

Mineralogical mosaics from the Carpathian–Pannonian region 2.

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Ásványtani mozaikok a Kárpát–Pannon régióból 2.

Összefoglalás

Tanulmányunkban további mozaikszerű információkat közlünk a Kárpát–Pannon régió új ásványtani eredményeiből. Az adatokat országok és lelőhelyek szerint csoportosítottuk. Az egyes „mozaikdarabokban” az ásványok pontos — döntően XRPD, SEM-EDX és EMPA általi — meghatározására, illetve a paragenézis tömör bemutatására koncentráltunk. A tanulmányunkban szereplő ásványok olykor első említések az egész régióból, vagy legalábbis az illető lelőhelyről.

Magyarországról a recski rézércesedés mélysíntjéről néhány Bi-szulfidot (bizmutin, galenobizmutit), a recens hidrotermás kiválásokból pedig réz-kloridokat (eriokalkit, atacamit) mutatunk be. A pátkai polimetallikus-fluoritós ércesedésből wulfenitet, míg egy bátonyterenyi széntelepből a benyomuló bazalttelérek hatására képződött phillipsit-Na-t ismertettünk.

Romániából másodlagos Bi-ásványokat (bizmutit, bizmutoferrit) dokumentáltunk műszeres vizsgálatokkal Vaskőről (Ocna de Fier). Brianyoungitot mutatunk ki a nagyági (Săcărâmb) bánya meddőhányójáról, illetve spertiniit a rézbányai (Băița [Bihar]) szkarnos polimetallikus ércesedésből. Rögzítettük a konyait előfordulását a Nagysármás (Șarmașu) melletti szikes kivirágzások között.

Szlovákiából amarantitot és butleritet azonosítottunk a szomolnoki (Smolník) ércesedésből, richelsdorfitot Iglóhutáról (Novoveská Huta). Végül egy sor járulékos szulfátásványt (hexahidrit, epsomit, thénardit, glauberit, konyait, eugsterit, blődít) mutatunk ki a gömörhorkai (Gemerská Hôrka) gipsz-anhidrit telepből.

Tárgyszavak: galenobizmutit, atacamit, eriokalkit, wulfenit, phillipsit-Na, bizmutoferrit, bizmutit, spertiniit, konyait, brianyoungit, amarantit, butlerit, richelsdorfit, blődít, hexahidrit, thénardit, epsomit, glauberit, eugsterit

Abstract

This paper focuses on the compilation of new, mosaic-like mineralogical data from the Carpathian–Pannonian region. The data are grouped into entries arranged by localities and countries. Individual entries are linked to the exact identification of a species (or some species). These are dominantly based on XRPD, EMPA and SEM-EDX data, and are completed by the description of its/their paragenesis. The details presented here contain either the first description of a species from the whole region or at least from the given locality.

1) Hungary. Two Bi-sulphide minerals (bismuthinite, galenobismutite) are reported here from the deep levels of the Recsk copper deposit, together with the description of two copper chloride species (eriochalcite, atacamite) deposited by recent hydrothermal fluids. Wulfenite from the polymetallic–fluorite-type mineralisation of Pátka (in the Velence Hills) is also presented. The last entry is phillipsite-Na from Bátonyterenye, where the mineral was formed by the effect of basalt veins penetrating the coal seams.

2) Romania. Secondary Bi-minerals (bismutite, bismutoferrite) are documented from Ocna de Fier (Vaskő), Banat. Brianyoungite is described from the waste material of the Săcărâmb (Nagyág) mine, and also spertiniite from the polymetallic mineralisation of Băița Bihar (Rézbánya). Konyaite was found in alkaline salt efflorescences near Șarmașu (Nagysármás).

3) Slovakia. Amarantite and butlerite from the pyrite-rich mineralisation of Smolník (Szomolnok), and richelsdorffite from the copper ore deposit Novoveská Huta (Iglóhuta), were identified. Numerous sulphate minerals (hexahydrate, epsomite, thénardite, glauberite, konyaite, eugsterite, blödite) are described from the gypsum-anhydrite deposit of Gemerská Hôrka (Gömörhorka).

Keywords: galenobismutite, atacamite, eriochalcite, wulfenite, phillipsite-Na, bismutoferrite, bismutite, spertiniite, konyaite, brianyoungite, amarantite, butlerite, richelsdorffite, blödite, hexahydrate, thénardite, epsomite, glauberite, eugsterite

Experimental methods

X-ray powder diffraction patterns were recorded on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation (40 kV and 40 mA). This also involved a 250 mm radius goniometer, with parallel-beam geometry obtained by Goebel-mirror optics, a 0.25° primary axial Soller with a 0.6-mm divergence slit, and a 0.12° detector side long-Soller. 1 to 5 mg samples were ground in agate mortar under acetone and loaded on Si single-crystal sample holders. All measurements were recorded in the $2\text{--}70^\circ$ (2θ) range with a 0.01° (2θ) / 2 sec scanning rate.

X-ray diffraction measurements were also performed with a 114.6-mm diameter Gandolfi camera. Analytical parameters: $\text{CuK}\alpha$ radiation, Ni filter, 40 kV accelerating voltage, 20–25 mA tube current, exposition time: 44 to 46 hours. Unit cell parameters were calculated with the Unit-Cell software (HOLLAND & REDFERN 1997). NIST SRM 640 silicon powder was used as the external standard for the correction of film shrinkage.

Scanning electron microscopy (SEM) studies, energy-dispersive X-ray spectroscopy (EDX), EDX mapping and electron microprobe measurements (EMPA), were done on a JEOL–JXA 8600 Superprobe unit equipped with four wavelength-dispersive spectrometers and an E2V Scientific Instruments EDX silicon drift detector (SDD). For the EDX measurements 15–20 kV acceleration was used, with a probe current of 10–20 nA. A $4\times 5\ \mu\text{m}$ area was scanned with a focused beam during the analyses (a stopped focused beam was used if the target area was too small).

Results

Hungary

Bismuth sulphides from the deep levels of the Recsk ore deposit

Bismuth-containing sulphides were first mentioned from Recsk (Lahóca deposit) by SZTRÓKAY (1944), based on his ore-microscopy investigations. He assumed the presence of galenobismutite in the enargite-dominant ores. Later, Pb–Bi sulphides were found by microprobe in the enargite–luzonite mineralisation of the Rm–48 inclined adit (“Lejtakna” deposit) (DOBOSI 1971, BAKSA 1975). These Pb–Bi sulphides formed inclusions in enargite and luzonite. In 1987–88 Gábor PAPP (then Department of Mineralogy, Eötvös Lorand University, Budapest, personal communication) studied bismuthinite from a similar paragenesis of the deep levels of the Recsk deposit. According to the X-ray spectroscopy (XRS) results the mineral contained a considerable amount of Se. In the 80s Gábor DOBOSI (then Geochemical Research Laboratory of the Hungarian Academy of Sciences) found 1.1–1.4 wt% Se by microprobe analysis in the small ($< 30\ \mu\text{m}$) grains. An XRS analysis of the acicular stibnite inclusions in calcite was also made in 1988 but did not reveal any trace elements.

