Sokolova dolina and Jánov grúň localities. Their size is from 4 to 12  $\mu$ m. Th ranged from 99 to 200 °C (Jánov grúň) and 138 to 200 °C (Sokolova dolina). Salinity ranges from 8 to 28 wt% (Jánov grúň) and 11 to 17 wt% NaCl equiv. (Sokolova dolina).

## PETROGENESIS OF THE TARNICA COMPLEX OF THE DITRĂU (DITRÓ) SYENITE MASSIF, TRANSYLVANIA, ROMANIA

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On the basis of field work and macroscopic, microscopic, mineral geochemical, thermobarometrical, petrogenetic studies as well as major and trace element analyses, I stated that rocks (hornblendites, diorites) of the Tarnica Complex (PÁL MOLNÁR, 1998) are characteristic products of the mixing boundary zone occurring between the solid ultrabasic body of mantle origin and the crustal syenites.

The petrogenetic model can be summarised as it follows:

1. Formation of the Tarnica Complex can be connected with tectonomagmatism of the activated platform (continental) areas (continental autonomous magmatic activation).

2. In the dissected continental platform areas, which were adjacent to aulacogens (tectonic depressions), the magmatic processes started from a slightly undersaturated to slightly oversaturated ultrabasic parental magma, the composition of which was a primitive melt of the upper mantle, and similar to the olivine-pyroxene hornblendites.

3. Hornblendites, nepheline syenites and granites are co-genetic and co-magmatic rocks. Developments of the ultrabasic magma is ended by an increase of SiO<sub>2</sub> and alkalis in the granite-nepheline syenite final system. The hornblendite  $\rightarrow$  nepheline syenite and the hornblendite  $\rightarrow$  granite developments are fractionated and AFC (fractionation + assimilation) magma developments, respectively. According to K/Ar data, this process happened in the Middle Triassic-Lower Jurassic period.

4. On the basis of K/Ar data, syenites are younger than hornblendites, nepheline syenites and granites. Syenites were formed under similar conditions to those of hornblendites, nepheline syenites and granites, however, it is possible that they come from a different magma source.

5. Mineral composition, textural and structural pattern, and K/Ar data of meladiorites and diorites indicate mixed rocks. They are hybridisation products of the hornblendites coming from the mantle and the syenites coming from the crust. The hybridisation process is synchronous with the syenite intrusion.

6. In fact the rock phase of the "host rock-boundary zone-magmatite" system, called hornblendite, is a slightly altered product of the original ultrabasic differentiate ("hornblendites after assimilation").

The alkali feldspar syenites penetrate hornblendites, diorites and even syenites as veins. They represent the latest Lower Cretaceous magmatic phase related to the syenites.

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# UNIVERSITY OF SZEGED, THE "SÁNDOR KOCH MINERAL COLLECTION"

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The "Sándor Koch Mineral Collection", one of the most important and, at the same time, least known mineral collections of Hungary, is located in the long-standing building of the University of Szeged at the Department of Mineralogy, Geochemistry and Petrology.

During its eighty-year-long history, the collection has often been enlarged through donation, purchase from abroad and exchange; nevertheless, the greatest improvement is related to Professor Sándor Koch (Head of Department) whose own collection was received by the department in 1965. At the institution new mineral species were classified and wrote down by him. These are the following: fülöppite, csiklovaite, matraite and "kiscellite".

The collection counts approximately 4000 pieces and bears the name of this outstanding personality of Hungarian mineralogy. The systematic unit is presented in 19 glass fronted cupboards from the point of view of geochemical classification. More than half of the specimens originate from the quarries of Central Europe.

Four large glass cases shelter the irreplaceable Carpathian Basin collection, which forms the essence of the collection. The minerals, in a rather unusual way, are arranged according to the genetics of their quarries, covering the magmatic, sedimentary and metamorphic geophases one by one. The collection is significant because it gives an overall view of the mineral world of the already classic quarries of the Carpathian Basin, located in present Hungary, Slovakia and Transylvania (Romania). Most of these quarries have been closed down or worked out, and the minerals originating from them are precious members of all collections.

Hereby, we would like to present the treasures of the collection with special regards to the tellurides (hessite, nagyagite, krennerite, sylvanite) of the Apuseni Mountains, the contact metamorphic minerals (garnet series, wollastonite, hematite, sylvanite) of Bánát area, the varied mineral world of the Szatmárian mining district (sulphides, sulphosalts, barite series) and the minerals of the oxidation-cementation zone of Rudabánya. The collection also contains fascinating minerals of several quarries exposed during the baleful era of World War II.

We have already re-examined several specimens of the collection, while other problematic ones are under continuous revision.

# EARLY REPORTS ON METEORITE FALLS IN THE CARPATHIAN BASIN

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Notes from 16–17<sup>th</sup> century chronicles and manuscripts on meteorite falls observed in the Carpathian Basin are discussed briefly. Original texts will be published elsewhere.

Keresztes-mező, S of Torda, Transylvania (= Turda, Romania), July 26, 1558. According to a short manuscript note of Forgáts (publ. 1903) three stones fell, measuring 26, 28 and 30 pounds. A similar note was taken by Sepsi Laczkó (see Mikó, 1858).

Miskolcz (= Miskolc), Hungary, May 10, 1560?

Istvánffy (1622) reports the fall of five stones accompanied by a strong detonation in clear sky, and suddenly rising then ceasing wind. One of the stones had been kept in Diósgyőr, the others had been sent to Vienna, but neither of them was traced by Chladni (1819). He and an 18<sup>th</sup> century manuscript (Pekár, 1904) date the event to 1559 (cf. Hey, 1966). Istvánffy, however, writes 1560, and Szent-Iványi (1699) reports the fall of five stones on May 10, 1560 at Mosócz, which is obviously an error for Miskolcz.

?Odranec, Moravia, Czech Republic (outside of the Carpathian Basin), June 11, 1619 Çelebi (in Karátson, 1916) describes the fall of black balls accompanied by loud noise, fire and smoke in the sky in North Hungary "in the Morava [= March] region" in mid-Sha'ban, 1028 (= mid-July, 1619). Hey misdates this fall to August, 1618, and lists it as "Steiermark", since Chladni claimed after Hammer (1816) that the stones had fallen "in the Mur district". The event may correspond to the Odranec fall (q.v. Burkart, 1953).

Between Gran (= Esztergom) and Ofen (= Buda), Hungary, December 11?, 1642 Stories on the appearance of five fiery balls in the sky accompanied by heavy detonations leading into a celestial battle of three hours with a subsequent shower of lead and tin may have been inspired by a meteorite fall. This event is dated by Chladni to November 30 or December 12 referring to unspecified sources (Hey gives December 2), but a copy of a contemporary manuscript (Anonymous, 1642) states December 11.

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# ARSENIC CONTAINING MINERALS IN THE HANKÓ VALLEY (COVASNA, ROMANIA). HISTORICAL BACKGROUND. DAWSONITE: A NEW MINERAL FOR ROMANIA

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The presentation consists of three parts: the first part concerns the history of the research of the mineralization, the presence of As in the mineral waters from Covasna. The second part presents the geological setting, the minerals in the assemblage as well as some genetic features, while the third part emphasizes the possibility of identification of such mineralization elsewhere.

The first mention of the mineralization in the Hankó Valley belongs to HAUER (1860). Only a few works have been done previously, and in various stages (BÁNYAI, 1932; LÁSZLÓ *et al.*, 1996). The presence of As in mineral water was identified long after the description of the As rich mineralization, in spite of the great number of water analyses carried by different researchers (FOLBERTH, 1860; PITULESCU *et al.*, 1953).

A brecciated carbonatic sandstone hosts the mineralization. Besides pyrite, marcasite and siderite, other minerals were deposited from the mineral waters: aragonite, sulphur, orpiment, realgar, dawsonite (first mention in Romania) and, according to Bányai (SZABÓ *et al.*, 1941), dimorphite. Recent studies prove that As is connected to the sandstone, from which it was dissolved by the mineral waters (LÁSZLÓ *et al.*, 1996).

The presence of As rich waters in several other places (Băile Malnaş, Turia etc.) in similar geological settings (SOÓS *et al.*, 1959; SZABÓ *et al.*, 1941), leads to the premise that the occurrence in Hankó Valley is not singular. Another proof is a borehole sample in the collection of the National Székely Museum in Sf. Gheorghe, consisting of a sandstone with calcite veins and orpiment from Bodoc (sample M.9.).

The identification of dawsonite and the premises of finding similar assemblages in other places are at least two reasons for continuing and deepening of this research.

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#### K/Ar DATING OF TERTIARY MAGMATISM IN HUNGARY

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Much geochronological data has accumulated during the last decades enabling us to draw a reliable picture of the distribution of Tertiary volcanism in Hungary in space and time.

Tertiary magmatism can be broadly classified into two types:

1. an earlier phase of volcanism of calc-alkaline affinity;

2. a generally later (though partly overlapping) phase of alkaline volcanism.

Within the calc-alkaline volcanism, two age groups can be distinguished: an older group, Eocene–Oligocene in age (42–25 Ma), and a younger one, Neogene in age (20–9.5 Ma).

Products of Eocene-Oligocene magmatism are located along and in the vicinity of the Balaton Line, from north Hungary (Bükkszék) to the Zala basin at the SW border of the country.

Miocene volcanic activity started with high volume siliceous calc-alkaline explosive eruptions about 20 Ma ago, and ceased around the Sarmatian/Pannonian boundary (11 Ma). The most intense phase of acidic volcanic activity took place in the Badenian (16.– 13.5 Ma). Ignimbrites, reworked tuffs and rare dome-flow complexes are widespread, extending over most of the Tertiary volcanic fields of Hungary. Their source areas are mostly yet unknown.

Acidic and intermediate calc-alkaline volcanic activity frequently occurred simultaneously, they can be alternating, however, andesitic volcanism generally postdates the acidic one. The oldest andesites (19 Ma) crop out in the Mecsek Mts. but are buried in SW Hungary, while the youngest eruptions (9.5 Ma) are confined to NE Hungary.

K/Ar data proved that the oldest extension related alkaline magmas are about 10 Ma old and erupted just as the calc-alkaline magmatism was waning.

Alkaline volcanism in Hungary is dominated by alkali basalts. K-trachytic (Danube basin, 12.0–10.5 Ma, and Balatonmária, 14.3 Ma) and ultrapotassic rocks (Bár, 2.17 Ma) are represented only by a few occurrences.

Alkaline basalts form significant volcanic fields in the SW part of the Transdanubian Central Range (Balaton Highlands and Bakony Mts., 8.0–2.3 Ma), in the Danube basin (5.5–3.0 Ma), in the Nógrád basin (5.4–2.0 Ma) and in the Danube-Tisza Interfluve region (Kecel–Kiskunhalas area, 10.4–8.1 Ma). The youngest alkali basaltic volcanism took place about 2 Ma ago, in the Nógrád basin.

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## THE PRESENCE OF MINOR ELEMENTS INTO THE MAIN SULFIDES FROM THE BAIA MARE METALLOGENIC DISTRICT, ROMANIA

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The sulfides represent a mineral class characterized by high retention capacity as "minor element" of great number of elements at very large variety of content value.

It is interesting to study the behavior of minor elements for the main sulfides – pyrite, chalcopyrite, sphalerite and galena. These minerals participate in a large rate at the internalization content of the main ore deposits of the Baia-Mare Metallogenetic District (Ilba, Nistru, Baia Sprie, Herja, Cavnic, Baiut, Cizma, Coasta Ursului).

Many minor elements are typical for Alpine metallogenesis. For the most of them, there were determined the highest contents of sulfide in Romania. More ores within the Alpine internalization, those of Neogene age are the richest in minor elements of the mentioned sulfides. The values are near richest but with some variation from a zone to another. Within mineralized sulfides from Baia-Mare, the richest contents of As, Se, Mn, Ga and others were determined.

So, the pyrite from Baia Sprie, Chiuzasa and Ilba contain up to 1% Mn, the pyrite and chalcopyrite from Cavnic up to 2% Mn and the sphalerite from Cavnic up to 4% Mn.

The highest contents of As for the pyrite are remarked at Cavnic, up to 3% and Baia Sprie (New vein), up to 4%. It is to be pointed out that at Cavnic ore deposit, the As richest pyrite is reached into the veins where the mispickel (FeAsS) is not reported into the paragenesis.

It is interesting to point out the presence of Se into galena, and the highest contents are remarked for galena in some veins from Speranta (Ilba zone).

