

Mineralogical mosaics from the Carpathian–Pannonian region 1.

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Ásványtani mozaikok a Kárpát–Pannon régióból 1.

Összefoglalás

Jelen tanulmány egy sorozat első része, melyben — és a továbbiakban is — mozaikszerű információkat adunk a Kárpát–Pannon régió új ásványtani eredményeiből. Az adatokat országok és lelőhelyek szerint csoportosítottuk. Az egyes mozaikokban az ásványok pontos — döntően XRD, SEM-EDX és EPMA általi — meghatározására, illetve a paragenezis tömör bemutatására koncentráltunk. A tanulmányunkban szereplő ásványok sokszor első említések az egész régióból, de minimum az illető lelőhelyről.

Az első részben a rudabányai ércesedés számos ritka másodlagos ásványát ismertetjük: ilyen a roxbyit, a réz-kloridok közül a connellit és claringbullit, illetve a greenockit és ramsbeckit. A roxbyit a korai kiválású réz-szulfidok (digenit és djurleit) átalakulási terméke. A réz-kloridok az oxidációs zóna kupritjához, a greenockit a mállásnak indult szfalerithez, míg a ramsbeckit a szupergén eredetű smithsonit-hoz kapcsolódik.

A második részben új romániai adatokat közlünk, így a macskamezői mangánérclelep oxidációs zónájából két másodlagos foszfátot, a strengit és kakoxént. A felsőbányai polimetallikus ércesedés felső szintjeinek ezüstben gazdag zónáiból nem meglepő az argentojarosit megjelenése. Vizsgálatainkkal érdekes, zónás jellegű kémiai helyettesítéseket mutattunk ki.

A harmadik részben új szlovákiai adatokat ismertetünk. A csucsomi mangánérclelepből kimutattuk a jacobsitot, mely ugyan a romániai Mn-szilikátos ércesedésekben jól ismert, de innen még nem mutatták ki. A muzeális példány nagysága arra enged következtetni, hogy ezt az ércípust akár bányászhatták is 100 évvel ezelőtt. Mikroszondás vizsgálatainkkal megkülönböztettünk egy ideális kémiai összetételű és egy Al-gazdag változatot. A nyilasi Sn-W-As greizenes képződményekből arsenopirit és löllingit mállásából első alkalommal észleltünk egy arseniosziderit. A vihorláti Bi-Te-Se indikációk, — melyek típuslelőhelyei a telluronyevszkit és vihorlátit ásványoknak — azok mállásából származó másodlagos Bi-Fe-szilikátot, a bizmutoferrit mutattuk ki. A mikroszondás és XRD vizsgálatok a fenti ásvány mellett változó Bi-tartalmú, rosszul kristályosodott vas-oxidokat rögzítettek.

Tárgyszavak: roxbyit, claringbullit, connellit, greenockit, ramsbeckit, strengit, kakoxén, argentojarosit, jacobsit, arseniosziderit, bizmutoferrit

Abstract

This paper is the first member of a series of publications in which the authors intend to present the scattered, mosaic-like nature of data acquired during recent mineralogical research from the Carpathian–Pannonian region. These data are organized by localities and/or genetics. Furthermore, they represent an important addition to the modern mineralogical knowledge of the area. It was decided that these particular data could not be presented separately as individual papers and this is why they are illustrated in the format of this study. One mosaic is focused on the exact identification of a mineral, or some minerals — dominantly based on XRD, EPMA and SEM-EDX data — with the description of its/their paragenesis.

This paper is the first description of the minerals reported here (at least from the specific localities mentioned).

The first part of deals with some rare secondary minerals from Rudabánya, Hungary: roxbyite, copper halides (connellite, claringbullite), greenockite and ramsbeckite. Roxbyite could be an alteration product of Cu-sulphides in the course of their early formation (e.g. digenite, djurleite). The copper halides are connected to the cuprite of the oxidation zone; the greenockite is related to the decaying sphalerite; and the ramsbeckite is associated with the smithsonite and brochantite, which are of supergene origin.

The second part of the paper presents secondary phosphates (strengite and cacoxenite) from the oxidation zone of the manganese deposit of Razoare, Romania. Argentojarosite is also described here from the silver-rich upper zone of the polymetallic mineralization of Baia Sprie, Romania. Its interesting chemical zonation is also illustrated.

The final part of the paper describes data from Slovakian localities — for example, with respect to jacobsite from the manganese deposit of Euema, Slovakia. This mineral is well-known from the Mn-silicate mineralizations of Romania, but it is new from this location. The jacobsite has two different compositions based on EPMA data. One is close to the Mn-Fe oxide formula, whereas the other contains an important Al substitution in its structure. Jacobsite could be one of the manganese ores which was mined at the location 100 years ago. An arsenate, arseniosiderite is characterized here from the Sn-W-As greisen mineralization of Hnílec, Slovakia; it was formed as an alteration product of arsenopyrite and löllingite. Bismutoferrite, a secondary Bi-Fe silicate, is described from the Bi-Te-Se indications of the Vihorlat Mts, Slovakia; this is the type locality of telluronevskite and viorlatite. Bismutoferrite was formed as an alteration product of the above-mentioned telluronevskite and viorlatite. A poorly crystalline phase with varying Bi content is also visible nearby the bismutoferrite.

Keywords: roxbyite, claringbullite, connellite, greenockite, ramsbeckite, strengite, cacoxenite, argentojarosite, jacobsite, arseniosiderite, bismutoferrite.

Introduction

This paper represents the start of a new series of research papers which will present new data for Carpathian–Pannonian mineralogy. It is the result of the successful cooperation of the Department of Mineralogy and Petrology, University of Miskolc, Hungary and the Department of Mineralogy, Herman Ottó Museum, Miskolc, Hungary.

A lot of new mineralogical data for the area of the Carpathian–Pannonian region were acquired as a result of the combination of extensive fieldwork and a detailed systematic study of the samples using instrumental mineralogy. Thousands of specimens are collected every year on the field by the above-mentioned institutes and also by professional mineral collectors. These are then investigated in the integrated X-ray diffraction (XRD), electron microprobe (EPMA), optical and thermo-analytical laboratories of the Department of Mineralogy and Petrology, University of Miskolc. These numerous unpublished data have created the basis for this new series of papers. It is impossible to present all the data in separate research papers. The value of some of them is such that they can be published separately in individual papers, but many of them can be presented only together. Yet whatever the case related to this issue, it was decided that it is important to present these data to the research community. This is because they provide a lot of new reliable information, and also clarify some of the ambiguous data evident in earlier literature. In each paper of the series an attempt will be made to group these scattered, but high-quality data according to localities or by different genetic types. Within this framework, the main focus will be on new minerals and the mineral paragenesis of the locations in the Carpathian–Pannonian region. The local geology and research history will be kept to a minimum because details concerning these factors are already available. The data which are presented here have been acquired during our recent investigations, and earlier reported knowledge or measurements are not included.

