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CHEMISTRY OF REE-BEARING ION ADSORPTION CLAYS IN TOKAJ MOUNTAINS, HUNGARY

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Ion adsorption clays (IAC) might be important collectors of rare elements such as REEs or Li and can be important resources for the European Union's economy and vital for various sectors, especially as the EU transitions towards cleaner energy and digital technologies. The ionadsorption clays are formed through the chemical weathering of volcanic rocks containing REEbearing minerals, followed by the subsequent chemical adsorption of REEs onto clay minerals, currently provide the world's dominant supply of heavy REE (ESTRADE *et al.*, 2019).

This study aims to investigate the chemistry of REE-bearing ion adsorption of lacustrine sediments surrounded by rhyolite tuff of south Tokaj mountains as prospective target using handheld gamma spectrometry (HGS) and X-ray fluorescence (XRF) methods. Petrological and geochemical analyses conducted in the Tokaj Mountains reveal that high lithium (Li), thorium (Th), uranium (U), rubidium (Rb), and cesium (Cs) contents associated with rhyolite tuff and diatomite could be related to shallow-depth hydrothermal alteration sedimentary and processes (BELAY et al., 2023).

XRF and HGS are conducted in this research to determine the chemical characteristics along with rare elements. All samples collected from Bodrogkeresztúr quarry, Mád III (Király Hill), Rátka V and VII quarries are rhyolitic volcanoclastic rocks in composition having 73.89–78.79 wt.% SiO₂, 11.69–14.31 wt.% Al₂O₃ and total alkali content of 4.5–6.35 wt.%; notably high concentration in Th, U, Rb, Pb and K.

ZELENKA *et al.*, (2012) studied the paleovolcanic reconstruction of Tokaj mountains and specified that uranium maximum values can be found around volcanic centers which are areas of hydrothermally altered rhyolite tuff with largest maximum values (5–8%) of potassium

indicate K-metasomatism (ZELENKA *et al.*, 2012). The HGS measurements show notably high U reaching up to 9.9 associated with high K.

BELAY *et al.*, (2023) studied the alkaline metals using LIBS and ICP-MS measurements of Erdőbénye basin showed high Rb up to 553 ppm, and Li up to 47 ppm.

XRF data from altered rhyolite tuffs of the four quarries show that increasing Ishikawa alteration index (AI) is different by quarries and correlates well with Rb values, while have negative correlation with U and Th (Fig. 1). It suggests that U and Th mobilizes with increasing sericite alteration, while Rb and K resists. XRF did not allow to detect lithium and REEs.

Multielement ICP-MS data from the Erdőbénye Ligeterdő diatomite quarry shows that there are very strong correlations between Rb, and K with Th, U, HREEs, LREEs in the diatomite and diatomic clay, while Li in these beds correlates with Mg, Ca and Mn. Conversely, in rhyolite tuff and tuffaceous sandstone beds of the Ligeterdő quarry Rb does not correlate with U and Th, while Li and LREEs have strong correlations with Th, Mg and Ca.

These complex correlation patterns indicate that shallow-depth hydrothermal alteration of rhyolite tuffs of south Tokaj mountains could mobilize LREEs and Li which could be fixed in diatomite and diatomaceous clay (Fig. 2).

These conclusions should be approved by multielement ICP-MS analysis of south Tokaj rhyolite tuff samples and more detailed sampling, separation and chemistry to search lithium related to the Ligeterdő quarry.

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References

- BELAY, M.A., FÖLDESSY, J., KUPI, L., MÁDAI, F. (2023): Carpathian Journal of Earth and Environmental Sciences, 18 (2), 405–413.
- ESTRADE, G., MARQUIS, E., SMITH, M., GOODENOUGH, K., NASON, P. (2019): Ore Geology Reviews, 112, 103027.
- ZELENKA, T., GYARMATI, P., KISS, J. (2012): Central European Geology, 55(1), 49–83.



Fig. 1: Correlation of Rb- and U-content with Ishikawa Alteration Index (AI) of samples from altered rhyolite tuffs of southern Tokaj Mountains. Ranges represent different rock types: 1: Bodrogkeresztúr rhyolite tuff quarry, 2: Mád Király Hill leached tuff quarry, 3: Rátka VII quarry zeolitic rhyolite tuff, 4: Rátka V quarry zeolitic rhyolite tuff, 5: Mád Király Hill quarry ignimbrite



Fig. 2: Correlation of La-content with U of samples from Erdőbénye Ligeterdő diatomite quarry

GOLD MINERALIZATION IN RUDABÁNYA, HUNGARY: INSIGHTS FROM BOREHOLE ANALYSIS AND GEOCHEMICAL CORRELATION STUDIES

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The Rudabánya mining area in north-eastern Hungary, within the Aggtelek-Rudabánya Mountains, presents significant mineralogical and geochemical interest due to its complex geological history and diverse mineralization processes. Positioned within the tectonically active Darnó Zone, a strike-slip fault zone associated with the Mid-Hungarian Lineament, this region's geological framework has been shaped by various tectonic and metasomatic events (BODOR *et al.*, 2013). This study aims to explore the gold mineralization in Rudabánya, an area that has been underexplored despite its potential.

The mineralization in Rudabánya is marked by multiple phases, contributing to the area's complex ore textures and mineral assemblages. The earliest phase includes stratiform Pb-Zn sulphide mineralization within the Szin Marl Formation, where galena (PbS) and sphalerite dominate. Iron ore mineralization (ZnS) followed, driven by metasomatic processes that replaced carbonate rocks with iron-rich minerals such as siderite (FeCO₃) and ankerite (Ca(Fe,Mg,Mn)(CO₃)₂). Breccia-hosted barite (BaSO₄) and Pb-Zn sulphide mineralization represent another crucial phase, filling tectonic fractures with barite and sulphide minerals, indicating multiple phases of fluid flow and mineral deposition. Copper mineralization, predominantly associated with chalcopyrite (CuFeS₂), is found in vein structures and disseminated within the host rocks, while supergene processes have enriched the oxidation zone, forming limonite (hydrous iron oxides) and other secondary minerals, thereby enhancing the economic potential of these deposits.

As part of the research, three boreholes out of the lot with notable gold values were analysed.

Specifically, Borehole 12/A, with a length of 86.6 meters, a dip of 55°, and an azimuth of 220°, revealed two significant gold (Au) anomalies. The first anomaly, located between depths of 68 meters and 69 meters, exhibited a gold concentration of 0.77 ppm and showed a strong correlation with barium (Ba), manganese (Mn), and iron (Fe), which were associated with spade breccia. The second anomaly, found between 85.40 meters and 86.60 meters, exhibited a higher gold concentration of 1.28 ppm and similarly demonstrated a strong correlation with manganese (Mn) and iron (Fe), associated with creamspar breccia. These findings highlight the interplay between geochemical complex elements and mineralization processes in the area.

Further geochemical analysis using ioGas software was conducted to investigate the correlation between gold and pathfinder elements. The analysis confirmed that there is no significant correlation between gold and traditional Carlin-type pathfinder elements, which contrasts with previous studies such as those by (KORPÁS et al., 1999). However, a strong correlation was observed between gold enrichment and specific lithological units, particularly those involving siderite and hydrothermal metasomatic alterations. underscoring the role of these processes in gold deposition.

The study's findings have significant implications for future exploration strategies in Rudabánya, providing new insights into the genetic relationship of gold mineralization. The recognition of the lack of correlation between gold and traditional pathfinder elements, alongside a strong correlation with specific lithological units, emphasizes the need for more

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targeted exploration approaches. These results contribute to the broader field of mineral exploration by offering a detailed understanding of the mineralogical and geochemical processes that govern gold and silver enrichment in Rudabánya, enabling more effective and innovative exploration strategies to uncover hidden resources in the region.

These insights are remarkable for guiding future exploration efforts and developing effective mining strategies in Rudabánya, thereby enhancing the potential for economic mineral extraction.

References

- BODOR, S., FÖLDESSY, J., KRISTÁLY, F., ZAJZON, N. (2013): Carpathian Journal of Earth and Environmental Sciences, 8(4), 147–153.
- KORPÁS, L., HOFSTRA, A. H., ÓDOR, L., HORVÁTH, I., HAAS, J., ZELENKA, T. (1999): Geologica Hungarica Series Geologica, 24, 197–293.



Fig. 1: Downhole diagram of borehole *T*-12/*A* for major target and pathfinder elements of the Rudabánya ore field.

MINERALOGICAL AND GEOCHEMICAL STUDY OF PERMIAN SAND-STONE WITH NATURAL GAMMA ANOMALY FROM BÁN VALLEY, BÜKK MTS.

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The Mecsek Ore Mining Company (MÉV) have conducted uranium prospecting between 1974 and 1981 on the Permian Szentlélek Formation of the Bükk Mts., composed from siliciclastic sediments. The survey was supported by drillings, and trenches. As a result, uranium mineralized bodies were explored, with the highest uranium concentration of 1880 ppm, mostly incorporated into kasolite (Pb(UO₂)(SiO₄) * H₂O). Besides U, polymetallic ore indications were also found. The three different ore-bearing paragenesis which were indicated are the following: (1) kasolite cerussite +/- U-Ti-oxides, uranites, U-bearing micas, sulphides; (2) cerussite +/- epigene Agminerals, kasolite, goethite, jarosite; and (3) galena (with Ag-content), sphalerite +/- Cusulphides, pyrite, hematite, goethite (SZABÓ, 2002, SZABÓ & VINCZE, 2002).

The University of Miskolc conducted new research on the area of the Bán Valley to sample the outcrops of the mineralization and to examine it from a point of view of HFSE. Surface sampling was supported by a Gamma Surveyor scintillation detector. On the field the instrument was used in searching mode to find locations with elevated gamma activity, where spectral measurements were also carried. Measured K concentrations are between 1.9-5.6 %, eU between 4 and 150 ppm, eTh between 6 and 16 ppm. Where eTh is relatively higher, eU is usually lower. Sampling points are often connected to rock debris exposed by abandoned trenches, roots of fallen trees, and only rarely are in situ rock bodies. The highest U concentrations were indicated in debris-rich soils. The measuring points are often in the close vicinity of former trenches.

Samples were collected from debris and rocks indicated to have high U or Th content, as well as from high U-rich soils. Chemical composition of nine selected samples was measured by ICP-AES and ICP-MS. Results shows high SiO₂ and Al₂O₃ (about 60–80 wt% and 10–20 wt%, respectively) with low CaO and MgO (maximum 1-2 wt%, but generally below 1 wt%) furthermore slightly various Fe₂O₃, Na₂O and K₂O (1-7 wt%, 1-4 wt% and 0.5-6 wt%). Relatively higher Al₂O₃ and K₂O as well as lower SiO₂ concentration values of the soil samples suggest the presence of clay minerals. The sample which is indicated by the scintillation detector as U-poor, and relatively Th-rich, have the highest Al₂O₃, Fe₂O₃, MgO and K₂O concentrations, indicating its higher mica content. The highest U-concentration (114 ppm, about 42 times enrichment compared to the upper crust; RUDNICK & GAO, 2003) measured is connected to a rock debris sample, while the second higher value (78 ppm) to a soil sample. Although the soil sample contain other trace elements (REEs, Zr, Th) in slightly elevated concentrations, the U-rich rock debris is poor in them. On the other hand, the sample which is low in U is relatively rich in other trace elements, however highest values are connected to an aleurolite sample with medium U-concentration. High trace element contents of soil sample are probably the result of absorption processes.

Mineralogically the samples mainly consist of quartz, muscovite and albite, other minerals are not detectable with the XRD. With electron microprobe analyses abundant carbon-bearing Pb-Fe minerals (surite?) were detected, which

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usually surround pyrite and include micrometric Ag-sulfide inclusions. Dispersed galena (with Se and Cd), in most of the cases in albite, is common, as well as Sr-bearing barite. Other accessory minerals are monazites (with Th, U, Sr and S), up to more ten μ m-s in diameter, xenotime, zircon, fluorapatite and Ti-oxide (with Nb or W). Until now, despite the significant amount of Pb-bearing phases present, no Ubearing phases were found, except some monazite grain, and a mineral phase which has Ti:U ratio about 1:1 (in wt%). This ratio is the closest to the mineral brannerite (or its Thbearing variety, absite), but the data are not reliable enough for clear identification.

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References

- RUDNICK, R. L., GAO, S. (2003): In: RUDNICK, R. L. (Ed.): The crust. Treatise on Geochemistry, Vol. 3. Elsevier, pp. 1–64.
- SZABÓ, I. (2002): In: SZAKÁLL, S., MORVAI,
 G. (Eds): Érckutatások Magyarországon a 20.
 században. Közlemények a Magyarországi Ásványi Nyersanyagok Történetéből XIII.
 Miskolc – Rudabánya: Miskolci Egyetem,
 Herman Ottó Múzeum, Érc- és Ásványbányászati Múzeum, MTA Miskolci Akadémiai Bizottság, pp. 217–234.
- SZABÓ, I., VINCZE, J. (2002): Földtani Közlöny 132, 181–221.

CRITICAL RAW MATERIAL OCCURRENCES IN HUNGARY

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Critical Raw Materials (CRM) are such kind of chemical elements and other raw materials, which are indispensable for modern technologies, thus, they have particular economic importance, but on the other hand, their supply is risky. In the European Union the first list of CRMs was published in 2011, only with 14 CRMs. The list is reviewed in every three years, the most recent one was issued in 2023, with 34 CRMs. Some examples for CRMs include Light and Heavy Rare Earth Elements (LREE and HREE), Ta, Ti, Li, B, Mg, Mn, Sr, graphite, barite, bauxite.

The first comprehensive work on the CRMs of Hungary was made during the CriticEl project, conducted by the University of Miskolc (SZAKÁLL, 2014). During the project, the main focus was on the REEs. The following occurrences were analysed: Recsk ore deposit, volcanics of Mecsek Mts., Velence Mts., Mn-Be anomaly of Bükkszentkereszt, Mn-deposit of Úrkút, Hungarian bauxite deposits, coal deposits in Mecsek Mts., Rudabánya ore complex, rock waste of Fehérvárcsurgó, and Palaeozoic metamorphic rocks of the Cserehát Mts. In the following paragraph the most interesting results are summarized.

In volcanics of the Mecsek, high REE concentrations were measured (500-550 ppm in phonolite), with at least 14 different REE-bearing minerals, including oxides and carbonates. In the granitoids of Velence Mts. the REEconcentration is not high (maximum 225 ppm), but on the other hand, oxidated beforsite from the same locality can contain REEs up to 740 ppm, mainly in monazite (in drillings) and florencitegoyazite (in the oxidated zone). REEs concentration of monchiquite of the same region is not too high, but it contains REE-phosphates, oxides and carbonates. In the Mn-Be-anomaly of Bükkszentkereszt, Bükk Mts., the HREE concentrations are surprisingly high, up to two times the value of the Mecsek phonolite. They are connected to apatite and Mn oxides. In the albite-quartz veins of the country rock metarhyolite xenotime-(Y), aeschynite-(Y) and pyrochlore were also found. In the Mn-deposits of Úrkút, REE-concentrations are between 90 and 387 ppm, and the middle REEs are enriched the mostly. The REEs are partly connected to apatites, and partly absorbed on clay minerals. can **Bauxites** have significant **REEs** concentration ppm), (400 - 800)in various minerals.

New research has also been carried out as a continuation of this project by the University of Miskolc, mainly in NE Hungary. In the SE and NE part of the Bükk Mts., significant REE + Y enrichment occur, up to 1900 ppm, in metavolcanics and siliciclastic metasedimentary rocks. The REE-minerals are REE-phosphates, carbonates, and Nb-Ti complex oxides. In these rocks several other elements are enriched, including Zr, Th, and among the CRMs Nb and Ta, and probably Li (NÉMETH *et al.*, 2023). Also, in the Bükk Mts. a highly B-enriched (with 1770 ppm) rock body occur, with rock-forming axinite-(Fe) (BALASSA *et al.*, 2023b).

In the Bükkalja region Miocene volcanics can have relatively elevated REE+Y (~280 ppm) and Ti-concentrations. These formations are also associated with placer deposits, rich in ilmenite, zircon and allanite. Occurrences sampled so far are in the vicinity of Tibolddaróc and Cserépváralja.

In rock bodies from Rágyincs Valley, Uppony Mts. and Rakaca Valley, Szendrő Mts., REE + Y concentrations are 130–590 ppm and 210–550 ppm, respectively, incorporated to phosphates and carbonates. TiO₂ concentration often reach 1%. In Uppony Mts., P concentration also can be relatively high (10 times enrichment compared to the upper crust), as well as V. These localities

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also have graphite as a CRM (BALASSA *et al.,* 2023a, LESKÓNÉ MAJOROS *et al.,* 2021).

It is clear from these few examples that there are many CRM occurrences throughout Hungary, and it is worth doing further research in this topic.

References

- BALASSA, CS., NÉMETH, N., KRISTÁLY, F. (2023a): Geosciences and Engineering, 11(1), 89–103.
- BALASSA, CS., NÉMETH, N., KRISTÁLY, F. (2023b): Tertiary and Quaternary Strata, 2, 4–7.

- LESKÓNÉ MAJOROS, L., LESKÓ, M.ZS., SZAKÁLL, S., KRISTÁLY, F. (2021): Multidiszciplináris Tudományok, 11, 90–97.
- NÉMETH, N., KRISTÁLY, F., BALASSA, Cs. (2023): Journal of Geochemical Exploration, 246, 107159.
- SZAKÁLL S. (ed.) (2014): Ritkaföldfémek magyarországi földtani képződményekben. CriticEl Monography Series V., Miskolc: Milagrossa Kft.

ORE GENETIC STUDY OF THE OSTRA POLYMETALLIC MINERALI-ZATION

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Discovered during barite exploitation in the 1960s, the Ostra (Suceava County, Romania) Cu-Zn-Pb massive sulfide (MS) mineralization is situated in the northern range of the Eastern Carpathians. Barite mining lasted until the 2000s, but only a few old studies addressed this mineralization, leaving detailed mineralogical, geochemical chemical, and mineral data unavailable. Its genesis is debated, and no detailed modern deposit model is set up. Some previous research considered the barite epigenetic and Mesozoic in origin (IANOVICI et al., 1963, 1966), while ILUTI & POPA (1970) considered it as syngenetic with the nearby Paleozoic Cu-Pb-Zn VMS mineralization (Leşu Ursului).

The study area is within the Ordovician Tulgheş terrane of the Alpine Bucovinian Nappes, known for containing Cu, Pb, Zn \pm Au, Fe-Mn, and barite (\pm sulfides) deposits. The main lithologies include sericite-chlorite schists, greenschists, acid metavolcanics, metacherts, and carbonate rocks. The known VMS base metal deposits are associated with rhyolitic-sedimentary rocks (KRÄUTNER, 1988).

Our study on the Ostra polymetallic mineralization evaluated its deposit type and economic significance as well as modelled oreforming fluids through detailed field mapping, microscopic petrography, SEM-EDS observations, electron probe microanalysis (EPMA), whole rock- and stable isotope geochemistry, as well as fluid inclusion studies (petrography, microthermometry, Raman spectroscopy).

We have identified several massive sulfide lenses, which were always associated to the porphyroid rock (metavolcanite with rhyolitic protolite). Clayey alteration of the immediate host rock is common. Barite can be either associated with distal parts of the massive sulfide lenses, or it can form massive bodies (without sulfides) in the altered porphyroid rock. It may also form barite rosettes in fine grained pyrite matrix and tabular coarse-grained texture in ironoxide matrix.

The polymetallic mineralization consists of pyrite, chalcopyrite, sphalerite, galena, Zntennantite, marcasite, and barite. Significant differences were found between the topographically upper and lower massive sulfide lenses. The lower lens contains As-rich pyrite (colloform and framboidal texture is also present, Fig. 1), Ag-bearing Zn-tennantite, sphalerite, galena, and chalcopyrite, while the upper lens is mainly composed of pyrite and marcasite. Gold (up to 13 ppm) and silver (up to 212 ppm) were found only in the lower lens.



Fig. 1: BSE image of colloform pyrite aggregates from the lower outcrop. Galena layers are also identified in the pyrite.

Primary L+V fluid inclusions of barite suggest trapping from a homogeneous parent fluid, which can be modelled in a methanebearing NaCl-H₂O system. Homogenization (i.e., minimum temperatures formation temperatures) are between 145–193 °C, while the observed salinities (5.26-7.59% NaCl equiv. origin. wt%) suggest evolved seawater Continuous cooling from proximal to distal zones were documented (Fig. 2).

The mechanism of barite formation and the textural characteristics of the barite rosettes are syngenetic (formed together) with pyrite, which is contradicting to the previously thought Mesozoic epigenetic origin. The Cu:Zn:Pb ratios and S isotope data support the submarine hydrothermal origin, as well as the continuous transition between the distal barite and massive sulfide bodies observed in the "lower outcrop" (Fig. 2), the appearing clay-rich rock alteration, and the presence of colloform and framboidal

pyrite in both proximal and distal zones. However, massive tabular barite might represent later remobilization processes.

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References

- IANOVICI, V., GIUȘCĂ, D., TĂNĂSESCU, F., PITULEA, G. (1963): 6th Congress of the Carpato-Balcanic Association.
- IANOVICI, V., PITULEA, G., LEMNE, G. (1966): Studii și Cercetări de Geologie, Geofizică, Geografie, Seria Geologie, 11, 331–340.
- ILUTI, M., POPA, I. (1970): Revista Minelor, 21, 159–164.
- KRÄUTNER, H.G. (1988): In: ZOUBEK, S.V. (Ed.): Precambrian in Younger Fold Belts. London: John Wiley & Sons, pp. 625–638.



Fig. 2: Photo of the sampling profile of the lower massive sulfide lens and its altered host rock. Sampling locations as well as the basic characteristics of the collected samples are also shown. (py-pyrite, sph sphalerite, gn-galena, ccp-chalcopyrite, fhl-fahlore, cv-covellite, brt-barite, qtz-quartz, kln-kaolinite, ms-muscovite, ilt-illite).

ERTLITE, NEW TOURMALINE-SUPERGROUP SPECIES WITH TETRA-HEDRAL BORON

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Ertlite is a new member of the tourmaline ideal formula supergroup. With the Na(Al₃)Al₆(Si₄B₂)(BO₃)₃O₁₈(OH)₃(O), it represents a new tourmaline species with tetrahedrally coordinated boron. It was found in a B-rich granitic pegmatite in the Sahatany Valley, central Madagascar, where it formed during a late stage of open pocket crystallisation in a highly fractionated granitic pegmatite dike of the LCT type. Pink crystals of the tourmaline are in part rimmed by, or intergrown with fibrous prisms in parallel growth of grey-yellowishbrown tourmaline, and are chiefly associated with behierite, quartz and K-feldspar.

The pink tourmaline type forms euhedral crystals up to c. 5–10 mm in diameter, which are transparent and have a vitreous lustre, conchoidal fracture and white streak. It has the Mohs hardness of ca. 7, a calculated density of 3.038 g.cm⁻³ and is uniaxial with $\omega = 1.659(2)$, $\varepsilon = 1.639(2)$ at 589.3 nm white LED light, while pleochroism is light grey in the omega direction and colourless in the epsilon direction.

The tourmaline has a trigonal symmetry, space group R3m, a = 15.6509(8) Å, b = 15.6509(8) Å, c = 7.0406(5) Å, V = 1493.55 (19) Å³ and Z = 3. The crystal structure was refined to $R_1 = 1.99$ % using 2192 unique reflections collected with MoKa X-ray source. The structure was refined using neutral scattering factors. Occupancies of X-, Y-, Z- and T- cation sites were refined as free variables. Occupancies of X-, Y-, and T-sites were refined using two major elements located in the respective sites, i.e., Na vs Ca at the X-site, Al vs Li at the Y-site, and Si vs B at the T-site. The hydrogen atoms were located in a residual electron-density map. The empirical formula of the potentially new tourmaline was calculated on the basis of Y+Z+T+B = 18 apfu and $(OH^-+F^-+Cl^-+O^{2-}) = 4$ apfu. The structural refinement showed full occupancies of the Y-, Z-, and T-sites, resulting in the final empirical formula:

The ideal formula of the potentially new tourmaline conforms to both the dominant-valency and dominant-constituent rules (BOSI *et al.*, 2019). The dominant end-member approach (HAWTHORNE, 2023) provided an identical result. Based on the analysis, the structural formula contains 57.3 mol. % of the end-member (limited by the 0.573 apfu Na at the X-site).