Within the framework of analyzed mineralization it is not possible to make any appreciation concerning the behavior of minor elements, with indication of a general tendency of enrichment or impoverishment within the frame of the metallogenetic district, but partial observations are still interesting:

- an enrichment of Cd in sphalerite from W to E. Thus the sphalerite from Herja and Baia Sprie, (the Main Vein, and Diagonal Vein) consist of less than 4,000 ppm in comparison with the other, which contains more than 4,000 ppm or usual content of 1-1,3% at Cavnic, Baia Sprie (New Vein). The weight center of enrichment is Cavnic, toward Baiut content is decreasing but not less than 5,000ppm;

- an impoverishment of Ag in the galena from W to E, the richest content being up to 40,000 ppm into the galena from Fata Mare (Ilba) internalization. The lowest content was at Herja - 3,150 ppm, Cavnic - less than 4,000 ppm, Cisma - less than 2,000 ppm.

Analyzing the minor elements on minerals – pyrite, chalcopyrite, sphalerite and galena, they are common and they have the greatest values from the Romanian ore deposits. They present a series of qualitative and quantitative variations, depending of the metallogenetic district character, which they are belonging to.

### TRACE ELEMENTS OF SULPHIDE ORE HOSTED IN THE EAST CARPATHIAN (ROMANIA) EPIMETAMORPHIC ROCKS

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The subject of this study is the distribution of the trace elements from ores hosted by epimetamorphic rocks belonging to the Tulgheş series (East Carpathians). The ores are located in Burloaia, Bălan, Fundul Moldovei and Leşu Ursului. We analyzed the common sulphides: pyrite, chalcopyrite, sphalerite and galena, which are present in great amounts. The trace elements permanently present in the analysed sulphides are the following: As, Co, Ni, Mn, Ti in pyrite; Co, Ni, Mn, In, Bi, Sn in chalcopyrite; Cd, Mn, Ga, Ge, Sn, In in sphalerite; Ag, Bi, Sb in galena.

From the trace element data the following observations have been made. The sulphide ores associated with epimetamorphic rocks of the Tulghes series contain a large number of trace elements in high concentration: Co in pyrite, chalcopyrite and sphalerite, Ni in pyrite and chalcopyrite, In in sphalerite, As in pyrite.

Tin has been recorded as a permanent element in chalcopyrite and sphalerite. In  $CuFeS_2$  it is present in concentrations up to 4000 ppm; in ZnS the maximum value is 450 ppm. The appearance of cassiterite and some Sn bearing sulphosalts prove a strong staniferrous character of fluid solutions that generated the analyzed ores.

The concentration of different trace elements varies from one location to another. In the same deposit there is variation both on the surface as well as in depth. This is the case of the Bălan ore body, where a heterogeneous repartition of different trace elements with depth was found. Thus, on the level + 50 a clear depletion in In, Ag, Ni, Mn content can be observed and a strong enrichment of Sn; In reaches the highest contents on the - 85 and Wetter levels. The analyses of trace element variations lead to an interesting observation concerning their repartition depending on ore type: massive ore and disseminated ore. This statement could be supported by the data from the Leşu Ursului mineralization. Thus, Mn in massive ore pyrite can reach values as high as 5000 ppm while the highest Mn values in pyrite from disseminated ores are only 500 ppm. The amount of Sn in massive ore is in between 10 and 50 ppm while in the disseminated ore the values are between 50 and 5000 ppm. In 70 % of the samples from massive ore, Sb content varies from 100 to 5000 ppm while in the disseminated ore only 30 % of samples reach values between 100 and 500 ppm. Co and Ni were found only in pyrite from massive ore and they are absent from the disseminated ore. The same observation is valid also for the Fundu Moldovei mineralization.

It is interesting to point out the behaviour of Mn from the Crucea–V. Bistriței– P. Sarpelui sulphide mineralization, hosted also in the Tulgheş series. The content of Mn in pyrite, chalcopyrite and sphalerite clearly increases with depth as follows: level 790 – py 0.7 %, cpy 0.03 %, sph 0.2%; level 690 – py 2 %, cpy 1.5 %, sph 3.5 %.

The sulphides hosted in epimetamorphic rocks of the Tulgheş series contain the typical trace elements for this mineral category. The correlation between trace element contents and the concentration of the major elements such as Cu, Pb or Zn do not substantially increase the economic value of the mineralization.

# HYDROGEN ISOTOPE SORPTION CAPACITY OF CLAY MINERALS

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The accumulation of hydrogen isotopes in different structural types of clay minerals is the subject of this work. The dependence of accumulation parameters from the ratio of heavy isotope concentration in the "water-mineral" system and from the time of watermineral interaction was investigated. IR spectroscopy,  $\beta$  spectroscopy and DTA were used for the determination of the quantitative characteristics of the exchange in perfect and imperfect kaolinite, palygorskite, and montmorillonite.

It was established that the concentration of heavy H isotopes in all structural positions of clay minerals increased with the increase of their concentration in the aqueous medium. The accumulation of H isotopes also depends on the structural type of clay minerals, e.g. greatest absorption ability in all items is characteristic for palygorskite. Three types of hydrogen isotope accumulation capacity within the clay minerals have been discovered: as superficially absorbed water ( $C_{sur}$ ), as interlayer water ( $C_{int}$ ) and as structural OH groups ( $C_{str}$ ). Absorption capacity is:  $C_{common} = C_{sur} + C_{int} + C_{str}$ , where  $C_{common}$  is the full capacity.  $C_{sur} = f(N_{ch} \ properties); C_{int} = f(cations, \ properties); C_{str} = f$ (properties);  $N_d$  is the number of active centres on the surface of the clay mineral.

Structural peculiarities of clay minerals determine their *properties*. Comparative quantity of the OH groups in clay minerals with 1:1 structure (e.g. kaolinite) is more than with 2:1 structure (montmorillonite). Therefore there are more H bonding positions that can be exchanged to the heavy isotopes in the first structure than in the second. *Cations* denotes the type of exchangeable cations. In some case this item can be zero. There are no exchangeable cations in the structure of kaolinite.

The basic attention in the estimation of absorption capacity of clays has been given to the study of the accumulation of isotopes in structural hydroxyl groups. For the estimation of the quantitative absorption capacity of clay minerals the fractionation factor of hydrogen isotopes  $\underline{\alpha}$  was used, which is calculated according to the formula  $\underline{\alpha} = (H^*/H)_m/(H^*/H)_w$ , where  $H^*$  is heavy hydrogen isotope (deuterium, tritium), H is hydrogen,  $(H^*/H)_m$  in the numerator is the ratio of heavy isotope to hydrogen in mineral,  $(H^*/H)_w$  in the denominator is the same ratio in water. Limiting theoretical significance  $\underline{\alpha}$ for montmorillonite is 0.94, and 0.97 for kaolinite. After the accumulation of tritium in the structure of montmorillonite the value of the coefficient  $\underline{\alpha}$  reached 0.6 (initial  $\underline{\alpha}$  was 0.002). Therefore the change of  $\underline{\alpha}$  expresses the levelling of heavy isotope concentration in the "clay mineral–heavy water" system which occurs during the short period time (to 180 days). In the case of kaolinite placed in heavy water  $\underline{\alpha}$  increased from  $1.5 \times 10^{-6}$  to  $4 \times 10^{-2}$  in 40 days.

# MINERALS OF SULPHUROUS SPRING SEDIMENTS FROM THE CARPATHIANS AND THE CARPATHIAN FOREDEEP

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In the Polish part of the Carpathians, 125 springs of sulphurous waters have been recorded (RAJCHEL, 2000), i.e. springs whose 1 dm<sup>3</sup> of water contains more than 1 mg of iodometrically determined sulphur. On the bottoms of those springs and of their outflows characteristic deposits of sulphur bacteria occur (mainly *Chromatium*, *Thiothrix* and *Beggiatoa*), as well as mineral products of bacterial metabolism. The deposits develop as white, creamy, pink, purple and violet festoons, coatings and webs, underlain by a black sediment (STRZESZEWSKI, 1913; RAJCHEL, 1996).

The deposits studied were collected from springs of the Carpathians (Magura and Silesian Unit) and the Carpathian Foredeep. Based on X-ray analyses and observations in optical and scanning electron microscopes, it has been found that the mineral components of the white deposits include colloidal sulphur with grain sizes of some  $\mu$ m, sporadically occurring as larger accumulations of flakes, and gypsum in the form of euhedral crystals some hundred  $\mu$ m in size.

The purple and pink deposits represent colonies of photoautotrophic bacteria of the *Chromatium* sp. (JAROCKA & KŁOSOWSKA, 1966) coloured by bacteriopurpurine. They contain sulphur developed in the same manner as in the white deposits, as well as gypsum in the form of subhedral crystals some tens of  $\mu$ m in size, often in rosette like intergrowths. The black sediment is composed of dead organic matter with a small admixture of bacterial pyrite in accumulations up to 15  $\mu$ m; sulphur and gypsum are also present but in amounts lower than in the deposits described above. Sulphur most often forms single grains with sizes of some  $\mu$ m; gypsum occurs as euhedral, anhedral as well as subhedral grains.

The white and white-creamy deposits called "*sulphur flowers*" represented the source of sulphur from ancient times and were also used for medicinal purposes (PAZDUR, 1960-61).

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91

## SEASONAL PECULIARITIES FORMATION OF SLOPE STRUCTURE OF SALT WASTE PILES

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At potassium mines of the Verkhnekamsky deposit (North Ural, Russia), waste of production is heaped on an earth surface as flat-topped salt waste piles. Matter going into waste piles is colourless or grey with a pink or yellowish shade natural grains and crystals of halite. Granulometric composition of salt waste is rather uniform and is determined by the technological parameters of cycles. High solubility of salt waste resulted in that the prevailing geomechanical process on the waste piles is dissolution.

There is a strong redistribution of substance. The initially homogeneous matter is divided, ready-soluble compounds are transported to deeper regions of waste piles and to their bounds, insoluble and fixed compounds are collected on the surface. The brines in waste piles go downwards, therefore on the surface mainly vertical structures of destruction are formed. The slopes of waste piles are covered with plenty of such structures, which we "name cavities of dissolution". The depths of these cavities reach more than 18-20 m, diameter 1-1.2 m.

Seasonal climatic changes of the region cause that on the surface there is a nonuniform distribution of cavities. The active formation goes on only in the summer, when plenty of water falls as rain and air temperatures are positive. Dissolved halite partially crystallizes and cements the un-altered grains of halite. Thus a strong skeleton fixing the initially highly porous rock is quickly formed. The free infiltration of moisture through its pores and the development of cavities goes with high speed.

In the winter, when free moisture is absent and negative temperatures are prevailing, the halite grains are cemented by hydrohalite. If the temperature is higher +0.15 °C (and even at negative temperatures) hydrohalite is destroyed with the formation of microcrystalline halite. This matter partially fills pores, initial porosity of rocks is reduced, and before the start of the period of active geomechanical processes the rock has time to be condensed. The development of cavities on such sites is difficult, the formation of a cavernous-cellular structure does not occur or this process happens on a rather insignificant scale.

Thus, on slopes of salt waste piles areas with a various degree of development of cavities are formed. The intensity of dissolution and evacuation of salts for the bounds of waste piles is maximal on sites leached out in the summer.

Such phenomena are characteristic for other regions where KCl salts are mined:

### GEOCHEMICAL STUDY ON MAREKANITIC PERLITE OF TOKAJ-LEBUJ – A HISTORICAL APPROACH

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The marekanitic perlite outcrop of Tokaj-Lebuj is well-known as a stop of geological field trips. Besides its petrographical value, it is important from a science historical point of view, because its perlite and rhyolite varieties were described by the pioneers of the geological knowledge of the mountains. Johann Ehrenreich von Fichtel (1732–1795) was the first who reported this perlite containing obsidian nuclei, which he called (together with other perlites, rhyolites and rhyolite tuffs of the Tokaj Mountains) as volcanic zeolite. A few years later, in 1793, Robert Townson (1762–1827) collected several samples here, made fire and acid tests, and revised Fichtel's description. He asked Martin Heinrich Klaproth, the famous German chemist, to analyse the "pearly matrix", and published the result. According to our recent knowledge this is the first published chemical analysis of the rock (TOWNSON, 1797). In 1794, the Norwegian Jens Esmark (1763–1839) studied this outcrop. He called this rock as "perlstein" (German version of perlite).

It is well known that József Szabó (1822–1894), the most excellent Hungarian geologist in the 19th century, devised his theory on perlite genesis (i.e. hydratation of obsidian) on the basis of petrographic and chemical analyses of samples from the Tokaj Mountains (SZABÓ, 1866). His samples collected from Tokaj-Lebuj were analysed by BERNÁTH (1866). This remarkable formation has been petrographically studied by several researchers since Szabó's work, however, a systematic mineralogical-geochemical study has not been performed. It would be useful to analyse obsidian, perlite and rhyolite samples of this classic outcrop using modern analytical methods in a correlative way. Mineral and glass phases were performed by using scanning electron microscopy; geochemical analyses were performed by using scanning electron microprobe (SEM-EDAX), particle induced gamma-ray emission (PIGE) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Water bound conditions of glass structures were investigated by thermal analysis (DTA, DTG, TG) and infrared spectroscopy (IR).