All the examined samples presented here are deposited at the Herman Ottó Museum, Miskolc.

Experimental methods

X-ray powder diffraction results were recorded on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha_{1,2}$ radiation (40 kV and 40 mA) with a 250 mm radius goniometer, in

parallel-beam geometry obtained by Goebel-mirror optics, 0.25° primary axial Soller with 0.6 mm divergence slit and 0.12° detector side long-Soller. 1 to 5 mg samples were grinded in agate mortar under acetone and loaded on Si single crystal sample holders. All measurements were recorded in the $2\text{--}70^\circ(2\Theta)$ range with a $0.01^\circ(2\Theta)/2$ sec scanning rate.

X-ray diffraction measurements were also performed with a 114.6 mm diameter Gandolfi camera (UB/61, Officina Elettrotecnica di Tenno, Trento, Italy) with Kodak Instrumex MX 125 film. Unit cell parameters were calculated with UnitCell software (HOLLAND & REDFERN, 1997). Film shrinkage was corrected with NIST SRM 640 silicon powder (as a basic external standard). Analytical parameters were the following (X-ray generator, radiation, filter, accelerating voltage, tube current, exposition time):

— Claringbullite: Siemens Kristalloflex 710, $\text{CuK}\alpha$, Ni-filter, 40 kV, 20 mA, 46 hours.

— Connellite: Seifert ISO-Debyelex 1001, $\text{CuK}\alpha$, Ni-filter, 40 kV, 20 mA, 44 hours (Institute of Material Sciences, Univ. Miskolc)

— Ramsbeckite: Seifert ISO-Debyelex 1001, Co tube, no filter, 30 kV, 30 mA, 44 hours (Institute of Material Sciences, Univ. Miskolc)

— Greenockite: Siemens Kristalloflex 710, $\text{CuK}\alpha$, Ni-filter, 40 kV, 25 mA, 46 hours.

Scanning electron microscopy (SEM), with the combination of energy dispersive X-ray spectroscopy (EDX), EDX mapping and electron microprobe measurements (EPMA), were performed on a JEOL–JXA 8600 Superprobe unit. The latter was equipped with four wavelength dispersive spectrometers and an E2V Scientific Instruments EDX silicon drift detector (SDD). During the analyses, for the EDX measurements 15–20 kV acceleration was used, with a probe current of 10–20 nA and a $4\times 5\ \mu\text{m}$ scanned area with focused beam during the analyses. (If the specimen size was not suitable for this, then a stopped focused beam was used.)

For roxbyite the following analytical parameters were used: 20 kV accelerating voltage, 20 nA beam current, and $5\ \mu\text{m}$ stopped spot size. S, Fe and Cu were measured by wavelength dispersive spectrometers with the following standards: synthetic MnS_2 (for S), ilmenite USNM 96189 (for Fe), and pure Cu (for Cu). No other elements could be

intensities. Roxbyite could be an alteration product of djurleite and/or digenite. This is the first occurrence in the Carpathian–Pannonian region.

CLARINGBULLITE AND CONNELLITE

Both copper chlorides were identified in the cavities of massive cuprite from the Adolf open pit. Light blue micaceous lamellae of claringbullite show excellent cleavage and have size up to 0.6 mm. Verification of claringbullite was based on XRD (Table III) and EDX data

Table III. XRD data of claringbullite from Adolf open pit, Rudabánya

III. táblázat. Claringbullit XRD adatai. Rudabánya, Adolf külfejtés

Claringbullite from Rudabánya (this study)		Claringbullite from Nehanga open pit, Zambia (FEJER <i>et al.</i> 1977) - ICDD 29-539				
d (Å)	Int. (%)	d (Å)	Int.	h	k	l
5.788	100	5.75	vvs	1	0	0
4.897	22	4.89	s	1	0	1
4.628	20	4.58	s	0	0	2
3.597	6	3.59	mw	1	0	2
3.338	3	3.336	w	1	1	0
2.892	26	2.889	ms	2	0	0
2.707	72	2.700	vvs	1	1	2
2.446	51	2.445	vs	2	0	2
2.297	7	2.276	m	0	0	4
		2.178	vvw	2	1	0
2.136	8	2.133	mw	1	0	4
2.103	7	2.099	w	2	0	3
		1.891	vw	1	1	4
1.799	16	1.797	ms	2	0	4
1.780	16	1.775	m	3	0	2
		1.749	vvw	1	0	5
1.669	24	1.669	ms	2	2	0
1.635	1	1.630	vw	3	0	3
1.603	3	1.604	vw	3	1	0
1.583	7	1.583	mw	2	1	4
1.571	5	1.568	w	2	2	2
		1.540	vvw	2	0	5
1.514	2	1.514	w	3	1	2
		1.475	vvw (b)	3	0	4
1.446	3	1.445	w	4	0	0
1.393	2	1.392	w	1	1	6
1.379	8	1.378	mw	4	0	2
1.353	12	1.352	ms	2	0	6
1.326	1	1.327	vw	3	2	0

Unit cell (Rudabánya sample): $P6_3/mmc$ space group, $a = 6.677(3)$, $c = 9.225(7)$ Å, $V = 356.2(4)$ Å³.

(Figure 2). It contains few percent of fluorine, which most probably substitutes chlorine in the structure. Accompanying minerals are connellite and malachite.