The closest end-member compositions of valid tournaline species are olenite, aluminooxy-rossmanite, and darrellhenryite, related by the substitutions: ${}^{T}Si^{4+} + {}^{V}O^{2-} \rightarrow {}^{T}B^{3+} + {}^{V}OH^{-}$ accompanied by the disorder exchange ${}^{V}O^{2-} + {}^{W}OH^{-} \rightarrow {}^{V}OH^{-} + {}^{W}O^{2-}$; ${}^{X}\Box + {}^{T}Si^{4+} + {}^{T}Al^{3+} \rightarrow {}^{X}Na^{+} + 2({}^{T}B^{3+})$; and ${}^{Y}Li^{+} + 2({}^{T}Si^{4+}) \rightarrow {}^{Y}Al^{3+} + 2({}^{T}B^{3+})$, respectively.

Tourmalines with high ^TB contents seem to be stable especially in low-temperature hydro-thermal systems oversaturated in boron and high $f(CO_2)$ in fluid phase.

References

- BOSI, F., BIAGIONI, C., OBERTI, R. (2019): Minerals, 9(10), 591.
- HAWTHORNE, F.C. (2023): Mineralogical Magazine, 87(3), 494–504.

REVISION OF THE MINERALS OF THE ROMÉITE GROUP FROM HUNGARIAN LOCALITIES

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Roméite group belongs to the pyrochlore supergroup, which has a general formula of $A_{2-m}B_2X_{6-w}Y_{1-n}$, where (in the roméite group) ^[8]A = **Ca**, **Pb**, Fe^{2+} , Sb^{3+} , Bi^{3+} , Cu^{2+} , Ag, Na, []; ^[6]B = **Sb**⁵⁺, Si, Ti, Fe³⁺; X = **O**, OH, F; Y = **OH**, **F**, **O**, [], H₂O (dominant ions are indicated by bold letters), and m = 0-2, w = 0-0.7, n = 0-1(ATENCIO et al., 2010). The roméite group (B =Sb⁵⁺, X = O) currently includes five mineral species approved by the IMA ("A" status): fluorcalcioroméite (Y = F, A =Ca). hydroxycalcioroméite (Y = OH, A = Ca), hydroxyferroroméite ($Y = OH, A = Fe^{2+}$), oxycalcioroméite (Y = O, A = Ca),and oxyplumboroméite (Y = O, A = Pb). In addition to these species, there are five more questionable members in the group ("Q" status): bindheimite (Y = O, OH?, A = Pb), bismutostibiconite (Y = O, OH?, A = Pb)A = Bi), monimolite (Y = O, A = Pb; should be discredited according to HÅLENIUS & BOSI, 2013), stetefeldtite (Y = O, OH?, A = Ag) and stibiconite (Y = OH, $A = Sb^{3+}$). It is also worth mentioning the non-approved ("N" status) fluornatroroméite (Y = F, A = Na) and the discredited ("D" status) partzite (Y = O, OH?, A = Cu).

The occurrences of antimony-oxide minerals in Hungary were reviewed by SZAKÁLL *et al.*, (2000), who mentioned the following members of the roméite group (the localities are given in parentheses at the level of settlement): stibiconite (Pátka, Lovasberény, Parádfürdő, Gyöngyösoroszi, Mátraszentimre, Gyöngyössolymos, Parádsasvár, Gyöngyös-Mátraháza, Rudabánya, Erdőbénye, Rátka), bindheimite (Szabadbattyán, Pátka, Lovasberény, Parádfürdő, Rudabánya) and partzite (Rudabánya). In the present study, re-examination of some of these occurrences is reported. The examined minerals form white, pale yellow, yellow, rarely brown and green, powdery coatings or earthy aggregates. They often appear on stibnite or form pseudomorph after it (Fig. 1).

In other cases, they are weathering products of tetrahedrite-tennantite mixed with poorly crystalline arsenates. Well-crystallized specimens are not found in any of the localities in Hungary.

First, X-ray powder diffraction investigations were performed, which determined that the samples belong to the roméite group. This is not always an easy task, as only very few reflections from roméite-group minerals appear on X-ray patterns, since they are generally poorly crystallized, mixed with other phases, as well as crystallize in the cubic system, so they have few peaks anyway. Even in better cases, the determination was made based on only five or six reflections at 5.92–5.95, 2.96–3.16 (doublets on lead-free samples), 2.55–2.60, 1.82–1.84 and 1.55–1.57 Å.



Fig. 1: Hydroxycalcioroméite pseudomorph after stibnite from the Teréz Hill, Mátraszentimre. Width of the picture: 2.5 cm. Collection of the Herman Ottó Museum, Miskolc. Photo: S. Szakáll.

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The chemical composition was determined by electron microprobe analyses. Since the materials were examined mostly porous aggregates, the totals of the analyses were often considerably less than 100%. For this reason, the water contents of the minerals could not be estimated as the differences between analytical totals of 100 wt% and the total oxide concentrations determined by microprobe. Although no quantitative data on water content were obtained, the intensity of the OH band of the IR curves around 2500 - 3750 cm^{-1} was found to be a suitable indicator for the water content: where the OH band is absent or weak, no or little OH content (i.e. oxyspecies) was assumed; in the case of hydroxyspecies, the OH band is medium or strong, while in the case of very strong OH band, the sample also contained admixed hydrated minerals.

In the following paragraphs, the occurrences of the roméite-group minerals in Hungary will be discussed by mineral species. As studies are still ongoing, further results and clarifications are expected in the future.

Hydroxycalcioroméite was identified on the Teréz Hill, Mátraszentimre; Fehér-kő Hill, Parádfürdő; Hercegköves Hill, Rátka and Andrássy-I mine, Rudabánya. In the earlier literature they were referred to as stibiconite.

Oxycalcioroméite was detected at Ligetmajor, near Erdőbénye; Hercegköves Hill, Rátka and Andrássy-III mine, Rudabánya. Previously, they were also described as stibiconite.

Hydroxyferroroméite was identified from the Fehér-kő Hill, Parádfürdő, which is the fourth occurrence of this species in the world according to the mindat.org database.

Oxyplumboroméite ("bindheimite"): among the minerals listed as bindheimite in the previous Hungarian literature, the presence of oxyplumboroméite has been confirmed in the following localities based on this study: dumps of the abandoned lead ore mine at Szabadbattyán; Fehér-kő Hill, Parádfürdő and Polyánka and Andrássy-I mines, Rudabánya. It should be noted that bindheimite is still a valid, albeit questionable mineral species according to IMA.

"Stibiconite" is also a valid, but questionable species. In the older Hungarian literature (e.g., SZAKÁLL *et al.*, 2000, 2016), it is mentioned from numerous localities, but the new instrumental tests carried out so far have only confirmed its presence in the following sites: Asztag-kő Hill, Gyöngyössolymos and Teréz Hill, Mátraszentimre.

"Bismutostibiconite" is also a questionable species and has only been described from a few localities in the world. At the *A*-site Bi-dominant roméite-group mineral was identified from the Meleg Hill, Lovasberény, but more detailed study of this mineral is planned for later.

"Partzite" was discredited by MILLS *et al.*, (2016). In Hungary, it has been described from the Andrássy-III mine, Rudabánya, in some publications as "cuproroméite" according to the new nomenclature of the pyrochlore-supergroup minerals (ATENCIO *et al.*, 2010). However, our current studies suggest that this is not a single phase, but a mixture of (oxy- or hydroxy-) calcioroméite and amorphous hydrated Cu and Fe arsenates.

References

- ATENCIO, D., ANDRADE, M. B., CHRISTY, A. G., GIERÉ, R., KARTASHOV, P. M. (2010): Canadian Mineralogist, 48, 673–698.
- HÅLENIUS, U., BOSI, F. (2013): Mineralogical Magazine, 77, 2931–2939.
- MILLS, S. J., CHRISTY, A. G., RUMSEY, M. S., SPRATT, J. (2016): European Journal of Mineralogy, 28, 1019–1024.
- SZAKÁLL, S. FEHÉR, B., TÓTH, L. (2016): Minerals of Hungary. Szeged: GeoLitera (in Hungarian).
- SZAKÁLL, S., PAPP, G., SAJÓ, I., KOVÁCS, Á. (2000): Acta Mineralogica-Petrographica, 41, 31–62.

DISTINGUISHING UNSTABLE HEMIHYDRATE POLYMORPHS BY X-RAY POWDER DIFFRACTION

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Gypsum binders are widely used in the building products industry. Due to their good crystallinity, they can provide excellent performance and are suitable for use in various practical applications, e.g. to improve the mechanical strength of self-leveling mortars and plasters.

Gypsum belongs to the group of hydrous sulfate minerals, the dihydrate of calcium sulfate (CaSO₄·2H₂O). Calcium and sulfate ions are bound in ring-shaped units whose threedimensional arrangement results in tubular structures. The water molecules of the crystal water are incorporated into these tubes. As this water is only loosely bound by adsorption, dehydration is possible in all stoichiometric ratios (FELDMANN & DEMOPOULOS, 2012). If gypsum is heat-treated at a temperature of over 90 °C, a calcium sulfate hemihydrate is formed by the removal of three quarters of the water with the following reaction (VAN DRIESSCHE *et al.*, 2017):

$CaSO_4 \cdot 2H_2O + dQ \rightarrow CaSO_4 \cdot 1/2H_2O + 3/2H_2O$

A distinction is made between two types, the α -hemihydrate, which is produced by wet processes (e.g. autoclaving) and represents a fully formed hexagonal crystal form, and the β -hemihydrate, which is produced by dry methods (e.g. calcination) and represents a fine crystalline formation due to the rapid transformation of the dehydrate. Above 120 °C, all crystal water is removed and anhydrite is formed, of which two forms are known: the reducible anhydrite II modification, which is stabilized by heat treatment, and the still reactive, soluble anhydrite III phase (VAN DRIESSCHE *et al.*, 2017; SINGH & MIDDENDORF, 2007).

Depending on the treatment conditions, the α hemihydrate binders may contain β -hemihydrate and AIII and AII as undesirable products, which can have a significant effect on the important product properties (e.g. setting time) of the material.

It was reported that the morphologies of α and β -hemihydrates (i.e., the changes in their surface conditions) strongly influence their thermal behavior, since crystals with high aspect ratios show an apparently higher thermal stability than that with low aspect ratios. Further, α hemihydrate differs from the b-form in terms of several parameters (crystal structure, specific surface area, solubility, and effects of thermal analysis) (ZHANG *et al.*, 2019). It is known α hemihydrate has a monoclinic structure, while β hemihydrate is trigonal, AIII is hexagonal and AII is orthorhombic. (ZHANG *et al.*, 2019; CHRISTENSEN *et al.*, 2008; BEZOU *et al.*, 1995; KIRFEL & WILL, 1980)

However, the designation of these phases is associated with many challenges. One of the most suitable methods is the detection of their different crystal structures by XRD analysis. In this study, we determined the phase components of an industrially produced α -hemihydrate binder.

X-ray powder diffraction analysis was carried out on a Bruker D8 Discover instrument, with Cu-K α radiation (40 kV, 40 mA generator settings). The measurements were run in Bragg-Brentano geometry, with symmetric 2,5° axial Soller slits. Recording was done with LynxEye XE-T position sensitive detector (PSD) in high energy resolution mode, 2° window opening. Scans were recorded in the 2–110°(2 θ) range, with 0.007°(2 θ)/4 sec counting time for the first scan, then 20-36°(2 θ) range, with 0.006°(2 θ)/39 settings to observe the time dependent

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transformations. The powder specimens were arranged in top loaded shallow low background Si single crystal sample holder. Identification of components crystalline was done bv Search/Match, on ICDD PDF2 (2005) database in the Bruker DiffracPlus EVA software. Quantitative composition was calculated with Rietveld refinement in Bruker TOPAS4. instrumental profile determined on SRM640a Si standard. Crystallographic information for the identified phases was taken from ICSD and AMCSD databases.

During the measurements, we found that this task is challenging because the peaks of the individual modifications are very close to each other and it is not possible to reliably identify them based on the PDF cards and the peak maxima alone, so Rietveld refinement is required. Moreover, short measurements are required, since in contact with air the metastable modifications are rapidly changing into the monoclinic structure. After refining on the available monoclinic, orthorhombic and trigonal hemihydrate structures, on the residual pattern peaks resembling that of hexagonal the hemihydrate were observed. The measurements and Rietveld refinement were repeated on a newly synthesized sample, returning the same quantitative results, unit cell parameters and fitting residual. Thus, we can assume the existence of a hexagonal modification, which has the shortest period of stability. Unfortunately, our current work could not solve its structure, and data from literature was not found to fit the measured patterns. However, our assumption is supported by the frequent reports of ideally symmetrical hexagonal hemihydrate plates obtained by hydrothermal synthesis. These hexagonal crystals always present monoclinic structure (SEUFERT et al., 2009, ZHANG et al., 2022, SUN et al., 2020), independent on platy or prismatic habit, controlled by salt concentration of the hydrothermal media. In our samples the needle and prismatic crystals are dominant, thus

the hexagonal shape is less obvious, but its visible.

A noteworthy observation is the absence of amorphous material(s). Also, the very fast transformation of unstable hemihydrates into the monoclinic α -type present a challenge for the phase identification by XRD, leaving only minutes for sample preparation and measurements.

References

- BEZOU, C., NONAT, A., MUTIN, J-C., LEHMANN, M. S. (1995): Journal of Solid State Chemistry, 117(1), 165–176.
- CHRISTENSEN, A. N., OLESEN, M.,
- ERENIUS, Y., JENSEN, T. R. (2008): Chemistry of Materials, 20, 2124–2132.
- FELDMANN, T., DEMOPOULOS, G.P. (2012): Hydrometallurgy, 129, 126–134.
- KIRFEL, A., WILL, G. (1980): Acta Crystallographica, B36, 2881–2890.
- SEUFERT, S., HESSE, C., GOETZ-NEUNHOEFFER, F., NEUBAUER, J. (2009): Cement and Concrete Research, 39, 936–941
- SINGH, N.B., MIDDENDORF, B. (2007): Progress in Crystal Growth and Characterization of Materials, 53, 57–77.
- SUN, X., LI, Z., WANG, X., ZHANG, G., CUI,
- P., SHEN, H. (2020): Industrial & Engineering
- Chemistry Research, 59(31), 13979–13987.
- VAN DRIESSCHE, A. E. S., STAWSKI, T. M., BENNING, L. G., KELLERMEIER, M. (2017): In: VAN DRIESSCHE, A. E. S., KELLERMEIER, M., BENNING, L. G., GEBAUER, D. (Eds.): New perspectives on mineral nucleation and growth. Springer, pp. 227–256.
- ZHANG, X., JIN, B., WANG, X., LIU, X., YANG, L. (2019): Polyhedron, 173, 1–5.
- ZHANG, X., JIN, B., WANG, X., LIU, X., LI, S., YANG, L. (2022): Particuology, 62, 98–103.

EVIDENCE FOR AN ULTRA UNSTABLE HEMIHYDRATE POLYMORPH BY X-RAY DIFFRACTION

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Hemihydrate types are usually differentiated based on particle or crystal morphology, in relation with characteristically different physical specific properties. However, beyond experiments, structure based analytical results show the presence of the stable monoclinic α type, bassanite. Beyond the existence of trigonal orthorhombic, and hexagonal polymorphs - the latter being less explored, it is plausible to assume, that at least more varieties of the polymorphs should exist, according to retained structural water amount and molecular orientation in the lattice (ZHANG et al., 2019; BEZOU et al., 1995).

X-ray powder diffraction analysis was carried out on a Bruker D8 Discover instrument, with Cu-K α radiation (40 kV, 40 mA generator settings). The measurements were run in Bragg-Brentano geometry, with symmetric 2,5° axial Soller slits. Recording was done with LynxEye XE-T position sensitive detector (PSD) in high energy resolution mode, 2° window opening. Scans were recorded in the $2-110^{\circ}(2\theta)$ range, with $0.007^{\circ}(2\theta)/4$ sec counting time for the first scan, then 20–36°(2 θ) range, with 0.006°(2 θ)/39 settings to observe the time dependent transformations. The powder specimens were arranged in top loaded shallow low background Si single crystal sample holder. Identification of crystalline components was done by Search/Match, on ICDD PDF2 (2005) database in the Bruker DiffracPlus EVA software. Quantitative composition was calculated with Rietveld refinement in Bruker TOPAS4, instrumental profile determined on SRM640a Si standard. Crystallographic information for the identified phases was taken from ICSD and AMCSD databases.

Results have revealed that there is at least one phase which in air is transforming into the stable

polymorphs, most likely monoclinic. However, since the monoclinic type is the end product, the transformation steps through trigonal and orthorhombic types could be too quick to be observed by our method. A peculiarity of the measurements is that no sample preparation can be applied, and the as-synthesized material has to be kept under cooling (<5 °C) and air-tight, to be immediately measured after unpacking. Grinding, either dry or under alcohol or acetone, leads to the disappearance of the characteristic peaks. The measurements were repeated several times for statistical observations, showing the dependent same pattern and same time important transformations. The most transformations occur in the first 5 to 10 minutes of the contact with air.

We assume the existence of at least one hexagonal polymorph, unevidenced by now due to its instability. This assumption is based on the resemblance between characteristic ICDD PDF cards and fitting residual of Rietveld refinement performed on the stable hemihydrate structures.

Our observations were only made possible by the use of the energy dispersive detector in high resolution mode, allowing acceptable statistics for the short counting time, yet small recording intervals. With any other settings, the overlapping peaks are not distinguished and the materials transformations occur well before being detected.

References

- BEZOU, C., NONAT, A., MUTIN, J-C., LEHMANN, M. S. (1995): Journal of Solid State Chemistry, 117(1), 165–176.
- ZHANG, X., JIN, B., WANG, X., LIU, X., YANG, L. (2019): Polyhedron, 173, 1–5.

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CONNECTING EAST WITH WEST: CONSTRAINING POLYGENETIC VARISCAN TO POST-VARISCAN METAMORPHISM IN THE MARMAROSH/MARAMURESH MASSIF, UKRAINE/ROMANIA

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The Carpathian Mountains belt in the Central Europe extends for more than 1300 km and is composed of the internides, deformed mainly in the Mesozoic and containing crystalline cores of Pre-Alpine (mostly Variscan) basement, and the externides that were deformed during the Cenozoic (SCHMID et al., 2008). The Outer Carpathians consist of a complex nappe system which verges towards the outer parts of the arcuate orogen and formed during Cretaceous to Neogene times. The basement of the folded sedimentary basin(s) is known only from olistoliths and exotic pebbles (POPRAWA et al., 2006; GAWEDA et al., 2019). In the Eastern Carpathians, the crystalline basement underlying the Outer Eastern Carpathians sedimentary basins is exposed as Marmarosh/Maramuresh Massif, located at the Ukrainian/Romanian border. This work reports the first data on the metamorphic Variscan evolution of the (Ukraine) Marmarosh and Maramuresh (Romania) massifs in the Outer Eastern Carpathians. Geothermobarometry determinations coupled with U-Th-Pb dating of monazite, apatite, titanite and rutile was used to construct P-T-t paths. These clockwise P-T-t paths evolve from 560-630 MPa and 515-535 °C to c. 900-1180 MPa in the north (Ukraine), while in the southern nappe (Romania), the P-T-t conditions evolve from 455-620 MPa and 545-555 °C, (M1) through to 670–745 MPa and 540–560 °C,

(M2) to 910–965 MPa and 645–660 °C, (M3). The northernmost nappes were likely the structurally lowest in relation to the southern Variscan progressive metamorphism ones. related to nappe stacking climaxed at c. 350 Ma, as documented by U-Pb rutile and U-Th-Pb monazite dating. In both regions post-kinematic exhumation to 700-500 MPa, 550-630 °C MPa (M3/M4) and then to the titanite stability field (M4/M5) was dated at 330–317 Ma, using the U-Pb system on apatite and titanite. Subsequent Permian retrogression and exhumation was constrained to 290-280 Ma by U-Pb rutile and apatite and U-Th-Pb monazite dating. These data link the Marmarosh/Maramuresh massifs to the Central European Variscides that represented part of the external zone of the Variscan orogen.

Both the age and P-T conditions of the Marmarosh/Maramuresh Massif are similar to that of pre-Mesozoic crystalline basement of the Alps (SCHULZ, 2021), recording the same Variscan and post-Variscan collision-related crustal thickening, exhumation and Permian shearing. The principal difference is the lack of Meso-Variscan granitoids and HP/HT rocks in the Marmarosh/Maramuresh Massif, that is typical of the pre-Mesozoic basement of the Alps (VON RAUMER *et al.*, 2013 and references therein). The metamorphic basement of the Marmarosh/Maramuresh Massif thus likely formed part of the external zone of Variscan

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orogen, most probably overthrust onto the Baltica/Laurussia margin. We infer that all Variscan crystalline basement fragments in the Alps and Carpathians probably represent remnants of the same microcontinent, collided to Laurussia during Variscan orogenesis and dismembered during Alpine orogenesis.

References

- GAWĘDA, A., GOLONKA, J., WAŚKOWSKA, A., SZOPA, K., CHEW, D., STARZEC, K., WIECZOREK, A. (2019): International Journal of Earth Sciences, 108, 1409–1427.
- POPRAWA, P., MALATA, T., PÉCSKAY, Z., KUSIAK, M.A., BANAŚ, M., PASZKOWSKI, M. (2006): Geolines, 20, 110–112.
- SCHMIDT, S.M., BERNOULLI, D., FÜGENSCHUH, B., MATENCO, L., SCHEFFER, S., SCHUSTER, R., TISCHLER, M., USTASZEWSKI, K. (2008): Swiss Journal of Geosciences, 101, 139–183.
- SCHULZ, B. (2021): Minerals, 11, 981.
- VON RAUMER, J.F., BUSSY, F., SCHALTEGGER, U., SCHULZ, B., STAMPFLI, G.M. (2013): Geological Society America Bulletin, 125, 89–108.

THE 250-YEAR-OLD EÖTVÖS MUSEUM OF NATURAL HISTORY: NEW ROLE FOR THE 21ST CENTURY

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Natural history, in its 17-19th century sense (LINNÉ, 1766-68), incorporates all objects of nature, organised into three kingdoms - plants, animals and minerals (or better: natural solids). Natural history as a separate subject, including elements of mineralogy, was introduced to the curricula of the Faculty of Philosophy of the 1635-founded Jesuit University of Nagyszombat (Trnava in Slovak / Tyrnau in German) in 1774 (BUDA et al., 2004). The Styrian-born ex-Jesuit Mathias Piller, as the first professor of natural history started teaching with his own natural history collection that was later bought for the university. This way, 2024 September is regarded as the 250th anniversary of both the natural history collection (named today Eötvös Museum of Natural History) and the start of natural history (incl. mineralogy) education at the Eötvös Loránd University (Budapest, Hungary). At an anniversary like this, a rare occasion in a human lifetime (not for all generations), it is time to consider the role of such collections.

By 1774, at the university, natural history included only two kingdoms of nature, the animal and the mineral kingdom. Botany was separated earlier, in 1770, when the Department of Chemistry and Botany was established within the newly formed Faculty of Medicine. The history of mineralogy education at the Eötvös University and the Eötvös Museum of Natural History are summarised in English by BUDA et al., (2004), further information about the collections is given in Hungarian by HARMAN-TÓTH & FELKER-KÓTHAY (2021, mineral and rock collection), HOLLÓ-SZABÓ (2021, mathematics collection), SZENTE (2021,paleontology collection) and TÖRÖK (2021, biology and paleontology exhibition).