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## THE MINERALOGICAL, PETROLOGICAL AND GEOCHEMICAL CHARACTERS OF THE BASIC INCLUSIONS IN THE GRANITOID ROCKS OCCURRING IN BOREHOLES NEAR ÜVEGHUTA, MÓRÁGY MTS., HUNGARY

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The Hungarian National Project on the low and intermediate level radioactive waste disposal has been performed in 3 phases since 1993. The site exploration is being carried out by the Geological Institute of Hungary with dozens of partners. Seven deep and a lot of shallow boreholes were drilled near Üveghuta, in the Mórágy Mts. (BALLA *et al.*, 1998, 1999).

The main rock types in the boreholes are (BUDA, 1998, 1999):

1. white or pinkish microcline bearing granitoid with microcline megacrysts (monzogranite);

2. basic inclusions;

3. microgranite and pegmatite.

The aim of the current study is to find out the origin of the basic inclusions and to determine the composition of the primary melt. The inclusions are syenite, monzonite and quartz monzonite according to the modal and normative compositions.

I have distinguished four groups of inclusions that contain biotite and hornblende:

1. with microcline, without quartz;

2. with quartz, without microcline;

3. with microcline and quartz;

4. without microcline and quartz.

The total REE, Ba and Th content is high because there are a lot of accessory minerals. The quantity of REE elements in the microcline bearing granitoid is high, too. The inclusions are strongly differentiated, similar to the granitoid. So it means that there was an equilibrium in REE content among the two melts (acidic and basic) during the generation, and these melts crystallized at about the same time.

According to the major elements analysis the character of the basic inclusions is metaluminous (A/CNK=1), meaning that its origin is mixed crust and mantle. The basic inclusions probably originated from a volcanic arc and mixed with the partially melted continental crust during the post-collision uplift.

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#### POLYMORPHISM IN MINERALOGY

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Pyrite, gypsum, barite, celestine, calcite and other mineral types are very impressive in their multiformity. Obviously, the mineral morphology depends on the growing media, but the details of the growing processes are still unknown. Complex system approach can be used to create the new mineral forming theory. Crystal forming, stats and decay are different processes according this theory and these processes run by their own elements. Therefore, the mineral atomic structure or the mineral dissolving to the ions has no influence at the crystal growth processes. The observations on te minerals in nature show that the crystallization processes run via molecule and supramolecule particles.

The atomic and ionic point of view of crystallization cannot resolve some nonagreements. Salts pretend to be ionic crystals because they dissolve to ion solutions. On the other hand, salt crystallization is impossible in dilute ion solutions. The physical sense of the solution, saturation and supersaturation does not elucidate. Obviously, salt growth in dilute solutions is impossible because salts do not grow by ions. The saturation point marks the beginning of the NaCl molecule appearance in the solution. The supersaturation means the enlargement of particles of growth (clusters). That is why salt growing in the supersaturated solutions yields muddy crystals.

The particles of crystal growth (clusters) can be defined by the system analysis and design procedures on the base of the crystal chemistry and crystal morphology theories. The result of the definition is the table of atomic coordinates in the cluster structure. The clusters of the minerals differ by the forms and sizes, but they have got the same chemical composition. Pyrite clusters have the  $n(FeS_2)$  composition, with n value from 1 to 10 and more. The variety of the mineral morphologies depends on the cluster multiformity.

Clusters of mineral growth are the main objects of the theory. They are the good indicators of the crystal growing media. The pyrite morphologies differ in the various occurrences, but a single morphological type prevails in the specific ore deposit. This effect takes place because of the cluster's exact dependence on the mineral growth condition. The cluster structure, form and size are the strict parameters of the growing media.

Cluster is the starting point for the more detailed investigations. Firstly, the large cluster consists of the smaller particles and the nucleation processes may be studied. The kinetics of the nucleation processes is the field of the geochemistry interest. On the other hand, the crystal surface processes may be defined more exactly on the cluster structure base. According this theory, the mineral surface is not an atomic plane, but the cluster-size relief one. Therefore, the undulating atomic structure of the mineral surface may be determined by this methodology.

Complex system approach leads to the molecular conceptions in mineralogy. These ideas do not depreciate the significance of the atomic structure conception. Each of these theories prevail in the different processes and states, but some of the mineral forming phenomena, and polymorphism phenomenon especially, may not be resolved on the base of the molecular conception.

## A BURIED LATE MIOCENE ALKALINE TRACHYTE VOLCANO AT THE AXIS OF THE LITTLE HUNGARIAN PLAIN, NW HUNGARY

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Alkaline volcanism developed in two main stages in the Little Hungarian Plain Volcanic Field. In the late Miocene, dominantly trachyandesite-trachyte volcanism took place, building up a more than 2000 m thick stratovolcano at the axis of the Little Hungarian Plain, right at the Rába low angle fault. It was followed by an alkaline basaltic volcanism after a few Myr quiescence. The trachytic stratovolcano was penetrated by several boreholes (Pásztori, Tét, Mihályi, Szany, Bősárkány) beneath 2000 m thick Quaternary to Late Miocene sequence. This volcanic activity could be related to the narrow rift stage (TARI & HORVÁTH, 1995) of the LHP.

This volcanic association is particularly important since it is unique in the Pannonian Basin. The volcanic series consists of pyroclastic rocks and lava flows. At the lower parts alkaline trachytic lithology dominates that changes upwards to trachyandesitic composition. The upper levels are penetrated by alkaline basaltic dyke rocks. It is hard to estimate the thickness of different rock types because coring was sparse. The only thing to be said is that alkaline basalt occurs at the top of the series at about 1800–2000 m, trachyandesite is between 2200–2400 m and trachyte occurs deeper than 2400 m.

Petrographically, basalts are the freshest rocks. They have porphyritic intergranular texture, with phenocrysts of slightly iddingsitic olivine, less augite and labradoritic plagioclase. The groundmass contains plagioclase, magnetite and apatite. Trachyandesitic rocks have porphyritic holocrystalline texture with large zoned oligoclase-andesine plagioclase phenocrysts enriched in glass inclusions. Large aegirinaugite, brown amphibole and biotite occur as phenocrysts and apatite, magnetite and ilmenite as accessories in groundmass. Trachyte has porphyritic holocrystalline, fluidal texture with large, rarely antiperthitic sanidine lath. The groundmass consists of sanidine laths, carbonate and quartz, with accessories such as rutile, zircon and apatite. Several rocks also contain aegirine, riebeckite and aenigmatite.

Geochemical composition suggests clear intraplate character. The isotopic composition of the trachytes is consistent with derivation from an asthenosphere derived mafic magma by fractional crystallisation and without assimilation of crustal material (HARANGI *et al.*, 1995).

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## MINERAL ASSOCIATIONS OF THE BURNING DUMPS OF THE RUSSIAN AND EUROPEAN COAL BASINS: SIMILARITIES AND DIFFERENCES

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Mineral associations of the burning dumps of coal mines have been studied in Europe since the twenties of the 19<sup>th</sup> century. Today the total number of mineral species described on such dumps approximates 300. The number of minerals found in each basin is diverse; it is 21 for the L'vov-Volinsky basin, Ukraine (SREBRODOLSKY, 1986), 57 for burning dumps of Hungary (SZAKÁLL & JÁNOSI, 1996), 95 for Bohemia, Czech Republic (ŽÁČEK, 1995; ŽÁČEK & ONDRUŠ, 1997) and more than 200 for the Chelyabinsk coal basin, Russia (CHESNOKOV, 1999; CHESNOKOV & SHCHERBAKOVA, 1991).

The similarities and differences between mineral lists of these areas may easily be discovered. For example, the dominance of sulphates and the presence of ammonium and organic minerals are typical for every of them. What is more, there is a whole series of minerals, such as sulphur, sal ammoniac, mascagnite, tschermigite (or K-alum), gypsum, anhydrite, alunogen, pickeringite, copiapite, epsomite, hematite and one of the mineral forms of silica, more often quartz, which have been described in every coal basin, regardless of the total amount of minerals known there. These phenomena reflect the same genetic essence of mineral forming processes occurring in the burning dumps, that is, the interaction of the volatiles (products of the decomposition of residual dump coal) and their influence to primary dump rock.

On the other hand, appearance of some unique or rare minerals such as compounds of As and Sb in Bohemia or the rarest Fe chlorides in Chelyabinsk are connected, first of all, with the geochemical character of a basin as a whole and regional climatic conditions.

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97

# PYROPHYLLITE MINERALIZATION OF THE URALS AND THE CARPATHIANS

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Deposits and occurrences of pyrophyllite can be divided into five types on the basis of geology and genesis (SINYAKOVSKAYA *et al.*, 1996). The first two are associated with hydrothermally altered rocks in felsic and intermediate volcanogenic suites. They differ by the character of their metasomatites and their subsequent transformations in varying volcanic conditions. The third type includes deposits and occurrences of metamorphic-metasomatic genesis and is caused by greenschist facies transformations of terrigenous-sedimentary interbeds in felsic volcanites. The fourth type is associated with low and mid-temperature stages of hydrothermal vein formation at the limits of volcanogenic and metamorphic strata. Pyrophyllite weathering crusts on metamorphic strata and Carpathians is interesting from an economic (types 2 and 3) and a mineralogic point of view (type 4).

Pyrophyllite mineralization of the Urals is believed to be deposits of metasomatites in ensimatic island arcs and Paleozoic marginal seas. Bodies of pyrophyllite are associated with apical and peripheral parts of extrusive and effusive domes. Initial flows of rhyolitic-dacitic lavas have interlayered volcanogenic sedimentary rocks of the same composition. Syn-ore metasomatism is accompanied by a loss of bases and alkali elements, and the introduction of alumina. Titanium and silica are inert. The host rocks are thus transformed to pyrophyllite containing metasomatites in conditions of aggressive waters (pH 1.2–3.0, temperature 250–290 °C) at the presence of H<sub>2</sub>S, SO<sub>2</sub>, CO<sub>2</sub>, HCl, to the subsequent oxidation of SO<sub>2</sub> up to H<sub>2</sub>SO<sub>4</sub>. (SINYAKOVSKAYA & MASLENNIKOV, 1999).

Mesozoic metamorphosed terrigenous argillaceous strata with pyrophyllite are known in the Carpathians. The Triassic pyrophyllite containing Shela Formation (Carpathians) consists of chlorite, muscovite and coaly slates interstratified with metaconglomerates and psammites. The interlayers contain up to 70 % of pyrophyllite.

Pyrophyllite occurrences in quartz vein hydrothermal systems of the Urals are found in Paleozoic metamorphic rocks. Pyrophyllite was identified as a mineral species by R. Germann in 1829 in the gold-quartz veins at the Berezovsk gold deposit. Pyrophyllite mineralization in Alpine quartz veins of the Carpathians was investigated by G. Popescu and E. Constantinescu. Thermobarometric research indicates a formation temperature of 160–180 °C, at a pressure of no more than 1 kbar.

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## MINERALOGICAL AND PETROLOGICAL STUDIES OF EPITHERMAL ORE INDICATIONS AT MÁTRAKERESZTES, WEST MÁTRA MTS., HUNGARY

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The indications are situated at the western border of the Gyöngyösoroszi-Mátraszentimre low sulfidation ore field, in the Neogene part of the Mátra Mts., representing a characteristic part of the polymetallic-epithermal zone of the Inner Carpathian Volcanic Belt. This mineralization is situated in a caldera structure, which was formed in andesitic type stratovolcanic series. The direct host rocks exhibit slight acidic features (trachytes). According to the K/Ar data, the age of the whole volcanic sequence is about 12–16 Ma.

The host rock shows intensive silicification and K metasomatic alteration. The argillitization (montmorillonite, sericite) and hydrohematitization are of secondary importance. The poor, original sulfide mineralization (marcasite and arsenic pyrite with 2 wt% As) is accompanied by silicification, in form of stockworks and little veins with banded structure. In these objects the hydrothermal K-feldspar ("adularia") is frequent. Later these minerals were transformed into goethite and jarosite during the gossan formation, indicating the high potassium content (max. 13 % K<sub>2</sub>O) of the host rock. In the area there is a high As-Sb(-Hg-Ba) anomaly (8500 ppm As, 1000 ppm Sb) which is due to the Fe bearing secondary minerals.

The low sulfidation type mineralization proceeded at 190–200°C. The total salinity of solutions was low (0.2–5 NaCl equiv. wt%) compared to other deposits of the western Mátra Mts. The composition of the fluids was mainly Ca-Na chloride type (the vein forming stage), but subordinately alcali bicarbonate/sulfate fluids also occur (in open cavities of the host rock, in the so-called "apophysis" stage) with lower salinity. The dilution of solutions was characteristic, since the originally mixed fluids could be diluted-cooled by the direct influence of the meteoric water.