A copper chloride-sulphate, connellite was found in a similar environment as claringbullite. It has azure blue

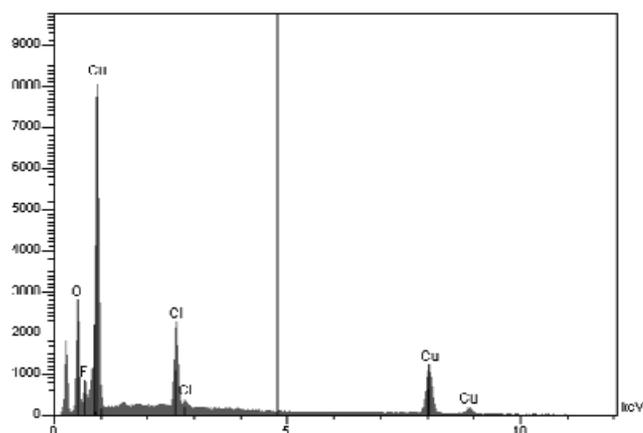


Figure 2. EDX spectrum of claringbullite. Adolf open pit, Rudabánya

2. ábra. Claringbullit EDX spektruma. Rudabánya, Adolf külfejtés

colour. Massive aggregates, prismatic crystals, needles (up to 0.2 mm), and star-like aggregates (up to 0.5 mm) can be found in cuprite. According to SEM images the crystals are hexagonal prisms (Figure 3). Connellite was identified by XRD (Table IV) and EDX observations (it contains Cu, Cl,

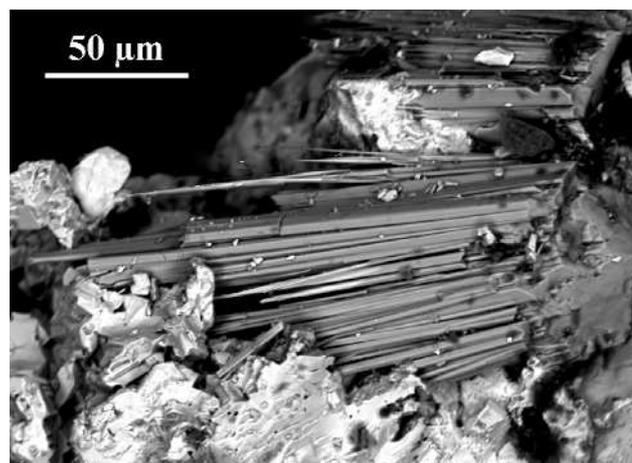


Figure 3. Prismatic connellite crystals in cuprite. Adolf open pit, Rudabánya. BSE image

3. ábra. Prizmás connellitkristályok kupritban. Rudabánya, Adolf külfejtés. BSE kép

S and O). Both copper-chlorides are rare, but their presence is characteristic for the oxidation zone of Rudabánya. This is the first time they have been documented from the Carpathian–Pannonian region.

GREENOCKITE

Sphalerites of Rudabánya contain more, or less cadmium. The cadmium content always shows strong correlation with zinc in the bulk rock samples. The Cd:Zn ratio is usually between 2–3.5 per thousand (N. Németh, personal communication). However, up to now a cadmium mineral has not been identified from the location. Very rarely, lemon yellow, powdery aggregates (up to 1–2 mm in diameter) can be found in fissures of massive fine-crystalline sphalerite in the Andrassy II. open pit. These aggregates contain only

Table IV. XRD data of connellite from Adolf open pit, Rudabánya*IV. táblázat.* Connellit XRD adatai. Rudabánya, Adolf külfejtés

Connellite from Rudabánya (this study)		Connellite from an unspecified locality ICDD 8-135				
d (Å)	Int. (%)	d (Å)	Int. (%)	h	k	l
13.647	73	13.7	99	1	0	0
7.947	100	8.0	100	1	1	0
6.879	5	6.9	10	2	0	0
5.496	19	5.51	59	2	0	1
5.198	35	5.20	69	2	1	0
4.578	13	4.59	59	0	0	2
4.335	14	4.35	59	1	0	2
3.970	4	3.98	20	1	1	2
3.814	18	3.82	59	2	0	2
3.434	15	3.48	59	3	1	1
3.232	23	3.27	89	3	0	2
		2.96	20	3	2	1
2.859	8	2.85	20	4	1	1
2.747	34	2.75	99	4	0	2
2.631	11	2.62	69	5	0	1
2.597	12	2.59	59	3	2	2
2.507	22	2.51	79	4	1	2
2.476	11	2.46	10	5	1	0
2.382	5	2.38	40	3	1	3
2.289	38	2.29	99	0	0	4
2.258	12	2.25	50	4	3	0
2.196	9	2.19	50	3	2	3
2.095	4	2.09	40	2	1	4
2.044	3	2.04	40	6	0	2
1.979	7	1.97	50	4	2	3
		1.91	20	7	0	1
		1.855	20	6	2	1
		1.811	50	4	3	3
		1.799	50	5	3	2
1.759	7	1.754	69	5	4	0
		1.725	10	6	3	0
		1.673	20	7	2	0
		1.644	10	7	2	1
1.618	14	1.613	89	4	0	5
1.585	7	1.580	59	3	2	5
		1.546	40	6	4	1
		1.520	20	7	3	1
1.489	8	1.488	79	2	0	6
		1.464	10	2	1	6
		1.443	20	9	0	2
1.425	4	1.419	40	8	1	3
1.394	5	1.392	50	4	0	6
		1.371	20	3	2	6
		1.354	40	10	0	1
		1.333	10	5	0	6
1.316	5	1.313	70	4	2	6

Unit cell (Rudabánya sample): $P6_3/mmc$ space group, $a = 15.81(2)$, $c = 9.16(2)$ Å, $V = 1984(6)$ Å³.

cadmium and sulphur (based on SEM-EDX data). Despite of the large exposition time (46 hours) of the XRD measurement, only four diffuse reflections appeared on the film of the Gandolfi camera, with very weak intensities. These reflections, as well as the most intensive peaks of the greenockite and hawleyite data, are shown in Table V. Comparing these data, it is clear that the Cd sulphide phase of

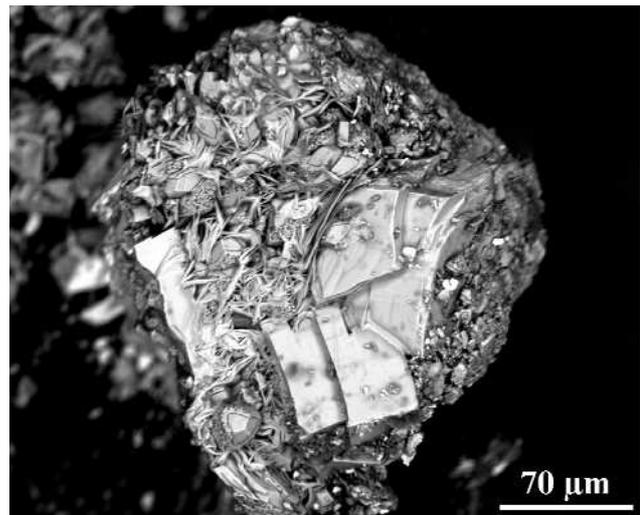
Table V. XRD data of greenockite from Andrassy II open pit, Rudabánya*V. táblázat.* Greenockit XRD adatai. Rudabánya, Andrassy II külfejtés

Cd sulphide Rudabánya	Greenockite (synthetic) ICDD 41-1049			Hawleyite from the Hector-Calumet mine, Yukon, Canada ICDD 10-454		
	d (Å)	I_{rel} (%)	hkl	d (Å)	I_{rel} (%)	hkl
3.573	3.5861	62	100			
3.339	3.3599	91	002	3.36	100	111
3.136	3.1638	100	101			
				2.90	40	200
2.046	2.0705	48	110	2.058	80	220
	1.8998	50	103			
				1.753	60	311

Rudabánya is greenockite. Peaks at 3.573 and 3.136 Å indicate the presence of greenockite structure. Based on the visual intensity estimation of the reflections, the intensity of the 3.339 Å peak is similar to that of above-mentioned ones, and therefore the presence of a hawleyite-type structure is improbable. This greenockite has a secondary origin, and it is an alteration product of sphalerite.