Higher amounts of Bi-containing sulphides were found in the exoskarn ores explored by the West 3rd adit on the –900m level. They are enclosed in coarse crystalline calcite associated with serpentine minerals, talc and chlorite and subordinate anhydrite and fluorite are also present. Calcite is frequently dark grey due to the dense, hair-like sulphide inclusions. The needle-like inclusions frequently form patches of 1–2 mm in diameter, while the felt-like aggregates can reach 1 cm in size. These aggregates are mainly built up of bismuthinite and galenobismutite (Figure 1). 1–3 wt% lead (Pb) is always present in bismuthinite, while the

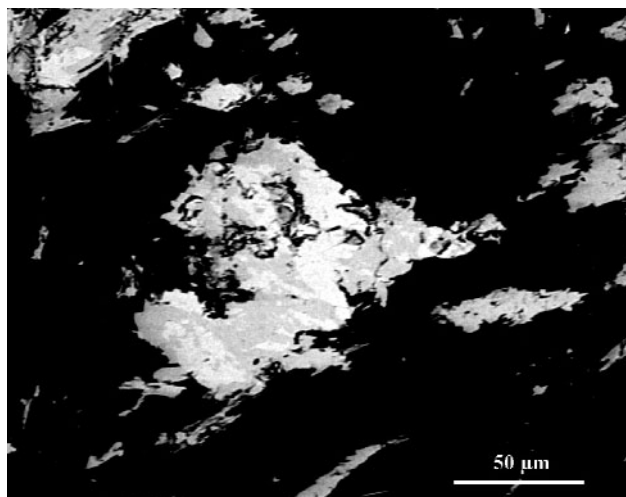


Figure 1. Galenobismutite (dark grey) and bismuthinite (pale grey) in calcite (black) from the deep levels of the Recsk ore complex, Hungary. BSE image

I. ábra. Galenobizmutit (sötétszürke) és bizmutin (világosszürke) kalcitban (fekete). Recsk, mélyszint. BSE-kép

chemical composition of galenobismutite is close to the ideal formula (Tables I–II). Both sulphides were identified by XRPD. The observed characteristic reflections of galenobismutite were: $3.45\ \text{Å}$ ($3.47\ \text{Å}$), $3.41\ \text{Å}$ ($3.45\ \text{Å}$), $2.05\ \text{Å}$ ($2.05\ \text{Å}$) — (data of ICDD card 20-0571 are in brackets). Some unique 1–3 μm size “flakes” were found by micro-

Table I. Analytical data (EMPA, wt%) of bismuthinite from the deep levels of the Recsk ore complex, Hungary

I. táblázat. Bizmutin vegyelemzési adatai (EMPA, tömeg%). Recsk, mélyszint

	1	2	3	4	5	Average	Theoretical
S	18.51	18.78	18.49	18.53	18.45	18.55	18.7
Pb	1.26	2.27	3.19	2.51	2.80	2.41	-
Bi	79.59	79.90	77.64	78.55	78.21	78.78	81.3
Total	99.36	100.95	99.33	99.59	99.46	99.74	100

Table II. Analytical data (EMPA, wt%) of galenobismutite from the deep levels of the Recsk ore complex, Hungary

II. táblázat. Galenobizmutit vegyelemzési adatai (EMPA, tömeg%). Recsk, mélyszint

	1	2	3	4	5	Average	Theoretical
S	16.88	16.85	16.84	16.69	16.66	16.78	17.02
Pb	27.77	27.86	27.48	26.69	27.88	27.54	27.50
Bi	54.82	55.63	55.07	56.17	54.87	55.31	55.48
Total	99.47	100.35	99.38	99.55	99.41	99.63	100

probe with compositions close to tetradymite and “csiklovaite”, but these phases need further investigations. It is to be noted that a few sulphide inclusions of the coarse crystalline calcite from the deep levels of the deposit proved to be stibnite.

Copper chlorides from the deep levels of the Recsk ore deposit

The recent mineral paragenesis that precipitated from the thermal waters (35–44 °C) in the adits driven on the –690 m and –890 m levels of the Recsk ore deposit was investigated in detail by KISS & JÁNOSI (1994); they gave special attention to the magnesium-bearing phases. Hydrocarbonate, sulphate and chloride anions were found in the thermal waters using wet chemical methods. The cations of the minerals that crystallised from the ion-rich fluids could be derived either from the surrounding sedimentary (Ca, Mg) and magmatic rocks (Na, K) or from the ores (Cu, Zn). The high amount of chloride may come from sedimentary formations. The dominant chloride of the hydrothermal association is halite, but hydrohalite is also mentioned (albeit without any further data). Atacamite and eriochalcite — with “question mark” — are also mentioned as being present in the rare greenish, bluish chloride patches of the –890 m adit, but there is no documentation of this. The present research was able to identify both atacamite and eriochalcite with XRD and EDX measurements.

Atacamite — $\text{Cu}_2\text{Cl}(\text{OH})_3$ (which is orthorhombic), is the most common Cu chloride in the studied greenish, bluish crusts from Recsk. It was formed in the oxidation zones of copper deposits, especially during periods of arid climatic conditions. It is frequently observed in fumaroles (ANTHONY et al. 2003). At Recsk, atacamite forms dark green xenomorphic grains, irregular aggregates, 1–2 cm² size encrustations, or pulverulent coatings. It is to be noted that malachite, brochantite and some other green minerals were also mentioned by KISS & JÁNOSI (1994) from the mineralisation of the deep levels of the Recsk deposit, but without any further data. Atacamite from Recsk was identified by XRPD (Table III). The calculated cell parameters (for *Pnam* space group) are $a = 6.056 \text{ \AA}$, $b = 9.073 \text{ \AA}$, $c = 6.877 \text{ \AA}$, $V = 377.9 \text{ \AA}^3$. Cu and Cl were identified by EDX. Halite, blödite and tamarugite were identified in close association with atacamite. The most spectacular varieties are the intense green, dust-like coatings or encrustments of atacamite on 5–10 cm-long white, stalactitic aggregates of halite and blödite.

Eriochalcite — $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ (which is orthorhombic), is a sublimation product of fumaroles, or an oxidation product of copper deposits produced during periods of arid climatic conditions (ANTHONY et al. 2003). However, in Recsk it was precipitated from hydrothermal fluids rich in copper and chloride ions. Eriochalcite forms bluish or yellowish green aggregates 2–4 mm in size; these are associated with halite, tamarugite and hexahydrite. Atacamite was not identified in its close association. Thick tabular intergrown eriochalcite crystals sometimes form dense

Table III. XRPD data of atacamite from the deep levels of the Recsk ore complex, Hungary