Consequently, the upper region of the vein system of a low sulfidation type mineralization can be identified, which is located in a shallower depth than the vein systems of the Gyöngyösoroszi–Mátraszentimre mineralization. Later these rocks were exposed on the surface, and were transformed under oxidizing conditions.

99

# Sb-Au MINERALIZATION IN NIŽNÁ BOCA (NÍZKE TATRY MTS., SLOVAKIA)

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Sb-Au hydrothermal mineralization is one of the most abundant ones in the Nízke Tatry Mts. (CHOVAN *et al.*, 1996). Occurrences of Sb-Au mineralization in Nižná Boca are located in the Zach mine field, to the south from the village. Veins and veinlets are located in the Ďumbier type Variscan I-type granitoid and rarely in metamorphic rocks, not intersecting Mesozoic autochthonous sedimentary sequences. Veins typically have a N–S strike, dipping 50ş E with a supposed length up to 1 km. Sb-Au ore was exploited till the end of 19<sup>th</sup> century.

Based on a detailed mineralogical-paragenetical research (only from old mine dump material), we can distinguish the following paragenetic associations:

- 1) quartz arsenopyrite, pyrite
- 2) quartz gold (?)
- 3) quartz-dolomite stibnite
- 4) quartz ferroan dolomite pyrite sphalerite galenite, boulangerite, zinckenite, bournonite, berthierite gold
- 5) quartz carbonates tetrahedrite, chalcopyrite

6) barite - carbonates - hematite, pyrite

Sb-Au veins consist predominantly of quartz and carbonates that occur always in position of the younger mineral. Arsenopyrite is the oldest sulphide at the deposit, Au content varies from 0.5 to 1150 ppm. Gold occurs mostly in milky and grey-white quartz, scarcely in carbonates, boulangerite, pyrite and arsenopyrite. It forms irregular grains of typical yellow colour. The biggest gold grain was 2 mm in size, but the majority of grains is less than 0.04 mm in size. Au content varies from 79–90.5 wt%, Ag 9–18 wt%, concentration of other analysed elements (Bi, Cu, Fe, Te, Sb, Hg) do not exceed 0.8 wt. %. Stibnite was found to form veins and veinlets up to 4 cm in quartz and carbonates, needle shaped or acicular crystals are rare. Pb-Sb sulphosalts are abundant, they are represented mainly by zinckenite and boulangerite that form needle shaped and acicular crystals up to 0.5 mm in milky and grey-white quartz and carbonates. Secondary minerals are represented by malachite (?), goethite, jarosite, rozenite, and stibiconite.

Gold was also found in the adjacent Boca Creek (max. 112 grains per panned sample). Its morphological and chemical features were presented by SMIRNOV (1999).

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## CORUNDUM BEARING ROCKS FROM THE NÍZKE TATRY MTS. CRYSTALLINE COMPLEX, WESTERN CARPATHIANS, SLOVAKIA

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Corundum bearing rocks were found in the banded amphibolite rocks at Jasenie, Nízke Tatry Mts. They occur as small irregular lenticular bodies on the contact of ultrabasic rocks with host gneisses. They have an inhomogeneous structure made up of phlogopite matrix containing large corundum grains. Corundum content in the rocks varies, locally it gives up to 40% of the rock volume. There are also other minerals present in accessory aounts there: white mica, two types of amphiboles (tschermakite and magnesiohornblende), plagioclase (An<sub>40</sub>), zircon, apatite, chlorite, allanite and Cr-spinel.

Corundum is not regularly distributed in the rock, its usual size is 8-10 mm (rarely as big as 15 mm). It forms irregular shapes, often cataclased and on the rims altered to a fine schistose aggregate of white micas. Its chemical composition is homogenous with no considerable amounts of admixtures.

Chemical composition of corundum bearing rocks is variable and depends on modal composition. The analysis of a typical rock (phlogopite 60%, corundum 30%, white mica 6%, hornblende 2%, accessory minerals 3%) gives the following (main elements in wt%, trace elements in ppm):  $SiO_2 - 42.75$ ,  $TiO_2 - 0.39$ ,  $Al_{23} - 22.90$ ,  $Fe_2O_3$  total – 5.94, MnO – 0.07, MgO – 14.07, CaO – 3.12, Na<sub>2</sub>O – 1.74, K<sub>2</sub>O – 5.39, LOI – 3.45, Ba – 550, Sr – 112, Zr – 690, Cr – 720, Co – 28.8, Ni – 129, Y – 46, V – 26.3, La – 30. The analysis shows that the rock is rich in  $Al_2O_3$ , MgO, K<sub>2</sub>O, Ni, Cr, Zr, La and Y, and/or poor in  $SiO_2$  and CaO. High content of MgO, Cr and Ni document a close geochemical affinity to ultrabasic rocks, high  $Al_2O_3$  and K<sub>2</sub>O contents reflect the specific mineral composition (corundum, phlogopite and white mica) and high contents of Zr, La and Y show high zircon and allanite quantities. Corundum bearing rocks are very rare and generally they may have originated in two possible ways:

- they represent metamorphosed rocks with equivalent specific composition (Al rich sediments, laterites and o., cf. BOL et al., 1989);
- corundum bearing rocks represent metasomatites with specific composition having originated as a result of the reaction of ultrabasic rocks with host rocks.

With the corundum bearing rocks of Jasenie the second possibility seems probable. It is suggested by: 1 - inhomogenous mineral composition, 2 - occurrence of these rock only close to ultrabasic rocks, 3 chemical composition of the rocks (high contents of elements typical of ultrabasic rocks - Cr, Ni), 4 - presence of Cr-spinel (aluminum-chromite according to STEVENS, 1944); spinel is a typical mineral of Al rich rocks and frequently associated with corundum, however, it is always Al-spinel, not Cr-spinel.

#### PIEMONTITE AND SPESSARTINE IN LOWER PALEOZOIC METASEDIMENTS OF THE INNER WESTERN CARPATHIANS

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In the Lower Palaeozoic of the Inner Western Carpathians (Rakovec group, Gemericum) a 22 m thick layer of manganese enriched metasediments has been encountered by borehole RHV-1 south of Rudňany. During epigenetic processes the increased Mn content in the original lithofacies gave rise to manganese nodules (concretions). In the subsequent greenschists facies regional metamorphic recrystallization process, the Mn nodules were altered into an anchimonomineralic aggregate of garnet of spessartine composition. Simultaneously, they were partly disintegrated and folded jointly with the country rocks, i.e. the chlorite-sericite-quartz schists.

Garnet is the basic mineral of nodules (isometric grains – approx. 0.2 mm in size). The spessartine nodules are encompassed by a 1–20 mm broad rim, intensely coloured in red to violet-red, formed dominantly of piemontite and Fe oxides, which passes gradually into the adjacent rocks. The schists also contain sporadic garnets of microscopic size (0.02 mm) and epidote.

The analyses of garnets from different parts of nodules have shown that they have practically identical composition and azonal structure. They contain 80–87 % spessartine, 0.2–0.4 % pyrope, 3–8 % almandine, 7–11 % grossular components. The piemontites form short prismatic crystals (below 0.03 mm) and/or irregularly shaped pink coloured grains with strong pleochroism. Piemontites are zonal and contain 6–16 % piemontite component ( $Mn^{3+}$ ) (selected analysis: SiO<sub>2</sub> – 36.70, TiO<sub>2</sub> – 0.12, Al<sub>2</sub>O<sub>3</sub> – 22.86, Fe<sub>2</sub>O<sub>3</sub> total – 7.94, Mn<sub>2</sub>O<sub>3</sub> + 8.00, MnO<sup>\*</sup> – 2.52, MgO – 0.04, CaO – 20.52, Na<sub>2</sub>O – 0.00, K<sub>2</sub>O – 0.03, \* – recalculated). Piemontites occur only in rocks with a high oxidation ratio and rather high MnO content (chlorite-sericite-quartz schist with piemontite and spessartine: SiO<sub>2</sub> – 55.58, TiO<sub>2</sub> – 0.72, Al<sub>2</sub>O<sub>3</sub> – 16.74, Fe<sub>2</sub>O<sub>3</sub> – 7.87, FeO – 0.53, MnO – 1.48, MgO – 2.07, CaO – 1.81, Na<sub>2</sub>O – 2.75, K<sub>2</sub>O – 4.41, LOI – 2.69, oxidation ratio – 94).

The rocks studied presumably represent pelagic sediments enriched in manganese. The increased Mn content in primary sediments was due to the presence of the products of basic volcanism, possibly also to the exhalation and hydrothermal activity associated with this volcanism.

## APPEARANCES OF NICKEL MINERALIZATION ON ORE DEPOSITS IN THE MALÉ KARPATY AND NÍZKE TATRY MTS., WESTERN CARPATHIANS, SLOVAKIA

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Until recently, occurrences of Ni mineralization in the Malé Karpaty Mts. were known in the mineral deposit near the village of Častá (CAMBEL & KRIŠTÍN, 1977) and an indication of secondary annabergite in the Pezinok mineral deposit (POLÁK, 1955). Suitable geochemical data about Ni contents in this area were substantially extended by the mineralogical work of ANDRÁŠ *et al.* (1998). According to this, Ni mineralization in the Malé Karpaty Mts. is much wider than was assumed.

Beside locality Častá (ANDRÁŠ, 1996), appearances of Ni minerals were verified in the Pezinok and Trojárová ore deposits (ANDRÁŠ & CHOVAN, 1995). There are exsolutions of Ni in pyrite, identification of ullmannite, gersdorffite, korynite and Nitetrahedrite.

Occurrences of Ni mineralization in the Nízke Tatry Mts. are rarer but important to complete the summary of mineralization in this region. They are known in the Jasenie (STANKOVIČ & JANČULA, 1982), Vyšná Boca (OZDÍN & CHOVAN, 1998) and Dúbrava (CHOVAN *et al.*, 1998) ore deposits by appearances of ullmannite, gersdorffite and an unidentified Ni sulphidic phase.

In both presented ore districts Ni mineralization is accompanied most frequently by carbonates, quartz, sulphides and sulphosalts of Cu, Sb, Zn. It is not impossible that detailed research in the future will bring more data about Ni mineralization in this region (IVAN & HOVORKA, 1980; SPIŠIAK *et al.*, 1998; ROJKOVIČ & HOVORKA, 1979). It is supposed that the origin of nickel is connected to the Ni content in surrounding rocks.

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#### ELECTRON MICROSCOPICAL INVESTIGATION OF THE SHAPE AND SIZE OF HALLOYSITE FROM DIFFERENT OCCURRENCES IN THE WESTERN CARPATHIANS, SLOVAKIA

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In geological scientific literature the shape and size of different minerals is frequently used to various applications. Relation between the length and width of minerals gives an often useful information e.g. about its genetic conditions of formation and development. Dimension of shape and size of minerals offers to gain conclusions for evaluation in connection with their eventual environmental risk. Needle shaped and acicular forms of halloysite yield an effective possibility for the study of this relation.

Because halloysite is not a rare mineral in the West Carpathian region, occurrences of halloysite from different localities of Slovakia is treated in the works of numerous authors (ČÍČEL:, 1960; KRAUS, 1989; LINTNEROVÁ, 1995, 1996; RADZO, 1987; ŽÁKOVÁ, 1988; and others).

In the foregoing years halloysites were studied from the viewpoint of growth mechanism (GERTHOFFEROVÁ & ŠUCHA, 1992), mineral particle size distribution (GERTHOFFEROVÁ & KRAUS, 1979), their transformation and stability under weathering conditions (DUBÍKOVÁ, 1998), assemblage minerals (NOVOTNÁ *et al.*, 1993; ŠAMAJOVÁ & FEJDI, 1995) and comparing home and foreign localities (GIESE, 1988; LINDQVIST & ALVIOLA, 1995; and others).

The investigation of halloysite is a part of our wider programme. In the last years, essential intention of the investigation of halloysite was to present fundamental data and survey of size and shape on separated minerals from individual deposits.

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### CORRELATION AND MAGMA TYPES OF THE MIOCENE SILICIC PYROCLASTIC FORMATIONS IN THE BÜKKALJA REGION, HUNGARY: A ZIRCON MORPHOLOGY STUDY

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During the Miocene, repeated explosive eruptions of silicic magmas occurred in the Pannonian Basin, simultaneously with the main period of basin formation. Unfortunately, the majority of the volcanic products are covered by post-Miocene sediments that make the study of these volcanic rocks difficult. Traditionally, the Miocene silicic pyroclastic rocks of the Pannonian Basin have been divided into three horizons based on primarily stratigraphic observations. Nevertheless, we still do not know the mechanism of the eruptions, the source areas of the explosive events, the source of the magmas and the geodynamic relationship of these major volcanic events.