RAMSBECKITE

Ramsbeckite was identified in the Andrassy I. open pit, where it could be rarely found, albeit rarely, in the cavities of supergene earthy smithsonite. Their crystals are short prismatic to isometric (up to 50–80 µm in size) and have an emerald green colour (Figure 4). The identification was

**Figure 4.** Isometric ramsbeckite crystals with smithsonite and brochantite. Adolf open pit, Rudabánya. BSE image

4. ábra. Izometrikus ramsbeckitkristályok smithsonittal és brochantittal. Rudabánya, Adolf külfejtés. BSE kép

Table VI. XRD data of ramsbeckite from Adolf open pit, Rudabánya

VI. táblázat. Ramsbeckite XRD adatai. Rudabánya, Adolf külfejtés

Ramsbeckite from Rudabánya (this study)		Ramsbeckite from Ramsbeck, Germany ICDD 39-365		
d (Å)	Int. (%)	d (Å)	Int. (%)	hkl
7.102	100	7.09	100	001
5.580	2	5.596	4	220
4.388	7	4.40	12	320, 221
4.139	6	4.136	5	-311
3.554	24	3.549	25	002
3.242	12	3.244	11	202
2.996	5	2.997	8	222
2.884	7	2.884	16	132, 132
2.693	19	2.694	30	350, -251
2.562	4	2.559	7	160
2.515	42	2.516	75	-351, 351
2.143	20	2.145	25	352, 352
1.777	20	1.776	20	-603, 004
1.707	6	1.707	2	082
1.557	5	1.558	7	10.1.1
1.522	3	1.522	5	524
1.483	7	1.483	11	354, 354

proved by XRD (Table VI) and EDX analyses (it contains Cu, Zn, S and O). Accompanying minerals are rhombohedral, or earthy smithsonite and needle-like brochantite; however, the wider paragenesis contains some other secondary copper minerals, such as aurichalcite, malachite, linarite, hydrozincite and rosasite. Ramsbeckite usually has a secondary origin. This is the first known occurrence in the Carpathian–Pannonian region.

Romania

The Răzoare (Macskamező) manganese ore deposit

STRENGITE AND CACOXENITE

The metamorphosed Mn-Fe deposit of Răzoare has a very interesting Mn-silicate mineral assemblage (UDUBAŞA et al. 1996). The manganese ore was mined from the oxidation zone in the first decade of 1900s. Here, pyrolusite was the main ore-forming mineral. The manganese oxide ore was very rich in calcite, with the occasional presence of quartz veinlets. This type of ore has been found in some old waste dumps at the western part of the abandoned open pit. In the cavities of the quartz veinlets two secondary phosphates were identified: cacoxenite and strengite. Cacoxenite forms pale yellow sprays or felt-like aggregates which consist of needles up to 20–40 µm in length (Figure 5). The XRD pattern shows a poorly crystalline material and only the strongest reflections of cacoxenite appear: 21.78 Å (22.0 Å), 11.84 Å (11.94 Å) and 3.34

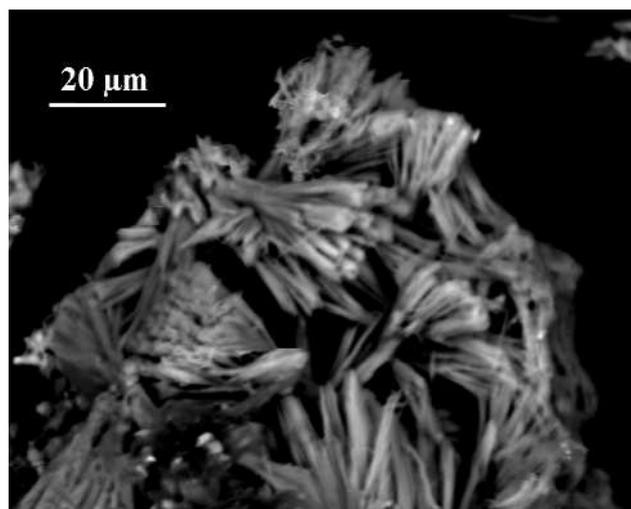


Figure 5. Spray of cacoxenite. Manganese mine, Răzoare. BSE image
5. ábra. Kakoxén sugaras halmaza. Macskamező, Mn-bánya. BSE kép

Å (3.34 Å) (the data of ICDD 01-075-1346 card in brackets). Strengite was found as colourless to pale grey rhombic dipyramids (up to 0.5–1 mm in size) in the cavities of quartz veinlets (Figure 6). It was proved by XRD (Table VII) and

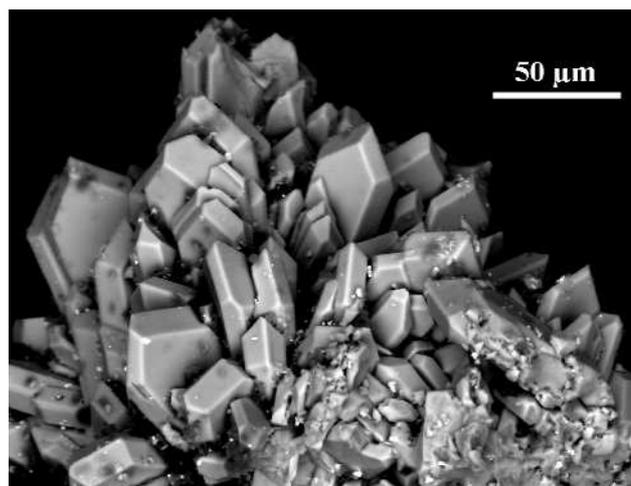


Figure 6. Short prismatic strengite crystals. Manganese mine, Răzoare. BSE image

6. ábra. Zömök prizmás strengitkristályok. Macskamező, Mn-bánya. BSE kép

EDX analyses that it contains only Fe, P and O. According to BSE images and EDX measurements, strengite is chemically homogenous. Primary euhedral, corroded apatite and muscovite were identified with it in close association (Figure 7). Both secondary phosphates could possibly have been formed from the apatite in the oxidation zone. This is the first description of strengite in Romania.