III. táblázat. Atacamit XRPD-adatok. Recsk, mélyszint

Atacamite, Recsk (observed)		Atacamite, 00-025-0269 (PDF2-2005)				
d (Å)	I (%)	d (Å)	I (%)	h	k	l
5.481	100	5.480	100	0	1	1
5.037	79	5.030	70	1	1	0
4.064	10	4.050	12	1	1	1
3.211	6	3.220	7	1	2	1
*3.028	24	3.040	5	0	3	0
		3.010	8	2	0	0
2.840	39	2.836	50	1	1	2
2.769	96	2.779	50	0	3	1
		2.759	55	2	0	1
2.740	28	2.742	25	0	2	2
2.706	39	2.711	20	1	3	0
2.651	12	2.641	14	2	1	1
*2.518	53	2.525	14	1	3	1
		2.515	40	2	2	0
*2.268	20	2.278	70	0	4	0
*2.273	19	2.265	45	2	0	2
2.204	25	2.198	17	2	1	2
2.140	26	2.141	11	2	3	0
2.126	49	2.130	25	1	3	2
2.043	30	2.043	17	2	3	1
1.971	12	1.964	12	3	1	0
1.827	43	1.829	11	0	3	3
		1.824	35	2	0	3
1.817	83	1.817	25	2	3	2
1.807	44	1.812	9	1	4	2
1.792	17	1.788	10	2	1	3
1.755	9	1.758	10	2	4	1
1.738	17	1.747	13	1	5	0
1.719	16	1.717	20	0	0	4
1.710	12	1.706	10	3	1	2
1.608	46	1.606	55	0	2	4
1.564	9	1.563	13	2	3	3
1.557	19	1.561	9	2	5	0
		1.560	9	1	4	3
1.551	22	1.556	25	1	5	2
1.509	8	1.507	7	3	3	2
1.493	11	1.488	13	4	1	0
1.473	8	1.473	11	3	4	1
1.420	15	1.418	9	2	2	4
1.384	24	1.390	25	0	6	2
1.381	35	1.381	7	3	4	2
1.370	25	1.372	13	0	4	4

* overlapped with calcite.

*átfed a kalcittal.

aggregates (Figure 2). Cu and Cl were identified by EDX. The XRPD data shows a good match with ICDD card 00-033-0451 (Table IV). The cell parameters of eriochalcite from Recsk (calculated for *Pbnm* space group) are $a = 7.420 \text{ \AA}$, $b = 8.092 \text{ \AA}$, $c = 3.751 \text{ \AA}$, $V = 225.2 \text{ \AA}^3$.

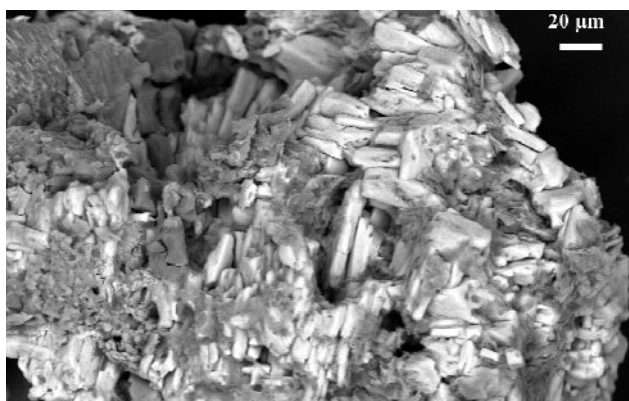


Figure 2. Tabular crystals of eriochalcite from the deep levels of the Reckseck ore complex, Hungary. BSE image

2. ábra. Eriokalkit táblás kristályai. Reckseck, mélysínt. BSE-kép

Table IV. XRPD data of eriochalcite from the deep levels of the Reckseck ore complex, Hungary

IV. táblázat. Eriokalkit XRPD-adatai. Reckseck, mélysínt

Eriochalcite, Reckseck (observed)		Eriochalcite, 00-033-0451 (PDF 2-2005)				
d (Å)	I (%)	d (Å)	I (%)	h	k	l
5.469	100	5.467	100	1	1	0
4.046	51	4.050	56	0	2	0
3.751	10	3.750	11	0	0	1
3.710	6	3.708	6	2	0	0
3.348	21	3.346	21	1	0	1
3.093	33	3.093	40	1	1	1
2.735	13	2.734	14	2	2	0
2.638	67	2.638	82	2	0	1
2.579	17	2.578	18	1	2	1
2.535	14	2.534	17	1	3	0
2.366	7	2.365	9	3	1	0
2.210	22	2.209	29	2	2	1
2.100	11	2.100	13	1	3	1
2.065	5	2.064	5	3	0	1
2.023	20	2.024	22	0	4	0
2.001	35	2.001	17	3	1	1
1.876	5	1.874	5	0	0	2
1.855	11	1.854	14	4	0	0
1.839	4	1.839	5	3	2	1
1.823	6	1.822	6	3	3	0
1.781	4	1.781	4	0	4	1
1.774	8	1.774	9	1	1	2
1.731	3	1.731	5	1	4	1
1.686	6	1.686	9	4	2	0
1.674	4	1.673	5	2	0	2
1.663	4	1.662	3	4	0	1
1.659	6	1.658	6	1	2	2
1.639	10	1.639	6	3	3	1
				2	1	2
1.605	16	1.605	23	2	4	1
1.581	3	1.582	5	1	5	0
1.508	2	1.507	3	1	3	2
1.495	2	1.494	3	3	0	2
1.470	2	1.469	3	3	1	2
1.460	6	1.459	8	5	1	0
1.457	5	1.457	4	1	5	1
1.445	4	1.445	5	3	4	1
1.402	5	1.402	6	3	2	2
1.367	5	1.367	7	4	4	0

Wulfenite from the Szűzvár deposit, Pátka

The Pb-Zn-Cu-containing sulphide paragenesis and the secondary mineral associations formed from them were first described by KISS (1954). These were found in the adits opened for fluorite exploitation in the early 1950s, near the former Szűzvár Mill, Pátka. Near the sulphides, the strongly-altered parts of the silica-rich veins contain cavities usually filled with secondary minerals; these cavities are a product of weathering processes close to the surface. A strongly-weathered quartz vein of this type can be found on the surface even now, close to the original entrance of the mine. The investigated wulfenite specimens were collected here. The secondary minerals, especially plumbogummite, were examined by ZAJZON et al. (2004). They mentioned wulfenite in this paragenesis for the first time. Wulfenite — tetragonal, PbMoO_4 — usually occurs here together with pyromorphite, as pale yellow or off-white, tabular crystals, 2–4 mm in size. However, sometimes crystals up to even 2–4 cm in diameter can be found. The dominant form is the {001} basal pinacoid; {011}, {112}, {114} and {013} forms are represented by smaller faces only. A common crystal habit is where the small bipyramids alternate, producing a peculiar zigzagged shape (Figure 3). A “pure” bipyramidal habit is much rarer, the largest crystals of this type being 1–2 mm in size.

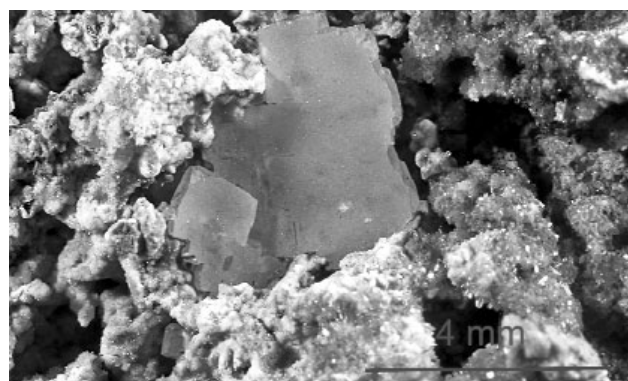
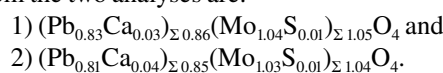


Figure 3. Tabular crystals of wulfenite with pyromorphite from the Szűzvár deposit, Pátka, Hungary

The largest crystal is 0.5 cm. Collection: S. KLAI, photo: L. TÓTH.