The Bükkalja region provides an excellent area to study these volcanic products, since they have several outcrops here. Recent investigations (SZAKÁCS *et al.*, 1998; MÁRTON & PÉCSKAY, 1998) have pointed out that each of the three horizons are represented in this area. However, correlation of the magmas are still a subject of debate.

Zircon is an important accessory mineral in silicic rocks. Morphology of this mineral depends upon the type of magma (calc-alkaline, alkaline or peralkaline). This lead PUPIN (1980) to introduce a method to distinguish different granitic magmas, based on the morphology of their zircon population. We apply this method for silicic volcanic rocks in the Bükkalja area with an attempt to see similarities and/or differences among the previously distinguished Miocene pyroclastic horizons.

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105

## SULPHIDE AND Ba-Sr SULPHATE BLEBS IN CLINOPYROXENE MEGACRYSTS FROM NEOGENE ALKALI BASALTS (THE BAKONY-BALATON HIGHLAND, HUNGARY)

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Neogene to Quaternary alkali basalts in the Carpathian–Pannonian Region contain a large number of sulphide bearing upper mantle xenoliths and clinopyroxene megacrysts. Sulphide inclusions of the clinopyroxene megacrysts of this area have not been studied yet in details.

Twenty-one clinopyroxene megacrysts and one clinopyroxenite xenolith from the Bakony–Balaton Highlands were selected to characterize the sulphide inclusions. Two types of the clinopyroxene megacrysts were identified: 1) clinopyroxenes with several olivine and spinel inclusions and a high abundance of sulphide inclusions (> 0.05 vol%); 2) clinopyroxenes which contain no olivine and spinel and less sulphide inclusions (<0.05 vol%). The sulphide occurring in clinopyroxene, in olivine and in spinel form blebs or equant negative crystals. These inclusions often form linear arrays parallel to the clinopyroxene growth faces. Most sulphide inclusions are monomineralic: Ni rich pyrrhotite, or MSS with 6–8 wt% Ni whereas some show lamellae or rims of exsolved chalcopyrite.

Sulphides could have been trapped as immiscible primary phases on the surface of the clinopyroxene that later grew around them. This mechanism was published by (ANDERSEN *et al.*, 1987).

Sulphates occur also as blebs along with the sulphide inclusions, showing the same structure and distribution as sulphides. These sulphates are Sr rich barites with minor Ca content. Similar Sr bearing barites were found in mantle rocks as a result of metasomatic events (PYLE & HAGGERTY, 1994).

P, T conditions were estimated from the same samples (TÖRÖK & DE VIVO, 1995), therefore we assume that three immiscible liquids (sulphide, sulphate and silicate) were present at mantle depth at 1029-1048 °C and at a pressure of about 1.0-1.1 GPa.

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# KAŇKITE FROM NAGYBÖRZSÖNY, BÖRZSÖNY MTS., A NEW MINERAL FOR HUNGARY

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The base metal deposit at Nagybörzsöny produced ores for centuries. In the large amount of waste dumps of the mine several secondary minerals have been formed (according to the latest studies, for example 13 sulphates and 4 arsenates). As the main type of sulphides in the mineralization is arsenopyrite one of the most widespread arsenate is scorodite.

However, based on XRD, thermoanalytical, and IR studies a porous, encrusting-like precipitation in the waste disposal of Lower Rózsa adit proved to be kaňkite. The examination data show strong similarity to the results of the examination at the type locality: Kaňk, near Kutná Hora, Czech Republic (CECH et al., 1976). The IR spectrum confirms the presence of a minor amount of sulfate ions. The typical sulfate absorption band at 1072 cm<sup>-1</sup> is well defined on the absorption curves of kaňkite. The yellowish green, spherical aggregates of kaňkite are maximum 0.5 mm in size. According to the SEM studies, they are built up by thin tabular crystals of 5–20  $\mu$ m. In a close association with them, scorodite, gypsum and muscovite also appear.

Similarly to the type locality, the kaňkite was formed by the weathering of the arsenopyrite on the waste dump of the mine.

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# NEW DATA ABOUT BI-Te MINERALS FROM THE MÁTRA MTS., HUNGARY

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Bi-Te minerals have been described in the Central Mátra ore district only in Gyöngyössolymos (Nyirjes) and in the surroundings of Gyöngyössolymos, Asztagkő Hill. At the Nyirjes area, tetradymite nests appear rarely disseminated in quartzite and are accompanied by secondary Bi-Te-bearing minerals, so-called "tellurium-ochres" (KISS, 1960; DÓDONY & GATTER, 1987). Tetradymite and tellurobismuthite were found in a drilling core near the Asztagkő Hill by microprobe analyses as microscopic inclusions in pyrite, accompanying arsenopyrite and sphalerite (NAGY, 1986).

The identification of these minerals was completed by X-ray diffraction, optical examination (Budapest), EDS analysis and SEM methods (Miskolc).

## Gyöngyössolymos, Nyirjes area

The tetradymite and tellurobismuthite appear in the quartzite as fine-grained, dissemination and also forming lamellar aggregates of 0.5–1 cm size. The accompanying sulphides are pyrite and arsenopyrite. Some of the sulphides, especially in a fissured, vuggy environment are rimmed by secondary minerals as montanite, goethite, more rarely jarosite and scorodite. The montanite usually forms yellowish brown, thin encrustations or more thicker crusts of globular and reniform aggregates.

## Gyöngyösoroszi, pit heading at the 100 m level

The polymetallic ore deposit occurring in altered, pyrite-bearing andesite, andesite agglomerate is associated in several areas with fissures filled of quartz, adularia, fluorite and calcite. In these areas tetradymite occurs sometimes among the sulphides.

The tabular and rhombohedral tetradymite crystals (up to 1.8 mm) appear usually enclosed in quartz and fluorite. Thin-tabular crystals with forms {0001} and {10 $\overline{1}$ 1} and scale aggregates of the tabular crystals occur more rarely. According to microprobe analyses, a mineral phase close to tetradymite and an other one with composition between tetradymite-ingodite-"csiklovaite" were found. In the succession order, tetradymite follows the pyrite whilst it is followed by arsenopyrite, bismuthinite etc.

Based on the mineral paragenesis and the succession order, the Bi-tellurides of the Mátra Mts. presumably had been formed before the formation of the Zn-Pb-Cu-type hydrothermal ores that are well-known in this territory.

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## SULPHO-HALIDES OF Ag-Hg FROM RUDABÁNYA, HUNGARY

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Hg-bearing tennantite and Ag-bearing galena had been formed, accompanying other sulphides and barite during the hydrothermal ore formation stage of the Rudabánya iron ore deposit. Weathering of these minerals and activation of halogen-bearing solutions resulted in the formation of some Ag-halides (chlorargyrite, bromargyrite, iodargyrite) (SZAKÁLL & KOVÁCS, 1995) and some Ag-Hg sulpho-halides (perroudite, capgaronnite, iltisite?) in the zone of oxidation of the Adolf mine. This paragenesis that occurs in the silicified limonite is accompanied by copper- and lead-carbonates, - sulphates and -arsenates.

The identifications of sulpho-halides of Ag-Hg made by X-ray diffraction (Geneva), optical examination, EDS analysis and SEM method (Miskolc).

<u>Perroudite</u> (SARP et al., 1987): transparent bright red micro-crusts, and crystals are elongated along [001]. Size of the crystals are to 0.06 mm. Some crystals are fluted with hollow terminations. Rarely were observed penetrated twins as well. It has adamantine lustre and reddish-orange streak. Pleochroism marked from brownish-red to yellow to brownish yellow.

<u>Capgaronnite</u> (MASON et al., 1992): crystals are prismatic, elongated along [001] and flattened on (010). Translucent to opaque, grey to black with subadamantine-submetallic luster. Size of the crystals are to 0.3 mm.

<u>Iltisite</u> (SARP et al., 1997): hexagonal tabular crystals up to  $2-20 \mu m$  in diameter. Sometimes were identified zigzag aggregates, which were built up from intergrowth crystals. It has bright red to brownish red colour and adamantine lustre. It is not verify by X-ray diffraction yet (only EDS and SEM).

Sulpho-halides of Ag-Hg occur in a strongly siliceous limonite in the Adolf mine, Rudabánya. The siliceous limonite is reddish from hematite and cinnabar, and in the cavities are found the sulpho-halides of Ag-Hg as minute crystals or micro-crusts. Accompanied minerals are: cinnabar, tennantite, hematite, malachite, cerussite, barite, chlorargyrite, bromargyrite (common); iodargyrite, mimetite, beudantite, acanthite, mercury, moschellandsbergite (rare).

They have crystallized following decomposition of Hg-bearing tennantite and Agbearing galena by halide-bearing solutions, probably of marine origin.

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# MINERAL COMPOSITION OF CENOZOIC SANDS AND SANDSTONES IN HUNGARY

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The evaluated data of references published before 1984 represent more than 8500 Cenozoic sand and sandstone samples of Hungary, mainly the 0.1–0.2 mm fraction of them. The mineral composition was measured by counting the grains under microscope.

The samples contained 80 different mineral species, 15 mineral groups, 140 mineral varieties, 34 types of rock fragments. On an average, 4–6 different light minerals and 7–15 different heavy minerals occurred in a sample. The older the samples are the higher sandstone ratio they have, the smaller heavy mineral content they have, the more mature they are on the basis of the most resistant heavy minerals (zircon, tournaline and rutile), and the fewer types of minerals they contain. This fact may be caused by diagenetic processes and by the climate, which was warmer and more humid in the older ages of Cenozoic in this area. The average number of heavy mineral species in the samples representing different ages is similar to the data published by PETTIJOHN (1941).

Quartz is the most frequent light mineral in the samples of different ages, followed by the more rare feldspars and rock fragments or muscovite, except the Eocene sandstones, which contain more rock fragments than feldspars. The garnets are the most frequent heavy minerals in the samples of different ages. They are followed by magnetite in the Paleogene, pyrite in the Miocene, chlorites in the Pannonian (Upper Miocene–Pliocene), and amphiboles in the Quaternary samples. Biotite, limonite, epidotes and tourmalines are also among the most frequent heavy minerals.

The degree of similarity of the source rocks or source areas of the samples was pointed out by cluster analysis of the detrital heavy minerals. According to this, the samples of the Eocene, Oligocene and Miocene sands and sandstones are similar to each other. It is because of having similar source areas in the Alps and in the Western Carpathians and having less material from metamorphic rocks. The Pannonian and Quaternary samples are different from the older ones and slightly similar to each other. This may be due to their higher metamorphic component and the fact that their source areas were located not only in the Alps and in the Western Carpathians, but in other parts of the latter and in the Transylvanian (Apuseni) Mountains as well.

The cluster analysis seems to be an effective tool in this case, for example the Quaternary sands brought by the Danube are well distinguishable from the sands brought by the Tisza and Körös rivers, and it also helps to recognise the recycling of sedimentary rocks.

<u>Reference</u> PETTIJOHN, F.J. (1941). J. Geol. 49: 610–625.

## THE STATE OF ASBESTOS IN HUNGARY

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Due to their excellent refractory and insulating properties, chemical stability and solidity, asbestos has been widely used all over the world since the last decades of the 19<sup>th</sup> century. In Hungary, the production of asbestos-containing goods began in 1902 in Nyergesújfalu. Building industry became the main consumer of asbestos: it was used in roofing slates, insulating materials, paints and pipe-works. Among other consumers car manufacturing, shipbuilding and military industry can be listed.

The success story of asbestos broke when attention was drawn to the lung diseases induced by these minerals in the last quarter of the  $20^{\text{th}}$  century. Recently, the word "asbestos" – which refers mainly to amphibole and chrysotile developing fibrous habit – arises only fear and rejection in public.

Since different minerals with different chemistry carry different health risks, mineralogy is a suitable device to evaluate asbestos-containing materials. To estimate the health risks of asbestos that induces disease only if its fibres accumulate in the respiratory system, we investigated the potential of various asbestos-containing products to release individual fibres. Based on these results, the existing epidemiological literature, the manufacturing and import data available in Hungary, we tried to estimate the amount, quality and hazards of asbestos that has been processed in the last hundred years in Hungary. As the basic co-ordinator of usage, removal and waste-management of asbestos, the Hungarian Asbestos Association is presented, too.

Concerning law, the usage of the inevitably carcinogenic amphibole asbestos is already prohibited. Since 1992, it has not been used in Hungary, either. In spite of the fact that the epidemiological effect of chrysotile is still debated, legislative bodies show a tendency to withdraw all kinds of asbestos from circulation all over the world. This approach, irrespective of the quality of asbestos is highly dangerous as: (1) resources for asbestos removal are limited; (2) by demolition of asbestos-containing materials vast amounts of waste would be produced; (3) no appropriate substitute for asbestos that meets health, industrial and economic requirements at the same time has been found so far.