The Baia Sprie (Felsőbánya) ore deposit

ARGENTOJAROSITE

It is well-known, that the upper level of the Baia Sprie deposit was rich in silver (BORCOŞ et al., 1975). There is a small abandoned open pit in the western part of Dealul Mineii, where a zone with strong jarositization can be found

Table VII. XRD data of strengite from the manganese mine, Răzoare

VII. táblázat. Strengit XRD adatai. Macskamező, Mn-bánya

Strengite (measured)		Strengite 00-033-0667 (PDF-2 2005)					
d (Å)	I(%)	d	I(%)	h	k	l	
5.618	1	5.620	40	1	1	1	
5.494	48	5.509	60	1	1	1	
4.943	66	4.954	30	0	2	0	
4.378	100	4.383	85	2	0	1	
4.003	52	3.996	45	2	1	1	
3.991	23	3.996	45	0	1	2	
		3.959	13	1	2	1	
3.712	10	3.719	25	1	1	2	
3.277	19	3.281	17	2	2	1	
3.112	43	3.114	100	1	2	2	
2.999	27	3.002	45	3	1	1	
2.949	30	2.949	45	1	3	1	
		2.690	5	1	1	3	
		2.631	11	2	3	1	
		2.631	11	0	3	2	
2.545	22	2.546	50	1	3	2	
2.531	27	2.531	35	4	0	0	
2.443	2	2.472	6	0	4	0	
		2.444	25	2	1	3	
2.131	23	2.132	35	1	3	3	
		2.104	8	1	4	2	
		2.074	15	3	3	2	
2.002	16	2.003	20	2	0	4	
1.958	5	1.965	6	2	1	4	
		1.958	20	1	2	4	
		1.945	9	3	4	1	
		1.895	12	1	5	1	
		1.832	13	5	2	1	
		1.832	13	3	3	3	
1.805	23	1.806	16	5	1	2	
1.649	10	1.657	10	6	0	1	
1.648	10	1.649	19	2	0	5	
1.624	5	1.624	17	1	2	5	
1.614	5	1.615	19	1	4	4	
1.614	11	1.615	19	1	5	3	
1.604	11	1.604	17	5	3	2	
		1.600	15	3	3	4	
		1.566	14	2	6	0	
1.556	6	1.566	14	5	4	0	
1.556	6	1.556	20	2	4	4	
1.479	17	1.556	20	2	5	3	

Unit cell (Răzoare sample): *Pcab* space group, $a = 10.122 \text{ \AA}$, $b = 9.886 \text{ \AA}$, $c = 8.723 \text{ \AA}$, $\beta = 90.35^\circ$, $V = 872.9 \text{ \AA}^3$.

in the fissures of hydrothermally altered rocks. The primary silver minerals are acanthite, pyrargyrite and proustite. Jarosite minerals appear as yellowish powdery coatings or fine crystalline masses. The detailed examinations of these minerals show very interesting associations. The jarosite, Ag-rich jarosite and K-rich argentojarosite crystals show the following chemical zonations: the cores of rhombohedral

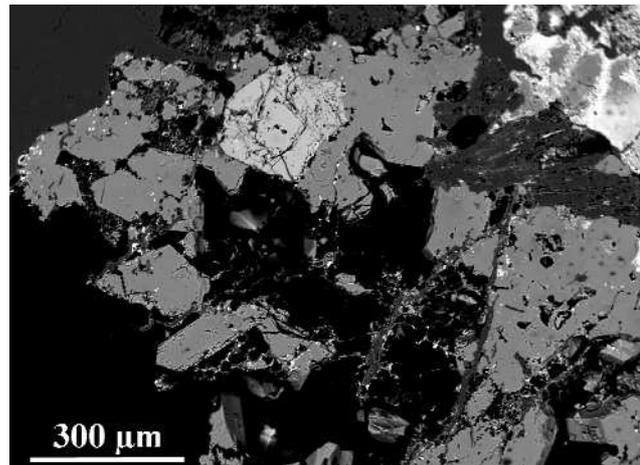


Figure 7. Strengite (grey), apatite (pale grey), muscovite and quartz (black). Manganese mine, Răzoare. BSE image

7. ábra. Strengit (szürke), apatit (világosszürke), muszkovit és kvarc (fekete) szöveti képe. Macskamező, Mn-bánya. BSE kép

crystals consist of Ag-rich jarosite with minor arsenic oxide grains; the following zone is jarosite with a lesser amount of Ag, while the outer rim is K-rich argentojarosite (Figures 8–9). All chemically different jarosites also contain a few

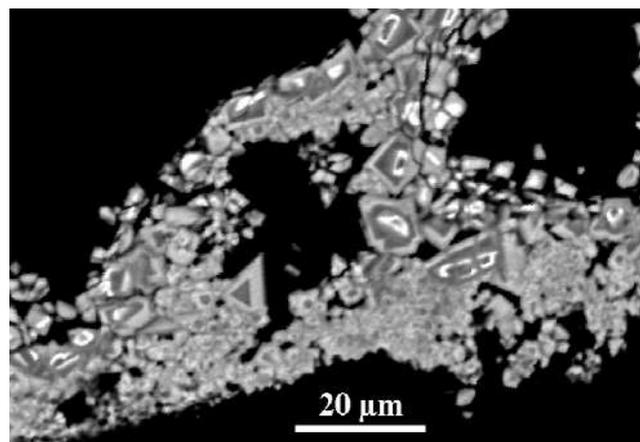


Figure 8. Chemical zoning of argentojarosite (light grey), jarosite (dark grey), and Sb-oxide (white). Dealul Mineii, Baia Sprie. BSE image

8. ábra. Argentojarosit (világosszürke) kémiai zónássága jarosittal (sötétszürke) és Sb-oxiddal (fehér). Felsőbánya, Bánya-hegy. BSE kép