3. ábra. Táblás wulfenitkristályok piromorfittal. Pátka, Szűzvár
A legnagyobb kristály 0,5 cm-es. KLAI S. gyűjteménye. Fotó: TÓTH L.

XRPD data show a good match with ICDD card 00-044-1486, with regard to both d -values and intensities (Table V). Cell parameters of wulfenite from Pátka (calculated for a $I4_1/a$ space group) are $a = 5.433 \text{ \AA}$, $c = 12.110 \text{ \AA}$, $V = 357.4 \text{ \AA}^3$. Wet chemical analyses revealed minor $\text{Ca} > \text{Pb}$ and $\text{S} > \text{Mo}$ substitutions (Table VI). The chemical formulae calculated from the two analyses are:



Pyromorphite and cerussite are the most common associated minerals and these were formed earlier than wulfenite. Sometimes oxyplumboroméite (formerly bindheimite), malachite, azurite, more rarely plumbogummite and mimetite can follow them. The cations of the secondary

Table V. XRPD data of wulfenite from the Szűzvár deposit, Pátka, Hungary*V. táblázat.* Wulfenit XRPD-adatai. Pátka, Szűzvár

Wulfenite, Pátka (observed)		Wulfenite 00-044-1486 (PDF2-2005)				
d (Å)	I (%)	d (Å)	I (%)	h	k	l
4.957	10	4.958	11	1	0	1
3.244	100	3.245	100	1	1	2
3.027	17	3.027	15	0	0	4
2.717	18	2.718	20	2	0	0
2.378	5	2.378	6	1	1	4
2.212	3	2.212	3	1	0	5
2.082	4	2.082	4	1	2	3
2.022	24	2.022	22	2	0	4
1.921	15	1.921	9	2	2	0
1.791	10	1.791	5	3	0	1
1.787	19	1.787	12	1	1	6
1.653	25	1.653	17	3	1	2
1.622	15	1.622	8	2	2	4
1.514	5	1.514	1	0	0	8

Table VI. Analytical data (wet chemical analyses, wt%) of wulfenite from the Szűzvár deposit, Pátka, Hungary. Analyst: A. BARTHA*VI. táblázat.* Wulfenit nedveskémiai elemzési adatai (tömeg%). Pátka, Szűzvár. Elemző: BARTHA A.

	1	2	Theoretical
PbO	54.10	54.01	54.29
CaO	0.45	0.68	
MoO ₃	43.50	44.21	45.71
SO ₃	0.22	0.34	
Total	98.27	99.24	100

minerals are the same as those of the primary sulphides of the mineralisation; however, Mo could have originated from the molybdenite of a granite pegmatite of the closer environment (JANTSKY 1957). Nevertheless, optical spectroscopy results published by KISS (1954) did not indicate the presence of Mo in any of the samples collected from the oxidation zone of the ore-bearing veins at the Szűzvár mine.

Phillipsite-Na from the Bátonyterenye coal mine

The investigated coal specimens are preserved in the mineral collection of the Herman Ottó Museum, Miskolc, Hungary. According to their registration label they came from an unspecified coal mine of the Nógrád coalfield, probably collected by István VITÁLIS. Phillipsite-filled veins penetrate these samples. The coal specimens show a hexagonal columnar structure, similar to that observed in the coked coal seams in the Pécs-Vasas open pit. In the latter, magmatic veins penetrated the coal beds and “baked” them on making contact. According to the XRPD data, the cracks are filled with a colourless, transparent mineral: phillipsite (Figure 4). The dominant extra-framework cation is Na, as proven by EMPA; thus the mineral is phillipsite-Na (Table VII). The crystals are always fourlings with pseudo-tetragonal symmetry (Figure 5). Phillipsite-Na is a product of the hydrothermal activity of the basalt dykes penetrating

**Figure 4.** Phillipsite-Na crusts in the cracks of natural coke. Bátonyterenye coal mine, Hungary. Width of the picture: 8 cm*4. ábra.* Phillipsit-Na bevonatok természetes kokszt repedéseiben. Bátonyterenye, szénbánya. Képszélesség 8 cm**Table VII.** Analytical data (EMPA, wt%) of phillipsite-Na from the Bátonyterenye coal mine, Hungary*VII. táblázat.* Phillipsit-Na vegyelemzési adatai (EMPA, tömeg%). Bátonyterenye, szénbánya

SiO ₂	54.16	55.42	55.41
Al ₂ O ₃	18.88	18.46	17.85
Fe ₂ O ₃	0.00	0.05	0.12
MgO	0.00	0.00	0.00
CaO	0.84	1.06	0.49
BaO	2.50	2.08	2.50
Na ₂ O	6.61	5.69	6.62
K ₂ O	4.07	4.13	4.53
Total	87.07	86.90	87.52
Cation numbers based on 32 oxygens			
Si	11.36	11.54	11.56
Al	4.67	4.53	4.39
Fe	0.00	0.01	0.02
Mg	0.00	0.00	0.00
Ca	0.19	0.24	0.11
Ba	0.21	0.17	0.20
Na	2.69	2.30	2.68
K	1.09	1.10	1.21

Total Fe as Fe₂O₃
Összes Fe mint Fe₂O₃

the coal seam. Basalt dykes with up to 20 cm-wide coked contact were reported first from the area of the Károly shaft at Salgótarján by SCHAFARZIK (1893a, b).

Table VIII. Continued
VIII. táblázat. Folytatás

Observed		Bismutite, 00-041-1488 (PDF2-2005)				Bismutoferrite, 00-047-1848 (PDF2-2005)				Goethite 01-081-0464 (PDF2-2005)						
d (Å)	I (%)	d (Å)				I (%)	h	k	l	d	I (%)	h	k	l	d	
2.517	47					2.527	47	1	3	4	2.527	5	1	0	1	
											2.490	13	0	4	0	
2.450	42										2.449	62	1	1	1	
2.383	21					2.383	19	1	1	-3						
2.305	9										2.302	2	2	0	0	
2.285	15	2.279	10	0	0	6										
2.259	25										2.254	10	1	2	1	
2.250	28	2.233	3	0	1	5	2.248	11	1	3	-2	2.243	3	2	1	0
						2.223	15	2	2	0						
2.201	27					2.202	6	0	2	3	2.190	15	1	4	0	
2.163	34					2.160	16	0	4	1						
2.134	20	2.135	30	1	1	4										
2.083	16					2.085	13	2	2	-2	2.090	1	2	2	0	
2.042	22					2.040	17	2	2	1						
2.011	15										2.011	3	1	3	1	
1.935	29	1.933	20	0	2	0	1.938	16	0	4	2					
1.921	26										1.922	5	0	4	1	
1.904	30					1.907	17	1	3	-3	1.892	1	2	3	0	
1.831	15	1.860	5	0	2	2	1.837	5	2	2	-3	1.828	1	1	5	0
						1.787	3	2	2	2	1.801	8	2	1	1	
1.764	13	1.750	25	1	1	6					1.774	2	1	4	1	
1.749	13	1.745	20	0	1	7										
1.718	42					1.720	12	1	3	3	1.719	28	2	2	1	
1.713	31	1.714	15	1	2	1										
1.693	37	1.682	10	0	2	4	1.697	4	2	4	-1	1.690	8	2	4	0
1.658	21										1.660	3	0	6	0	
1.635	14															
1.611	33	1.617	35	1	2	3	1.606	19	1	3	-4	1.604	6	2	3	1
1.588	21					1.590	17	1	5	-2						
1.508	21					1.503	18	3	3	-1	1.512	8	0	0	2	
1.484	21	1.474	10	2	0	6	1.472	5	0	6	1	1.475	2	2	4	1