Classical systematic natural history collections played a rather important role in

scientific research throughout the 18–20th century. The general knowledge about nature stemmed partly from the study of museum specimens, mineral and rock specimens contributed both to the description of new species and also, to the discovery of new chemical elements. Systematic collections were developed at that time with a holistic approach. The organisation state / arrangement of collections, represented by catalogues, have depicted the overall knowledge about the given kingdom, too.

Collections have grown large, needing space and restructuring from time to time. A large systematic investment into the university natural history collection took place at the end of the 19th century: in 1886, the Natural History building at Múzeum körút 4A (Budapest) was accomplished, and was opened by the Emperor of Austria and king of Hungary, Franz Joseph I. The four exhibition spaces served both education and research. The zoology and comparative anatomy exhibitions have been designed by the zoology professor Tivadar Margó, the Mineral and Rock Exhibition Halls by the professor of mineralogy and geology, József Szabó. From these four exhibition spaces, only one survived the 20th century: the biology exhibitions were destroyed by a bomb at the end of the second world war (1944/45), while the Rock Hall was demolished in 1952 as new functions needed place in the building. The Mineral Hall, complemented with the 6 showcases of the demolished Rock Hall, has been transferred to the new Lágymányos (Buda) campus of the university (Fig. 1).

Natural history collections can be statefinanced or private collections. Both survive and develop, flourish until the financial support and

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Fig. 1: Exhibition spaces of the Eötvös Museum of Natural History, around 2020, on the Lágymányos campus. 1a. The Mineral and Rock Hall in its original, protected, end of 19th century furniture (photo by Árpád Palotás). 1b. The Biology and Paleontology Exhibition is hosted in a modern glass pyramid, with recent end extinct species arranged parallel, in the sequence of evolution (photo by Tamás Váczi). 1c. The Mathematical Collection is arranged into an interactive playroom (photo by Eszter Hegyesi).

the intention for development and maintenance exist. State-financed institutions with only museum role are probably more apt to survive on the long term, embedded into the collective responsibility of a nation, but university collections, representing a small facet only of a large institution, are more sensitive to financial problems.

As our knowledge about nature increases, information is more and more separated from the objects of study. It is quite normal in the case of the living organisms, to shoot videos and photographs of observations in nature and keep data in accessible databases, but even in this case, museums keep skeletons, whole body (stuffed and wet) and anatomical preparations, too. The collection, storage and preservation of minerals and rocks are more simple, yet may involve challenges, too. In the 21st century natural history collections need to redefine their role, rethink their mission statement. The author of this paper is following with a kind of anxiety the breakthrough and spread of artificial intelligence, especially in the field of visualization. Images, videos on the web will soon contain only traces of reality. People of the 21st century, when collecting information, are largely dependent on the internet, which is invaded by spectacular, improved or created photolike images (Fig. 2) and realistic videos. Individuals soon will not be able to judge properly the real size and possible impact of animals, the weight of stones, *etc*.

In this context, while keeping the important role of scientific repository (type specimens, archived research material, *etc.*), well-known to scientists but less seen and respected by the society, the main new aim of natural history

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collections will become to be the reliable source of information, the representation of nonaugmented, real nature. Removal of the glass – let it be the showcase in an exhibition or any kind of screen, through which the modern people "observe" – is a necessity to offer and facilitate the experience of nature as it is. A new opportunity for our museum is the Árpád Juhász Exploration Room (freshly installed, still to be inaugurated), where visitors will get the real touch-on experience.

References

BUDA, Gy., PAPP, G., WEISZBURG, T. G. (2004): Acta Mineralogica-Petrographica, 45/1, 5–20.

Fig. 2: Fake crystal cave image, suggested to be from the Naica Mine-related Cave of the Crystals (Mexico), appearing on community pages in the spring and summer of 2024. (e.g., https://www.facebook.com/photo/?fbid=4202303042 70167&set=a.102502422709625). Most mineralogists are still able to recognize that the crystals depicted mostly resemble giant quartz crystals, all placed in a dripstone cave, while the Cave of the Crystals is famous for the giant monoclinic gypsum crystals. The challenge of the location is partly its limited accessibility, partly the harsh conditions, also from the photographic point of view (up to 58 °C air temperature, 90-99% relative humidity). Probably all fields of natural history – mineralogy and petrology, botany, zoology and paleontology alike – face these challenges of human wishful imagination combined with AI visualization technology.b. A real photograph of the Cave of the Crystals from 2010, by Alexander Van Driessche, from Wikipedia (https://en.wikipedia.org/wiki/File:Cristales_cueva_ de_Naica.JPG).

- HARMAN-TÓTH, E., FELKER-KÓTHAY, K. (2021): In: SCHLAY, G., TÓTH, K. (eds.): Az ELTE muzeális gyűjteményeinek jelene és jövője. Budapest: ELTE Egyetemi Könyvtár és Levéltár, pp. 55–78.
- HOLLÓ-SZABÓ, F. (2021): In: SCHLAY, G., TÓTH, K. (eds.): Az ELTE muzeális gyűjteményeinek jelene és jövője. Budapest: ELTE Egyetemi Könyvtár és Levéltár, pp. 125–134.
- LINNÉ, C. (1766–68): Systema naturæ per regna tria naturæ. 12th edition, Vol. 1–3. Holmiæ, Salvius.
- SZENTE, I. (2021): In: SCHLAY, G., TÓTH, K. (eds.): Az ELTE muzeális gyűjteményeinek jelene és jövője. Budapest: ELTE Egyetemi Könyvtár és Levéltár, pp. 115–124.
- TÖRÖK, J. K. (2021): In: SCHLAY, G., TÓTH, K. (eds.): Az ELTE muzeális gyűjteményeinek jelene és jövője. Budapest: ELTE Egyetemi Könyvtár és Levéltár, pp. 79–113.

ASSESSING OF THE PHYSICO-CHEMICAL IMPACTS OF NATURAL ZEOLITE ADDITIVES ON THE CEMENTITIOUS IMMOBILIZATION OF Cs AND Ba ISOTOPES IN BORIC ACID LIQUID WASTE

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In pressurised water reactor (PWR) systems, boric acid is used as an effective neutron absorber for activity management, assisting in the preservation of steady state operational temperature regulation. One of the primary waste streams produced by PWR during operation is liquid boric acid waste (2000 m³/year) (SUN & WANG, 2010). Low amounts of radioisotopes produced by nuclear fission, such as ¹³⁷Cs and its metastable decay daughter ^{137m}Ba, may be present in liquid waste of the system. The environmental significance of adequately storing this high-volume liquid waste has been on the increase, and if it is not properly immobilized, the radioisotopes can become bioavailable in the natural system.

Certain hydrated cement mineral phases can immobilise borates, which is how cementitious matrices can achieve physical and chemical stability (ROSTAMIPARSA *et al.*, 2023). This technique is used in several repositories across Europe, including the subterranean disposal site in Bátaapáti, Hungary (BENEDEK *et al.*, 2009).

The aim of our research is to assess the geochemical effects of two natural zeolites (i.e., clinoptilolite and mordenite) additives in sulfoaluminate cement (SAC) and ordinary Portland cement (OPC) blends for optimizing chemical and mechanical stability for immobilizing boric acid liquid waste and contained fission isotopes in solidified cement paste waste forms.

In the northeastern part of Hungary, the Tokaj-Hegyalja region is well-known for its zeolite-rich rhyolite-tuff (ZAJZON *et al.*, 2021). Two quarry sites in the region are the sources of the rhyolite-tuff samples for our study: 1) Rátka quarry, mined by JOSAB Hungary Ltd., with geo-locational position (decimal) 48.21186, 21.23374, where we collected sample ZC, Figure 1, 2) Bodrogkeresztúr quarry, mined by COLAS Hungary Ltd., with geo-locational position (decimal) 48.17386, 21.33974, where we collected sample ZM, Fig. 1).

The rhyolite-tuff samples ZC and ZM were characterized using several analytical methods, scanning electron microscopy including (secondary electron) SEM-SE, Xray- diffraction XRD, and inductively coupled plasma mass spectrometry ICP-MS. The SEM-SE results showed the presence of cylindrical and flake-like shaped grains in sample ZC, whereas sample ZM showed the presence of fibre-shaped grains within matrices. The XRD its results indicated the presence of clinoptilolite Ca₃₋₆(Si₃₀Al₆)O₇₂·20H₂O (in 54 m/m %) in sample whereas sample ZC, ZM indicated the presence of mordenite (Na₂,Ca,K₂)₄(Al₈Si₄₀)O₉₆·28H₂O (in 49 m/m %). Furthermore, the ICP-MS analyses provided concentrations of Ba (59.5±1.7 mg/kg), B (2.85±0.32 mg/kg) and Ce (0.631±0.052 mg/kg) in sample ZC, and Ba (15.2±0.7 mg/kg), B (3.18±0.53 mg/kg) and Ce (0.465±0.064 mg/kg) in sample ZM.

Furthermore, to determine if the zeolite-rich samples ZC and ZM could potentially adsorb Cs^+ and Ba^{2+} ions in boric acid liquid waste, a batch

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Fig. 1: Showing the sample collection sites (i.e. sample ZC collected from Rátka quarry and sample ZM collected from Bodrogkeresztúr quarry).

adsorption experiment was conducted. Additionally, to assess their selectivity towards Cs^+ and Ba^{2+} , samples ZC and ZM were treated with potassium copper (II) hexacyanoferrate (CuSO₄+K₄Fe(CN)₆) (KAZEMIAN *et al.*, 2006; RI *et al.*, 2023) to assess the effect of KCuHFC on the adsorption of the stated ions.

Samples ZC and ZM were crushed and sieved to $200-400 \mu m$ grainsize range. Then 50% of each sample was treated in KCuHFC solution for 48 hours, then dried in room temperature for 24 hours, whereas the other 50% of the samples were left untreated.

The adsorption test was performed by immersing both the treated and untreated samples in pure borate (40000 ppm) liquid, borate + cesium nitrate (300 ppm) liquid and borate + barium nitrate (300 ppm) liquid to simulate the Ba and Cs isotopic ratios in low level liquid waste, respectively, and then mixed at 530 rotations/minute at room temperature for 24 hours until equilibrium concentration between the liquid and solid phases is attained. The liquid phases were, then, carefully decantated from the solid phase without perturbation. The elemental concentrations of the resultant solid and liquid phases were measured using inductively coupled plasma - optical emission spectrometry (ICP-OES).

According to the ICP-OES data, the untreated sample ZC, showed the highest concentration of

 Cs^+ adsorption, whereas the KCuHCF treated sample ZM indicated the highest concentration of Ba^{2+} adsorbed. Hence, Cs adsorption capacities of the natural zeolite-rich samples did not appear to be enhanced by the KCuHCF treatment.

References

- BENEDEK, K., BOTHI, Z., MEZO, G., MOLNÁR, P. (2009): Hydrogeology Journal, 17(5), 1219–1232.
- KAZEMIAN, H., ZAKERI, H., RABBANI, M. S. (2006): Journal of Radioanalytical and Nuclear Chemistry, 268(2), 231–236.
- RI, S. H., KIM, Y. N., IM, S. J., CHOE, S. G., KIM, C. H. (2023): Journal of Radioanalytical and Nuclear Chemistry, 332(6), 2329–2337.
- ROSTAMIPARSA, M., TOLNAI, I., CZÖMPÖLY, O., FÁBIÁN, M., HEGEDŰS, M., FALUS, G., SZABÓ, C., ÓVÁRI, M., TÓBI, C., KÓNYA, P., VÖLGYESI, P., SZABÓ-KRAUSZ, Z. (2023): Journal of Radioanalytical and Nuclear Chemistry, 332(7), 2543–2557.
- SUN, Q., WANG, J. (2010): Nuclear Engineering and Design, 240(10), 3660– 3664.
- ZAJZON, N., FEHÉR, B., SZAKÁLL, S., KRISTÁLY, F. (2021): Földtani Közlöny, 151(1), 27–36.

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PERMIAN SEDIMENTARY SEQUENCE CONTAINING ANALCIME AND AUTHIGENIC AEGIRINE FROM THE BOSKOVICE BASIN (BOHEMIAN MASSIF, CZECHIA)

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The Boskovice Basin is ca. 100 km long and 3–10 km wide half-graben situated in the eastern part of the Bohemian Massif. The basin is divided into southern and northern sub-basins (JAROŠ & MALÝ, 2001). The southern Rosice-Oslavany sub-basin sediments range between late Gzhelian and Asselian, the north-ern Letovice sub-basin sediments range between the early Asselian and late Asselian or possibly up to the earliest Kungurian (OPLUŠTIL et al., 2017). The overall thickness of sedimentary record in both depocentres is uncertain, but estimated between 2 to 6 km (JAROŠ & MALÝ, 2001). Sedimentary fill of the basin consists of four formations. The two oldest formations, the Rosice-Oslavany and Padochov, occur in the southern sub-basin, while younger Veverská Bítýška and Letovice formations are present only in the northern Letovice sub-basin (JAROŠ & MALÝ, 2001).

The level of geological recognition is much better in the southern Rosice-Oslavany sub-basin due to presence of coal seams, extracted from 1755 to 1992 (HOUZAR & HRŠELOVÁ, 2016).

Apart of the coal and the diachtonous coarsegrained facies (conglomerates) at the eastern part of the basin, the most significant basin infill is alternating sandstones and mudstones of fluvial origin. Lacustrine horizons are usually X to X0 meters thick, comprising of grey sandstones, mudstones and claystones, with intercalations of bituminous limestones (JAROŠ & MALÝ, 2001; HOUZAR *et al.*, 2017).

Volcanic rocks in the Boskovice Basin are rare. They were described as keratophyres, basic andesites, trachyandesites, and subalkaline dacites (summary in HOUZAR *et al.*, 2017). The share of volcaniclastic rocks (tuffs, tuffites) is also negligible (summary in JIRÁSEK et al., 2019).

Bačov locality was first mentioned by AUGUSTA (1926) and its rich fossil record evaluated by many authors, e.g. HAVLENA & **Š**PINAR **SCHNEIDER** (1955),(1984). MIKULÁŠ & MARTÍNEK (2006), ŠIMŮNEK & MARTÍNEK (2009), and ŠTAMBERG (2014). It contains diverse flora, amphibians, actinopterygians, insects, and ichnofossils. Due its paleontological and stratigraphic to significance it was declared a natural monument in 1986, with the restricted collecting and sampling.

Despite its stratigraphic importance and number of paleontological studies, only very limited attention was paid to the lithology of the sedimentary sequence. HAVLENA & ŠPINAR (1955) divided local sedimentary sequence into 77 layers with the overall thickness 68.76 m. Rocks were reported as pelocarbonate shales, shales, claystones, laminated limestones, marls, and sandstones. Its most recent description goes for fine-grained sandstones and sandy siltstones with reddish to grey color, including laminated bituminous limestone fossiliferous horizon (MIKULÁŠ & MARTÍNEK, 2006).

The sedimentary environment for the local sequence was described as lacustrine, with alternations of the offshore and nearshore facies. The fossiliferous shaly limestone rich in organic carbon was interpreted as alluvial plain facies (ŠIMŮNEK & MARTÍNEK, 2009).

With the permission of the landowners and the natural protection authorities, we collected 55 samples in Bačov III quarry, 32 samples in Bačov II quarry, one sample in Bačov I quarry, and several samples from the natural outcrops in their vicinity.

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It turned out that predominant are siliciclastic rocks with grain sizes equivalent to mudstones, siltstones, and fine-grained sandstones, with intercalations of carbonate concretions and one single carbonate shaly horizon rich in organic carbon (fossiliferous bituminous shale). But in contradiction to previous studies, we have found out that common parts of the rocks are analcime (up to 54 wt.%), albite (up to 38 wt.%), microcline (up to 58 wt.%), and aegirine (up to 11 wt.%). Among accessory minerals, we can mention apatite, magnetite, rare zircon, and from the thin fissures filled by hydrothermal mineralization also calcite, baryte, sphalerite, celestine, and strontianite.

We can presume that the origin of the sedimentary sequence was significantly affected by the volcanoclastic influx into the sedimentary basin. It might be also responsible for the fertilizing the freshwater lake long enough to produce the fossiliferous bituminous shaly horizons.

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References

AUGUSTA, J. (1926): Sborník Státního geologického ústavu československé republic, 6, 143–219.

- HAVLENA, V., ŠPINAR, Z. (1955): Sborník Ústředního ústavu geologického, Oddíl paleontologický, 27, 7–47.
- HOUZAR, S., HRŠELOVÁ, P. (2016): Acta Musei Moraviae, Scientiae Geologicae, 101, 3–32.
- HOUZAR, S., HRŠELOVÁ, P., GILÍKOVÁ, H., BURIÁNEK, D., NEHYBA, S. (2017): Acta Musei Moraviae, Scientiae Geologicae, 102, 3–65.
- JAROŠ, J., MALÝ, L. (2001): In: PEŠEK, J. (ed.): Geologie a ložiska svrchnopaleozoických limnických pánví České republiky. Praha: Český geologický ústav, pp. 208–223.
- JIRÁSEK, J., MATÝSEK, D., SIVEK, M., MARTÍNEK, K. (2019): Geoscience Research Reports, 52, 53–61.
- MIKULÁŠ, R., MARTÍNEK, K. (2006): Bulletin of Geosciences, 81, 81–91.
- OPLUŠTIL, S., JIRÁSEK, J., SCHMITZ, M., MATÝSEK, D. (2017): Bulletin of Geosciences, 92, 95–122.
- SCHNEIDER, J. (1984): Freiberger Forschunghefte, C 395, 19–37.
- ŠIMŮNEK, Z., MARTÍNEK, K. (2009): Review of Palaeobotany and Palynology, 155, 275–307.
- ŠTAMBERG, S. (2014): Freiberger Forschunghefte, C 548, 45–60.

MULTI-LAYERED MINERAL DEPOSITS IN BIOGAS ENGINES: LESSONS FOR AND FROM GEOLOGISTS

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Biogas is a renewable source of energy, produced as a byproduct of waste management practices such as solid waste landfilling and wastewater treatment. According to the Renewables 2023 report by the Internal Energy Agency (IEA), biogas is considered as a domestic energy source that can lessen reliance on imported natural gas, thus strengthening energy security (IEA, 2024).

Combined Heat and Power (CHP) or cogeneration is a proven and ready-to-use technology where engines fuelled with biogas produce dual energy output: electricity and heat (WANG *et al.*, 2019). Energy produced is used to support the waste facilities (onsite), and excess is sold to the local utility grid.

One of the primary operational challenges of biogas based engines is the buildup of solid deposits within the combustion chambers. These deposits directly damage the engine by causing pre-ignition, physical damages: scratches and wears (ÁLVAREZ-FLÓREZ & EGUSQUIZA, 2015), leading to engine failure and significantly increasing maintenance requirements.

Here we are presenting a part of a larger investigation, formation of a layered mineral deposition on a piston crown of combustion chamber at Pusztazámor the landfill, nearby Budapest, Hungary.

On the piston surface the deposit developed into a 3-layered crust (Fig. 1) with the thickness of $\sim 2 \text{ mm}$ in ~ 13 months operation period: a dark-greyish layer attached directly to the engine surface (Layer 1), a white layer facing the combustion space where the biogas combustion occurs (Layer 3), and a layer in between (Layer 2). There is no clear boundary between Layer 1 and Layer 2, while the boundary between Layer 2 and Layer 3 is clearly marked by the texture.



Fig. 1: A cross-section showing different layers. Layer 1: microgranular aggregates; Layer 2: mixed texture (aggregated, lamellar, massive); Layer 3: glass layer with vesicles (bubble voids). BSE image.

Multiple phases, both crystalline and noncrystalline (only short-range order, amorphous) could be identified in each layer.

Layer 1 is made up mainly of amorphous granular silica aggregates with grain size less than 1 μ m, with a skeletal structure growing on the engine surface. Anhydrite (CaSO₄^{orthorhombic}) is a minor phase, and cervantite (Sb₂O₄^{orthorhombic}) is a subordinate phase here.

Layer 2 is heterogenous in texture, ranging from granular over lamellar to massive. The main phase is anhydrite, with minor amorphous silica and quartz (?), again with subordinate cervantite.

Layer 3 is a calcium-silicate glass layer (Si:Ca ~ 1:1). The glass is massive, exhibits conchoidal fracture and spherical vesicles (indicative of outgassing from the melt). Minor crystalline phases, cristobalite (SiO₂^{tetragonal}) and calcium antimonate (CaSb₂O₆^{hexagonal}) are hosted inside the glass (Fig. 2). The textural position of cristobalite resembles that of the snowflake obsidian. Calcium antimonate is a well-known opacifier in glass artefacts. A subordinate amount of wollastonite (CaSiO₃^{triclinic}) is also present.

We managed to track the source of the elements in that relatively simple fivecomponent system (Ca-S-Si-Sb-O(-H)): 1) biogas (methane with H_2S – sourcing S, and siloxanes – sourcing Si as contaminants) and 2) the lubrication oil derivatives (Ca, Sb). The progressive growth of the oxides-based heat insulating crust on the metal surface created an improperly cooled system, resulting in progressive overheating in time.

The phases and their conversion across the layers represent the temperature condition and chemical stability from "bottom to the top". Solids (amorphous silica, anhydrite, cervantite) deposited first on the metal surface. Thickening crust got overheated, leading finally to the decomposition of anhydrite, degassing of SO₂

and formation of reactive CaO, contributing to calcium silicate melt formation and ending with the crystallization of cristobalite, the fully oxidized antimony phase and wollastonite.



Fig. 2: Close-up of Layer 3 showing the textural position of relevant phases in calcium silicate glass matrix. BSE image.

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References

- ÁLVAREZ-FLÓREZ, J., EGUSQUIZA, E. (2015): Engineering Failure Analysis, 50, 29– 38.
- IEA (2024): Renewables 2023. Paris: International Energy Agency (IEA), pp. 131.
- WANG, J., YOU, S., ZONG, Y., TRÆHOLT, C., DONG, Z. Y., ZHOU, Y. (2019): Applied Energy, 252, 113445.

STRUCTURAL CHANGES AS FUNCTION OF TEMPERATURE IN THE $Y_X Ti_{1-X}$ OXIDE SYSTEM

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Rare earth oxides are frequently solid solutions of two or more rare earth cations and other heterovalent cation(s) of similar size. They can adopt wide range of crystal structures, as function of cation ratios and crystallization Mapping the possible crystal conditions. structures with changing parameters promotes both understanding crystallization conditions of rare earth oxide minerals and fine tuning synthesis pathways for technological applications. In this contribution, we applied a micro-combinatorial method to synthesize two component Y-Ti oxide layers for subsequent structure analysis as function of temperature. Our aim was to reveal the correlations between composition, structure and annealing temperature and thus to create a phase map that covers the entire Y-Ti-O system regarding the Y/Ti ratio. Variable composition samples $(Y_xTi_{1-x}O_y)$ were prepared by dual DC magnetron sputtering, in the $0 \le x \le 1$ concentration range. The structure and morphology of the oxide phases in both asdeposited and annealed samples at 600, 700, and 800 °C, were studied with transmission electron microscopy (TEM), as a function of Y/Ti ratio. A comprehensive map showing the appropriate amorphous and crystalline phases, and their occurrence regions of the whole Y-Ti-O layer system up to 800 °C. was revealed

(OLASZ *e al.*, 2024). Thanks to the applied method, it was shown that at the given experimental conditions, the $Y_2Ti_2O_7$ phase with a pyrochlore structure forms already at 700 °C without the TiO₂ and Y_2O_3 by-phases, which is remarkably lower than the required temperature for most physical preparation methods. These results demonstrate the importance and benefits of creating phase maps in materials science and technology and may contribute to modelling the crystallization conditions of more complex geological rare earth oxide minerals.