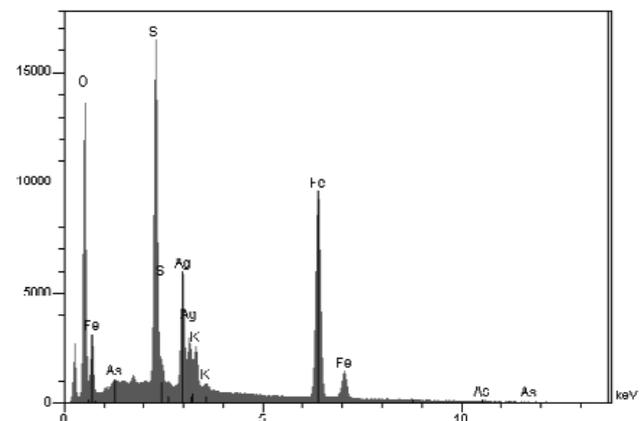


Figure 9. EDX spectrum of K-rich argentojarosite. Dealul Mineii, Baia Sprie

9. ábra. K-gazdag argentojarosit EDX spektruma. Felsőbánya, Bánya-hegy

wt% arsenic. So, according to BSE images the following characteristic rhythm could be described: Ag-rich jarosite → jarosite → K-rich argentojarosite. The crystals of a jarosite-argentojarosite solid solution have rhombohedral-pinacoid combinations. The crystals are minute, with their size only being up to 2–12 μm in diameter (Figure 10).

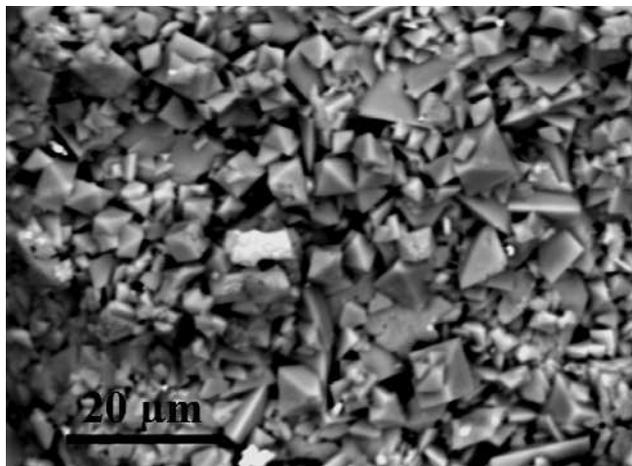


Figure 10. Rhombohedral argentojarosite crystals. Dealul Mineii, Baia Sprie. BSE image

10. ábra. Romboéderes argentojarosít-kristályok. Felsőbánya, Bánya-hegy. BSE kép

Table VIII. XRD data of argentojarosite from Dealul Mineii, Baia Sprie

VIII. táblázat. Argentojarosít XRD adatai. Felsőbánya, Bánya-hegy

Argentojarosite (measured)		Argentojarosite 00-041-1398 (PDF-2 2005)				
d (Å)	Int. (%)	d (Å)	Int. (%)	h	k	l
5.946	100	5.960	50	1	0	1
5.551	9	5.530	2	0	0	3
5.057	24	5.060	9	0	1	2
3.675	20	3.682	24	1	1	0
3.484	4	3.470	1	1	0	4
3.126	37	3.129	22	0	2	1
3.064	62	3.061	100	1	1	3
2.973	51	2.976	14	2	0	2
2.776	31	2.765	44	0	0	6
2.528	41	2.526	29	0	2	4
2.381	10	2.381	8	2	1	1
2.311	21	2.310	10	1	2	2
2.228	12	2.220	56	1	0	7
2.083	1	2.079	2	2	1	4
1.982	39	1.979	23	3	0	3
1.905	3	1.899	2	0	2	7
1.837	16	1.838	26	2	2	0
1.756	12	1.757	2	1	3	1
1.742	9	1.735	7	2	0	8
1.653	7	1.647	7	1	1	9
1.625	10	1.626	1	1	3	4
1.584	11	1.586	1	4	0	1
1.560	4	1.562	8	3	1	5

Unit cell (Baia Sprie sample): $R\bar{3}m$ space group, $a = 7.34 \text{ \AA}$, $c = 16.65 \text{ \AA}$, $V = 776.5 \text{ \AA}^3$

They show close intergrowth in the cavities, and the yellow to golden yellow crystals or coatings have an adamantine lustre. There are also small amounts of chlorargyrite and an unspecified antimony oxide in close association with these jarosites. The XRD data show good agreement with reference data (Table VIII). This is the first mention of argentojarosite in the Carpathian–Pannonian region.

Slovakia

The Čučma (Csucsom) manganese ore deposit

JACOBSITE

There are two historical specimens from Euema which are rich in jacobsite, and which can be observed in the collection of Herman Ottó Museum, Miskolc, Hungary. Their exact locality is the “manganese mine, upper adit” (this is what is written on the old labels). These specimens most probably were collected in the first decade of 1900s. Jacobsite is black and coarse-granular in hand specimens, and its powder has a dark brown colour.

The anhedral to subhedral crystals are up to 5–50 μm, and form a close intergrowth. Quartz grains and pyrite veinlets appear together with jacobsite. The crystals sometimes show chemical variation, and at least two

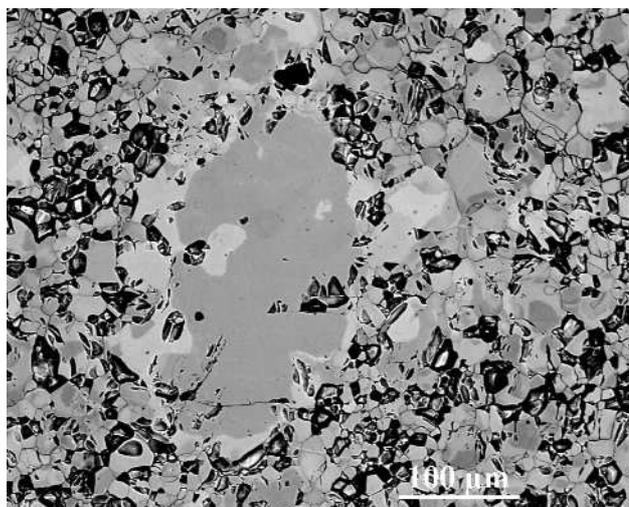


Figure 11. Chemical zoning by Al of jacobsite. Manganese mine, Čučma. BSE image

11. ábra. Al-beépülés okozta kémiai zónásság jacobsitban. Csucsom, Mn-bánya. BSE kép

composition types were identified: Al-poor and Al-rich; commonly the core is Al-rich, while the outer zone is Al-poor (Figure 11). According to EPMA and EDX analyses there are no other substitutions in the jacobsite (Table IX). The XRD pattern shows good accordance with reference data (Table X). Jacobsite could have been one of the mined ore types of manganese from the upper level, based on the quite big size (25 cm in diameter) of the investigated specimens.