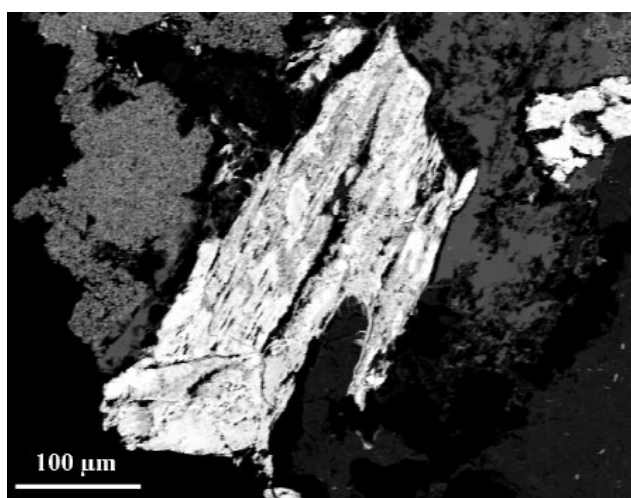


Figure 6. Bismutoferrite (pale grey) and bismutite (white) with goethite (dark grey) from the Ocna de Fier ore deposit, Romania. BSE image

6. ábra. Bismutoferrit (világosszürke) és bismutit (fehér) goethittel (sötétszürke). Vaskő. BSE-kép

Brianyoungite from the Săcărâmb (Nagyág) ore deposit

This rare $Zn_3(CO_3,SO_4)(OH)_4$ mineral was first described by LIVINGSTONE & CHAMPNESS (1993) as a recently-formed phase, found in an abandoned lead-zinc mine at Nenthead, Cumbria, England, UK. The mineral was accompanied by gypsum, smithsonite, goethite and pyrite.

At Săcărâmb, brianyoungite forms hair-like or radial aggregates of needles and laths up to 0.5 mm on quartz (Figure 7); these are in the cavities of tetrahedrite-pyrite rich quartz vein fillings. The investigated specimens were collected at the old waste site. Tetrahedrite, pyrite, sphalerite, and gypsum were identified from its close environment. XRPD data show a good match with those on the ICDD card (Table IX). According to the EDX data, brianyoungite from Săcărâmb contains a few wt% of Sb in addition to the major detectable constituents (Zn and S).

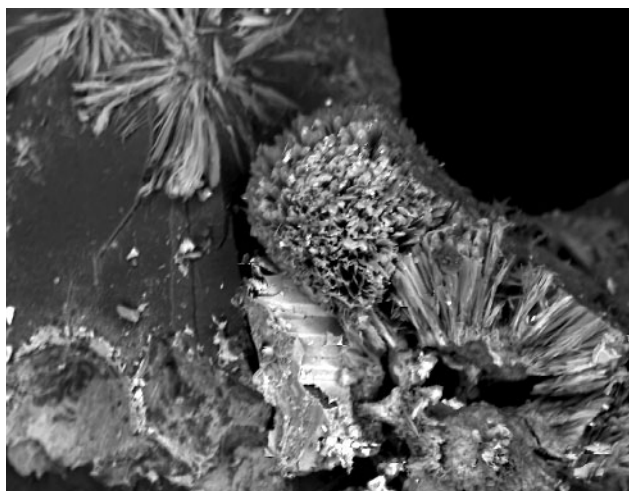


Figure 7. Radial aggregates of brianyoungite from the Săcărâmb ore deposit, Romania. BSE image

7. ábra. Brianyoungit sugaras halmazai. Nagyági ércesedés. BSE-kép

Table IX. XRPD data of brianyoungite from Săcărâmb, Romania (compared to selected reflections of ICDD card 00-046-1431). Gandolfi record

IX. táblázat. Brianyoungit XRPD-adatai. Nagyág (Săcărâmb), Románia (összehasonlítva a 00-046-1431-es ICDD-kártya válogatott reflexióival). Gandolfi-felhétel

Brianyoungite Săcărâmb, Romania		Brianyoungite (ICDD 00-046-1431) Brownley Till mine, Nenthead, Cumbria, England	
I_{rel}	d (Å)	I (%)	d (Å)
m	15.75	100	15.44
s	7.86	100	7.88
w	5.23	20	5.25
vw	4.14	5	4.13
vw	3.121	10	3.128
vw	2.991	10	2.976
vw	2.803	10	2.802
m	2.708	40	2.714

Abbreviations: m = medium, s = strong, w = weak, vw = very weak. (X-ray generator: Siemens Kristalloflex 710; Radiation: Co; Filter: None; Accelerating voltage: 35 kV; Tube current: 30 mA; Exposition time: 71 hours)

Rövidítések: m = közepes, s = erős, w = gyenge, vw = nagyon gyenge. (Röntgen-generátor: Siemens Kristalloflex 710; Co-sugárzás, szűrő nem volt. Gyorsítófeszültség: 35 kV, csőáram: 30 mA, expozíciós idő: 71 óra.

Spertiniite from the Băița [Bihor] (Rézbánya) ore deposit

Spertiniite — $\text{Cu}(\text{OH})_2$ (which is orthorhombic), is a very rare mineral. At its type locality (Jeffrey mine, Québec, Canada) it was formed from chalcocite, in a ringite dyke near the contact zone with a serpentinized dunite; this took place in the presence of alkaline groundwater (GRICE & GASPARRINI 1981). It was identified as thin, blue crusts on the surface of native copper from the deep

Table X. XRPD data of spertiniite from Băița [Bihor], Romania

X. táblázat. Spertiniit XRPD-adatai. Rézbánya (Băița [Bihor]), Románia

Spertiniite, Băița [Bihor], (observed)		Spertiniite, 01-080-0656 (PDF2-2005)				
d (Å)	I (%)	d (Å)	I (%)	h	k	l
5.297	94	5.297	90	0	2	0
3.732	100	3.731	100	0	2	1
2.634	62	2.628	65	0	0	2
2.507	39	2.498	34	1	1	1
2.266	56	2.263	62	1	3	0
1.716	42	1.715	41	1	3	2

levels of the molybdenum mine at Băița [Bihor]. XRPD data show a good match with those on the ICDD card 01-080-0656 (Table X). Only Cu and O were identified on the EDX spectra. It is most likely that it is an alteration product of native copper.