The future of asbestos is still open today. On the one hand, it is possible that all kinds of asbestos will be withdrawn from circulation. In this case, removal and wastemanagement of asbestos-containing materials are going to be vitally important in the coming decades. Should there be no appropriate substitute to find, however, the processing of chrysotile might go on with some technological restrictions. We think that analytical methods of mineralogy (SEM and TEM basically) will be essential in testing substitutes as well as in handling asbestos-containing materials and waste, no matter what the future brings.

# ON TYPOMORPHISM OF SEMICONDUCTOR MINERALS OF ENDOGENIC ORIGIN, RACHIVSKY ORE REGION (UKRAINIAN CARPATIANS)

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Physical and decrepitation properties of semiconductor minerals of Sauliak, Berlibash, Biluy Potik, Rachivskiy, Banskiy, Yaseniv, Tukalo and other deposits, and ore fields have been investigated.

Semiconductor minerals such as pyrite, galena, arsenopyrite, chalcopyrite, magnetite and others were studied in detail.

Based on the typomorphic characteristics and parameters, the search-estimation criteria of endogenic ore mineralization has been developed.

## DISTRIBUTION OF THE Au-Ag TELLURIDE MINERAL FAMILY: FACTS AND LIMITATIONS

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Unlike many chemically related mineral groups or families, gold-silver tellurides (GSTs) occur always together, forming as a rule fine intergrowths and showing various paragenetic relationships. Other tellurides such as frohbergite, weissite, rickardite, montbrayite, coloradoite, tellurantimony and native tellurium may also be present in minor amounts within the GST dominated assemblages. As against other tellurides, GSTs occur mostly under hydrothermal conditions at relatively low temperatures. The Bi tellurides are typically associated with skarn deposits, whereas the PGE tellurides are restricted to magmatic deposits of Sudbury–Norilsk type.

In many books GSTs are presented together, mainly due to the late solving of their crystal structures, but also to their strong tendency to occur together, not dispersed in other types of ores (except hessite). The approach to group together the GSTs could be still accepted as in this case the chemical link is stronger than the structural one. KOSTOV & MINCEVA-STEFANOVA (1981) include all the GSTs into the "Au-Ag-Te assemblages" either in the planar type (krennerite, sylvanite, nagyagite) or in the (pseudo-) isometric type (hessite, petzite, stuetzite, empressite, calaverite).

As shown by ZEMANN (1994), the mineralogy of gold and silver tellurides is grossly different, i.e. in the gold rich part of the ternary diagram Au-Ag-Te dominate the Te rich phases, while in the silver rich part Te poor phases are dominant. The phase relations in the Ag-Au-Te system or parts thereof are quite well known from experiments carried out by MARKHAM (1960), SHTCHERBINA & ZARYAN (1964), CABRI (1965), KRACEK *et al.* (1966) and LEGENDRE *et al.* (1980). Among other facts the experimental data showed that (1) krennerite is a single mineral entity rather than a polymorph of AgTe<sub>2</sub>, (2) there is a continuous solid solution between the highest polymorphs of hessite and petzite, (3) there exists a new phase, the "x" phase, stable along the hessite-petzite join from about 2.3 to 14.5 wt% gold within the temperature interval from 50 to 415 °C, (4) a phase of composition  $Au_2Te_3$  does not exist in the pure Ag-Au-Te system (CABRI, 1965) (montbrayite occurs only if stabilized by Sb).

AFIFI *et al.* (1988) and ŞIMON *et al.* (1996, 1997) gave pertinent insights into the formation conditions and the limiting factors governing the telluride (and selenide) occurrences, i.e. the Te<sub>2</sub>, S<sub>2</sub>. and O<sub>2</sub> fugacities. However, "the reason for enrichment of some systems with tellurium are open to speculations" (AFIFI *et al.*, 1988, p. 402). In addition, tellurium abundancy anomalies should also be taken into consideration (COHEN, 1984), as well as the different valencies, i.e. Te<sup>-2</sup>, Te<sup>+4</sup> and Te<sup>+6</sup>, tellurium can possess, as a part of a generalized explanation for the restricted occurrences of GSTs.

Among the GSTs hessite is the most "wandering" mineral species, occurring as the sole telluride in some massive sulphide deposits, e.g. Porz-Mellec, France; sometimes in association with gold and altaite (Jabal Say'id, Saudi Arabia; Mattagami Lake, Quebec), to which petzite sometimes is added (Noranda, Quebec). Hessite also seems to be common in some skarn deposits, e.g. Dawson City, Yukon, Canada; Tsumo, Japan; Hedley, British Columbia (associated with petzite), or in magmatic deposits such as Kambalda, Australia; Sudbury, Ontario, where altaite is also known.

Such a different behaviour of hessite (and altaite, too) is perhaps related to a high affinity of Te for Ag and Pb at relatively low tellurium fugacity. It is thus reasonable to consider that the affinity of Te for the GST forming elements decreases in the following sequence: Ag, Pb, Au, Sb, Fe, Cu, Hg, which at least formally explains the scarcity of Hg, Cu, Fe, Sb tellurides, as well as of the complex sulphotelluride, nagyagite.

# NIOBIUM-TANTALUM MINERALS OF THE WEST CARPATHIAN GRANITIC PEGMATITES, SLOVAKIA

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A detailed mineralogical, mainly EPMA study during the 1990's revealed a broad variety of disseminated Nb-Ta minerals in West Carpathian granitic pegmatites. The pegmatites form veins to lenses, up to several m thick, in parental Hercynian granites or neighbouring metamorphic rocks. The pegmatite bodies are azonal or zonal with graphic, coarse grained quartz-feldspar-muscovite(-biotite), blocky K-feldspar and core quartz (± beryl) zones, locally late saccharoidal albite and cleavelandite zones occur. The West Carpathian granitic pegmatites with Be and Nb-Ta mineralization belong to the beryl-columbite subtype of rare-element class and LCT-family.

Two groups of Nb-Ta mineralization can be distinguished (UHER & BROSKA, 1995):

(1) Ti poor Nb-Ta assemblage occurs in albite rich or muscovite bearing units of the pegmatites in the Malé Karpaty (the Bratislava region), Považský Inovec and Žiar Mts. Concentric, oscillatorily or mosaic zonal ferrocolumbite-ferrotantalite, rarely manganocolumbite and manganotantalite are the most widespread minerals, generally with increasing Ta/(Ta+Nb) and Mn/(Mn+Fe) atomic ratio from center to rim of crystals and from primitive to more fractionated units and pegmatites; both ratios vary between 0.1 to 0.7 for all studied bodies. Ferrotapiolite + ferro- to manganotantalite pairs show the widest compositional variability within a single pegmatite body known up to now (Moravany pegmatite, NOVÁK *et al.*, in press). Microlite, pyrochlore, uranmicrolite and fersmite are alteration products of columbite-tantalite along the fractures and rims.

(2) Ti rich Nb-Ta assemblage occurs in azonal quartz-feldspar-muscovite or biotite pegmatites in the Nízke Tatry Mts. (Sopotnica Valley, Dúbrava mine). Nb-Ta rich rutile with armalcolite exsolutions, titanian ixiolite and ferro- to manganocolumbite (Ta/(Ta+Nb) < 0.4), belong to primary phases (UHER *et al.*, 1998a). Locally, they are extensively replaced by pyrochlore, microlite, betafite, uranpyrochlore, uranmicrolite, plumbomicrolite, stibiomicrolite, stibiobetafite, stibiotantalite, fersmite, Nb-Ta rich titanite and Nb-Ta-U rich roméite. The secondary Sb-Pb-U rich association is probably a product of hydrothermal overprint from an external source (UHER *et al.*, 1998b).

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# CALCIAN DRAVITE IN MARBLE AND ACTINOLITE SCHIST FROM HNÚŠŤA–MÚTNIK MAGNESITE-TALC DEPOSIT, SLOVAKIA: COMPOSITION AND ORIGIN

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Recent electron microprobe study of unusual tourmaline, previously determined as "uvite" by classic wet analysis from the Hnúšťa–Mútnik magnesite-talc deposit (BOUŠKA *et al.*, 1973) shows calcian dravite compositions and reveals other associated minerals which improve our mineralogical and genetical knowledge.

Dravite forms 0.5-2 cm large crystal clusters in fine grained calcite marble or fan shaped aggregates in actinolite schist at exocontact zones of the magnesite-talc lenses of the metamorphic stratiform deposit. Dravite hand specimens show dark greyish-blue to brownish-black color with slight pleochroism under the microscope. Dravite from marble is relatively homogeneous (Table 1A), dravite from actinolite schist (Table 1B) reveals increasing of Ca and Mg toward the rim in some cases. Dravite from marble have higher Ca/(Ca+Na) and Mg/(Mg+Fe) values than dravite from actinolite schist: 0.33-0.44 vs. 0.05-0.46 and 0.89-0.91 vs. 0.79-0.88, respectively.

A plenty of minute mineral inclusions (~ 0.01 to 0.5 mm large) occur in both dravite types. Diopside, calcite, rarely quartz, titanite, apatite, galena and a Bi phase are included in dravite from the marble; actinolite, dolomite, rarely quartz, titanite, apatite and zircon form inclusions in dravite. Phlogopite (Mg/(Mg+Fe) = 0.82-0.85), partly altered to clinochlore, locally associates together with dravite in actinolite schist. The size and composition of actinolite (locally magnesiohornblende and tremolite) from the inclusions and adjacent actinolite schist is the same: Mg/(Mg+Fe) = 0.85-0.90, Si = 7.41 - 7.85 apfu.

Tourmaline is probably a product of younger (Alpine?) metamorphic overprint of Paleozoic metacarbonates or metabasic rocks with external influx of fluids, rich in B, Na, K (also Fe in marbles). A reaction between the fluids and Ca-Mg bearing rocks resulted in nucleation of calcian dravite poikiloblasts with numerous inclusions of primary metamorphic minerals.

$(A) (Na_{0.6}Ca_{0.3-0.4}\Box_{0-0.07})_1 (Mg_{2.6-2.7}Fe_{0.3})_3 (Al_{5.6-5.9}Mg_{0.1-0.3})_6 (BO_3)_3 (Al_{<0.1}Si_{\sim 6}O_{18}) (OH)_4$
$(B) (Na_{0.5-0.9}Ca_{<0.1-0.4}\Box_{<0.15})_{I} (Mg_{2.2-2.6}Fe_{0.3-0.7})_{3} (Al_{5.6-6}Mg_{0.1-0.3})_{6} (BO_{3})_{3} (Al_{<0.1}Si_{-6}O_{18}) (OH)_{4}$
Table 1. Dravite formulae from marble (A) and actinolite schist (B), Hnúšťa deposit.

#### <u>Reference</u>

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# GARNET ANDESITES FROM THE BÂRGĂU MOUNTAINS, EAST CARPATHIANS, ROMANIA

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Garnet bearing igneous rocks are uncommon worldwide, and consequently limited data are available. The rare occurrences of primary igneous garnets could be explained by the special chemical, p-T and tectonic conditions required for their formation and stability (HARANGI, 1999).

The aim of our study is to bring new data on garnet bearing rocks by a petrological, geochemical and genetical characterisation of the garnet andesites from the Peşii–Mal Neogene intrusive structures from the Bârgău Mountains, East Carpathians.

The Pleşii and Mal structures are located at the contact between the Rodna crystalline massif (Rebra series) and Oligocene–Lower Miocene sedimentary rocks, between Sângeorz Băi and-Măgura Ilvei localities. Both structures are built up of quartz andesites with hornblende and garnets. They consist of a main intrusive body, tabular in shape, elongated in a NE–SW direction.

The Pleşii and Mal intrusive structures represent the only primary igneous garnet bearing outcrops within the volcanic arc of the East Carpathians (NITOI *et al.*, 1995). These features lead us in considering the quartz andesites with hornblende and garnets as a special petrographic type.

The quartz andesites show a porphyritic structure, with a fine to medium granular crystalline matrix. Plagioclase feldspars, quartz, hornblende and garnets represent the phenocrysts.

There are small variations in the distribution of major and minor elements. Thus,  $SiO_2$  varies between 58,6–63,7 %, typical values for andesites and quartz andesites. Other mean values are  $Al_2O_3 = 17.62$  %,  $Fe_2O_3 = 5.32$  %, MnO = 0.12 %, MgO = 2.4 %, CaO = 6.21 % and water = 1.86 %.