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Reference

OLASZ, D., KIS, V.K., CORA, I., NÉMETH, M., SÁFRÁN, G. (2024): Nanomaterials, 14, 925.
MORPHOLOGICAL CHARACTERIZATION OF BIOGENIC MAGNETITE NANOPARTICLES WITH DISTINCT SHAPES

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We used electron tomography to study the shapes of magnetite nanoparticles from the cells of magnetotactic bacteria (MTB). MTB synthesize chains of membrane-bound magnetic nanocrystals (magnetosomes) intracellularly, and use them to navigate along magnetic field lines, in order to find their optimal position in aquatic vertical chemical habitats with gradients (BLAKEMORE, 1975). Each bacterial strain produces single crystals with distinct morphologies, many of which are unusual for magnetite, including "prismatic" and "bullet" shapes (MANN et al., 1987). The morphologies of magnetite nanoparticles from MTB have been the subject of numerous studies that addressed the issue from various perspectives: e.g., the use of special magnetite morphologies as biomarkers, as indicators of crystal growth processes, or as proxies for MTB evolution (PÓSFAI et al., 2013). However, magnetite morphologies from MTB have been described mostly on the basis of two-dimensional projections in electron micrographs. Therefore, we used an advanced technique, high-angle dark-field (HAADF) electron annular tomography (ET) in the scanning transmission electron microscope (STEM), for characterizing several distinct magnetite shapes from MTB, and interpreted the results in terms of crystal growth processes.

We studied magnetite crystals from MTB collected directly from the mud of a pond that collects the water of Kinizsi-spring, in the Bakony Mountains, Western Hungary. A large variety of cell types - including various cocci, vibrio and spirilla - were present. Cells of MTB were magnetically enriched, then the enriched suspensions were placed on TEM support grids. We characterized the distinct cell types, the

structure of chains of magnetosomes, and magnetite morphologies using TEM techniques.

Magnetite magnetosomes occurred either in single, double, or two double chains, or in disordered arrangement, depending on the particular cell type. Spirilla, vibrio and cocci typically contained magnetite with elongated prismatic and nearly octahedral morphologies (Fig. 1). Facets could be indexed on 3D reconstructions, and the crystals were bound primarily by the {111}, {110}, and {100} forms, in agreement with previously published models (PÓSFAI *et al.*, 2013). Rod-shaped cells containing magnetite with 'bullet' morphologies also occurred. The bullets are elongated along [100] and consist of an octahedral base and an elongated, pointed part (Fig. 2).



Fig. 1: Composite Fe-P elemental map of a cell of a coccus bacterium. The cell contains huge polyphosphate inclusions with two double chains of nearly octahedral magnetite magnetosomes.

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Contrary to previously published models, the elongated portion of the crystal is bound neither by large-index faces, nor a curved surface; instead, high-resolution images suggest that short steps of low-index (primarily {110}) faces occur, bestowing a staggered, sawtooth-shaped outline on the nanocrystal. The observed morphology could indicate a rapid, anisotropic growth along the elongation direction, probably taking place through the addition of precursor nanoparticles.

Cocci with disordered chains of magnetosomes displayed magnetite particles with "ladyfinger" morphologies. Facets were not indexable on this magnetite type, and 3D reconstructions show that the crystals contain a large number of voids. We interpret the presence of voids as suggestive of a crystal growth process by particle attachment. The voids may be remnants of gaps between individual precursor nanoparticles that attached and recrystallized to form the single crystals as we observe them.

In summary, our ET results showed that previously published models properly describe the cubooctahedral and "prismatic" shapes of magnetite magnetosomes. However, the sawtooth-like surfaces of bullet-shaped magnetosomes, as well as the numerous voids in "ladyfinger"-shaped nanoparticles are novelties that could shed light on crystal growth processes. In addition, a precise characterization of magnetite nanocrystal shapes could contribute to the understanding of their physical properties, including their magnetism, and the association of distinct cell types with certain magnetite morphologies may provide insight into the taxonomic relationships of MTB strains.

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References

- BLAKEMORE, R. (1975): Science, New Series, 190, 377–379.
- MANN, S., SPARKS, N. H. C., BLAKEMORE,R. P. (1987): Proceedings of the Royal Society of London, Series B, Biological Sciences, 231, 469–476.
- PÓSFAI, M., LEFÉVRE, C. T., TRUBITSYN, D., BAZYLINSKI, D. A., FRANKEL, R. B. (2013): Frontiers in Microbiology, 4, 344.



Fig. 2: *Electron tomographic reconstruction of the morphologies of bullet-shaped magnetite nano-crystals, each displaying an octahedral base and a pointed, elongated part*

"BIO-EVAPORITES", I.E. ENHANCED MINERALIZATION OF PLANTS

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Plants contain variable amounts of "minerals" – chemical elements in biological definition – which in turn can often be related to minerals, in geological sense. The major and minor nutrients have mostly mineral sources and although they exist in organic or mineral-organic complexes in live tissues, crystalline excretions are well known, even if categorized as oxalates, mostly. Some species known as hyperaccumulators are known to produce harvestable amounts of minerals. This process can be upgraded by enhanced mineralization, leading to biomass production rich in very rare and unique evaporitic minerals. Thus, a kind of bio-evaporites, although synthetic in nature.

Mineral nutrient content in plants is regularly monitored parameter in agriculture, based on solution extraction standards or modern spectroscopic methods allow solid-state analysis also. The crystalline phase content, however, is rarely investigated, being a less useful information in crop production. Dried and micronized biomass can readily be analysed by X-ray powder diffraction for bulk composition.

Investigations were conducted on laboratory grown 3 months specimens of maize, sunflower and Triticum monococcum. Experiments were run on live soil with rhyolite and andesite nanosuspension fertilizing and on lignite mining waste with andesite sand, in synthetic soil setting. Control groups were set for sprouting on cotton sponge, in soil without fertilizing and mining waste alone. Watering was solved with single distilled tap water. The mining-waste based set also included a batch with soil colloid inoculation, to observe effect on bacterial activity.

Harvested samples were undertaken to X-ray powder diffraction in raw and dried state.

Measurements were run on Bruker D8 Advance (Cu source, 40 kV and 40 mA, Göbel mirror) with Vantec1 position sensitive detector (1° opening) and Bruker D8 Discover (Cu source, 40 kV and 40 mA, Bragg-Brentano) with LynxEye XE-T position sensitive detector (2° opening) in high resolution mode. The first instrument gave better result for chopped but unground plant material, while the second instrument was better for < 0.1 mm ground samples. Control measurements were done by SEM+EDX (Jeol JXA 8600 Superprobe) by BSE imaging, EDX analysis and X-ray mapping.

The XRD sample preparation produces changes in the original composition, the gamma-KNO3 detected in dried plants was transformed into niter, by the mechanochemical effect of grounding. Characteristic differences were observed for the same species depending on fertilizer type, substrate and different parts of the plants. K-input enhances nitrate production, while Ca turns the balance towards sulphates and oxalates. Mining waste is further developed towards various sulphate rich compositions, enhanced by inoculating with soil colloid. The role of bacteria is highly evidenced, since the setting on cotton with fertilizers yielded no mineralization, while inoculated mining waste doubled the mineral nutrient uptake.

Although the living and green state of the samples could not be evaluated due to the elevated water content, the textural distribution and setting of the mineralized parts supports, that evaporitic phases are not developed solely due to drying, even if its effect cannot be neglected.

Dry biomass of up to 1/3 mineral content can be obtained, the type of mineralization being selective on plants species, parts and grooving substrate.

APPROXIMATING DETECTABLE LOWER CRYSTALLITE SIZE LIMITS FOR MINERALS IN X-RAY POWDER DIFFRACTION

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Definition of crystals based on diffracting ability is a more practical approach since it relies on analytically measurable parameters. Beyond the question of wavelength and instrumentation, to define crystallinity, also the range of periodicity shall be defined, preferably stronger than short or long. For such definitions the unit cell is a well-established base, the range of order being defined as the number of unit cells - even for anisotropic crystallite sizes and shapes. To test this approach, different pattern fitting algorithms have been tested, in which peak broadening can be fitted as size and strain related parameters. Simulations and measured pattern fitting also supports, that average size domains or (hkl) defined range of order can be extracted from powder X-ray diffraction patterns.

Experiments were done on single phase materials (ZnO, corundum, hematite) and mixtures of known and unknown compositions. Measurements were run in parallel beam and Bragg-Brentano geometry on two different instruments (Bruker D8 Advance with Cu source, 40 kV and 40 mA, Vantec1 position sensitive detector, 1° opening and Bruker D8 Discover Cu source, 40 kV and 40 mA, LynxEye XE-T position sensitive detector, 2° opening, in high resolution mode). Size and shape related parameters were correlated with transmission electron microscopy (TEM) data.

The modified double-Voigth approach was tested in detail, by Rietveld refinement based whole powder pattern deconvolution. In the same TOPAS4 software also simulation was run for different instrumental settings, to test size-based broadening prediction as compared to measured samples.

With the developments in detector technology, one must expect that nanocrystalline

materials in the size range around 10 nm-s are clearly recognized and parametrized, if the unit cell volume is not larger than 1/10 of the defined crystallite volume. Of course, the problem of anisotropic size broadening and size range distribution has to be addressed, which could become problematic in nanocrystalline mixtures. However, the major observation is, that whole pattern deconvolution methods have correctly predicted the low crystallite sizes even for instruments, of which angular resolution did not allow to define broadened peaks.

In Rietveld refinement, we have the option to selectively extract peaks after refining all instrument and specimen related parameters. Thus, the option to characterize shape related size distribution, interpreted as number of unit cells. Calculations related to TEM data show an agreement as usually reported in the literature.

Simulations and calculations indicate that a crystallite can produce recognizable diffraction for any metal target X-ray source if at least 10 unit cells have coherent periodicity inside its volume. In mixtures with variably sized phases, the presence of such nanocrystalline materials is erroneously overlooked by background fitting.

Observations also support, that Cu source instruments with at least FWHM at 30°(2Th) of at least 0.04 (K-alpha1) will be able to correctly detect materials with size around 10 unit cells (5–15 nm), if correct background treatment is applied.

Special cases, such as nanosheets (clay lamellas), highly strained structures and < 10 unit cells sized materials can be also recognized and treated accordingly to include in the deconvolution.

LEACHABILITY OF METAL(LOID)S FROM SLAGS AFTER HISTORICAL Cu PRODUCTION IN MIEDZIANA GÓRA, POLAND

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Historically (16th–18th century), copper in Miedziana Góra, Poland, was produced by pyrometallurgy, resulting in the slag formation. Nowadays, in the area of the former smelter, we can still observe slag on the surface and buried in the soil.

This study aims to determine how much metal(loid)s is released into the environment from slags created during the historical metallurgy in Miedziana Góra. During field works, slag, soil, and ground water samples were collected from profile (up to 50 cm) at depths: 0-5 cm; 5–10 cm; 10–30 cm; 30–35 cm; and >35 cm. Geochemical (ICP-MS/OES) and petrological tools (XRD, SEM-EDS, EPMA) were used to determine the slags' chemistry and phase composition. At the same time, leaching tests were performed to classify material (according to EN 12457-2) and to simulate various pH scenarios (pH – static leaching in the range 2-12; EN 14997). The natural pH of the slags was also measured during leaching tests. The soil samples were subjected to 0.01 M CaCl₂ leaching (simulating soil pore water) to determine metal(loid)s (bio)availability for plants. Based on the chemical composition of leachates, geochemical modelling was carried out using PHREEQC to determine pH-dependent phases' supersaturation in regard to leachate (PARKHURSTt & APPELO, 2013).

Slag analyses showed high concentrations of Pb (57 400 mg·kg⁻¹), Zn (9 000 mg·kg⁻¹), Cu (8 890 mg·kg⁻¹), Ba (7 120 mg·kg⁻¹), and As (325 mg·kg⁻¹). In terms of phase composition, slags consist mainly of glass with dispersed crystalline phases, among which most frequently observed are quartz (SiO₂), wollastonite (CaSiO₃), clinopyroxene (Ca(Mg,Fe²⁺)Si₂O₆), metallic copper (Cu) and litharge (PbO). Similarly, high concentrations of Pb (5 830–32 000 mg·kg⁻¹), Zn

(1 250–11 800 mg·kg⁻¹), Cu (6 470–13 900 mg·kg⁻¹), Ba (225–1 330 mg·kg⁻¹), and As (81.0–985 mg·kg⁻¹) were found in the soils. In terms of mineral composition, the soils mainly consist of quartz, muscovite (KAl₂(AlSi₃O₁₀)(OH)₂), plagioclase ((Na,Ca)[Al(Si,Al)Si₂O₈]), dolomite (CaMg(CO₃)₂), and kaolinite (Al₂(Si₂O₅)(OH)₄).

The slags are classified as non-hazardous waste based on leaching test results and European Council Decision 2003/33/EC (EUR-Lex, 2003). However, due to excessive leached concentrations of Pb (1.26 mg·kg⁻¹) and Sb (0.227 mg·kg⁻¹), these slags cannot be considered fully inert.

Based on the analysis of groundwater, it was found that the pH of the soil in Miedziana Góra was in the range of 6.58-6.75. The concentrations of metal(loid)s in groundwater were: 0.234-0.724 mg·l⁻¹ of Cu; 0.228-0.288mg·l⁻¹ of Zn; 0.105-0.165 mg·l⁻¹ of Pb; and less than 0.007 mg·l⁻¹ of As.

The pH static leaching showed that metal(loid)s are most easily leached under low pH conditions. At pH 2, 2 730 mg·kg⁻¹ of Pb, 726 $mg \cdot kg^{-1}$ of Cu, 335 $mg \cdot kg^{-1}$ of Zn, 144 $mg \cdot kg^{-1}$ of Ba, and 29.4 mg·kg⁻¹ of As were leached out from the slags. With the increase in pH, the amount of leached metal(loid)s decreases, reaching under soil pH conditions (6-7), up to 6.54 mg·kg⁻¹ of Pb, 4.51 mg·kg⁻¹ of Cu, 1.45 mg·kg⁻¹ of Zn, and 0.60 mg·kg⁻¹ of As. At high pH values (>10), Pb, Cu, and As concentrations in leachate rise again, reaching at pH = 12:265mg·kg⁻¹ of Pb; 5.38 mg·kg⁻¹ of Cu; and 2.94 $mg \cdot kg^{-1}$ of As.

When CaCl₂ solution was used, the most easily mobilized metal(loid)s was Zn. Still only max. 0.66 wt.% of the total amount in soils was released to leachate. Depending on the soil layer (horizon), 7.48–19.1 mg·kg⁻¹ of Zn, 5.05–7.15

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 $mg \cdot kg^{-1}$ of Cu, 0.557–6.37 $mg \cdot kg^{-1}$ of Pb, and less than 0.50 $mg \cdot kg^{-1}$ of As were leached.

Based on the results of the geochemical modelling, it was found that the leachate obtained at natural pH of the slags is supersaturated with numerous metal(loid)s concentrating phases e.g., delafossite (CuFeO₂), ferrite-Cu (CuFe₂O₄), ferrite-Zn (ZnFe₂O₄), PbHPO₄, pyromorphite (Pb₅(PO₄)₃Cl) and plumbogummite $(PbAl_3(PO_4)_2(OH)_5 \cdot H_2O).$ Their presence as solids may act as stable storage of metal(loid)s under natural conditions. SEM-EDS observations confirmed the presence of delafossite and ferrite-Cu in slags leached with deionized water. Additionally, crystallization of secondary Pb phosphates and Pb and Cu oxides/carbonates was observed in the leachate after test at pH 6–7.

References

- EUR-Lex, 2003. Council Decision 2003/33/EC of 19 December 2002 Establishing Criteria and Procedures for the Acceptance of Waste at Landfills Pursuant to Article 16 of and Annex II to Directive 1999/31/EC.
- PARKHURST, D.L., APPELO, C.A.J. (2013):
 Description of Input and Examples for PHREEQC Version 3eA Computer Program for Speciation, Batch-reaction, Onedimensional Transport, and Inverse Geochemical Calculations, U.S. Geological Survey Techniques and Methods, Book 6, Chap. A43.

TIMREX-CRM – IMPROVEMENT OF THE MINERAL EXPLORATION JOINT PROGRAMME TOWARDS CRITICAL RAW MATERIALS

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Critical Raw Materials Act (EC 2023) has been accepted by the European Commission in March 2024. Its major purpose is to secure the raw materials supply to the EU of raw materials - first of all metals - which have critical or strategic importance for the EU's economy. One of the major targets is to reach at least 10% raw materials extraction from European sources by 2030, which needs more intensive mineral prospecting and exploration activities in the Member States in the future. However, environmental, nature conversion and social achievements reached in last decades in the EU should be maintained, therefore future mineral exploration works should implement advanced technologies and approaches.

TIMREX joint master programme was established by the TIMREX EIT-RawMaterials project in 2022 to implement a joint curriculum focused on innovative raw materials prospecting and exploration methods with strong innovation and entrepreneurial components. TIMREX programme incorporates new exploration techniques and methodologies, portable and higher sensitive equipment and processing and interpreting of large, multidimensional datasets. The programme as a consortium of four European universities and eight non-academic partners, received the EIT-Label in 2022. Field geology, strong training in mineral deposits and application of advanced analytical methods are among the major targets of the programme (BOROJEVIC-SOSTARIC et al., 2023).

The follow-up project of TIMREX for period 2025-27 was submitted in January 2024 with the focus of improving the curriculum towards critical raw materials (TIMREX-CRM) and to meet the future demand to implement the CRM Act by the Member States and companies. Mineral exploration technology is in a

revolutionary change. Portability and miniaturisation of sensors and equipment make possible advanced measurements directly in field, allowing to take decisions already during field campaigns. The amount of exploration data produced by portable, laboratory and remote sensing equipment increased in several magnitudes and their complex evaluation and interpretation is possible with powerful "deeptech" computation technics and software systems.

TIMREX-CRM aims to tailor the curriculum to fit to mineral exploration-related targets of the CRM Act, especially developing:

• updates in mineralogy-geochemistry and regional and economic geology courses towards CRMs, especially with focus on key exploration target regions: Carpatho-Balkan-Dinaric and Scandinavian metallogenic provinces,

• updates in specific exploration technologies and approaches to CRMs,

• specialties of exploration methods for mine waste facilities with CRM potential, including understanding the mineralogy of alteration processes taking place in MWFs,

• skills towards resource qualification systems with focus on United Nations Framework Classification system (ECE, 2010).

Based on the Mineral Intelligence for Europe (Mintell4EU) database, relevant critical and strategic raw materials for the Carpatho-Balkan-Dinaric region are summarized in Table 1.

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(HAPAKO) - 2021-1.2.1-EIT-KIC-2021-00003" project.

References

BOROJEVIC SOSTARIC, S., PASZKOWSKA, G., JANSSON, N., LOPES, L., MIRAVALLES, A. S., MARIČIC, A., MÁDAI, F. (2023): Materials Proceedings, 15(1), 8. ECONOMIC COMMISSION FOR EUROPE (2010): ECE ENERGY SERIES No. 39, pp. 1–25.

EUROPEAN COMMISSION (2023): COM(2023) 160. MINTELL4EU (2024):

https://geoera.eu/projects/mintell4eu7/

Table 1: Critical and strategic raw materials for the Carpatho-Balkan-Dinaric region. ALB: Albania; BIH: Bosnia and Herzegovina; HRV: Croatia; HUN: Hungary; MNE: Montenegro; ROU: Romania; SRB: Serbia; SVK: Slovakia; SVN: Slovenia.

Critical and Strategic Raw Material	Countries	Deposit types
Antimony (metal)	SVK, SRB, BIH, SVN	Vein, polymetallic replacement, shale-hosted, skarn
Baryte	SVK, SRB, ROU, HUN	Vein, shale-hosted, epithermal
Bauxite	ALB, BIH, MNE, HRV, SVN, ROU, HUN	Bauxite
Borates	SRB	Phosphorite
Cobalt (metal)	BIH, ROU	Laterite, Layered complex, BIF, mafic to ultramafic rocks
Graphite	SVK, ROU	Skarn and carbonate replacement, metamorphic, alluvial placer
Lithium (metal)	SRB, SVN, ROU	Phosphorite, granitic igneous rocks and pegmatites
Niobium (metal)	ROU	Syenitic and alkali granitic intrusives and pegmatites
Phosphate rock	ALB, ROU	Phosphorite, sedimentary
Tantalum (metal)	ROU	Syenitic and alkali granitic intrusives and pegmatites
Titanium and TiO ₂	ROU	Mafic to ultramafic rocks, alluvial placers
Total Rare Earth Elements	ROU	Syenitic and alkali granitic intrusives and pegmatites
Vanadium	ROU	Mafic to ultramafic rocks, alluvial placers

TRACING CONTAMINATION IN URBAN SOILS USING STABLE STRONTIUM ISOTOPES: A CASE STUDY FROM SALGÓTARJÁN, HUNGARY

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Urban soil contamination is a significant consequence of human activities, particularly in areas with industrialization (CRAUL, 1985). In the city of Salgótarján, located in northern Hungary, where soils have accumulated high concentrations of potentially toxic elements (PTE) including heavy metal(loid)s, over the course of centuries due to various anthropogenic activities and pollution sources. This study specifically investigates the distribution of Sr and its stable isotopic ratios (⁸⁷Sr/⁸⁶Sr) in urban soils with a focus on contamination linked to the former coal-fired power plant (CFPP) in Salgótarján.

A total of 15 urban soil samples were selected from residential areas of the northern part of Salgótarján. Additionally, samples of local brown forest soil, coal ash and brown coal were also collected to serve as reference materials for natural and anthropogenic PTE sources. The sampling strategy was designed to capture the spatial variability of Sr concentrations and isotopic ratios across different land uses, including parks, playgrounds, kindergartens, roadsides, and areas in close proximity to former industrial sites. The collected samples were subjected to a series of physicochemical analyses, including pH determination, total organic carbon (TOC) and total nitrogen (TN) content measurements, and grain size distribution analysis. Composition of bulk

chemistry performed by inductively coupled plasma mass spectrometry (ICP-MS) and ⁸⁷Sr/⁸⁶Sr isotopic ratios were determined using thermal ionization mass spectrometry (TIMS).

The physicochemical analyses revealed significant variability in urban soils across Salgótarján. The studied urban soil samples exhibited pH values ranging from acidic (5.86 in sample STN09: park) to weakly alkaline (7.62 in sample STN10: playground), with mean of 7.28 pH value. The elevated pH levels in most urban soils are linked to artificial infills (e.g., containing calcareous materials) due to land use changes. A notable exception was STN09 (park), where the soil is acidic due to smelter slag used for filling up material during landscape process.

Contents of TN and TOC varied in the samples: TN ranges from 0.09 m/m % (STN16: playground) to 0.25 m/m % (STN11: park) with mean value of 0.18 m/m %, whereas TOC ranges from 0.78 m/m % (STN16: playground) to 2.55 m/m % (STN29: park) with mean value of 1.55 m/m %. The highest TN and TOC content was found in STN11 (park) and STN29 (park), respectively, reflecting the impact of land use change (HILLER *et al.*, 2015). However, the lowest one for both was found in STN16 (playground), which is located in proximity to former industrial sites.

Grain size distribution shows high variability: most samples have sandy loam to silty clay loam

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textures. The clay fraction ranges from 4.0 m/m % (STN21: roadside) to 32.4 m/m % (STN07: kindergarten), whereas the silt fraction ranges from 37 m/m % (STN31: roadside) to 58.8 m/m % (STN12: kindergarten). The sand fraction is the lowest one (17 m/m %) in STN07 (kindergarten) and the highest one is 57.3 m/m % in STN21 (roadside). The coal ash sample has the highest sand fraction (62.3 m/m %), exceeding the range of studied urban soils, indicating feature characteristics of bottom ash from coal combustion residuals.

The Sr concentration in the urban soils ranges from 17.5 to 51.3 mg kg⁻¹, with a mean of 30.6 mg kg⁻¹. Notably, the highest Sr content is found in STN29 (park) (51.3 mg kg⁻¹) and STN21 (roadside) (48.6 mg kg⁻¹), close to former industrial sites, whereas STN16 (playground) (35.8 mg kg⁻¹) and STN14 (playground) (37.5 mg kg⁻¹) also exhibited elevated Sr values. The coal ash sample had the highest Sr concentration (113.6 mg kg⁻¹) highlighting its significant contribution to the urban soil Sr levels. Brown coal from Salgótarján contains 52.8 mg kg⁻¹, consistent with regional geological variations (LANDIS *et al.*, 2004).