Table IX. Chemical composition (EPMA) of jacobsite in weight per cent from the manganese mine of Čučma
IX. táblázat. Jacobisit kémiai elemzése (EPMA) tömegszázalékban. Csucsom, Mn-bánya

Wt. %	Jacobsite						Al-rich jacobsite				
	1	2	3	4	5	avr.	6	7	8	9	Avr.
Al ₂ O ₃	1.91	1.93	1.74	2.17	1.83	1.93	4.50	4.72	4.91	4.48	4.65
MnO	34.54	34.46	34.54	33.92	34.70	34.44	34.95	34.41	34.36	34.44	34.54
Fe ₂ O ₃	61.82	61.39	61.28	61.28	60.73	61.31	58.15	58.29	58.62	58.88	58.48
Extra O*	0.43	0.43	0.46	0.39	0.48	0.45	0.45	0.39	0.37	0.39	0.40
Summ.	98.70	98.21	98.02	97.76	97.74	98.13	98.05	97.81	98.26	98.19	98.07
Λ.p.f.u.											
Mn ²⁺	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fe ³⁺	1.79	1.78	1.79	1.79	1.77	1.78	1.67	1.67	1.67	1.69	1.68
Mn ⁴⁺	0.12	0.13	0.13	0.11	0.14	0.13	0.13	0.11	0.11	0.11	0.11
Al ³⁺	0.09	0.09	0.08	0.10	0.08	0.09	0.20	0.21	0.22	0.20	0.21
Summ ³⁺	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Oxygen	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

* Mn²⁺/Mn³⁺ calculated from the stoichiometry.

Table X. XRD data of jacobsite from the manganese mine of Čučma

X. táblázat. Jacobisit XRD adatai. Csucsom, Mn-bánya

Jacobsite (measured)		Jacobsite 00-010-0319 (PDF-2 2005)					
d (Å)	I (%)	d (Å)	I (%)	h	k	l	
4.891	12	4.906	20	1	1	1	
2.998	25	3.005	35	2	2	0	
2.557	100	2.563	100	3	1	1	
2.449	4	2.450	12	2	2	2	
2.122	34	2.124	25	4	0	0	
1.733	12	1.734	20	4	2	2	
1.633	32	1.636	35	5	1	1	
1.500	31	1.503	40	4	4	0	

Unit cell (Čučma sample): *Fd* $\bar{3}m$ space group, *a* = 8.499 Å, *V* = 613.908 Å³.

Medvedí potok locality, Hníflec (Nyilas)

ARSENIOSIDERITE

The Medvedí potok occurrence has Sn-W-Mo accumulations in greisen (DRNŽÍK et al., 1973). As-containing sulphides (e.g., arsenopyrite, löllingite) are common in quartz veins. The near-surface oxidation of these sulphides produced jarosite, scorodite, different iron oxides and rare arseniosiderite. The latter forms brown globular aggregates consisting of lamellae (up to 0.2 mm), or golden yellow to brown lamellae or lath-like crystals with silky lustre (up to 1–3 mm) in the narrow fissures (Figure 12). Ca, Fe, As and O were detected according to EDX analyses. The mineral was identified by its XRD pattern. The following reflections prove the presence of arseniosiderite (the data of ICDD 00-047-1848 card in brackets):

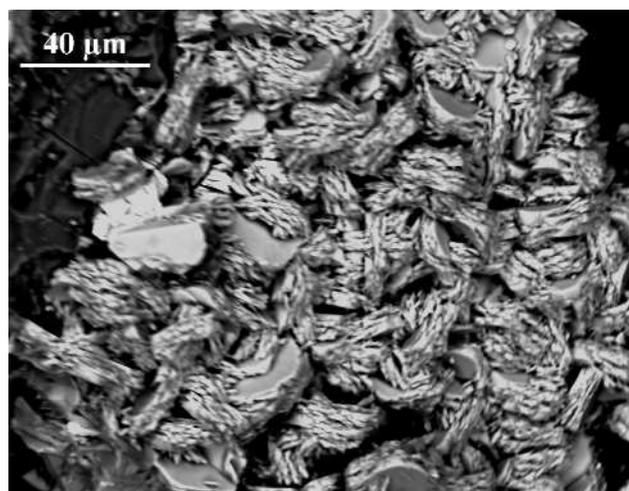


Figure 12. Arseniosiderite lamellae. Medvedí potok, Hníflec. BSE image
12. ábra. Lemezes arseniosiderit. Nyilas, Medve-patak. BSE kép

7.574 Å (7.554 Å), 3.891 Å (3.864 Å), 3.574 Å (3.566 Å), 3.171 Å (3.168 Å), 2.597 Å (2.590 Å). It has secondary origin, formed by decomposition of arsenopyrite and löllingite. This is the first mention of arseniosiderite from Slovakia.

The Poruba pod Vihorlatom (Németvágás) occurrence

BISMUTOFERRITE

The mineralization of bismuth selenides-tellurides, located in the central part of the Vihorlat Mts is bound to bodies of strongly silicified rocks near Lake Morske, and the Porubsky and Sokolsky valleys. The aggregates of telluronevskite and vihorlatite can be found in opal-quartz veinlets, and they are also present in a disseminated form in fine

crystalline silicified rocks. This area is the type locality of telluronevskite and vihorlatite. Telluronevskite occurs as massive aggregates of lamellar crystals up to 1 mm in size (RIDKOŠIL et al. 2001). Earthy or film-coated aggregates containing secondary minerals can be found around telluronevskite and vihorlatite because of their near-surface

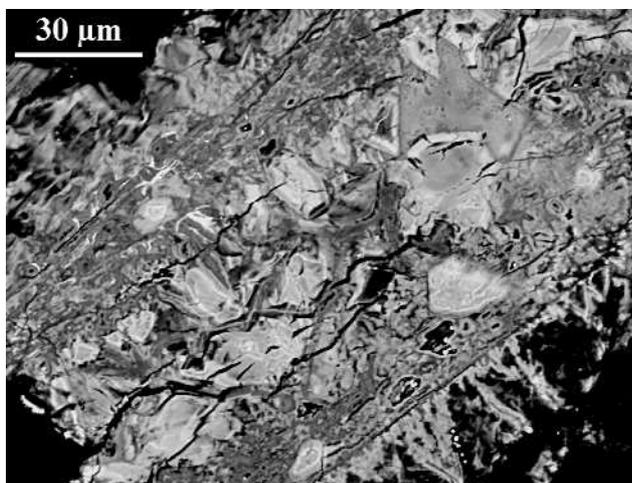


Figure 13. Bismutoferrite (pale grey) with iron oxides (dark grey). Poruba pod Vihorlatom. BSE image