The garnets (Alm = 46-55 %, Pir = 21-28 %, Andr = 12-15 %) are quantitatively subordinate (1-2 % of the rock volume). They form phenocrysts with subhedral or euhedral morphologies, 0.5–2.5 mm in size. Garnets are fresh, with no inclusions and reaction zones. They are not randomly distributed within the rock mass; most of the garnet crystals form the core of plagioclase and rarely of hornblende megacrystals. The plagioclases hosting garnet crystals are similar to other plagioclases in the rocks, as far as optical and chemical features are concerned, indicating that the feldspars and garnets formed from the same magma. It is also worth mentioning that the garnets are associated only with acidic to intermediate rocks, having corundum in their norm composition. Genetic relationship between garnets and their host rock is thus proved in this way.

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# OPTICAL PROPERTIES OF FIBROUS ZEOLITES OF THE BAKONY-BALATON HIGHLANDS, HUNGARY

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We studied fibrous zeolites occurring in cavities of young (7–3 Ma) alkaline basalts of the western part of the Bakony-Balaton Highlands Volcanic Field (BBHVF), Hungary. This small scale mineralisation is characterised by zeolites and calcium carbonates.

Fibrous zeolites can be divided into two groups on the basis of Si/Al ordering. One can distinguish fully ordered species (natrolite, mesolite, scolecite) and ones with different degrees of disorder (e.g. gonnardite, thomsonite). The fully ordered fibrous zeolites have very constrained composition fields, while the disordered ones constitute crystalline solution series (ROSS *et al.*, 1992).

The problem in the investigation of this mineral group lies in the fact that all fibrous zeolites share a common silicate framework, for which reason they are rather difficult to identify with standard XRD methods. However, their optical properties and optical orientation related to morphology are highly subject to changes in chemical composition (GUNTER & RIBBE, 1993). This offers a fairly straightforward way to their identification by spindle stage.

The fourteen samples investigated were originated from five localities of the BBHVF. The crystals are colourless, mostly clear, acicular, (pseudo)tetragonal in habit, with pyramidal ending forms. Sizes of crystals are up to ca.  $1.5 \times 0.2$  mm. Macroscopically there is no discernible difference between crystals from any of the localities.

Before measurement the crystals were fully hydrated by keeping them in a vapour rich atmosphere for at least 24 hours.

Three kinds of fibrous zeolites were documented. The results can be summarised as follows. (The data given are mean values.)

1. Orthorhombic,  $\gamma = c$ ,  $2V = 56^{\circ}$ ,  $\alpha = 1.481$ ,  $\beta = 1.484$ ,  $\gamma = 1.493$ . These data allow to identify the mineral as natrolite.

2. Very close to isotropic, n = 1.502-506. These are characteristic for mesolite.

3. Monoclinic,  $\beta \wedge c \approx 30^{\circ}$ ,  $2V = 54^{\circ}$ ,  $\alpha = 1.482$ ,  $\beta = 1.485$ ,  $\gamma = 1.494$ . There is no fibrous zeolite cited with similar optical properties, we use "**Type 3**" as working notation for that phase. Paranatrolite (unstable variety, not approved by IMA) is given as monoclinic but with 2V lower than 10°. Furthermore, it is established that paranatrolite, if kept dry, dehydrates to tetranatrolite (TSCHERNICH, 1992). It is not stated whether it is a reversible process or not. However, all examined samples were kept without any special treatment, except for the full hydration prior to measurement.

At least 9 different crystals from two localities showed "Type 3" optical features, therefore we believe that "Type 3" is a stable, until now not described fibrous zeolite phase. The full mineralogical characterisation of this phase is in progress.

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# THE HERCYNIAN GRANITOID COMPLEX OF NORTHEASTERN SERBIA

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The Hercynian granitoids in northeastern Serbia are one of the main geological features of the Carpatho–Balkanian composite terrane e.g. its terranes: Kucaj, Stara planina–Porec and Vrska cuka–Miroc (KARAMATA & KRSTIC, 1996).

The Hercynian granitoid complex (Fig. 1) consists of four large (Neresnica, Brnjica, Gornjane, Plavna) and eight small (Veliki Greben, Turija, Popovica, Veliki grabor, Mali goli vrh, Donja Bela reka, Pecka bara, Barjaktar) plutons intruded into Proterozoic high grade metamorphics, Rifeo-Cambrian "green complexes" and Lower Paleozoic slightly metamorphosed sediments. Structural features indicated their early to late sin- (Brnjica) and post-kinematic (Neresnica, Gornjane, Plavna) emplacement.

The granitoid complex comprises principally granitic rocks (tonalite-granodioritemonzogranite) with subordinate quartz monzodiorite, quartz diorite and diorite, rarely gabbro bodies. Most intrusions show zonal distribution of rock types and the character of polyphase intrusions. These rocks consist of plagioclase (7–30 An to 35–65 An), Kfeldspar (commonly with microperthite), amphibole, biotite,  $\pm$  quartz, and relics of clinopyroxene; accessory are zircon, allanite, apatite, titanite, magnetite,  $\pm$  monazite.

The whole rock chemistry indicates a broad variation and a nearly smooth trend of major elements, calcic to calc-alkali and peraluminious character of all granitoids.

Mineral composition as well as whole rock chemistry suggest I-type (with subordinate S-type) origin of the North-eastern Serbia Hercynian granitoids.



Fig. 1. Distribution of Hercynian granitoids in the northeastern part of Serbia.

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# GLAUCONITIC FORMATIONS IN AND AROUND THE CARPATHIAN–PANNONIAN REGION

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Glauconitic minerals are defined as Fe-rich layer silicates with structures varying from a Fe-rich smectite to a dioctahedral Fe-rich mica. The glauconitic facies (glaucony) is characterized by the granular morphology of the aggregates, by a heterogeneous but mainly monophase glauconite-type composition and by a distinctive genesis, the glauconitization process. Thus, it can be approached in mineralogical, petrographical and sedimentological ways. Comparative and regional case studies of the glauconite formations can provide important criteria for stratigraphical correlations as well as for structural and paleoenvironmental models of genetically connected areas. Based on several criteria estimated for various glauconitic levels outcropping in the same region, AMOROSI (1996) defined three genetic types: autochthonous, parautochthonous and detrital glauconite.

Our aim is to monitor the glauconite formations with their main occurrences in and around the Carpathian-Pannonian region, taking into account mineralogicalpetrographical features of glauconitic minerals (size, concentration in the host-rock, morphological type of the green grains, the amount of the main cations (total Fe, Al, K) and the mineralogical type defined by the polytypes 1M, 1Md, <1Md) as well as geological criteria (the geological unit, the lithostratigraphical unit, the age and the host rock). The information included in the database originates both from our previous research on significant glauconite occurrences in Romania and Hungary, and from comprehensive mineralogical, petrological and stratigraphical reference data in the literature of the region (Slovakia, Ukraine, Poland, Czech Republic, Croatia, Slovenia). With only one exception (Paleozoic, Poland), the glauconite formations in this region are not older than Jurassic. The most abundant formations are known from the Paleogene, then from the Neogene and then from the Upper Cretaceous. The most common host rocks are the detrital, from conglomerate to shale, dominantly sandstone, but other types of rocks were mentioned as well (limestone, phosphorite, chert).

Plots of the glauconite occurrences according to their stratigraphical ages offer the frame for a discussion of the geologic relationship between the synchronous formations, taking into account the possible genetic types (autochthonous vs. detrital) of glauconites.

This study intends to be a first stage in a larger project, which should emphasize the geological importance of glauconitic minerals, as well as another example of an applied mineralogical research.

This work was supported by OTKA Grant # T25873.

<u>Reference</u> AMOROSI, A. (1996). Sedimentary Geology, 22: 1–19.

# PLUMBOGUMMITE FROM PÁTKA, VELENCE MTS., HUNGARY: A NEW MINERAL FOR HUNGARY

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Plumbogummite, a new mineral for Hungary occurred in one of the samples which were collected in 1996 from the oxidation zone of Szűzvár mine, Pátka, Velence Mountains.

The new phase appeared as a crust in fissures of the leached vuggy textured quartz dike, associated with galena, fluorite, pyromorphite, cerussite. Stereomicroscope showed the mineral as a white-coloured powder mass. At some parts of the sample the surface is covered by a colourless microcrystallized mass composed of submicroscopic crystal needles.

According to SEM images the phase appears to be intergrown with pyromorphite. Distinct single crystals exhibit pseudo-octahedral, isometric habit. They are of the size of about  $30-50 \ \mu\text{m}$ . Twinned crystals also occurred (ZAJZON *et al.*, 2000).

We tried to separate plumbogummite from pyromorphite by using different methods. The separation based on different densities failed because of the tight intergrowth of the two phases. Therefore, measurements that require monomineralic separations could not be carried out on the new phase.

X-ray powder diffraction confirmed the presence of plumbogummite in the powder mixture of pyromorphite and plumbogummite.

Wavelength and energy dispersive X-ray microanalyses revealed that the newly appeared phase is plumbogummite  $(Pb_{1.08}Ca_{0.02}Al_{2.93}[PO_4](PO_3(OH))_{0.86}[(OH)_{6.78}])$ .

Textural patterns in optical and electron microscopes showed that plumbogummite appears to have been inter- and overgrown on pyromorphite, and/or replacing pyromorphite as an alteration product.

The authors express special thanks for Dr. Géza Nagy (HAS) for the WDX analytical data.

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ZAJZON, N., VÁCZI, T. & WEISZBURG, T. G. (2000). Acta Miner. Petr. (Szeged), 41, Suppl.: 121

## A NEW TWIN LAW FOR THE ALUNITE GROUP MINERALS

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Plumbogummite, an alunite group mineral was recently described from Szûzvár mine, Pátka, Velence Mts., Hungary by ZAJZON & SZENTPÉTERI (2000).

SEM studies demonstrated that part of the plumbogummite crystals are characterized by systematic regular intergrowth, penetration twins (see Fig. 1). None of the twin laws published previously for the alunite group minerals produce twin crystals of that shape. The aim of this study was to describe the geometrical characteristics of the new twin law and to find the structural background of twinning.

The size of the crystals (maximum 0.02-0.03 mm) did not allow us to use the standard method (reflection goniometry) for the determination of the geometrical relationship between the crystals. We could use only the SEM pictures, where the measurement of the directions and angles, related to the trivial morphological features of the individual crystals, could not be made with an error smaller than a few degrees, even if we measured several crystals in different orientations. Based on these rough data, we started to reconstruct the twin through comparison of the observed crystals and the models created by a computer program (SHAPE). The models suggested a rotational twin (twin axis: [2131], rotation: approximately 65°).

To confirm this, we searched for evidences in the crystal structure of alunite by using another computer program (ATOMS). The structure was plotted both perpendicular to and (by rotations) parallel with the suggested twin axis. It became obvious that there are two planes in the structure (both containing the  $[21\overline{3}1]$  direction and the  $a_1$  and  $a_3$ Bravais axes, respectively) where the polyhedral ribbons were found to be identical. On the  $[21\overline{3}1]$  view, an angle of 70° was measured between the planes.

Thus we suppose a twin law for the alunite structure, with a 70° rotation about  $[21\overline{3}1]$ . Further occurrence of alunite group crystals of that type of twinning will give a chance for further refinement of these data.

Reference

ZAJZON, N. & SZENTPÉTERI, K. (2000). Acta Miner. Petr. (Szeged), 41, Suppl.: 120

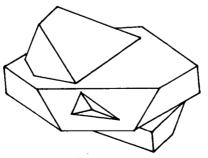


Fig. 1: Penetration twin of plumbogummite from Pátka, Hungary.

121

# DELAFOSSITE (Cu<sup>1+</sup>Fe<sup>3+</sup>O<sub>2</sub>) FROM MARTONYI, NE HUNGARY; A NEW MINERAL FOR HUNGARY

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Martonyi, a smaller metasomatized iron rich carbonate ore body (KOCH *et al.*, 1950) is to be found in NE Hungary, in the neighbourhood of the well-known iron ore deposit of Rudabánya. Although Rudabánya is much richer in mineral species than Martonyi, we are to present now a rare mineral, delafossite, that is new not only for Martonyi, but also for Hungary.

## Physical properties, crystal morphology

The mineral occurs in botryoidal masses, up to 3 mm in diameter. These aggregates consist of individual platy, euhedral crystals of 0.1 mm in diameter as a maximum. The crystals are brownish black with metallic lustre.

Based on SEM observations, three morphological types can be distinguished. The most common is the thin, "specularite like" variety, with traces of narrow rhombohedron faces at the rim of the dominating basis. Less frequent are the thicker plates formed by the combination of the basis and the  $\{10\overline{1}1\}$  rhombohedron, just as well as the barrel shape pyramidal crystals, combinations of the  $\{0001\}$ ,  $\{11\overline{2}1\}$  and  $\{11\overline{2}5\}$  crystal forms.