The ⁸⁷Sr/⁸⁶Sr isotopic ratios range from 0.71030 to 0.71956, with an average of 0.71510. The highest ratio was observed in STN31

(roadside) (0.71956), whereas the lowest value (0.71030) is in STN16 (playground). The data show positive correlation between 87 Sr/ 86 Sr ratios and distance from the coal-fired power plant, proving that coal ash is a significant Sr source.

Despite the prevalence of coal ash near the CFPP, specific samples (STN12: kindergarten, STN32: roadside, and STN09: park, and STN16: playground) show high contributions from anthropogenic sources even though they are not the closest to the CFPP. In contrast, natural sources contributed much higher Sr to samples (STN11: park and STN22: roadside, and STN31: roadside), which were not collected farthest from the CFPP. This variation highlights the complexity of Sr distribution in urban soils including mixture of additional unidentified sources with variations in ⁸⁷Sr/⁸⁶Sr ratios.

References

CRAUL, P. J. (1985): Journal of Arboriculture, 11(11), 330–339.

- HILLER, E., LACHKÁ, L., JUROKOVIČ, Ľ., VOZÁR, J. (2015): Environmental Earth Sciences, 73(11), 7147–7156.
- LANDIS, E. R., ROHRBACHER, T. J., GLUSKOTER, H. J., FODOR, B., GOMBAR, G., SEBESTYEN, S. (2004): US Geological Survey Circular, 1272.

NEW RESULTS AND ATTEMPTS TO LINK ORE MINERALIZATIONS TO TECTONOTHERMAL EVOLUTION OF THE CENTRAL WESTERN CARPATHIANS

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Many ore deposits and occurrences are hosted by the Variscan basement of the Central Western Carpathians, much less commonly by the Mesozoic sedimentary cover. The distinction between Variscan and Alpine mineralization has been obliterated by convergence of the hydrothermal processes of diverse age, remobilization by the young Alpine processes, mineralizations. and reworking of the Recognition of the age of the mineralizations can to link them closely help to the tectonometamorphic evolution of the orogens (Variscan or Alpine) and attempt to identify the sources of fluids and metals. In this work, we are presenting some of our recent results that link ores, tectonic, metamorphic, and igneous events in the Central Western Carpathians.

The Paleovariscan synsedimentary mineralizations at Pezinok, Hel'pa, and Smolník experienced Variscan and Alpine overprint. They consist of refractory minerals which survived that overprint and remobilized mineralization of uncertain age. They can be related to the evolution of the early Variscan crust and its mafic and ultramafic components, formation of rifts and ophiolite complexes. Some of these mineralizations can be traced in sulfur isotopes of younger ores in the same area, confirming remobilization of sulfur and perhaps also metals into younger fluids.

Historically important Sb-Au mineralization, developed especially in the Nízke Tatry Mountains, is of late-Variscan age, as shown by U-Pb dating of carbonates (MAJZLAN *et al.*, 2020). This mineralization was deposited by hydrothermal, H₂O-CO₂ fluids of low salinity

could be linked regional that to the metamorphism of the Variscan crust (CHOVAN et al., 1995). Our new work on Sb isotopes from these deposits suggests large-scale crustal flow of the ore-bearing fluids and subsequent formation of the ore deposits. Sparse occurrences of molybdenite, spatially associated with the Sb-Au mineralization, are directly related to the igneous processes that yielded the voluminous Variscan granites. The age and the tectonic regime of the scheelite mineralization is not known yet.

The Permian, late Variscan granitic rocks brought also mineralizations. One of the manifestations of their action was steatitization of the magnesite bodies at Gemerská Poloma (MAJZLAN et al., 2024). The Permian granites also produced occurrences of U-Mo mineralization in Čučma (FERENC et al., 2021) accumulations and larger of Sn-Mo mineralization in Hnilec (KOHÚT & STEIN, 2005).

The incipient stages of the Alpine orogeny produced limited remobilization of the preexisting mineralizations (ŠTEVKO *et al.*, 2014) in the Gemeric unit. Small occurrences of ores can be linked to the opening of the Tethys Ocean in the Middle Triassic (MAJZLAN *et al.*, 2022). Their mineral and chemical content is dependent on the lithology of the host rocks, suggesting that they were produced by small hydrothermal cells that leached these rocks. Examples are the Ni-Co occurrence Kolba or the barite-galena occurrence at Nižné Matejkovo.

The Jurassic times are present clearly in the ages of the clay minerals associated with faults in

the Variscan basement, but so far not in the ore mineralizations. The main pulse of hydrothermal activity is discernible in Cretaceous. In the Lower Cretaceous, siderite veins in Dobšiná (Gemeric unit) were formed (KIEFER et al., 2020), co-incident with the metamorphic maximum in the Gemeric unit. We assume, by analogy, that all siderite veins (also in the Veporic and Tatric units) have similar age. Work is underway to test this hypothesis. The Ni-Co hydrothermal mineralization in Dobšiná is also of Cretaceous age, coincident with the formation of the Gemeric cleavage fan and partial exhumation of the unit. In roughly the same time, the Gemeric stibnite veins precipitated (URBAN et al., 2006). The regionally developed Cu mineralization with common Bi sulfosalts precipitated NaCl-CaCl₂-H₂O from fluids (HURAI et al., 2006); the exact age of this mineralization remains unknown.

In Middle Cretaceous, Veporic unit experienced the metamorphic peak, with the associated quartz veins with REE phosphates. Tectonic motion, including thrusting of Alpine nappes, appears to be responsible for small mineralizations, such as the hematite-quartz veinlets in the Triassic sediments in Nízke Tatry Mts. or the quartz-lazulite veinlets in the Tríbeč Mts. Dolomite veins at the Sb-Au deposits, with clear geological evidence for their younger age with respect to the Sb-Au ores, formed also in Middle Cretaceous. The age and provenance of their Cu mineralization is not clear. We are striving to distinguish older and younger generations of chemically similar sulfides by analyses of their S isotopes, with the assumption that the Variscan and Alpine S isotopic signatures are significantly different. The reason therefore is the addition of Permian/Triassic sulfur from evaporitic rocks into the Alpine fluids.

In different types of ores, Paleogene remobilization of carbonate minerals is visible. It could be a result of burial under a stack of Paleogene molasse sediments or the increase of geothermal gradient and swelling of the asthenosphere. These processes led to extensive Neogene volcanism with the associated rich ore mineralization which are not the topic of this contribution.

The terminal stages of the ore evolution in the Central Western Carpathians were marked by weathering during Miocene intense and formation of oxidation zones with rich mineralogy, for example those at Lubietová or Poniky. Using stable O and H isotopes, we could show that they were produced solely from meteoric water. Their preservation, however, was strongly dependent on protection by overlying rocks, in our case, the Neogene volcanic rocks.

References

- CHOVAN, M., HURAI, V., SACHAN, H.K., KANTOR, J. (1995): Mineralium Deposita, 30, 48–54.
- FERENC, Š., ŠTEVKO, M., MIKUŠ, T., MILOVSKÁ, S., KOPÁČIK, R., HOPPA-NOVÁ, E. (2021): Minerals, 11, 629.
- HURAI, V., LEXA, O., SCHULMANN, K., MONTIGNY, R., PROCHASKA, W., FRANK, W., KONEČNÝ, P., KRÁĽ, J., THOMAS, R., CHOVAN, M. (2008): Geofluids, 8, 181–207.
- KIEFER, S., ŠTEVKO, M., VOJTKO, R., OZDÍN, D., GERDES, A., CREASER, R.A.,
 SZCZERBA, M., MAJZLAN, J. (2020): Journal of Geosciences, 65, 229–247.
- KOHÚT, M., STEIN, H. (2005): Mineralogy and Petrology, 85, 117–129.
- MAJZLAN, J., CHOVAN, M., KIEFER, S., GERDES, A., KOHÚT, M., SIMAN, P., KONEČNÝ, P., ŠTEVKO, M., FINGER, F., WAITZINGER, M., BIROŇ, A., LUPTÁKOVÁ, J., ACKERMAN, L., HORA, J. M. (2020): Geologica Carpathica, 71, 113– 133.
- MAJZLAN, J., MIKUŠ, T., KIEFER, S., CREASER, R.A. (2022): Mineralium Deposita, 57, 621–629.
- MAJZLAN, J., DIANIŠKA, I., KIEFER, S., ACKERMAN, L., RENČIUKOVÁ, V. (2024): Lithos, 470–471, 107521.

- ŠTEVKO, M., UHER, P., ONDREJKA, M., OZDÍN, D., BAČÍK, P. (2014): Journal of Geosciences, 59, 209–222.
- URBAN, M., THOMAS, R., HURAI, V., KONEČNÝ, P., CHOVAN, M. (2006): Mineralium Deposita, 40, 867–873.

MINERALS OF THE TESCHENITE ASSOCIATION ROCKS IN THE BES-KYDY PIEDMONT AREA (CZECHIA & POLAND) – A CRITICAL REVIEW

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Early Cretaceous igneous rocks in the Podbeskydí area (Czech Republic & Poland) are investigated since their first mention in 1816 (FICHTEL, 1816; OYENHAUSEN, 1822). Since then, significant number of published papers, as well as monographies, explanatory notes to the geological maps, student theses, unpublished reports, and other documents related appeared. them They are scattered to in many languages - the older ones are mostly in German, later followed by the Czech, Polish, French, and in recent two decades mostly in English. While the availability of old publications is getting better than ever, meaning of both geological and mineralogical terms sometimes shifted, so it might be problematic to understand properly even with easily accessible machine translations. It is the reason why the time for the critical review of the published works came now.

The studied Cretaceous igneous and volcanoclastic rocks, known as Teschenite Association Rocks (hereinafter referred to as TAR), are embedded as lavas or penetrate as dykes and sills into the Early Cretaceous sedimentary sequences of the Outer Carpathians (MENČÍK *et al.*, 1983; WŁODYKA, 2010). The modern research in this geological setting is greatly complicated by the Carpathian thrusting (PICHA *et al.*, 2006), as well as poor exposure of the TAR bodies.

The TAR are characterised by highly variable mineral proportions, with Mg-rich olivine, clinopyroxenes, amphiboles, K-feldspars and plagioclases as the main primary rock-forming minerals. In addition to phaneritic rock types with a gabbroic appearance, the TAR also includes alkali lamprophyres and fine-grained porphyritic and aphanitic types of effusive or near-surface intrusive bodies (HOVORKA & SPIŠIAK, 1988; DOSTAL & OWEN, 1998; WŁODYKA, 2010; MATÝSEK *et al.*, 2018). Zeolitisation (mainly analcimisation), chloritisation, smectitisation, and carbonatisation are the most frequent alteration processes associated with this rock suite (*e.g.* DOLNÍČEK *et al.*, 2010; MATÝSEK *et al.*, 2018; MATÝSEK & JIRÁSEK, 2023).

Mineralogy of the TAR was for a long time matter of limited number of researchers and mineral collectors, since except the rock-forming minerals (amphibole–supergroup minerals, clinopyroxenes, dark micas, feldspars and feldspathoids) the interesting phases are usually microscopic to submicroscopic and hard to identify. Only a few localities produced limited number of samples worthy for collectors – e.g., zeolites (analcime, natrolite, clinoptilolite), calcite, baryte, pectolite.

Authors' review came into conclusion that the approximate numbers of TAR valid mineral phases in groups of the Nickel-Strunz classification systems are as follows: elements – 1, sulfides + arsenides + sulfarsenides – 13, halides – 2, oxides – 20, carbonates – 10, sulfates – 13, phosphates and vanadates – 8, and silicates – 65. Out of that number, ca. 60% was described in last 40 years, and ca. 45% in last 20 years (Fig. 1). So it is clear that the research is continuously improving our knowledge about the mineralogy of the TAR.

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References

DOLNÍČEK, Z., URUBEK, T., KROPÁČ, K. (2010): Geologica Carpathica, 61, 327–339.

- DOSTAL, J., OWEN, J.V. (1998): Geologische Rundschau, 87, 67–77.
- FICHTEL, von J.E. (1816): Mineralogische Bemerkungen von den Karpathen, Erster Theil, Zwente Ausgabe. Wien: Camesina'schen Buchhandlung.
- HOVORKA, D., SPIŠIAK, J. (1988): Vulkanizmus mezozoika Západných Karpát. Bratislava: Veda.
- MATÝSEK, D., JIRÁSEK, J. (2023): Applied Clay Science, 243, 107067.
- MATÝSEK, D., JIRÁSEK, J., SKUPIEN, P., THOMSON, S.N. (2018): International Journal of Earth Sciences, 107, 2553–2574.
- MENČÍK, E., ADAMOVÁ, M., DVOŘÁK, J., DUDEK, A., JETEL, J., JURKOVÁ, A., HANZLÍKOVÁ, E., HOUŠA, V., PESLO-VÁ, H., RYBÁŘOVÁ, L., ŠMÍD, B.,

ŠEBESTA, J., TYRÁČEK, J., VAŠÍČEK, Z. (1983): Geologie Moravskoslezských Beskyd a Podbeskydské pahorkatiny. Praha: Academia.

- OYENHAUSEN, von C. (1822): Versuch einer geognostischen Beschreibung von Oberschlesien und den nächst angrenzenden Gegenden von Polen, Galizien und Östreichisch-Schlesien. Essen: G. D. Bädeker.
- PICHA, F.J., STRÁNÍK, Z., KREJČÍ, O. (2006): In: GOLONKA, J., PICHA, J. (Eds.): The Carpathians and their foreland: geology and hydrocarbon resources. Tulsa: AAPG Memoir 84, pp. 49–175.
- WŁODYKA, R. (2010): Ewolucja składu mineralnego skał cieszyńskiej prowincji magmowej. Katowice: Wydawnictwo Uniwersytetu Śląskiego.



Fig. 1: Approximate number of valid TAR mineral species described over the time.

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A NOVEL APPROACH TO MINERALOGICAL SPECIATION OF SULPHI-DIC MINE WASTES: INTEGRATING X-RAY POWDER DIFFRACTION (XRD) AND SEQUENTIAL CHEMICAL EXTRACTION (SCE)

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Accurately determining the mineralogical composition of unknown rock or mineral samples has long posed a significant challenge scientists. Precise mineralogical for characterization is essential in geochemical analyses to gain a deeper understanding of the reactions that occur during weathering processes. X-ray diffraction (XRD) is a highly effective technique for this purpose. Nonetheless, its effectiveness can be markedly diminished when dealing with altered and poorly crystallized samples, leading to elevated detection limits that may be deemed unacceptable. This challenge is particularly prevalent in oxidized or oxidizing sulphidic samples undergoing acid rock drainage (ARD).

These secondary minerals exhibit considerable variability in both mineralogical properties and chemical compositions and often possess weaker crystallinity, along with increased defects or contaminating elements, compared to conventional rock-forming These factors pose substantial minerals. challenges for achieving accurate results with XRD analysis.

In the late 1970's, the Sequential Chemical Extraction (SCE) method was introduced to assess the mobility of heavy metals in soils. Unlike conventional bulk chemical elemental analysis, SCE involves multi-step leaching processes that link the composition of each leachate step to specific mineral or mineral group.

For the analysis of oxidizing sulphidic samples – often characterized by a high proportion of amorphous or poorly crystallized minerals – a novel approach involves leveraging XRD patterns. These patterns can provide a preliminary identification of the mineral groups present. For instance, while XRD patterns can confirm the presence of jarosite, distinguishing between its various members – such as potassium, hydronium, lead, ammonium, or sodium-containing jarosite – based on crystal structure alone can be challenging.

The SCE method enables the identification of mineral species by measuring the concentration of leached cations, facilitating the precise calculation of mineral species quantities.

The goal is to illustrate how XRD and SCE can complement each other. While each method has its limitations, their integration significantly enhances the efficiency of determining mineralogical composition. A case study further demonstrates the applicability of this combined approach for analyzing altered sulphidic mine waste materials, enabling the identification of amorphous phases and the quantification of altered sulphides present at extremely low concentrations.

The primary objective of this methodology is to identify strongly altered minerals and secondary oxidation products, even when their concentrations are below 0.01%. Accurate recalculations require a robust foundation in chemistry, geochemistry, and mineralogy, as well as a comprehensive understanding of both SCE and XRD methods. Although the range of potential minerals in a sample can be extensive, knowledge of the sample's origin significantly reduces the number of possible mineral candidate.

METAMORPHOSED MANGANESE MINERALIZATION AT THE DIELY OCCURRENCE NEAR PORÁČ: A UNIQUE MINERAL ASSEMBLAGE OF MANGANESE ARSENATES AND ARSENOSILICATES FROM SLOVAKIA

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The enrichment of manganese deposits with arsenic is a common process occurring during the development of Mn-rich environments in the initial stages. Formation of arsenic-bearing manganese minerals influenced is by mobilization of initial components in the pore subsequent solutions with redistribution, precipitation and metamorphic evolution via tectonometamorphic processes affecting iron and manganese-bearing systems.

The metamorphosed Mn mineralization in the Western Carpathians was extensively studied at the localities Čučma-Čierna baňa, Smolník-Malá Hekerová, Betliar-Július and currently at the Prakovce-Zimná voda occurrence (e.g. FARYAD, 1994; ROJKOVIČ, 2001; ŠTEVKO et al., 2015; 2023; MYŠĽAN et al., 2023 etc.), all of which represent As-free Mn mineralization embedded in the metamorphosed volcanosedimentary sequences of the Gelnica Group rocks. The new occurrence of manganese ores was recently discovered and is currently studied at the Diely occurrence in the vicinity of the Poráč village. The locality is formed by one small exploration pit ~4 m in diameter and one small road cut outcrop nearby.

Mineralization at the Diely occurrence is hosted in the Early Paleozoic (Early Ordovician– Silurian), mostly low-grade metamorphic rocks of the Rakovec Group belonging to the Northern Gemericum Unit. Mineral assemblages are developed in the quartz-rich lenses (metacherts) embedded in metabasalts and their metavolcanoclastic material, generated during the submarine volcanic activity (BAJANÍK *et* *al.*, 1981) with their affinity to the E-MORB/OIT types of basalts (IVAN, 2009). Metamorphic pressure-temperature conditions were estimated in the temperature interval 440–480 °C at a pressure of 6–8 kbar (FARYAD & BERNHARDT, 1996).

Manganese minerals occur in the siliceous lenses, which are dominantly laminated and contain an extensive amount of irregularly distributed nodules up to 5 mm in size, locally forming bigger pinkish accumulations. Mn ore is formed by quartz, rhodonite, nambulite, Na/Na-Ca pyroxenes and amphiboles, OH-bearing garnets, rhodochrosite, kutnohorite, braunite and hematite, cut by a system of the whitish to light orange veins with thickness up to 3 mm.

Increased content of As was observed in minerals embedded in the matrix, specifically in nambulite (up to 624 ppm) or braunite (A₂O₅ up to 3.22 wt. %; 0.17 *apfu* As⁵⁺ respectively), suggesting arsenic accumulation in the initial Mn-phases.

The mineralization is intersected by a network of narrow veins predominantly composed of Asenriched minerals from the pyrosmalite group (schallerite, mcgillite and friedelite), as well as tiragalloite, manganberzeliite, brandtite, sarkinite and svabite associated with hematite, rhodochrosite, kutnohorite, baryte and quartz.

The most widespread As-rich minerals are zoned pale yellowish crystals (up to 4 mm in size) of pyrosmalite group minerals (Fig. 1), consisting of the most abundant schallerite with the highest amount of As^{3+} (up to 3.14 *apfu*) and high Cl⁻ (0.48–1.26 *apfu*). Less often mcgillite

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occurs, it has As^{3+} up to 0.47 *apfu* and Cl^{-} in the range 1.02–1.40 *apfu*. Friedelite occurs rarely and it shows increased content of As^{3+} (0.36–0.45 *apfu*) with decreased Cl^{-} (0.96–0.99 *apfu*) as well.



Fig. 1: BSE image of zoned crystals of pyrosmalite group minerals (dominantly schallerite and mcgillite)

Tiragalloite forms homogenous orange crystals up to 3.5 mm in size with As⁵⁺ in the range 0.59–1.00 *apfu* and slightly increased Ca^{2+} , Fe³⁺ and V⁵⁺. Similarly, svabite forms homogenous anhedral grains up to 50 µm in size with T site mostly occupied by As^{5+} (up to 2.33) *apfu*) and P^{5+} (up to 0.87 *apfu*) reflecting a As⁵⁺ \leftrightarrow P⁵⁺ substitution. Sarkinite forms subhedral grains up to 100 µm in size or intergrowths with svabite and braunite. Chemical composition is close to the end-member formula with slightly increased content of Fe^{2+} (up to 0.02 *apfu*). Brandtite occurs in the form of anhedral grains up to 40 µm in size (Fig. 2). Increased content of Mg (up to 0.39 apfu) reflects its solid solution with wendwilsonite. Manganberzeliite occurs rarely in the form of isolated anhedral grains up to 50 μ m in diameter. At the Z site it dominantly contains As^{5+} (2.86–3.05 *apfu*) with increased Mg (up to 0.29 *apfu*) and Fe^{2+} (up to 0.17 *apfu*) at the *Y* site.



Fig. 2: BSE images of intergrowths of manganberzeliite (*light grey*) *and brandtite* (*dark grey*) *in quartz-rich matrix*

Manganese arsenosilicates and arsenates were presumably generated during the final stages of Alpine hydrothermal activity with fluids originated from As- and Mn-rich precursor hydrothermal solutions.

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References

- BAJANÍK, Š., VOZÁROVÁ, A., REICHWALDER, P. (1981): Geologické Práce, Správy, 75, 27–56.
- FARYAD, S.W. (1994) Neues Jahrbuch für Mineralogie, Monatshefte, 10, 464–480.
- FARYAD, S.W., BERNHARDT, H. (1996): Geologica Carpathica, 47, 349–357.
- IVAN, P. (2009): Lower Palaeozoic Basic volcanism in the Western Carpathians geochemistry and geodynamic position. Acta Geologica Universitatis Comenianae, Monographie series, Bratislava, pp. 110.
- MYŠĽAN, P., ŠTEVKO, M., MIKUŠ, T. (2023): Journal of Geosciences, 68, 313–332.
- ROJKOVIČ, I. (2001): Geolines, 13, 34–41.
- ŠTEVKO, M., MYŠĽAN, P., BIAGIONI, C., MAURO, D., MIKUŠ, T. (2023): Mineralogical Magazine, 87, 887–895.
- ŠTEVKO, M., PLECHÁČEK, J., VENCLÍK, V., MALÍKOVÁ, R. (2015): Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, 23, 39–42.

NEW DATA ON THE HIGH FIELD STRENGTH ELEMENT CONTENT OF THE TRIASSIC METAVOLCANICS OF THE BÜKK MTS, NE HUNGARY

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The Institute of Mineralogy and Geology of the University of Miskolc started to study the rare element content of the rocks of the Bükk Mts, Northeastern Hungary in the frames of the CriticEl project from the early 2010s. Trace elements, mainly HFSE of the Triassic metavolcanics helped delineate to the formations, remapping the known outcrops and finding outcrops not mapped before (NÉMETH et al., 2023a). As an unintended consequence, a new HFSE enrichment hosted by metavolcanics sedimentary rocks siliciclastic and was recognized, and studied as well (NÉMETH et al., 2023b).

The study was not considered to be finished at the stage which was introduced in the publications. Since then, both fieldwork and sample analysis were continued. HFSE enriched outcrops were detected by means of a scintillation detector, utilizing the gamma radiation from the radioactive decay series of Th. Here we want to introduce new results from two areas, (1) the Bükkszentlászló Block of the Szentistvánhegy Metavolcanics and (2) the Southeastern Bükk Unit.

 Two types of HFSE enriched metadacite or metarhyolite were sampled and studied here. The first type is enriched generally in all HFSE except Eu and Ti, and the HFSE are hosted by zircon, Ti-oxide minerals, apatite, and allanite. The second type is a silicified and K-metasomatic rock with strong negative Eu and positive Ce anomaly, enriched in Ta, Th, Zr, Y and heavy REE only. The HFSE enrichments are moderate, most

The HFSE enrichments are moderate, most possibly resulted from syn- or post-magmatic hydrothermal processes, overprinted by regional metamorphism.