13. ábra. Bizmutoferrit (halványszürke) Fe-oxidokkal (szürke, sötétszürke). Németsvágás. BSE kép

oxidation phenomena. The brown to yellowish brown earthy, powdery masses are mainly amorphous iron oxides or goethites (according to XRD and EDX analyses). In these iron oxide masses, bismuth-containing phases were sometimes identified, and they appear as thin lenses, or patches (Figure 13). According to BSE images, they are of a lamellar structure. On the close border of bismuth tellurides-selenides, however, only rarely can a bright yellow to greenish yellow powdery mass be found; according to EDX analyses

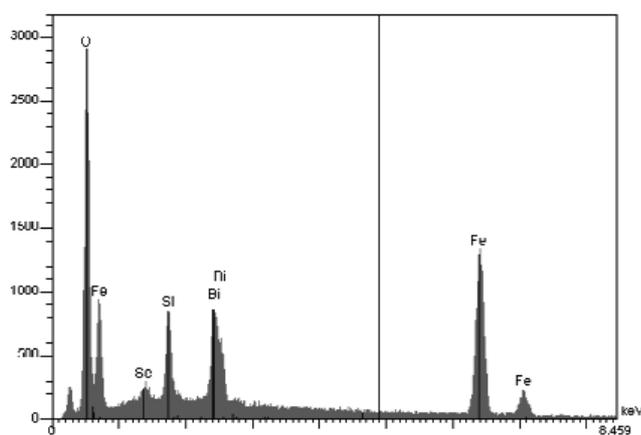


Figure 14. EDX spectrum of selenian bismutoferrite. Poruba pod Vihorlatom

14. ábra. Se-tartalmú bizmutoferrit EDX spektruma. Németsvágás

it has essential compounds of Bi, Fe, Si and O and a few wt% Se (see Figure 14). These earthy masses (up to 2–4 mm in diameter) consist of extremely small lamellae up to 2–3 µm, which form sheaf-like aggregates (Figure 15). These minute lamellae were identified by XRD examination as bismutoferrite. The following main reflections prove the presence of

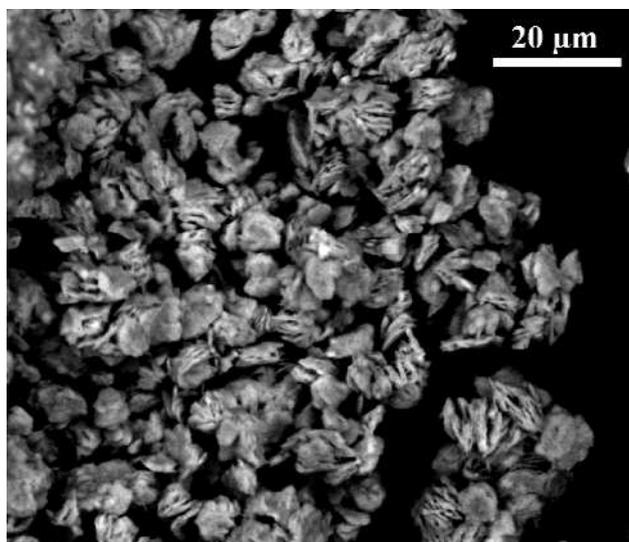


Figure 15. Sheaf-like aggregates of bismutoferrite. Poruba pod Vihorlatom. BSE image

15. ábra. Bizmutoferrit legyezős halmazai. Németsvágás. BSE kép

bismutoferrite (data of 00-026-1002 ICDD card in brackets): 8.922 Å (8.831 Å), 5.692 Å (5.609 Å), 3.274 Å (3.274 Å), 3.229 Å (3.229 Å), 2.949 Å (2.942 Å). Bismutoferrite is an uncommon mineral and around the world it is mainly produced by near-surface alteration of bismuth sulphides (e.g., MILTON et al. 1958, SEJKORA et al. 1994). It has a similar origin in the Poruba pod Vihorlatom occurrence, too. This is the first data about bismutoferrite from Slovakia.

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References — Irodalom

- BORCOȘ, M., LANG, B., BOSTINESCU, S. & GHEORGHÎȚA, I. 1975: Neogene hydrothermal ore deposits in the volcanic Gutâi Mountains. Part III. — *Revue Roumaine de Géologie, Géophysique et Géographie — Série de Géologie* **19**, 21–35.
- DRNZÍK, E., DRNZÍKOVÁ, L. & MANDÁKOVÁ, K. 1973: Geologičeskije predposilki, kriterii i perspektivy poiskov Sn-W-Mo orudnenija v Spišsko-gemerskich rudnych gorach (Slovakija). [Geological conditions, criteria and perspectives of Sn-W-Mo mineralization prospecting in Spiš-Gemer Ore Mts.]. — *Mineralia Slovaca* **5/2**, 157–164. (in Slovakian)
- FEJER, E. E., CLARK, A. M., COUPER, A. G. & ELLIOTT, C. J. 1977: Claringbullite, a new hydrated copper chloride. — *Mineralogical Magazine* **41**, 433–436.
- HOLLAND, T. J. B. & REDFERN, S. A. T. 1997: Unit cell refinement from powder diffraction data: The use of regression diagnostics. — *Mineralogical Magazine* **61**, 65–77.
- MILTON, C., AXELROD, J. M. & INGRAM, B. 1958: Bismutoferrite, chapmanite, and “hypochlorite”. — *American Mineralogist* **43**, 656–670.
- MUMME, W. G., SPARROW, G. J. & WALKER, G. S. 1988: Roxbyite, a new copper sulphide mineral from the Olympic Dam deposit, Roxby Downs, South Australia. — *Mineralogical Magazine* **52**, 323–330.
- RIDKOŠÍL, T., SKALA, R., JOHAN, Z. & ŠREIN, V. 2001: Telluronevskite, Bi_3TeSe_2 , a new mineral. — *European Journal of Mineralogy* **13**, 177–185.
- SEJKORA, J., ŠREIN, V. & ONDRUŠ, P. 1994: New data on bismutoferrite and chapmanite from the Bohemian occurrences. — *Vest. Česk. Geol. Úst.* **69/4**, 75–78.
- UDUBAȘA, G., HĂRTOPANU, P., ILINCA GH. & VALDMAR, ȘT. 1996: The regionally metamorphosed Mn-Fe deposit at Răzoare, Preluca Mts., Romania. — *Romanian Journal of Mineral Deposits* **77**, 3–20.
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