## Chemistry and crystal chemistry

The chemical composition was measured by EDX (quantitative measurement of Fe and Cu by using standards). The results confirm the formula  $Cu^{1+}Fe^{3+}O_2$  within the analytical error. There is no sign for any crystal chemical anomaly, as the XPD pattern of the hand-picked pure material fits quite well the reference data (JCPDS 12-752). The only minor differences are the increase of the intensity of the 006 reflection (from 30 % to 100 %) and the appearance of the 003 reflection (at 5.75 Å, of low intensity); both can be accounted for by preferred orientation.

## Paragenesis, genetical considerations

Delafossite occurred in the cavities of the brecciated oxidation zone of the ore deposit ("limonitic ore"). Its closest accompanying phases are goethite and cuprite, the latter forms octahedral crystals of mm size, in veinlets. The broader mineral assemblage includes also native copper, pyrolusite, calcite, malachite, azurite and cinnabar.

Delafossite is considered to have formed during the oxidation of the primary Fe-Cu sulphides of the ore body.

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## **Bi**<sub>3</sub>Te<sub>2</sub>: A NEW MINERAL PHASE FROM THE TYPE SPECIMEN OF PILSENITE ("WEHRLITE")

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Tellurides have been connected to the Carpathian–Pannonian Region since the discovery of the new element tellurium in Transylvania in the 18<sup>th</sup> century.

Nagybörzsöny (in German: Deutsch-Pilsen), Börzsöny Mts., Hungary, is one of the classical localities of bismuth tellurides in the region. It is the type locality of pilsenite (formerly: "wehrlite").

The type specimen of pilsenite, to be found in the Mineral Collection of the Eötvös L. University, was studied by reflected light microscopy in details by SZTRÓKAY (1946). Later SZTRÓKAY & NAGY (1982) gave local chemical data of the phases mentioned earlier, and thought to be found two new mineral phases, one of them member of the Bi-Te-S system. Preliminary results of the re-examination of the very mount used by SZTRÓKAY & NAGY (1982) was given by WEISZBURG *et al.* (1992). The new measurements and the revised interpretation of the data published by SZTRÓKAY & NAGY (1982) made it clear that the specimen really contains a new phase of the Bi-Te-S system, but different what was assumed earlier. The aim of the current paper is the presentation of this new phase, Bi<sub>3</sub>Te<sub>2</sub>.

 $Bi_3Te_2$  represents a surprisingly large, homogenous volume of the sample, occupies the central part of the massive, not lamellar half of it (lamellar = pilsenite). Its total volume is over 0.5 cm<sup>3</sup>. This amount of material made it possible to collect not only local chemical and optical, but also reliable XPD data, unavailable earlier. Based on the unit cell dimensions and the chemical formula assumptions could be made on the stacking order of the phase.

In the Nagybörzsöny sample the homogenous  $Bi_3Te_2$  is surrounded by homogenous joseite-B. Their boundary is sharp and clear. This fact, and some microprobe data of the composition of  $Bi_3Te_2$  published from other geological regions indicate that  $Bi_3Te_2$  is a stable, energetically favoured phase in nature along the pilsenite – native bismuth line. Nomenclatural consequences of the present results are under preparation for IMA CNMMN.

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# **RE-EXAMINATION OF MÁTRAITE FROM THE TYPE LOCALITY, GYÖNGYÖSOROSZI, MÁTRA MTS., HUNGARY**

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ZnS crystals with peculiar conical-pyramidal morphology were described from Gyöngyösoroszi, Hungary by KOCH (1958) and reported as representatives of a new polymorph of ZnS. Based on similarities of X-ray diffraction patterns (taken in a 114.6 mm oscillation camera) SASVÁRI (1958) suggested that these crystals are the natural counterparts of the 3R rhombohedral modification of ZnS reported by BUCK & STROCK (1955). The 3R structure was supposed to be the result of a slight distortion of the cubic close-packed, 3C sphalerite structure. The new natural ZnS polymorph was given the mineral name mátraite.

WEISZBURG & LOVAS (1982) studied the type material of mátraite by applying a broader range of single crystal X-ray diffraction techniques. They concluded that mátraite could not be a 3R modification, predicted strong real structure effects and suggested further TEM studies.

Recently we found again ZnS crystals of mátraite type morphology on samples from Gyöngyösoroszi. Our combined X-ray diffraction, optical, scanning and transmission electron microscopy study revealed that the "mátraite" crystals have a densely twinned 3C sphalerite structure, similar to the "pyramidal type" ZnS that was also reported from Gyöngyösoroszi (PÓSFA1 *et al.*, 1988).

These results indicate that matraite should be regarded as a morphological variety of sphalerite having a characteristically disordered (twinned) structure. Nomenclatural consequences of the present results are under preparation for IMA CNMMN.

This work was partly supported by OTKA Grant # T016628.

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# MELLITE (Al<sub>2</sub>C<sub>12</sub>O<sub>12</sub> • 16H<sub>2</sub>O) FROM CSORDAKÚT MINE, BICSKE, HUNGARY: A NEW MINERAL FOR THE CARPATHIAN–PANNONIAN REGION

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Mellite, a rare organic mineral  $(Al_2C_{12}O_{12} \cdot 16H_2O)$  was found in the Eocene coal mine Csordakút, Bicske (near Tatabánya), Hungary. The aim of the present study is the mineralogical characterisation of the Csordakút mellite.

The mineral occurs in euhedral, well developed pyramidal crystals up to 12 cm. Cm size crystals and parallel intergrowth of them are common.  $D_m = 1.6108(1)$  g/cm<sup>3</sup>. Most of the crystals are translucent, wax or honey yellow, but several fully transparent, colourless crystals were also found. Black colour, caused by coal inclusions, was also observed.

Based on morphological observations, two varieties can be distinguished. The most common is the perfect  $\{111\}$  dipyramid, rarely in combination with the subordinated  $\{100\}$  and/or  $\{001\}$  crystal forms. Less frequent are the distorted crystals, having two types of distortion: 1) platy crystals, where the plates form according to one of the faces of  $\{111\}$ , and 2) elongated, columnar crystals, where [111] is the axis of elongation. The distorted crystals are of the same crystal form(s) as the perfect ones. It is worth to mention that most of the transparent, colourless crystals belong to the distorted platy type.

No full chemical analysis has been performed on the mellite from Csordakút. We determined the water and the Al content by thermal analysis (combined DTA, TG and DTG analysis, both in air and in N<sub>2</sub> atmosphere, up to 1273 K). Our results support the data of GIACOVAZZO *et al.* (1973), who reduced the amount of water in the formula from 18 to 16. We hoped to find correlation between the colour and the trace elements (determined by AAS), but no significant differences could be found between the colourless and yellow samples (e.g. Fe 167 and 222 mg/kg, resp.). Unit cell parameters (XPD):  $c_0 = 23.12(2)$ ,  $a_0 = 15.34(2)$ ,  $D_{calc} = 1.615$  g/cm<sup>3</sup>. Systematic extinctions (based on single crystal patterns) confirm the I4<sub>1</sub>acd space group.

Mellite occurred in altered zones close to the bottom of the coal bed. Based on the heavily acidic environment (we measured pH down to 2 in water in the mine at places close to the "mellite adit"), we assume that mellite was formed by the interaction of organic acids and clay minerals present in the coal.

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## **AUTHOR INDEX**

Andráš P. 5, 6, 33, 103 Axente V. 89 Babić D. 36, 118 Bačo P. 7 Badics B 8 Bahna B. 9 Baida T. 10 Bainóczi B. 11 Bakos F. 12 Baláž B. 32 Bali E. 13 Balla M. 125 Balogh K. 87 Banerjee A. 14, 15 Bartha A. 73 Belkovsky A. I. 16, 17 Bendő Zs. 8 Berényi-Üveges J. 18 Bertalan É. 73 Bilonizhka P. 19 Blagojević S. 36, 118 Bliaean P. 62 Broska I. 20, 21, 22 Buda Gy. 52 Buriánek D. 80 Buseck P. R. 124 Cebulak S. 23, 45 Chovan M. 6, 24, 103 Činčura J. 25 Ciulavu M. 26 · Costea C. 58 Costin D. 27, 28 Damian F. 27, 28 Damian Gh. 27, 28 Denut I. 28, 29 Didenko P. 30 Ditrói-Puskás Z. 31 Dódony I. 65, 77, 78 Ďuďa R. 7, 32, 33 Dudok I. V. 34 Dumitras D. 69 Ehivanov V. 112 Elekes Z. 93

Emetz A. V. 35 Erić S. 36, 118 Fabian C. 37 Falus Gy. 38 Fehér B. 39, 40 Flaut C. 29 Földessy J. 41 Földvári M. 107 Franus W. 10, 42, 43 Gál Á. 44 Gál-Sólymos K. 31, 106 Galvánek J. 33 Gaweda A. 23, 45, 46, 47 Ghiurca V. 14, 15 Gibert R. 69 Gméling K. 8 Goławska B. 46 Haas J. 48 Háber M. 59 Hanak B. 45 Harangi Sz. 8, 49, 96, 105 Hîrtopanu P. 50 Holocsv A. 56 Horal M. 51 Horvat M. 52 Houzar S. 53 Hovorka D. 102 Hryniv S. P. 54 Hvožďara P. 55, 56, 57 lepure Gh. 28 Ion D. 58 Iró S. 57 Ízing I. 8 Jánosi M. 122 Jedrysek M. 46 Jeleň S. 7, 33, 59 Juhász T. 60 Katona I. 70 Kitley G. 60 Kóbor B. 84 Koděra P. 7, 59, 61 Komov I. 30, 81 Kondela J. 62

Konecny P. 20 Kostyuk O. 112 Kóthay K. 63 Kotuľák P. 7 Kovács Á. 108 Kovács G. 64 Kovács Kis V. 65, 78 Kovács-Pálffy P. 107 Kraczka J. 47 Kraus I. 104 Križáni I. 5 Kubovics I. 31 Kušnierová M. 5 Kvasnytsya I. 66 Laduron D. 79 Leichmann J. 46, 53 Loktina I. 16 Lovas Gy. A. 73, 124, 125 Lupulescu M. 67 Lytovchenko A. S. 90 M. Tóth T. 64 Macovel Gh. 28 Mádai F. 68 Manecki A. 42, 43 Manecki M. 10 Marias Z. 28 Marincea S. 69, 70, 79 Marszałek M. 91 Marusyak V. 112 Marynowski L. 23 Matkovsky O. 71, 72 Matviishyn Z. 72 Michéli E. 18 Mitsyuk B. M. 81 Mizák J. 73 Molnár F. 11, 74 Moravanský D. 75 Munteanu M. 79 Murphy P. 61 Nagy B. 31 Nagy T. 73, 124 Nagy-Balogh J. 31 Nedelcu L. 76 Németh P. 77 Németh T. 18, 78

Nesterov A. R. 17 Nikolenko A. 112 Nitoi E. 79 Novák M. 80, 114 Olijnyk T. 112 Ostapenko G. T. 81 Ozdín D. 51, 82, 115 Pál Molnár E. 83, 84 Papp D. C. 116 Papp G. 85 Papucs A. 86 Paulo A. 46 Pécskay Z. 87 Petrescu L. 89 Pieczka A. 47 Piwkowski R. 46 Pop D. 119 Popescu R. 88, 89 Popivnyak I. 112 Popivnyak Y. 112 Pósfai M. 124 Pršek J. 82 Pushkarev A, V. 90 Pushkareva R. A. 90 Puškelová Ľ. 25 Rajchel J. 91 Rajchel L. 91 Rankin A. H. 61 Repčiak M. 7 Rochev A. 92 Rosu E. 76 Rózsa P. 93 Rusu C. 58 Sajó I. E. 40, 108 Sallay E. 94 Samajová E. 104 Samodurov V. 95 Sapota T. 42 Sarp H. 109 Schléder Zs. 96 Schroll E. 6 Seghedi A. 26 Seres-Hartai É. 41 Shcherbakova E. 97 Siman P. 21

13051



Simulák J. 93 Sinyakovskaya I. 98 Sipos P. 99 Skakun L. Z. 35 Smirnov A. 100 Spišiak J. 101, 102 Stankovič J. 103, 104 Szabó Cs. 13, 38, 49, 63, 106 Szabó Zs. 105 Szakál J. A. 106 Szakáll S. 107, 108, 109, 122 Szentpéteri K. 120 Szöőr Gy. 93, 125 Thamó-Bozsó E. 110 Török K. 13, 63, 106 Tóth E. 111 Tóth M. 18 Tsikhon' S. 112 Tuček P. 12 Turanová L. 104 Udubaşa G. 113 Udubaşa S. S. 67, 89 Uher P. 22, 114, 115 Ureche I. 116 Váczi T. 117, 121 Varga Zs. 73 Vaselli O. 13, 38 Vasković N. 36, 118 Verkaeren J. 70 Vincze P. 125 Vovnyuk S. V. 34 Weiszburg T. G. 73, 111, 119, 121, 123, 124, 125 Wieser T. 43 Zajzon N. 120,121



**B**185444

128

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