(2) Newly found occurrences of metavolcanics (both Szentistvánhegy Metavolcanics and Szinva Metabasalt) were sampled here around Közép-szék, Bács-vár and Őr Hills, in the boundary zone of the Central and Southeastern Bükk tectonic units. The area contains siliciclastic beds affected by the HFSE enrichment, embedded in basin facies carbonates, while metavolcanics bodies are not HFSE enriched.

The new results increase the number of observations and support the conclusions of the referred studies, extending our knowledge to new locations of the study area.

References

- NÉMETH, N., KRISTÁLY, F., GÁL, P., MÓRICZ, F., LUKÁCS, R. (2023a): International Journal of Earth Sciences, 112/1, 297–320.
- NÉMETH, N., KRISTÁLY, F., BALASSA, CS. (2023b): Journal of Geochemical Exploration, 246, 107159

MODELING CARBONATE FORMATION IN LAKE BALATON ON A MESO-COSM SCALE

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We used a 'mesocosm' research facility for simulating carbonate mineral-forming processes in freshwater systems. The mesocosm scale allowed us to conduct studies under more control than would be possible in nature, while approaching the complexity of natural ecosystems. We wished to understand how environmental changes affect carbonate precipitation, and to test our hypotheses on the details of carbonate formation.

There are many observations in freshwater environments suggesting that photosynthesis by algae plays a major role in calcite precipitation (whiting events), by raising the pH and the cells providing surfaces for carbonate nucleation (DITTRICH & OBST, 2004). In addition, we found that inorganic surfaces (clay minerals) compete with cells in the nucleation process of calcite seeds (NYIRŐ-KÓSA et al., 2018; MOLNÁR et al., 2023, 2024). However, very few studies addressed questions related to the formation of distinct carbonate phases (including amorphous calcium carbonate (ACC), aragonite, calcite and dolomite) in association with algal blooms, the temporal dynamics of carbonate transitions, and phase how external environmental factors, such as temperature changes and precipitation events, impact the process.

In order to answer these questions and link our laboratory results with observations in Lake Balaton (PÓSFAI *et al.*, 2024), we performed a month-long mesocosm experiment. An algal bloom was induced artificially, and the changes in the properties of precipitating carbonate minerals were monitored.We controlled the experimental parameters in 12 basins, 5 m³ each, all filled with filtered Balaton water. Triplets of basins were treated in the same way, with the 4 types of basins set up as: (1) control, containing

only water, (2) a culture of algae (Chlorella vulgaris) added, (3) algae and smectite added (this clay mineral is always present in the water column of the lake as nanoscale flakes and provides a nucleation surface for calcite), (4) algae and smectite added, and the water kept at $\Delta T=5.7$ °C higher than in the other basins. The basins were daily sampled for water parameters, phosphorus chlorophyll, and nitrogen concentrations. Solid particles filtered from the water and taken from the sediment were characterized using a Thermo Scientific Talos F200X G2 scanning transmission electron microscope (STEM) and a Philips PW 3710Xray diffractometer (XRD).

During the one-month experiment there was a significant change in the weather: the initially warming, dry conditions were replaced by colder, wet weather with heavy precipitation (Fig. 1a), then towards the end of the experiment the weather became warm and dry. These changes allowed us to track the effects caused by extreme weather as well. Throughout the experiment we managed to replicate an algal bloom and its subsequent collapse as if it happened in the lake, while observing the formation of carbonates. We found that as photosynthesis created high supersaturation near the cells, Mg-rich amorphous calcium carbonate (Mg-ACC) nucleated first (Fig. 1b, c). Aging of Mg-ACC particles followed different pathways in the distinct basins. In the algae-only basin (2) Mg-ACC particles attached to cell walls and appendages (Fig. 1b), whereas in the algae+smectite basin (3) they attached to nmscale smectite flakes where they instantly transformed into calcite (Fig. 1c). Finally, in the heated pool (4) the entire process happened so quickly that only Mg-bearing calcite crystals could be detected. With further aging the clusters

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of Mg-ACC particles transformed into aragonite in the algae-only basin, then aragonite converted to Mg-bearing calcite that grew further and developed clearly visible crystal faces (Fig. 1b). In the algae+smectite basin dilution caused by heavy rains caused partial dissolution of Mgbearing calcite and reprecipitation of aragonite that again converted to Mg-bearing calcite (Fig. 1c). Finally, particles consisting of nanoscale dolomite within a matrix of Mg-bearing calcite developed, similar to those observed in another shallow lake by MEISTER *et al.* (2023).

Thus, in this mesocosm experiment we reproduced carbonate mineral phases that occur in the sediment of Lake Balaton. The formation of the dominant mineral of the sediment, Mgbearing calcite, involved at least two dissolutionreprecipitation cycles. The Mg content of calcite changed parallel with the water chemistry; in particular, dilution caused by heavy rains resulted in partial dissolution and less Mg in the calcite, while higher temperatures and evaporation increased the Mg content in the solid product and led to dolomite formation. The entire process of Mg-bearing calcite formation took place within hours to days, depending on the environmental factors; thus, the properties of calcite particles in the lake sediment are directly influenced by marked weather changes.

Our study successfully simulated a geological process, the accumulation of carbonate sediment in a shallow lake. By tracking the sequence of events, we obtained important details both on the time constraints of phase transformations and the



Fig. 1: Changes in environmental parameters and evolution of carbonate formation in two types of basins (one with algae only and another with algae and smectite added) over a one-month mesocosm experiment (with time progressing from bottom to top of the Fig.). (a) Precipitation events and changes in water temperature; the two temperature curves represent basin types 1–3 and type 4 (heated), respectively; (b) and (c) schematic illustration of the carbonate types observed by TEM that formed in basins treated with algae only and with algae and smectite, respectively (the vertical time scale is the same as in (a)).



external conditions affecting carbonate precipitation, including that of dolomite. Thus, mesocosm experiments can provide important insight into complex geological processes.

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References

- DITTRICH, M., OBST, M. (2004): Ambio, 33, 559–564.
- MEISTER, P., FRISIA, S., DÓDONY, I., PEKKER, P., MOLNÁR, Z., NEUHUBER, S., GIER, S., KOVÁCS, I., DEMÉNY, A., PÓSFAI, M. (2023): Crystal Growth & Design, 23, 3202–3212.

- MOLNÁR, Z., DÓDONY, I., PÓSFAI, M. (2023): Geochimica et Cosmochimica Acta, 345, 90–101.
- MOLNÁR, Z., PEKKER, P., REČNIK, A., PÓSFAI, M. (2024): Nanoscale, 16, 2012–2021.
- NYIRŐ-KÓSA, I., ROSTÁSI, Á., BERECZK-TOMPA, É., CORA, I., KOBLAR, M., KOVÁCS, A., PÓSFAI, M. (2018): Earth and Planetary Science Letters, 496, 20–28.
- PÓSFAI, M., MOLNÁR, Z., NYIRŐ-KÓSA, I., RÁCZ, K., PEKKER, P., ISTVÁNOVICS, V. (2024): In: STAICU, L. C., BARTON, L. L. (Eds.): Geomicrobiology, Volume 2: Natural and anthropogenic settings. Springer, pp. 261–280.

CARBONATE FORMATION, PARTICULATE PHOSPHORUS AND ALGAL BLOOMS: SEDIMENT MINERALS AFFECT LIFE IN A SHALLOW LAKE

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Minerals in the sediments of shallow lakes play important roles in nutrient cycling. The release of sediment-bound phosphorus (P) triggers blooms of cyanobacteria and other algal species (ISTVÁNOVICS et al., 2022). On the other hand, a consequence of photosynthesis is the precipitation of carbonate mineral particles (NYIRŐ-KÓSA et al., 2018) that sink and contribute to lake sediments, presumably adsorbing and thus removing P from the pore water. Our aim was to understand two specific phenomena related to algal blooms: carbonate mineral precipitation and the dynamics of P-rich particles between organisms and the sediment. The focus of our studies was Lake Balaton, a culturally and economically important, large (590 km² surface area), shallow (on average 3.5 m deep), calcareous lake in Hungary.

Water samples were obtained from the lake during algal blooms over the summers of the last four years; solid particles (including cells of algae and precipitated minerals) were either let to deposit or filtered and transferred to transmission electron microscopy (TEM) grids. We also collected samples from the upper 10 cm of the sediment. In addition to analyzing environmental samples, we performed laboratory experiments to precipitate carbonate minerals from solutions simulating lake water, and observed the physical properties and phase transformations of the products under controlled conditions. In particular, we focused on the effects of the clay mineral smectite, present in the water as nmscale flakes, on carbonate precipitation. We also performed a month-long mesocosm experiment, in order to link the laboratory results with phenomena observed in the lake. An algal bloom was triggered artificially, and both the changes in

the properties of precipitating carbonate minerals and the formation of P-rich nanoparticles were observed.

All solid samples were characterized using a Thermo Scientific Talos F200X G2 scanning transmission electron microscope, both in conventional transmission (TEM) and scanning transmission (STEM) modes. High-resolution annular TEM and high-angle dark-field (HAADF) STEM images were obtained, along with selected-area electron diffraction (SAED) patterns, and elemental maps were acquired using energy-dispersive X-ray spectroscopy (EDS) in STEM mode. HAADF STEM electron tomography was performed to study the 3D shapes of nanoparticles.

Concerning carbonate formation, the results obtained at the three spatial scales - lake, mesocosm and laboratory - were remarkably consistent, with each of the three types of observations providing some specific details. Amorphous calcium carbonate (ACC) precipitated in the immediate vicinity of photosynthesizing cells (PÓSFAI et al., 2024). ACC then transformed through dissolution and reprecipitation into aragonite with a peculiar morphology: spindle-shaped particles consisting of nm-scale crystals in a largely identical crystallographic orientation, forming mesocrystals (Fig. 1a-c) (MOLNÁR et al., 2024). The aragonite spindles then converted to Mg-bearing calcite particles, again by dissolution and reprecipitation. Whenever smectite clay flakes were present in the solution, the formation of the stable final product, Mg-bearing calcite, was accelerated, since the clay provided a suitable heterogeneous surface for nucleation and compartmentalized a space in which

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supersaturation could be achieved (MOLNÁR et al., 2021). The entire process of precipitation and transformations from ACC to Mg-bearing calcite took place within hours to days; thus, the typical Lake Balaton sediment contains only Mg-bearing calcite particles. A minor component of the sediment is a carbonate mineral with a calcitetype structure and a composition close to that of $(CaMg(CO_3)_2).$ High-resolution dolomite HAADF images of crystals of this material revealed that dolomite-like, perfect Mg-Ca ordering occurs in few-nm-large domains, alternating with domains characterized by disordered Mg-Ca distribution and a Ca-rich composition (Fig. 1d, e).

We identified P-rich nanoparticles both in association with algal blooms and in the Polyphosphate inclusions sediment. were abundant in cells of various cyanobacteria. Remarkably, outside but next to the cells similar P-rich particles occurred but with slightly different compositions. On the other hand, lake sediments typically contained P-rich particles adhered to clay minerals, ranging in structure from amorphous to that of apatite. By comparing algal cells from the lake and from laboratory cultures, a sequence of transformation of biogenic polyphosphate inclusions could be identified. Upon cell lysis, polyphosphate particles are liberated from cells and exposed to the lake water. These P-rich particles can then be



Fig. 1: (a) TEM image of spindle-shaped aragonite; (b) SAED pattern obtained from the area marked in (a), confirming a mesocrystalline nature of the particle; (c) 3D morphology of two interpenetrating aragonite spindles, reconstructed from HAADF-STEM electron tomography; (d) composite of STEM-EDS element maps obtained from a zoned Mg-rich calcite particle, with associated smectite clay flakes (in red); (e) atomic-resolution HAADF image obtained from the Mg-rich rim of the particle in (d), displaying alternating domains with ordered and disordered Mg–Ca distributions (each white spot in the image represents a cation position.

partly hydrolyzed, making their P content available to microorganisms, and partly captured by the surfaces of clay minerals and then permanently stored as apatite in the sediment.

Our results reveal a complex sequence of carbonate-forming events that result in Mgbearing calcite, the major carbonate mineral of the lake sediment. Carbonate precipitation is thought to provide a sink for P (by its adsorption on the mineral surface); however, the multistep process of carbonate formation that involves dissolution reprecipitation and cvcles complicates the understanding of the fate of adsorbed species, including that of P. Concerning the particulate forms of P, we identified a likely link between biogenic, intracellular polyphosphate inclusions in algae, extracellular P-rich particles, and nanoparticulate apatite in the sediment. Thus, biogenic P-rich nanoparticles may be important and hitherto unrecognized components of the P cycle in lakes. By accelerating carbonate nucleation and transformation, and by anchoring Ca phosphate nanoparticles, smectite clay flakes were found to play important roles in both carbonate formation and P immobilization.

In summary, inorganic sediment minerals and nutrient cycles are linked in complex ways in shallow Lake Balaton. In addition to the environmental significance of our results, highresolution HAADF imaging and electron tomography resulted in new mineralogical insight into Mg–Ca ordering on the nanoscale resulting in dolomite formation, and on the physical nature of spindle-shaped aragonite mesocrystals, respectively.

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References

- ISTVÁNOVICS, V., HONTI, M., TORMA, P., KOUSAL, J. (2022): Freshwater Biology, 67, 1091–1106.
- MOLNÁR, Z., PEKKER, P., DÓDONY, I., PÓSFAI, M. (2021): Earth and Planetary Science Letters, 567, 116971.
- MOLNÁR, Z., PEKKER, P., REČNIK, A., PÓSFAI, M. (2024): Nanoscale, 16, 2012–2021.
- NYIRŐ-KÓSA, I., ROSTÁSI, Á., BERECZK-TOMPA, É., CORA, I., KOBLAR, M., KOVÁCS, A., PÓSFAI, M. (2018): Earth and Planetary Science Letters, 496, 20–28.
- PÓSFAI, M., MOLNÁR, Z., NYIRŐ-KÓSA, I., RÁCZ, K., PEKKER, P., ISTVÁNOVICS, V. (2024): In: STAICU, L. C., BARTON, L. L. (Eds.): Geomicrobiology, Volume 2: Natural and anthropogenic settings. Springer, pp. 261–280.

SYMMETRIES OF PREHISTORIC PATTERNS

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A basic geometrical pattern-group whose origin can be traced back to the plaiting technique, was born in the end of the Upper Paleolithic and has survived up to the present day. The earliest motifs and religious symbols of our global cultural history, such as the chevron, checker-board, rectangle, square and the forms based on the meander hook belong to this pattern-group. Each can be found in the Neolithic cultures of Europe in different proportions and varied stylistic presentations.

The question arises: what kinds of phenomena cause the wide temporal and spatial spread of this pattern-group?

Following the results of earlier archaeological, technological, psychological and mathematical research during my own study I have found two fundamental conditions which can lead to this. The extensive occurrence was caused in all likelihood partly by the geometrical rules of plaiting technology and to some extent by the cognitive processes of the human brain. Together they resulted in and determined the development of the same patterns in different cultures.

The patterns are built up from rectangular modules (as base units) with inner symmetry.

The boundary lines of the modules are potential operation axes on which the different isometric operations (reflection, glide reflection, rotation, translation) can be implemented. The axes are the part of an underlying geometrical grid structure. Further rules can be conceived in the relationship of the visible patterns and their hidden complementary structure. The visible part of the patterns is built up of hypotenuses of right-angled triangles. The perpendicular legs of the right triangles correspond to the two sides of the base modules.

The classification of patterns takes place in accordance with a geometrical system. The ornamentations are formed from one another, not only indicating their close association, but also an opportunity to be born ongoing. At least a partial knowledge of this underlying structure and the use of symmetry operations are necessary to construct this type of patterns. Additionally, while repeating the motif, the application of calculation is a basic criterion.

In this universal pattern-group, geometric form creation is based on isometric operations and counting, so the intuitive mathematical thinking is clearly manifested.

HUNGARIAN TO OTTOMAN TECHNOLOGY SHIFT PRESERVED IN MORTARS FROM THE SZOLNOK FORTIFICATION (16TH CENTURY)

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Investigation of historical mortars usually reveals information related building to technology and raw material sources which can not be obtained from other sources. Moreover, the technological changes related to historical ages, shift in long-term customs of empires or even changes in local raw material sources can be traced. A peculiar change in mortar technology was preserved in the ruins of late medieval Szolnok fortification, despite several centuries of turmoil and demolition on the site. Two mortar materials were investigated, Hungarian (HuM) shortly before the conquest, and Ottoman (OtM) shortly after the conquest.

X-ray powder diffraction analysis was run on a Bruker D8 Discover instrument, with Cu-K α radiation (40 kV, 40 mA), in Bragg-Brentano geometry, with LynxEye XE-T position sensitive detector in high resolution mode. Quantitative composition was calculated with Rietveld refinement in Bruker TOPAS4. Electron microprobe studies were run on a JEOL JXA 8600 Superprobe (20 kV accelerating voltage, 20 nA beam current, carbon coating), equipped with an SDD-EDX detector. Textural characteristics and mineralogy were investigated by optical microscopy (polished 30 µm thin sections, Zeiss Imager A2m AXIO polarization microscope, Zeiss AxioCam MRc5 camera).

The bulk composition of the mortar samples is dominated by quartz and calcite (almost double in HuM), with traces of phyllosilicates, in good accordance with SEM+EDX. Dolomite is observed in the HuM, while the OtM has significant feldspar content. Part of the calcite has a Mg-content observed by both XRD and SEM+EDX analysis. However, in the Hungarian sample the Mg-rich calcite occurrence is mostly related to the hydraulic matrix, in accordance with its nanocrystalline state. The latter brings evidence to the use of freshwater dolomitic limestone – calc-sinter – for lime. Calc-sinter is a material found in shallow lacustrine deposits of the Great Hungarian Plain. The OtM in contrast is more likely based on CaO from limestones of the Bükk Mts. and is of higher quality also reflected by the higher amorphous content, directly related to the hydraulic binder mass.

The acid insoluble residue reveals the presence of garnet in HuM, also observed by microscopy investigations.

The difference in feldspar mineralogy and ratios is due to the use of different sand sources. The garnet, clinochlore and albite in the HuM acid insoluble residue is more indicative for siltsand recovered from the Tisza or its tributary, the Zagyva rivers. The acid insoluble residue of the OtM on the other hand is more specific for rhyolitic tuffs of the Bükkalja range. It might also explain the cristobalite content – undetected by optical microscopy, meaning it could also have its origin from plant-based ash used as hydraulic accelerator. In spite of cristobalite absence, the X-ray mapping reveals matrix details in the HuM also with Ca-bearing and Cl-rich alumino-silicate gel, indicative for plant ash and lime hydraulic product.

Based on all results, the obvious conclusion can be drawn, that a sharp shift of walling technology happened. Probable reasons could be a higher quality mortar of the OtM recipe, or a lower quality but more economic production, since fortification was not required at that moment in history.

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OTTOMAN (16TH-17TH CENTURTY) MUDBRICK AND MUD BINDER FROM THE TURSKISH PALACE OF SZOLNOK FORTIFICATION

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After the Ottoman conquest of the Szolnok fortification, a rearrangement and redesign of buildings and wall system was devised and implemented. Walling and building based on mud brick is traditionally a cheap, fast, effective and large-scale form of construction technology. In flood plain and lowland regions, any clay-rich sediment which meets the adobe grade requirements, i.e. shaping and drying results in a hardened block, is suitable for mud brick production. In a more sophisticated technology, dried straw or grasses are used as fibre reinforcement, a high-tech equivalent product being the admixed ash and lime, for alkali activated or hydraulic binder. In our samples straw addition is not evidenced, however it's not elementary to detect reacted ash in a refined clay matrix.

A wall segment of a palace from the fortification was recovered, in a surprisingly good preservation state. Bricks and binder could be visually delimited, thus samples were collected. A sample preparation strategy of bulk powder and clay fraction mineralogy (XRD), particle size analysis (PSA) and electron microscopy analysis (SEM+EDX) were adopted. Differently coloured parts, patches, lumps were extracted and investigated separately.

X-ray powder diffraction (XRD) analysis was run on a Bruker D8 Discover instrument, with Cu-K α radiation (40 kV, 40 mA), in Bragg-Brentano geometry, with LynxEye XE-T position sensitive detector in high resolution mode. Quantitative composition was calculated with Rietveld refinement in Bruker TOPAS4. Electron microscopy (SEM+EDX) was done on a JEOL JXA 8600 Superprobe (20 kV accelerating voltage, 20 nA beam current, carbon coating), equipped with an SDD-EDX detector. Textural characteristics and mineralogy were investigated by optical stereo microscopy.

The sedimentation and particle size analysis revealed a fine, clay rich silt material, with high clay fraction. XRD analysis reveals low, < 35 wt% quartz and significant feldspar (~10 wt%), mostly albite and microcline.

The dominant clay mineral is illite, with chlorite (2–4 wt%), kaolinite (2–3 wt%) and smectite (3–4 wt%). In the binder material, clay content is enriched, on the expense of quartz and muscovite, supporting the idea of sedimentation processing of brick clay to obtain the binder. The composition of fired bricks fragments is supported by XRD to be clay material fired at high temperatures, diopside and labradorite indicating 950–1000 °C. This indicates that raw materials and technology existed for high quality brick firing prior to Ottoman occupation.

The carbonate content is supportive for the addition of lime paste to the binder base, as calcite content is significantly increasing in the binder, while dolomite is only moderately increased. In addition, the amorphous content of the binder is also higher and even if the use of plant ash can not be traced back, the use of hydraulic additives to the clay binder base seems supported.

The composition of the base material is very similar to clay deposits found in the Tisza River flood plain. Also, the use of local raw materials is logical for adobe bricks. However, it remains a mystery why to choose adobe instead of good quality fired brick, unless the use and simplicity of production.

DETECTION OF RADIOACTIVE MINERALIZATION-BEARING ALTERA-TION ZONES USING LANDSAT-8 REMOTE SENSING IMAGERY: A CASE STUDY FROM THE CENTRAL EASTERN DESERT, EGYPT

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The El-Missikat and El-Erediya areas in Egypt's Central Eastern Desert are notable for their potential for radioactive mineralization. This is largely due to prominent shear zones in the syenogranitoid plutons. These shear zones facilitate the flow of hydrothermal solutions rich in minerals, leading to the formation of alteration zones where radioactive minerals precipitate in the resulting cavities and fissures.

Previous studies have underscored the presence of multiple mineralized alteration zones in the study area, encompassing kaolinization, greisenization, silicification, fluoritization, carbonitization, and hematization (ABU-DEIF & EL-TAHIR, 2008).

Recent breakthroughs in remote sensing technology have showcased their efficiency in mineralization and alteration zone detection (AHMADIROUHANI *et al.*, 2017). This study used LandSat-8 FCCs and BR techniques, to accurately detect alteration zones hosting radioactive minerals.

Numerous alteration zones hosting radioactive minerals have been confirmed, particularly in the shear zone, matching previous study locations. It validates the effectiveness of satellite technology and also leads to the identification of new unexplored alteration zones (Fig. 1a-c).

The alteration zones detected by Landsat-8 satellite imagery were validated through extensive fieldwork and meticulous microscopic investigations. This was accomplished by extracting samples from the shear zones, which clearly exhibited signs of shearing and alteration.

The petrographic analysis identified various alterations, including silicification, hematization, kaolinization, sericitization, and epidotization, all linked to radioactive minerals like uranophane, kasolite, and autunite (Fig. 1d-i).

With a global focus on economically valuable regions, it's essential to thoroughly investigate newly recognized alteration zones in this study area using advanced technologies.

References

- ABU-DEIF, A., EL-TAHIR, M. (2008): Earth Sciences, 19 (1), 85–97.
- AHMADIROUHANI, R., RAHIMI, B., KARIMPOUR, H., SHAFAROUDI, M., SADEGH, A., NAJAFI, S., POUR, B. (2017): Journal of African Earth Sciences, 134, 600– 612.