Konyaite efflorescences from Sărmașu (Nagysármás)

According to ANTHONY et al. (2003), konyaite — $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \times 5\text{H}_2\text{O}$ (which is monoclinic), occurs in salt efflorescences on saline soils; it forms between 30 °C and 50 °C due to the evaporation of ground and surface waters. Its thin tabular crystals are 5–8 μm in diameter (Figure 8). White,

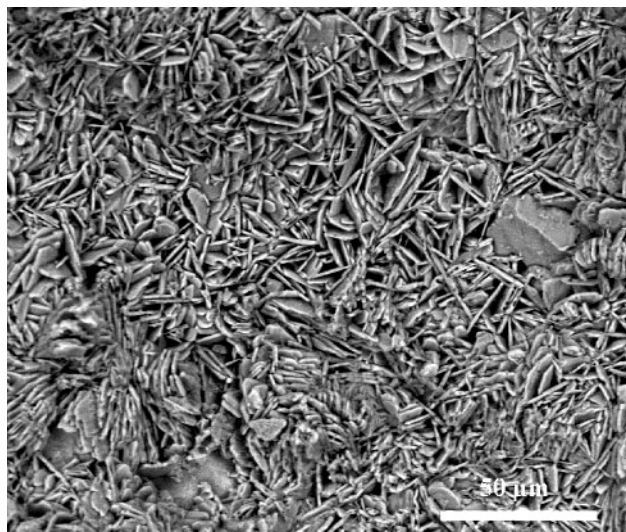


Figure 8. Tabular crystals of konyaite from Sărmașu, Romania. BSE image
8. ábra. Táblás konyaitkristályok. Nagysármás. BSE-kép

dust-like efflorescences collected on a hot, dry, summer day from the surface of the soil at Sărmașu proved to be konyaite with a minor amount of gypsum. It was identified by XRPD (Table XI). It is to be noted that salt efflorescences on soil surfaces are widespread in the Câmpia Transilvaniei (Mezőség) area, especially in the summer season. Their further mineralogical investigation is recommended.

Table XI. XRPD data of konyaite from Sărmaşu, Romania

XI. táblázat. Konyait XRPD-adatai. Nagysármás (Sărmaşu), Románia

Konyaite, Sărmaşu (observed)		Konyaite 00-035-0649					Quartz 00-046-1045	
d(Å)	I(%)	d(Å)	I(%)	h	k	l	d(Å)	I(%)
12.07	28	12.01	100	0	2	0		
7.62	5	7.61	6	0	1	1		
4.815	4	4.807	12	0	4	1		
				-1	1	1		
4.664	2	4.677	5	1	3	0		
4.546	20	4.546	55	-1	2	1		
4.412	6	4.410	10	1	1	1		
4.261	22						4.255	16
4.188	11	4.184	20	1	3	1		
4.008	24	4.002	70	0	6	0		
3.596	3	3.589	10	1	4	1		
				0	3	2		
3.422	5	3.416	10	1	1	2		
3.347	100	3.338	7	0	4	2	3.344	100
3.285	6	3.284	8	1	6	0		
				1	5	1		
3.186	3	3.156	6	1	0	2		
3.080	4	3.082	7	0	5	2		
3.032	3	3.054	2	1	2	2		
2.989	6	2.989	12	-1	4	2		
				1	6	1		
2.937	2	2.940	3	1	3	2		
2.817	9	2.811	14	0	8	1		
				1	7	1		
2.781	5	2.779	7	2	1	1		
2.726	7	2.725	14	1	7	1		
				2	2	1		
2.645	7	2.639	14	2	3	1		
				1	5	2		
2.598	7	2.598	16	2	4	0		
2.565	2	2.573	3	2	2	1		
2.459	6						2.457	9
2.436	3	2.433	7	-1	7	2		
				0	8	2		
2.405	4	2.403	10	-1	3	3		
				0	5	3		
2.337	4	2.336	10	2	6	0		
2.283	6						2.282	8
2.237	4						2.236	4
2.129	6						2.128	6
2.079	2	2.079	4	2	8	0		
1.995	5	1.995	5	2	3	3		
				2	7	2		
1.982	6	1.980	2	0	2	4	1.980	4
1.819	13						1.818	13
1.673	5						1.672	4
1.661	2						1.659	2
1.542	8						1.542	9

Slovakia

Amarantite from the Smolník (Szomolnok)
ore deposit

The pyrite deposit of Smolník — the type locality of three iron sulphates: rhomboclase, szomolnokite and kornelite — is

well known for its rich sulphate paragenesis (see ĎUĎA & OZDÍN 2012). A yellow, porous, sulphate-containing historical specimen from the collection of the University of Miskolc — labelled as copiapite — was reinvestigated. The reinvestigation was due to the presence of a few mm-size nests of orange-red, acicular crystal aggregates with vitreous lustre in the matrix. The yellow main mass proved to be butlerite — $\text{Fe}^{3+}(\text{SO}_4)(\text{OH}) \times 2\text{H}_2\text{O}$ (which is monoclinic), whereas the orange-red phase is amarantite — $\text{Fe}^{3+}_2\text{O}(\text{SO}_4)_2 \times 7\text{H}_2\text{O}$ (which is triclinic). It forms 1–1.5-mm long prismatic or lath-like crystals, which show perfect cleavage in one direction (Figure 9). Amarantite was identified by XRPD investigation (Table XII). The presence of iron and sulphur was proven by EDX.

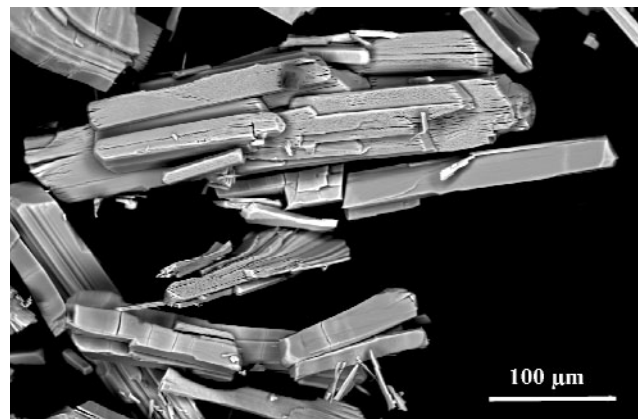


Figure 9. Elongated, lath-like crystals of amarantite from the Smolník ore deposit, Slovakia. BSE image

9. ábra. Nyúlt léces amarantitkristályok. Szomolnok. BSE-kép

Table XII. XRPD data of amarantite from Smolník, Slovakia

XII. táblázat. Amarantit XRPD-adatai. Szomolnok (Smolník), Szlovákia

Amarantite, Smolník, (observed)		Amarantite 01-071-1048				
d(Å)	I(%)	d(Å)	I(%)	h	k	l
11.53	45	11.481	64	0	1	0
		0				
8.89	100	8.8616	100	1	0	0
7.51	5	7.4935	4	-1	1	0
6.64	5	6.6284	6	0	0	1
				1	1	0
5.27	7	5.2640	10	1	0	1
5.10	10	5.0919	9	1	1	1
3.830	6	3.8270	2	0	3	0
3.748	7	3.7468	3	-2	2	0
3.719	9	3.7136	5	2	0	1
3.654	20	3.6551	18	2	-1	1
				2	0	1
3.465	5	3.4656	4	0	-3	1
3.179	11	3.1812	8	0	3	1
3.109	18	3.1095	14	-1	3	1
				0	1	2
3.054	8	3.0499	4	1	1	2
				2	2	1
2.884	5	2.8812	2	2	-3	1
				2	2	1

Table XII. Continued

XII. táblázat. Folytatás

Amarantite, Smolník, (observed)		Amarantite 01-071-1048					
d(Å)	I(%)	d(Å)	I(%)	d(Å)	I(%)	d(Å)	
2.733	5	2.7341	2	2	3	1	
				0	-4	1	
2.680	8	2.6764	6	3	0	1	
				-2	0	2	
2.601	6	2.6051	2	-2	-1	2	
				-2	1	2	
2.562	5	2.5631	2	-2	4	0	
1.819	6	1.8192	1	4	3	0	
				4	1	2	

Richelsdorffite from the Novoveská Huta (Iglóhuta) ore deposit

The Novoveská Huta ore deposit is famous for its secondary arsenates (see ĎUŘA & OZDÍN 2012) — $\text{Ca}_2\text{Cu}_5\text{Sb}(\text{AsO}_4)_4(\text{OH})_6\text{Cl} \times 6\text{H}_2\text{O}$ (which is monoclinic), which is also secondary in origin. It forms fan-shaped aggregates of 0.5–1 mm tabular crystals. According to the BSE images (Figure 10), these are chemically homo-

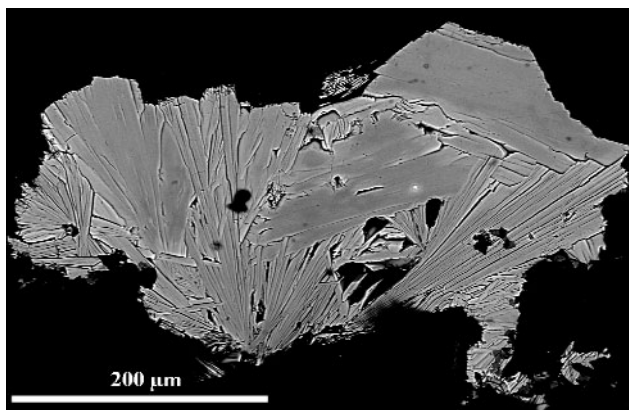


Figure 10. Richelsdorffite aggregate from Novoveská Huta, Slovakia. BSE image

10. ábra. Richelsdorffitalmaz, Iglóhuta (Novoveská Huta), Szlovákia. BSE-kép

Table XIII. Analytical data (EMPA, wt%) of richelsdorffite in weight % from Novoveská Huta, Slovakia. Analyst: P. KONEČNÝ

XIII. táblázat. Richelsdorffit vegyelemzési adatai (EMPA, tömeg%). Iglóhuta (Novoveská Huta), Szlovákia. Elemző: KONEČNÝ, P.

	1	2	3	Average	Theoretical
As_2O_5	35.11	35.61	35.68	35.47	34.80
Sb_2O_3	13.19	12.80	12.97	12.99	12.25
CaO	8.34	8.31	8.45	8.37	8.49
CuO	30.48	31.05	30.30	30.61	30.11
ZnO	0.04	0.00	0.06	0.03	
Cl	1.96	2.34	2.17	2.16	2.68
$\text{O} - \text{Cl}_2$	0.44	0.53	0.49	-0.49	-0.60
H_2O	n.d.	n.d.	n.d.	n.d.	12.27
Total	88.68	89.58	89.13	89.14	100

geneous, and their chemical composition is close to the theoretical values (Table XIII). The formula was calculated from the average of three analyses: $\text{Ca}_{1.94}\text{Cu}_{5.01}\text{Sb}_{1.04}(\text{AsO}_4)_{4.02}(\text{OH})_6[\text{Cl}_{0.79}(\text{OH})_{0.26}]_{\Sigma 1.05} \times x\text{H}_2\text{O}$. $x = 4.71$, if H_2O is calculated by difference. This is lower than the theoretical value (6) and is probably due to H_2O loss during analysis. The mineral is also identified by XRPD

Table XIV. XRPD data of richelsdorffite from Novoveská Huta, Slovakia

XIV. táblázat. Richelsdorffit XRPD-adatai. Iglóhuta (Novoveská Huta), Szlovákia

Richelsdorffite, Novoveská Huta (observed)		Richelsdorffite, 00-046-1462 (PDF2-2005)				
d(Å)	I(%)	d(Å)	I(%)	h	k	l
13.231	100	13.20	100	0	0	1
7.480	2	7.47	5	1	1	1
6.937	4	6.92	20	2	0	0
6.615	2	6.623	5	0	0	2
6.276	6	6.260	30	0	2	1
5.312	2	5.320	5	-2	0	2
4.972	4	4.963	30	2	2	0
4.417	4	4.413	25	0	0	3
				3	1	1
4.399	12					
4.249	13	4.261	20	2	2	2
3.844	1	3.823	<5	-1	3	2
3.545	2	3.552	10	0	4	0
3.138	5	3.132	90	-2	4	1
				3	3	2

(Table XIV). It is to be noted that these aggregates are overgrown on baryte crystals.

Some accessory sulphates from the Gemerská Hôrka (Gömörhorka) gypsum-anhydrite mine

Anhydrite and gypsum are the dominant sulphates of the Gemerská Hôrka evaporite deposit (LÓRINCZ 2008). Many accessory sulphates (hexahydrite, glauberite, blödite, epsomite, konyaite, thénardite and eugsterite) can be found in the thin or thick fibrous structures that fill the cracks of gypsum as products of secondary processes. XRPD (Figures 11–12) and EDX (major chemical components) were used to identify these species. Based on XRPD studies, here they form four typical associations:

- 1) epsomite–thénardite–gypsum,
- 2) glauberite–thénardite–gypsum,
- 3) konyaite–hexahydrite–blödite,
- 4) thénardite–eugsterite–gypsum.

Blödite forms white, flour-like masses and it is probably an alteration product of the very unstable konyaite and hexahydrite (see MILLS et al. 2010). Hexahydrite can also