Fig. 1: Mapping alteration zones using threshold values of various band ratios: (a) Ferric oxide, (b) Clay minerals, and (c) Sericite minerals. Photomicrographs illustrating uranium mineralization associated with various types of alteration: (d, e) uranium mineralization linked to the ferrugination process, (f, g) secondary uranium mineralization associated with the kaolinization process resulting from the hydration of perthite, and (h, i) uranium mineralization occurring alongside the sericitization process, which involves the alteration of K-feldspar into sericite. Symbols: UrP=Uranophane, Atn=Autunite, Tho=Thorite Qz=Quartz, Pr=Perthite, Pt=Pitchblende, Sr=Sericite, and IO=Iron Oxides.

LASER ABLATION AND LIBS APPLICATIONS IN GEOCHEMISTRY

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Laser Ablation (LA) combined with Laser-Induced Breakdown Spectroscopy (LIBS) has become a pivotal analytical approach in geochemistry, offering a rapid and precise method for the elemental analysis of geological materials. LA involves the use of high-energy laser pulses to ablate material from a sample surface, generating a microplasma. This plasma emission is then analyzed through LIBS, which identifies the elemental composition based on the characteristic spectral lines.

The LA-LIBS technique is distinguished by its ability to perform in-situ, real-time analysis with minimal sample preparation and high spatial resolution, making it particularly suited for complex and heterogeneous geological samples. This method provides significant advantages in geochemical investigations, such as the precise detection of trace elements and isotopic compositions, essential for understanding geological processes, provenance studies, and environmental assessments. In geochemistry, LA-LIBS is employed in a variety of applications, including the characterization of mineral deposits, the analysis of fluid inclusions, the study of volcanic products, and the examination of sedimentary records. Its capability to provide detailed compositional maps at microscale resolutions allows for the exploration of elemental distribution patterns, shedding light on the formation and alteration processes of geological materials.

Recent technological advancements have enhanced the sensitivity, accuracy, and detection limits of LA-LIBS systems, facilitating their widespread adoption in both field-based and laboratory-based geochemical research. Future developments are expected to further improve these capabilities, enabling more comprehensive geochemical analyses and contributing to a deeper understanding of the Earth's composition and the dynamic processes that shape our planet.

SPECIFIC TYPE OF ALTERATION OF CLINOPYROXENE (PERMIAN, BASALTS/LAMPROPHYRES, WESTERN CARPATHIANS)

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In the Permian basalts (Hronic Unit, Nízke Tatry Mts.), but also in the Permian lamprophyres (Tatric Unit, Malá Fatra Mts.), we found two genetically different types of clinopyroxenes (Cpx).

Based on their composition, the basaltic rocks were described as rift-related continental tholeiites (DOSTÁL *et al.*, 2003; VOZÁR *et al.*, 2015) and lamprophyres were classified as calcalkaline lamprophyres (SPIŠIAK *et al.*, 2018). The rocks are partially altered and the mineral composition of both rock types is very similar (plagioclase, clinopyroxene, magnesiohornblende, altered biotites, fine-grained dark matrix, and opaque minerals). The secondary minerals are represented by albite, chlorite, actinolite, hydrated garnets and occasionally pumpellyite-prehnite.

Two types of Cpx occur in these rocks. Both types of Cpx have a different chemical composition (SPIŠIAK *et al.*, 2017). The first type consists of porphyritic growths coexisting with other magmatic mineral phases, mainly

amphibole and plagioclase (Fig. 1a). Clinopyroxene (Cpx) phenocrysts are generally subhedral to euhedral and may occur as discrete crystals as well as aggregates. Based on microprobe analyses and following the IMA classification (MORIMOTO *et al.*, 1988), these clinopyroxenes correspond to augites (both types).

The second type forms xenocrysts. The xenocrysts are often lined with a newly formed pyroxene, which has a composition identical to the porphyry growths (Fig. 1b, 2a). Cpx xenocrysts in both types of basalts have a similar composition (they differ more significantly only in the contents of TiO_2 and Al_2O_3). In both types of basalts, we observed the same type of xenocrysts alteration. The Cpx xenocrysts are altered to form hydrated grossular-almandine garnets (katoite) and chlorite. The composition of hydrated garnets and chlorites is very similar in both cases. In addition to these chlorites, there are also chlorites in the matrix with an increased content of TiO_2 and K_2O (this may indicate their



Fig. 1: Back-scattered electron (BSE) images of two types of clinopyroxenes (Cpx1 – first type of clinopyroxene (porphyritic), Cpx2 – second type clinopyroxene (xenocrysts), HG – hydrated garnet Chl – chlorite. Sample DS-29 Dubná skala (lamprophyres, Tatric Unit, Malá Fatra Mts.)



Fig. 2: Back-scattered electron (BSE) images of two types of clinopyroxenes. Fig 2b Detail of the composition of hydrated garnets (HG) from Fig. 2a (Cpx1 – first type clinopyroxene (porphyritic), Cpx2 – second type clinopyroxene (xenocrysts), HG – hydrated garnet Chl – chlorite, Ttn – titanite, Sp – sphalerite. Sample NT-1 Malužiná (basalts, Hronic unit, Nízke Tatry Mts.).

formation triggered by biotite alteration). Hydrated garnets occur in irregular shapes prolonged in the direction of the original cleavage of clinopyroxenes, and/or it forms irregular oval shapes with diffuse (frayed) rims. Hydrated garnets contain inclusions of titanite and sphalerite (Fig. 2b). The presence of OH in their structure was confirmed by Raman spectroscopy. Following the garnet classification published by GREW et al. (2013), these garnets belong to the kenogarnets group; the content of katoite end-member varies from 2.3 to 5.1 mol. %. Dominant end members are grossular (from 37.6 to 44.9 mol. %) and andradite (from 46.7 to 53.4 mol. %). Elevated Ti content is reflected in the presence of morimotoite end-member (from 0.6 to 4.7 mol. %). Garnets thus correspond to a Fe³⁺ analogue of katoite.

Given that Cpx occur in form of xenocrysts, we must assume that they probably entered the basic melt at great depths, at the place of magma generation. At the same time, the transformation of anhydrous Cpx into a mixture of hydrated garnets and chlorite points to the presence of a relatively high water content.

Acknowledgement

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References

- DOSTÁL, J., VOZÁR, J., KEPPIE, J. D., HOVORKA, D. (2003): International Journal of Earth Sciences, 92(1), 27–35.
- GREW, E. S., LOCOCK, A. J., MILLS, S. J.,GALUSKINA, I. O., GALUSKIN, E. V.,HALENIUS, U. (2013): American Mineralogist, 98, 785–811.
- MORIMOTO, N., FABRIES, J., FERGUSON, A. K., GINZBURG, I. V., ROSS, M., SEIFERT, F. A., ZUSSMAN, J., AOKI, K., GOTTARDI, G. (1988): American Mineralogist, 73(1), 1123–1133.
- SPIŠIAK, J., VOZÁROVÁ, A., VOZÁR, J., FERENC, Š., MIKUŠ, T., ŠIMONOVÁ, V. (2017): Carpathian Journal of Earth and Environmental Sciences, 12(1), 293–299.
- SPIŠIAK, J., VETRÁKOVÁ, L., CHEW, D. J., FERENC, Š., MIKUŠ, T., ŠIMONOVÁ, V., BAČÍK, P. (2018): Geologica Carpathica, 69(5), 453–466.
- VOZÁR, A., SPIŠIAK, J., VOZÁROVÁ, A., BAZARNÍK, J., KRÁĽ, J. (2015): Geologica Carpathica, 66(1), 3–17.

A SOLUTION FOR THE AUTOMATED ANALYSIS OF GEOLOGICAL SAMPLES

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The analysis of geological materials in the SEM comes with a specific set of requirements – with the need for the microscope and analytical platforms to work closely together to achieve optimal results in the most efficient manner. Geological samples almost always contain a long list of elements (many of which have potential overlaps in EDS spectra) and there is frequently the need to analyse large samples or sample areas in order to develop an understanding of the populations of mineral grains that together form a rock.

Here, we present a comprehensive solution to this need that incorporates the cutting-edge analytical capabilities of Oxford Instruments' AZtecLive nanoanalysis platform with JEOL's IT710HR SEM. The analytical system incorporates at its core, Oxford Instruments' Tru-Q technology; a collection of algorithms which together enable industry leading spectral processing give superior elemental to identification, deconvolution, and quantification correcting for the physical processes that, if not accounted for, can harm the quality of data acquired. These algorithms are used in all EDS based analyses, including automated particle with AZtecLive's **AZtecFeature** analysis functionality and automated mineralogy with AZtecMineral.

The AZtecLive platform and functionalities within it enable the accurate identification of minerals in terms of both their major and minor elements. With this data in turn allowing full sample scale characterisation of relative mineral abundances and key properties such as mineral associations and, when needed, minerals processing properties such as liberation and grade recovery.

Combining this software with the high current at low or high acceleration voltage of the JEOL IT710HR and Oxford Instruments Ultim Max detectors means that a high resolution and fast analysis can be achieved.

The workflows that we will discuss offer the flexibility to handle multiple different sample types, allowing for a workflow that starts with manual investigation and moves on to whole sample compositional understanding. The combined system simplifies complex tasks, guiding users through the entire analytical workflow.

Further analyses of samples are possible through the direct integration of other analytical techniques such within the same software platform. Wavelength-dispersive spectroscopy (WDS), electron backscatter diffraction (EBSD), and backscattered electron + X-ray imaging (BEX) can all be utilised within a single workflow. This holistic approach enables comprehensive researchers to gain a understanding of sample characteristics and facilitates a more in-depth mineral analysis to address both current and potential future needs.

SUPERGENE MINERALS FROM THE WASTE DUMPS OF THE DOLEA MINE (BRUSTURI, ROMANIA)

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The Dolea Mine, a historic Pb-Zn-Cu ore mine located near the village of Brusturi in Arad County, Romania, ceased operations in the mid-19th century, leaving non-recultivated waste dumps behind. These waste dumps pose potential environmental hazards, which can best be understood by studying the secondary minerals that form there. Previous studies (e.g. PAPP, 1909) identified minerals such as

- cerussite (PbCO₃),
- linarite (PbCu(SO₄)(OH)₂),
- caledonite (Pb₅Cu₂(SO₄)₃(CO₃)(OH)₆),
- malachite (Cu₂(CO₃)(OH)₂) and
- leadhillite (Pb₄(CO₃)₂(SO₄)(OH)₂).

In recent years, the following minerals were identified from samples collected by mineral collector Gábor Koller:

- bechererite (Zn₇Cu(OH)₁₃[(SiO(OH)₃(SO₄)]),
- wroewolfeite (Cu₄(SO₄)(OH)₆ ·2H₂O),
- redgillite $(Cu_6(SO_4)(OH)_{10} \cdot H_2O)$, and
- namuwite $(Zn_4(SO_4)(OH)_6 \cdot 4H_2O)$.
- The aim of this project is to provide a detailed description of the secondary mineral paragenesis of the Dolea Mine, with a particular focus on sulfates and carbonates. The study seeks to understand why these minerals are found only in two small areas: a vein outcrop above an old adit and an adjacent waste dump.

Based on the results of SEM-EDS and Raman spectroscopy analyses, a diverse mineral

paragenesis is present, with a total of 30 secondary mineral species dominated by sulfates and carbonates, including many species that are rare on a global scale. Some new species were identified from the site, such as:

- antlerite (Cu₃(SO₄)(OH)₄),
- dundasite (PbAl₂(CO₃)₂(OH)₄ \cdot H₂O),
- felsőbányaite (Al₄(SO₄)(OH)₁₀ · 4H₂O),
- ktenasite $(ZnCu_4(SO_4)_2(OH)_6 \cdot 6H_2O)$,
- langite $(Cu_4(SO_4)(OH)_6 \cdot 2H_2O)$,
- lautenthalite (PbCu₄(SO₄)₂(OH)₆ \cdot 3H₂O),
- posnjakite ($Cu_4(SO_4)(OH)_6 \cdot H_2O$),
- ramsbeckite ((Cu,Zn)₁₅(SO_4)₄(OH)₂₂ · $6H_2O$),
- rosasite $((Cu,Zn)_2(CO_3)(OH)_2)$,
- serpierite $(Ca(Cu,Zn)_4(SO_4)_2(OH)_6 3H_2O)$
- woodwardite $(Cu_{1-x}Al_x(OH)_2(SO_4)_{x/2}$ · $nH_2O(x < 0.5 n < 3x/2)).$

The presence of carbonates is due to the unique location of the deposit. Directly above it lies a forest, where CO_2 produced from the decomposition of organic matter reacts with meteoric waters and oxidizing sulfides to form secondary carbonates. This helps prevent heavy metal pollution, as Pb, Zn, and Cu remain in place thanks to these minerals.

Reference

PAPP, K. (1909): Bányászati és Kohászati Lapok, 42, 612–625.

POSSIBLE HUNGARIAN MINERAL-BASED CATALYST CARRIERS

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Two types of catalysis are used in industrial processes - heterogeneous and homogeneous catalysis. In homogeneous catalysis, the catalyst and the reactant are present in one phase and form an intermediate product during the reaction, which eventually leads to the final product (SHELDON et al., 2007). In heterogeneous catalysis, the reactant and the catalyst are in different phases, and as a consequence, the reactants come into contact with the catalyst surface where they adsorb, and the catalysis takes place in the presence of the active phase. In addition to the active phase that performs heterogeneous catalysis, the geometry of the catalyst has an important role in the selectivity and rate of the reaction and can even determine the catalysis reaction completely (TÉTÉNYI et al., 2002). The right geometry for a certain catalytic reaction is significantly influenced by the chosen catalyst, carrier and synthesis method.

The catalyst carriers can be divided into two groups: natural and synthetic substrates. Synthetic catalyst supports have a well-defined, homogeneous structure and 99.9% purity, but they are expensive to produce. Natural carriers have relatively low costs and lower negative environmental impacts, but their structure is not always well defined, and they contain a higher proportion of pollutants. Such materials may include diatoms, clay minerals (smectitemontmorillonite, kaolinite), zeolites (mordenite) and perlite.

The diatomaceous earth is made up of the skeletons of algae, with a high amorphous SiO_2 content due to $[SiO4]^{4-}$ dissolved in the aqueous environment (lakes, lagoons). The pitted structure of the algae skeletons provides the material with high macro- and mesoporosity, thus increasing the quantity of active surfaces. High grade diatomite is available at the Erdőbénye deposit, requiring low cleaning

processes (Fig. 1). Due to the high SiO_2 content, it is inert to acids and alkalis and is heat resistant. (BENAYACHE *et al.*, 2018). Because of the properties which have been described above, the material is widely used as a carrier or base for catalysts carrier (NAZHIPKYZY *et al.*, 2022) and has also been successfully used in photocatalytic processes (SUN *et al.*, 2015).



Fig. 1: *BSE-SEM* image of the raw diatomite from the Erdőbénye deposit.

A significant part of the properties of perlite can be considered similar to those of diatomite due to their high SiO_2 content, which is lower than 80% for perlite. The advantages of the material include the development of its porosity thermal expansion, creating a porous, lowdensity and high specific surface area material. High grade perlite suitable for expansion is exploited and beneficiated at Pálháza, untested yet in catalytic processes.

Among the main advantages of zeolites are their selective adsorption and cation exchange capacity and their catalytic ability. These properties result from their unique structure, where the SiO_4 and AlO_4 tetrahedra are coupled to build up an open cage and channel cavity

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system in the lattice. The cation exchange in the structure is caused by the exchange of Si⁴⁺ with Al^{3+} , which allows the cations to be integrated into the structure due to the disruption of the charge equilibrium (SZAKÁLL, 2005). Zeolites are used as molecular sieves with pre-produced well-defined structural and elemental composition as catalyst supports for the industry. Several experiments with clinoptilolite and/or mordenite rich rhyolite tuffs are reported in the literature. Such materials are available in the Mád-Tokaj area, beneficiated for various applications. The deposits have two groups, with clinoptilolite mordenite or dominant compositions (Fig. 2).



Fig. 2: BSE-SEM image of the mordenite-dominant rhyolite tuff from the Mád-Tokaj area.

The clays, in particular smectite and kaolinite, are used in the synthesis of metal catalysts

because of their structural properties, where the tetrahedral and octahedral t-o-t layer structure can exchange a large number of cations. Metal complexes are integrated into the layers to moderate the physicochemical interaction of reactants in interlamellar reactions, thus increasing selectivity. The high-grade bentonite deposits of Hungary are currently unexploited, however the diatomite and zeolite deposits all have significant montmorillonite bearing parts. A similar situation is found for kaolinite, although the small deposits in Zemplén Mts. are not suitable for other industrial applications.

References

- BENAYACHE, S., ALLEG, S., MEBREK, A., SUNOL, J. J. (2018): Vacuum, 157, 136–144.
- NAZHIPKYZY, M., NEMKAYEVA, R. R., NURGAIN, A., SEITKAZIOVA, A. R., DINISTANOVA, B. K., ISSANBEKOVA, A. T., MAMATOVA, G. U. (2022): Nanomaterials, 12(11), 1817.
- SHELDON, R. A., ARENS, I., HANEFELD, U. (2007): Green chemistry and catalysis.Weinheim: John Wiley & Sons.
- SUN, Z., YAN, Y., ZHANG, G., WU, Z., ZHENG, S. (2015): Advanced Powder Technology, 26(2), 595–601.
- SZAKÁLL, S. (2005): Ásványrendszertan. Miskolc: Miskolci Egyetemi Kiadó.
- TÉTÉNYI, P., LÁZÁR, K., PAÁL, Z., SIMÁNDI, L. (2002): Magyar Tudomány, 1548–1556.

DIATOMITE SUPPORTED MAGNETIC Pd CATALYST

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The high specific surface area, porosity, chemical stability and low density all are in favour of a suitable catalyst carrier. Most of the silica is amorphous but diatomites may contain quartz, opal, cristobalite, clay minerals, carbonate and feldspars, and may dispose of organic matter. These substances act as pollutants for catalyser formulations, requiring purification and treatment. The situation better for bedded deposits, such as Ligetmajor (Erdőbénye, Hungary), where the highest-grade layers have a SiO₂ content of 90.8–99.8%, with low clay and iron minerals. The material density is 1.95-2.3 g/cm³ and its bulk density is around 0.8 g/cm^3 .

Spinel-type magnetic carriers are a promising area among catalyst carrier materials, due to platinum metals affinity to their surface and also easier recovery from their application media (NASROLLAHZADEH *et al.*, 2018). High surface area and structural porosity materials are ideal for their support, making diatomite a possible raw material (SUN *et al.*, 2017).

Composition and purity of diatomite and all synthesized products was investigated with XRD and SEM+EDX, surface activity of raw diatomite measured by Z-potential. HRTEM investigations were carried out to observe magnetite dispersion on the silica surface. ATR-FTIR was applied to observe the state of surface hydroxylation and changes in chemical structure of the silica during experiments. After catalytic experiments the measurements were repeated to observe stability of catalyser and carrier.

Crystallization of magnetite on the diatomite surface is facilitated by the presence of unbalanced structural oxygens. The precursor for magnetite was Fe^{+3} -cytrate, applied as amorphous film in water-based dispersion. Crystallization was resolved at 400 °C in nitrogen flow, followed by r.t. Pd deposition. All crystallization reactions are supported by XRD results, a good degree of dispersion observed by SEM+EDX. HRTEM reveals the development of 10-20 nm magnetite crystals both on the surface and in the pores of diatom shells. According to ATR-FTIR the state and structure of silica was not changed during the processing. Catalytic activity was tested by hydrogenation of nitrobenzene to aniline, monitoring rate of transformation by mass spectrometer-based gas chromatography. The catalytic efficiency of magnetite and noble metal doped magnetites in the hydrogenation of nitrobenzene has been discussed in several literatures, on selectivity and reaction time bases, accounting for pressure, temperature and amount of catalyst. For Pd doped maghemite, at 20 and 30 °C in the presence of 0.2 g of catalyst, nitrobenzene to aniline conversion occurred in 80 min with 97% selectivity (HAJDU et al., 2020). In our experiment the reaction was complete in 15 minutes with 97% selectivity at the same temperatures, using only 0.1 g catalyst.

References

- HAJDU, V., PREKOB, Á., MURÁNSZKY, G., KOCSERHA, I., KÓNYA, Z., FISER, B., VANYOREK, L. (2020): Reaction Kinetics, Mechanisms and Catalysis, 129, 107–116.
- NASROLLAHZADEH, M., SAJJADI, M., MAHAM, M., SAJADI, S. M., BARZINJY, A. A. (2018): Materials Research Bulletin, 102, 24–35.
- SUN, Z., YAO, G., LIU, M., & ZHENG, S. (2017): Journal of the Taiwan Institute of Chemical Engineers, 71, 501–509.

HISTORICAL RECONSTRUCTION OF THE 18–19TH CENTURY MINERAL COLLECTION OF THE PANNONHALMA ARCHABBEY, NW HUNGARY

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In today's Hungary, four major mineral collections date back to the 18th and early 19th centuries: the Schemnitz (Selmec) Collection at the University of Miskolc (1763), the Collection of the former Royal Hungarian University, today Eötvös Museum of Natural History, Eötvös Loránd University, Budapest (1774), the collection of the Hungarian Natural History Museum, Budapest (1802) and the collection of the Benedictine Abbey of Pannonhalma (1802) (PAPP et al., 1991). While the history and scientific importance of the first three are well documented, the latter had been latent for more than seven decades, only a preliminary study was published on it (MAYER & SZAKÁLL, 1991).

The scientific reconstruction of the Archabbey's mineral collection began in 2021, as the first stage of a project to professionally reconstruct the more than 20 thematic collections of the Archabbey Museum.

The Pannonhalma Benedictine Abbey, with its 996 AD foundation has been the oldest, continuously active institution in Hungary. The only short pause in its activity started in 1786, when King Joseph II suspended the order. In 1802 King Francis I restored the order and in return imposed an educational obligation, in accordance to Queen Maria Theresa's Ratio Educationis (1777).

As the Ratio Educationis requested a practice based regular teaching of natural history in lower and secondary schools, a mineral collection had to be established in the Archabbey to help the students there to study.

The present-day mineral collection of the Benedictine Archabbey of Pannonhalma was founded on the acquisition of two large collections, both having roots back to the 18th century: the Spaits Collection in 1802, and the Mitterpacher Collection in 1833.

The former bears the name of its original owner, Stephanus/Stephan/István Spaits, an ex-Jesuit monk, priest, teacher, and member of the Jena Mineralogical Society who was the of a Székesfehérvár. principal Hungary secondary school when, at the downhill of his life, he sold his mineral collection. The obviously 18th century collection was listed in an "original" catalogue written both in Latin and German, available still today. According to MAYER & SZAKÁLL (1991) the collection originally contained 920 specimens and they estimate the number of still identifiable specimens from that collection to be 350.

The second collection, which arrived at the Abbey in 1833, was assembled by Ludovic/Ludwig/Lajos Mitterpacher (von Mitterburg) and his nephew Georg/György Mitterpacher. Ludovic Mitterpacher, originally a Jesuit monk-teacher, was a natural scientist and later became the first university professor of agriculture at the Royal Hungarian University. Following his death in 1814, his predominantly 18th century mineral collection was inherited by his nephew, Georg Mitterpacher.

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Georg Mitterpacher served as a surgeon major Komarno/Komárom/Komorn (now at the Slovakia) garrison's hospital. His main interest was collecting minerals and rocks, he broadened his uncle's collection for almost two decades, but his collections covered other objects, too. Though no "original" catalogue/inventory of that combined Mitterpacher Collection could be found, the total number of specimens, representing the 18th century and the first third of the 19th century period, was estimated to be 980, out of which about 300 specimens were still identifiable years ago (MAYER 25 & SZAKÁLL, 1991).