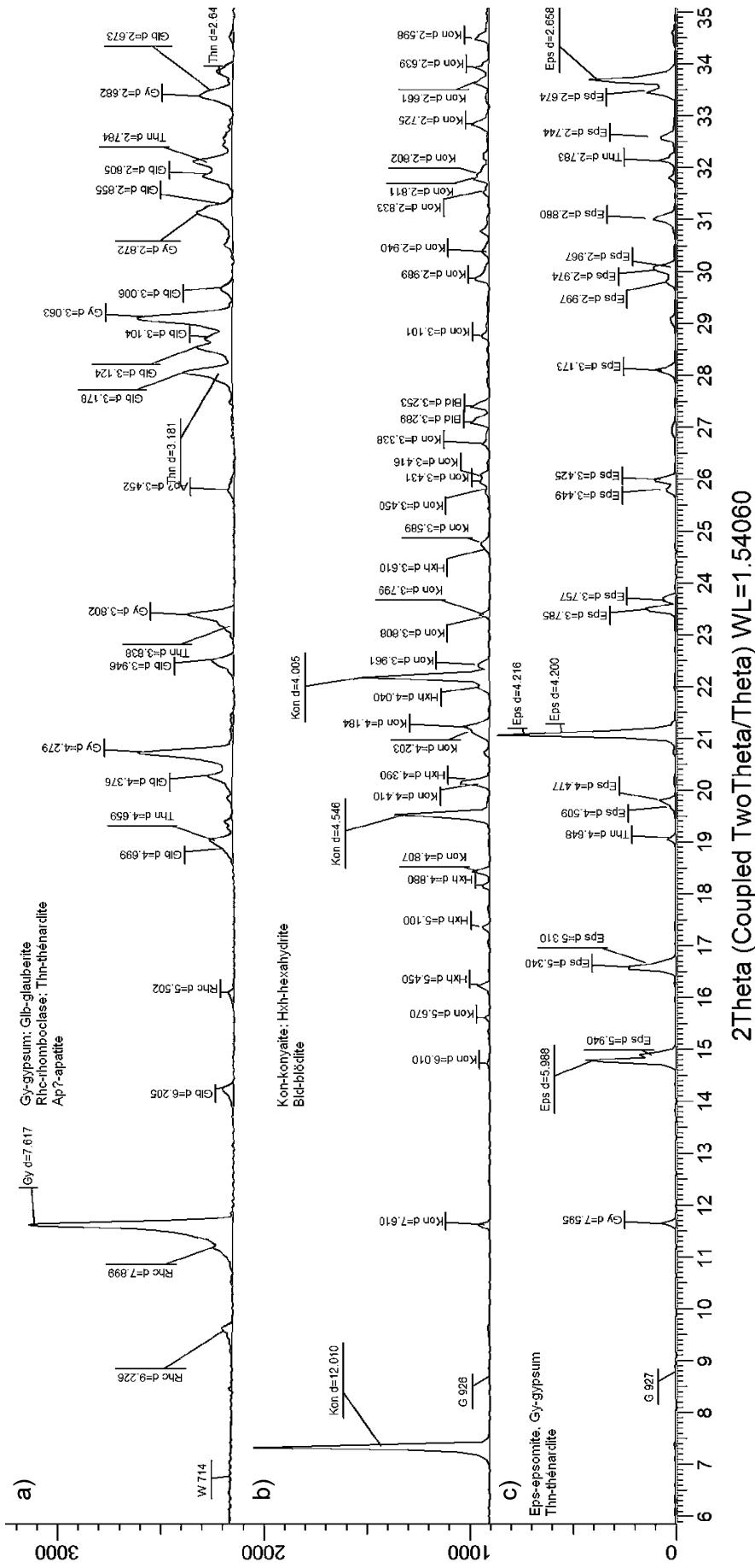


Figure 11. XRPD patterns of sulphates from Gemerská Hôrka, Slovakia
 a) Glauberite, thenardite and rhomboclase, b) Konyaite, hexahydrate and blödit, c) Epsomite, thenardite and gypsum
 II. ábra. Gömöhörkai (Gemerská Hôrka, Szlovákia) szulfátok XRPD-jéhezelei
 a) Glauberit, thenardit és romboklasz, b) Konyait, hexahidrit és blödit, c) Epsomit, thenardit és gipsz

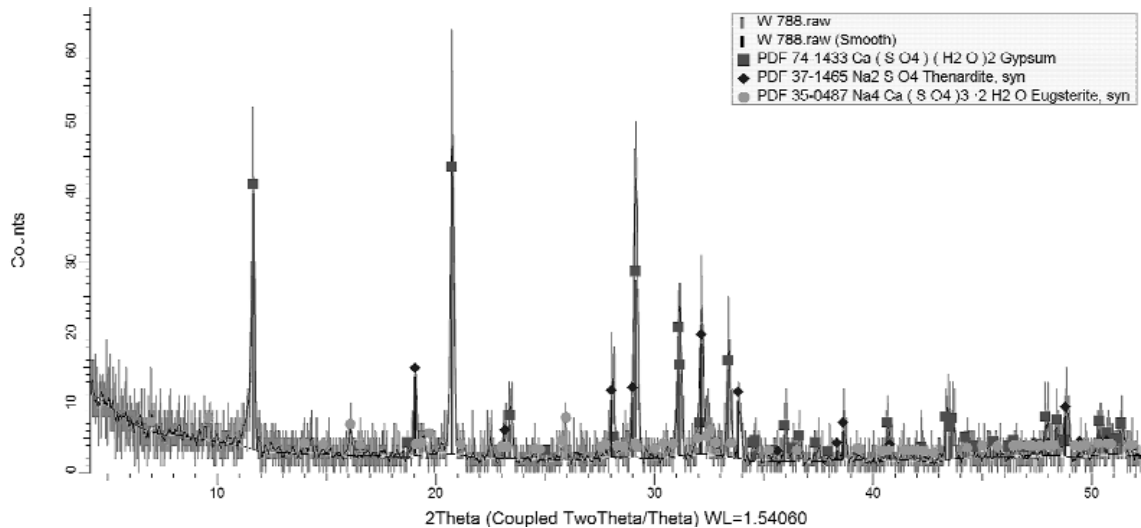


Figure 12. XRPD pattern of eugsterite, thenardite and gypsum from Gemerská Hôrka, Slovakia

12. ábra. Eugsterit, thenardit és gipsz XRPD-felvétele. Gömörhorka (Gemerská Hôrka), Szlovákia

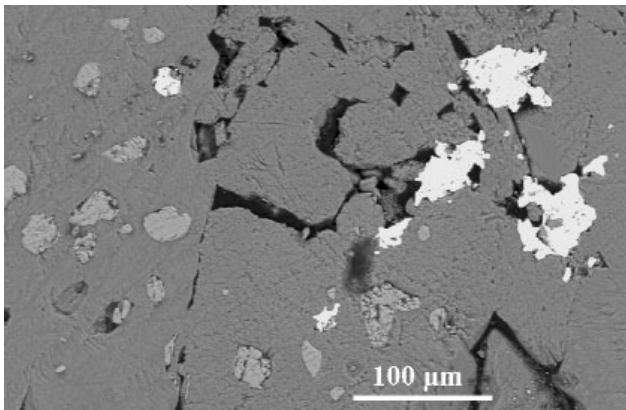


Figure 13. Celestine (white) and anhydrite (pale grey) crystals in gypsum. Fortuna adit, Gemerská Hôrka, Slovakia. BSE image

13. ábra. Idiomorf cölesztin- (fehér) és anhidritkristályok (halványiszürke) gipszben (szürke). Gömörhorka (Gemerská Hôrka, Szlovákia), Fortuna-táró. BSE-kép

occurs alone as fibrous aggregates of white needles or laths.

Epsomite and glauberite were described in the cracks of gypsum from the gypsum-anhydrite mine of Perkupa, Hungary by MAURITZ & CSAJÁGHY (1953), while MIKLÓS (1987) mentioned hexahydrate, thenardite, glauberite and

epsomite from the gypsum-anhydrite mine of Alsótelekes, Hungary. Both localities are similar in age and genetics to that at Gemerská Hôrka.

It is important to add that celestine crystals of 20–40 μm size were identified in the massive gypsum deposit, together with idiomorphic anhydrite (Figure 13); these most probably represent a product of relict phases. Similar celestine occurrences were also reported by MIKLÓS (1987) from Alsótelekes.

Acknowledgements

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