The scientific reconstruction of the whole mineral collection started on two parallel tracks in 2021: 1) a complete electronic text and photo documentation of the specimens, including all pieces of information (*e.g.*, labels of earlier inventories, locality *etc.*) to be found on/next to the items; 2) a complete comprehensive and comparative electronic compilation of all the mineral and rock catalogues (both Latin and German) from the 1802–1850 period to be found in Pannonhalma were created. At the closing phase of the project the two databases were harmonized for the most basic parameters.

Our final data show that out of the total 4500 samples of the present day collection about 950 can be directly connected to the two large founding collections. Out of the original 874 inventory items of the Spaits catalogue 485 physical specimens could be labeled today as Spaits. For the Mitterpacher Collection we could identify (reconstruct) about 880 catalogue items, out of which 457 physical specimens are to be found currently in the collection. An interesting discovery related to the Mitterpacher Collection was a small booklet containing Abraham Werner's actual mineral and rock system, published in Brünn/Brno in 1804 by ANDRÉ (1804). The classification/notation applied in that booklet was the key for deciphering the labels on the Mitterpacher rock samples. The booklet is full of handwritten extensions, clearly its first owner, Ludovic Mitterpacher used the printed material as a template for listing his own collection (Fig. 1 and 2).

By comparing the specimen types and the locality representation of the Spaits and Mitterpacher collections we found two characteristic differences: an increased number (104 items) of rock specimens in the Mitterpacher collection and a large positive anomaly (about 110 items) of the Sicily and Naples related localities, including a set of volcanic ash from the famous October 1822 eruption of Vesuvius. The increased interest in rocks in the second and third decades of the 19th century represents the dawn of geology. That part of the collection should clearly be connected to the activity of the younger Mitterpacher.



Fig. 1: Annex to the 1804 New Year's issue of the Patriotisches Tageblatt, Brno. Part of the title page with a greeting from the publisher, Christian Karl André.

SZÜCS *et al.* (2023) showed that the increased number of the Naples and Sicily samples, some of them clearly dated to the 1820ies, the period of Georg Mitterpacher, was connected to a family network: Katalin Mitterpacher was the wife of the from 1821 commanding general of Naples, Johann Philipp Frimont. Currently we could specify further the relationship between the two Mitterpachers: Katalin was the sister of Georg (Fig. 3).

In the 222 years since its purchase, the collection has undergone many changes and events that have affected its role in education and the position of its owner, the Benedictine Order. Among these, the reform of secondary education in 1849 had a particularly direct impact on the

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Fig. 2: Annex to the 1804 New Year's issue of the Patriotisches Tageblatt, Brno. Internal pages of the booklet with Werner's mineralogical system (printed) and Ludovic Mitterpacher's related handwritten catalogue notes (Museum of Benedictine Archabbey, Pannonhalma)

collection. The reform made illustrative teaching a priority, and the Archabbey transferred many items from its own collection to other, less wellequipped schools of the Benedictine Order. The collection survived the tumultuous changes of the 20th century, including two years of nationalisation of the grammar school, as well as the abolition of the separate secondary teaching of classical natural history, including mineralogy in 1948.

As a conclusion we can confirm that the Pannonhalma mineral collection is the second largest collection of verifiably 18th century material in Hungary, and the only collection overarching the 1815–1830 period, otherwise blank in the other Hungarian historical collections.

As a result of the 3 years long collective work of practically all Hungarian mineralogical research institutions, beside the electronic databases, a complete new storage system hosts the cleaned and labeled minerals, and, in 2024, even a small, unorthodox mineral exhibition has been opened for the audience in the Abbey.

The current status of the collection's documentation offers a good base for future detailed individual research work, among others, on specific regional, topographic mineralogy, ore geology or mining history questions.

The authors which to thank the Baranya County Archives of the Hungarian National Archives for their permission to publish the document on Fig. 3.

References

- ANDRÉ, C. K. (1804): Werners Neustes Mineral System. Brünn: Patriotisches Tageblatt, 18 p.
- MAYER, F., SZAKÁLL, S. (1991): In VITÁLIS, GY., KECSKEMÉTI, T. (eds.): Museums and Collections in the History of Mineralogy, Geology and Paleontology in Hungary. Annals of the History of Hungarian Geology, Special Issue 3, Budapest: Hungarian Geological Survey, Hungarian Geological Society, pp. 347–364.
- PAPP, G., SZAKÁLL, S., WEISZBURG, T. (1991): In VITÁLIS, GY., KECSKEMÉTI, T. (eds.): Museums and Collections in the History of Mineralogy, Geology and Paleontology in Hungary. Annals of the History of Hungarian Geology, Special Issue 3, Budapest: Hungarian Geological Survey, Hungarian Geological Society, pp. 15–26.
- SZÜCS, L. CS., GHERDÁN, T., PAPP, G., WEISZBURG, T. (2023): The role of a nobleman from Bihor in the transfer of samples from the 1822 eruption of Mount Vesuvius to the Mitterpacher Collection of the Benedictine Archabbey of Pannonhalma. pp. 83–90, Proceedings of XVIth History of Science and Technology Conference, Salonta/Nagyszalonta, Hungarian Technical Scientific Society of Transylvania, Romania. (In Hungarian with English abstract and captions.)

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Fig. 3: An official document from 1832, related to the testimony of Georg Mitterpacher. The Hungarian text lists two sisters and one brother of Georg, among them Katalin, widow of Johann Frimont. (Baranya County Archives of the Hungarian National Archives, # 1262/1832)

REE ACCESSORY MINERALS: TRACERS OF MAGMATIC TO HYDRO-THERMAL EVOLUTION OF THE ROCHOVCE GRANITE, SLOVAK ORE MOUNTAINS, SLOVAKIA

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The Rochovce granite (RG) is a hidden subsurface intrusion. emplaced into Carboniferous to Permian metapelitic to metapsammitic phyllites, basaltic metavolcanics, and micaschists along Alpine tectonic zone (the Lubeník fault), between the Veporic and Gemeric Unit of the Western Carpathians (ca. 15 km SW of Dobšiná town, Slovak Ore Mountains, Slovakia). The Rochovce granite complex is related to the W-Mo porphyry mineralization in endo- and exocontact of RG. The granitic rock material is available from several boreholes (up to ca. 1560 m depth).

Coarse-grained, commonly porphyritic biotite monzogranite (rarely granodiorite and syenogranite) with pink K-feldspar, locally with mafic microgranular enclaves (HRAŠKO et al., 1998) represents the main G1 intrusive phase of RG. Younger leucocratic granite porphyries and aplitic granites (syenogranites to alkali-feldspar granites) of G2 intrusive phase usually form veinlets to dykes (several cm to 10 m thick), penetrated the G1 granite or surrounding metamorphic rocks. Geochemical features of RG (e.g., IVANOV, 1984; HATÁR et al., 1989) indicate their high-K calc-alkaline, slightly peraluminous metaluminous to character (A/CNK = 0.9-1.6) with mildly to highly fractionated, transitional I- to A-type affinity, and with elevated contents of REE in G1 (Sum REE = 270-430 ppm; IVANOV et al., 1984; our data); increased Rb, Nb, and Th contents in G1–G2; and Mo, W and F enrichment especially in the G2 phase of RG.

Moreover, hydrothermal disseminated to stockwork Mo-W ore mineralization (molybdenite, wolframite, scheelite) and lowertemperature veins with quartz, calcite, fluorite and sulfide minerals (pyrite, sphalerite, galena, chalcopyrite) are developed in RG (Mo) and its exocontact aureole (Mo-W).

The zircon U–Pb and molybdenite Re–Os isotopic dating reveal Upper Cretaceous, Campanian (76–82 \pm 1 Ma) age of RG magmatic solidification (HRAŠKO *et al.*, 1999; POLLER *et al.*, 2001; KOHÚT *et al.*, 2013). The RG represents the only known occurrence of Cretaceous granitic magmatism in the Western Carpathians and it could be correlated with Upper Cretaceous granitic rocks of the Banatitic Magmatic and Metallogenetic Belt with numerous related ore deposits in Romania, Serbia and Bulgaria (KOHÚT *et al.*, 2013).

Despite a lot of detailed petrographic and geochemical data, chemical composition of RG accessory minerals as main carriers of rare lithophile elements (especially REE, Nb, Th) is still unknown. Our contribution brings new electron-microprobe (EPMA) data illustrating compositional variations of REE accessory minerals, as indicators of RG magmatic to hydrothermal evolution.

Principal REE accessory minerals in G1 intrusive phase of RG include Ca-REE silicate phases: allanite-(Ce) and REE-rich titanite (up to $6.4 \text{ wt.\%} \text{ REE}_2\text{O}_3, \leq 0.09 \text{ apfu} \text{ REE};$ with REE³⁺ + Fe³⁺ = Ca²⁺ + Ti⁴⁺ substitution). Th-rich monazite-(Ce), xenotime-(Y) and REE-rich thorite are characteristic accessory minerals mainly for more evolved G1 and G2. In addition, complex REE-U-Ti-Nb oxide minerals [euxenite-(Y) and uranopolycrase] occur in G2

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phase of RG. Moreover, REE carbonate minerals [synchysite-(Ce) and parisite-(Ce)] were detected in porphyritic leucogranites (G1–G2). Accessory zircon and fluorapatite contain lower REE concentrations (usually up to 2 wt.% of REE₂O₃). Other, probably magmatic accessory minerals of RG include widespread magnetite, rarely rutile, and pyrite.

Euhedral to subhedral crystal shape, textural relationships with associated minerals and regular fine-oscillatory or sector zoning indicate primary magmatic crystallization of allanite-(Ce), titanite, zircon, and fluorapatite. Th-rich monazite-(Ce). xenotime-(Y), thorite and euxenite-(Y) to uranopolycrase probably originated during magmatic to late-magmatic stage of RG evolution, showing mostly subhedral shape and partly to complete altered internal texture, probably due to younger, dissolutionreprecipitation processes.

On the contrary, domains rich in small, disseminated crystals of Th-poor and sulfur-rich monazite-(Ce) (up to 4.6 wt.% SO₃, 0.12 *apfu* S) and anhedral aggregates of synchysite-(Ce) containing narrow parisite-(Ce) lamellae in close association with calcite document hydrothermal

stage of RG evolution, under fluid regime rich in CO₂, and F.

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References

- HATÁR, J., HRAŠKO, Ľ., VÁCLAV, J. (1989): Geologica Carpathica, 40(5), 621–654.
- HRAŠKO, Ľ., HATÁR, J., HUHMA, H., MÄNTÄRI, I., MICHALKO, J., VAASJOKI, M. (1999): Krystalinikum, 25, 161–171.
- HRAŠKO, Ľ., KOTOV, A. B., SALNIKOVA, E. B., KOVACH V. P. (1998): Geologica Carpathica, 49(2), 125–138.
- IVANOV, M. (1984): Mineralia Slovaca, 16(2), 173–179.
- KOHÚT, M., STEIN, H., UHER, P., ZIMMERMAN, A., HRAŠKO, Ľ. (2013): Geologica Carpathica, 64(1), 71–79.
- POLLER, U., UHER, P., JANÁK, M., PLAŠIENKA, D., KOHÚT, M. (2001): Geologica Carpathica, 52(1), 41–47.

CHEMICAL COMPOSITION OF HOLOCENE ALLUVIAL AND SLOPE SEDIMENTS BETWEEN THE BUDA CASTLE HILL AND THE DANUBE RIVER

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The Holocene geomorphological evolution of the Buda Castle Hill's eastern footslope and the connected floodplain of the Danube were studied by I. Viczián, Jr., in relation to the archaeological excavation at 2 Fő Street in Budapest, carried out by the Budapest Historical Museum (VICZIÁN, Jr. et al., 2023). The study involved sedimentological and XRD mineralogical analysis of 10 samples, GIS modelling and geomorphological mapping of the sites' wider area.

The thickness of the studied sequence is 2.6 m. It represents the Boreal, Atlantic and Subboreal climatic periods of the Holocene, and, according to the archaeological framework, spans from the Middle Neolithic and the Copper Age and the Early to Middle Bronze Ages. VICZIÁN, Sen. *et al.*, (2022) reported detailed mineralogical results from the XRD analysis.

The current study focuses on the chemical composition of the samples. The chemical

analysis was carried out in Mosonmagyaróvár, at the laboratory of MOTIM Co., by XRF spectroscopy using an instrument of type ARL 9900 (see Table 1).

Chemical data were interpreted from two aspects.

1. First, they were used to check the accuracy of the quantitative XRD data of mineralogical composition used in the previous study by VICZIÁN, et al., Sen. (2022).Molar composition of oxidic components of minerals was computed and multiplied by the quantitative percentages of the mineral. The computed amounts were compared to the analytical data. Only the components that are essentially contained in one or two minerals were used, such as CaO that is found in calcite and dolomite, K₂O that is in illite and K-feldspar and Na₂O that is in plagioclase. The composition of muscovite was considered for illite, while albite was considered for plagioclase. CaO data were corrected

Table 1: Results of chemical analysis by XRF. Data in mass per cents, m/m. Archaeological site Fő u., No. 2, Budapest.

	F1	F2	F3	F 4	F5	F6	F 7	F8	F9	F10
Al ₂ O ₃	6.66	4.69	6.17	6.88	8.29	8.67	9.42	8.81	8.69	8.88
SiO ₂	34.76	23.18	32.39	33.33	41.44	42.06	43.3	39.06	38.64	39.54
TiO ₂	0.346	0.22	0.338	0.335	0.442	0.456	0.466	0.42	0.43	0.45
Fe ₂ O ₃	2.38	1.7	2.45	2.42	2.98	3.12	3.35	3.06	3.06	3.16
MnO	0.061	0.043	0.053	0.056	0.068	0.066	0.059	0.05	0.047	0.052
ZrO ₂	0.021	0.012	0.02	0.015	0.023	0.021	0.023	0.022	0.022	0.026
SrO	0.07	0.1	0.079	0.076	0.057	0.057	0.056	0.051	0.047	0,052
CaO	25.81	35.9	28.81	26.54	20.1 8	20.33	18.48	21.05	21.04	19.42
MgO	2.61	1.47	1.64	2.31	2.74	1.97	2.62	3.19	3.89	4.83
K ₂ O	1.23	0.83	1.11	1.31	1.57	1.62	1.7	1.57	1.55	1.59
Na ₂ O	0.6	0.27	0.46	0.56	0.73	0.63	0.92	1.02	1.08	1.17
P2O5	1.01	0.47	0.86	0.76	0.77	0.64	0.44	0.31	0.25	0.2
LOI at 900°C	24.87	31.09	25.84	25.24	20.45	20.48	19. 14	21.24	21.11	20.42

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considering the isomorphic substitutions of Mg and Sr in the calcite structure.

It was found that computing the total carbonate mineral contents from XRD analysis in the previous studies was correct, data independent from the XRD analysis were considered. When only the routine method of XRD quantitative analysis was used, the carbonate mineral contents were overestimated while non-carbonate minerals, such as illite, Kfeldspar and plagioclase were underestimated. Considering the CO₂ contents, there was relatively good agreement between the computed and measured values in most samples. The wereslightly quantitative mineral contents corrected by incorporating the chemical data and reviewing the X-ray method. However, in a few samples, exceptionally high differences occurred that cannot be simply explained by analytical error. These differences may result from sample inhomogeneity or potentially erroneous qualitative mineral determination in the case of feldspars.

2. The second goal of the interpretation was to evaluate chemical data from the point of view of sedimentation processes and the impact of human activity in the ancient times. The results of the previous studies can be summarized in the following way:

The geomorphological evolution of the area revealed environments from a low-lying floodplain to an elevated river terrace surface. The evolution of the narrow band between the Danube and the Castle Hill was predominantly driven by fluvial processes before the early Bronze Age, while the slope erosion of the Buda Castle Hill (predominantly built up by Upper Eocene Buda Marl and Quaternary fresh-water a key role later limestone) played in sedimentation. A significant increase in colluvial sediment deposition and accumulation during the Middle Bronze Age (MBA) was revealed, which can be attributed to the humid climatic conditions, deforestation and cultivation of the catchment slopes as well as resultant slope erosion.

In order to demonstrate the effect of these processes on chemical composition, the variation of each of the oxide components with depth in the sequence was considered. CaO followed the variation in the colluvial accumulation of carbonate rock debris, the maximal value being in sample No. 2. Components forming typical non-carbonate detrital minerals, like SiO₂ in quartz and silicates, Al₂O₃ clay minerals and feldspars, Fe₂O₃ chlorite and hydroxides, K2O illite and K-feldspar and TiO₂ independent Timinerals, vary in the opposite way than CaO. It is remarkable that their internal relations remain approximately the same.

On the other hand, MgO and Na₂O display almost continuous decrease upwards because the minerals carrying these components, dolomite and chlorite for MgO % and plagioclase for Na₂O % are missing in the rocks of Buda Castle Hill.

Intensive soil formation in the Early Bronze Age (samples No. 7. and especially No. 6.) and probably also on the top of the sequence (sample No. 1) is reflected in the dissolution of part of CaO which in turn causes increase in the noncarbonatic components. Dissolution in this level can be observed also at Na₂O. On the other hand, MnO seems to be enriched in the periods of soil formation.

 P_2O_5 is a special case showing continuous increase throughout the sequence, likely due to the increasing influence of human activity. In some samples (No. 5. and 3.) bone fragments were observed. The only interruption is at sample No. 2. when denudation probably also hindered agriculture.

The general tendency of the evolution of the sequence is well expressed in the variation of the chemical index of alteration (CIA, see Fig.1), introduced by NESBITT & YOUNG (1982). The continuous increase of this parameter in due to the increasing proportion of the sediment material derived from the top of the Castle Hill, which is more altered than the Danube River sediments on the bottom of the sequence. CIA values of fluvial sediments were also determined on the coasts of the Danube in Kulcs area, ca. 50 km south of Budapest, by UDVARDI *et al.*

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(2016). Our data agree well with those of this study. The most intensive soil formation is also reflected in the increased CIA values (samples No. 7. and 6.).

References

- NESBITT, H. W., YOUNG, G. M. (1982): Nature, 299, 715–717.
- UDVARDI, B., KOVÁCS, I. J., SZABÓ, CS., FALUS, GY., ÚJVÁRI, G., BESNYI, A., BERTALAN, É., BUDAI, F., HORVÁTH,

ZS. (2016): Environmental Earth Sciences, 75, 1299.

- VICZIÁN, I. Sr., VICZIÁN, I. Jr., SZABÓ, M. (2022): In: FEHÉR, B., MOLNÁR, K., LUKÁCS, R., CZUPPON GY., KERESKÉNYI, E. (Eds.): Calce et malleo Mésszel és kalapáccsal, 12th annual Petrology and Geochemistry Assembly, pp. 131–134.
- VICZIÁN, I. Jr., TÓTH, F. M., SZABÓ, M., VICZIÁN, I. Sr. (2023): MΩMOΣ XI. Aquincum Museum, 2019. 137–155.



Variation of CIA in the sequence

Fig. 1: Variation of Chemical Index of Alteration (CIA) in the sequence

UV-FLUORESCENT SPHALERITES OF MEŽICA, SLOVENIA

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The Mississippi-Valley-Type (MVT) leadzinc ore deposits of Mežica in the Eastern-Karawanken (Slovenia) are well-known since the Roman times. They were exploited in the last ca. five hundred years, which was finished in 1994 with the depletion of the know resources. Since then, the mine operates as a tourist attraction. The MVT deposits here can be correlated with two nearby locations (Bleiberg and Raibl). More than 350 orebodies were mined round Mežica, which were deposited from hydrothermal fluids in almost vertical Alpine fault-systems of karstic limestones with Triassic age. The youngest part of the deposit (Topla) is considered to be syngenetic. The main ore minerals are galena and sphalerite, which were oxidized by meteoric waters down to 2 km depth, creating the most interesting and well-known mineral association of the location. The most common secondary mineral is the wulfenite (the location is Worldfamous after this) which was even mined for molybdenum. Nearby wulfenite the other common minerals are anglesite, cerussite, hemimorphite, smithsonite and descloizite. Although numerous studies investigated the minerals of the location, still there are lot more areas which needs further research.

During the field-test of the Robominers Horizon 2020 project we performed "in-situ" measurements in two orebodies and collected samples for further investigations. The two locations were the Level 5 part of the Grabenmine in Žerjav with sphalerite rich ore and Mežica-mine (Podzemlje Pece) in Glančnik with galena rich ore. The massive galena rich ore was easily recognizable on the field, till the sphalerite rich ore was rather uncharacteristic by naked eye. Thus, the best way was to locate it with UV-light, as the sphalerite and the accompanying other (dominantly secondary) phases have strong fluorescence with varying colours. This strong fluorescence of sphalerite was studied further by us.

The main minerals of the samples are galena, sphalerite, dolomite and calcite by X-ray powder diffraction. Different sphalerite generations can be distinguished even by normal light in optical microscopes, which are even more characteristic in UV-light, as they have different fluorescent colours (Fig. 1). The fluorescence of the different sphalerite generations and the dolomite were measured in a photo-spectrometer excited with various monochrome sources. Generally, the sphalerites are light brown coloured with low iron content.

The coarse-crystalline, brown parts have blue luminescence with fine zonation from deep-dark shades to light blue. The outer zones nearby the carbonates were dominantly dark, till the inner parts of this zone have bright, light blue fluorescence. The brown sphalerite shows multiple peaks between ca. 310–335 and 500–510 nm when excited with 270 nm, and around 460 nm if 365 nm excitation wavelength applied.

The next zone has dark brown to black colour under visible light, and intense deep red colour in UV light illumination. This part is fine zoned, even sector zoning can be recognized in the UVfluorescent images, backscattered images and element maps. The intensity of the red fluorescence shows correlation to the concentration of few tenths of wt% of cadmium, till the sector zonally distributed copper causes the extinction of the fluorescence. This black coloured sphalerite shows peaks at ca. 360 and ca. 440-450-460 nm excited with 270 nm, and



Fig. 1: Sphalerite and dolomite in visible (left) and 365 nm UV-light (right) from Glančnik, Mežica. 1: dolomite, 2: brown sphalerite, 3: mixed, fine crystalline sphalerite. (Field of view ca. 8 mm)

ca. 560, 600–610, 620 and 670 nm peaks excited with 365 nm.

The third (last) innermost big zone of the sphalerite is a mixed fine crystalline mass with varying luminescent colours, where the different colours can be seen separately and most probably with mixed interferences also. The luminescent spectra of this zone contain all the peaks characteristic both for the brown and black sphalerite and dolomite, where the peaks of the black sphalerite are the way more dominant.

The above-described zonation and sector zonation are also spectacular in the monochrome SEM-CL (cathodoluminescent) images. The intensity of the SEM-CL images sometimes correlates with the intensity of the UVfluorescence, sometimes they are reverse. The associated dolomite has strong violet / purple luminescence under UV-light. At an excitation wavelength of 270 nm, dolomite exhibits luminescence peaks at approximately 350 and 390 nm. However, when excited at 365 nm, the emission bands around 410, 440, and 490 nm dominate the spectra.

REČNIK *et al.*, (2014) mention small amounts of Fe, Cu, As, Cd, Ag, Ga, Ge, Hg, Bi, Mn, Mo, Ni, Pb, Sb and Tl in the sphalerites of Mežica, but no qualitative data nor their distributions are described. Few newer papers (SALEH *et al.*, 2019; ŠOSTER *et al.*, 2023) examine the fluorescent colours of sphalerites caused by their trace elements, but the exact effect of the different trace elements is not characterized yet, as in the case of their simultaneous incorporation, their effects are combined.

To further characterize the luminescence of the Mežica sphalerites, we plan to perform more "in-situ" analyses which have lower detection limits for trace elements (e.g. LA-ICP-MS mapping).

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References

- REČNIK, A., ZAVAŠNIK, J., FAJMUT-ŠTRUCL, S. (2014): The Mineralogical Record, 45, 507–548.
- SALEH, M., LYNN, K. G., JACOBSOHN, L. G., MCCLOY, J. S. (2019): Journal of Applied Physics, 125, 075702.
- ŠOSTER, A., BERTRANDSSON ERLANDS-SON, V., VELOJIČ, M., GOPON, P. (2023): Ore Geology Reviews, 157, 105474.

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