

Original paper

Dobšináite, $\text{Ca}_2\text{Ca}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new member of the roselite group from Dobšiná (Slovak Republic)

Jiří SEJKORA*¹, Martin ŠTEVKO^{2,1}, Radek ŠKODA³, Eva VÍŠKOVÁ⁴, Jiří TOMAN⁴, Sebastián HREUS³, Jakub PLÁŠIL⁵, Zdeněk DOLNÍČEK¹

¹ Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193 00 Prague 9, Czech Republic; jiri.sejkora@nm.cz

² Earth Science Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 840 05 Bratislava, Slovak Republic

³ Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, 611 37, Brno, Czech Republic

⁴ Department of Mineralogy and Petrography, Moravian Museum, Zelný trh 6, 659 37 Brno, Czech Republic

⁵ Institute of Physics, Academy of Sciences of the Czech Republic v.v.i, Na Slovance 2, 182 21 Prague 8, Czech Republic

* Corresponding author



Dobšináite, ideally $\text{Ca}_2\text{Ca}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, is a new supergene mineral from the Dobšiná deposit, Slovak Republic, associated with phaunouxite, picropharmaocolite, erythrite-hörnesite, gypsum and aragonite. It forms white to pink clusters or polycrystalline aggregates up to 1–4 mm in size consisting of densely intergrown, slightly rounded thin tabular to platy crystals up to 0.1 mm in size. Dobšináite has a white streak, vitreous luster, does not fluoresce under either short- or long-wave ultraviolet light. Cleavage on {010} is good, the Mohs hardness is ~3, and dobšináite is brittle with an uneven fracture. The calculated density is 3.395 g/cm³. Dobšináite is optically biaxial negative, the indices of refraction are $\alpha' = 1.601(2)$ and $\gamma' = 1.629(2)$ and $2V_{\text{meas}}$ is 60° (+/– 20°). Dobšináite is monoclinic, space group $P2_1/c$, $a = 5.990(2)$, $b = 13.013(4)$, $c = 5.726(2)$ Å, $\beta = 108.47(3)^\circ$, $V = 423.3(3)$ Å³, $Z = 2$. The seven strongest lines in the X-ray powder diffraction pattern are as follows: d (Å)/ $I(hkl)$: 5.197/37(110); 3.443/38(130); 3.385/66(031); 3.249/77(040); 3.201/42(13–1); 3.026/100(121) and 2.822/60(10–2). The chemical analyses by electron microprobe yielded (in wt. %) CaO 36.74, MgO 0.89, NiO 0.37, CoO 0.51, P₂O₅ 0.03, As₂O₅ 52.75, SO₃ 0.18, H₂O_{calc.} 8.31, total 99.78. The resulting empirical formula on the basis of 10 O atoms per formula unit is $\text{Ca}_2(\text{Ca}_{0.84}\text{Mg}_{0.10}\text{Co}_{0.03}\text{Ni}_{0.02}\text{Σ}_{0.99})[(\text{AsO}_4)_{1.99}(\text{SO}_4)_{0.01}]_{\Sigma 2.00} \cdot 2\text{H}_2\text{O}$. Dobšináite is the Ca-dominant member of the roselite group as confirmed by stoichiometry, X-ray powder diffraction data and Raman spectroscopy. It is named after its type locality Dobšiná, Slovak Republic. Dobšináite was formed during weathering of primary Co and As-bearing ore minerals (safflorite, arsenopyrite) in a Ca enriched environment under relatively dry conditions.

Keywords: dobšináite, calcium arsenate, new mineral, roselite group, Dobšiná, Slovak Republic

Received: 20 March 2021; **accepted:** 28 June 2021; **handling editor:** J. Zachariáš

1. Introduction

During our long-term systematic mineralogical research focused on supergene arsenate minerals from various occurrences (Sejkora et al. 1999, 2009, 2018; Plumhoff et al. 2020; Steciuk et al. 2021), dobšináite, a new Ca dominant member of the roselite group, was discovered; in this paper, we report its description. Arsenate members of the roselite group comprise monoclinic minerals of generalized composition $\text{Ca}_2M(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$. The octahedral M site is occupied mainly by Mn²⁺ (brandtite, Herwig and Hawthorne 2006), Co²⁺ (roselite, Hawthorne and Ferguson 1977), Cu²⁺ (ruffite, Yang et al. 2011), Mg²⁺ (wendwilsonite, Kolitsch and Fleck 2006) and Zn²⁺ (zincroselite, Keller et al. 2004).

Dobšináite is named after its type locality Dobšiná, which represents the most important accumulation of Ni arsenides and sulfarsenides in the Western Carpathians

and in the past, it was a significant producer of the high-grade Ni and Co ores in Europe.

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2020-81). The holotype sample of dobšináite is deposited in the collections of the Moravian Museum in Brno, Department of Mineralogy and Petrography, Zelný trh 6, Brno, Czech Republic, under the catalog number B12257.

2. Occurrence

Dobšináite was found in several specimens collected in the short abandoned adit at the Dionýz mining field, Zemberg-Terézia vein system, which is located 2.2 km NE of the Dobšiná town, Spišsko-gemerské rudohorie



Fig. 1 Aggregates of dobšínáite consisting of densely intergrown, slightly rounded thin tabular to platy crystals; holotype sample, the field of view is 1.6 mm.



Fig. 2 White (with pink tint) dobšínáite aggregates consisting of densely intergrown thin tabular to platy crystals associated with hemispherical aggregates of minerals from erythrite-hörnésite solid-solution; holotype sample, the field of view is 1.8 mm.

Mts., Rožňava Co., Košice Region, Slovak Republic (48.837977°N, 20.383550°E).

The Zemberg-Terézia vein system is represented by siderite-ankerite hydrothermal carbonate-quartz veins with Ni-Fe-Co-Cu ore mineralization hosted in the Early Paleozoic gneiss-amphibolite complex of the Klátov group belonging to the Gemic tectonic unit (Rozložník 1959, 1965; Halahyiová-Andrusovová 1964a; Grecula et al. 1995). The vertical extent of the veins exceeds 1.5 km, generally with the SW-NE orientation and moderate to steep dip (40° to 70°) to the S or SE. The veins are usually 0.7 to 1.5 m thick. The two different ore mineralization types were distinguished: carbonate (siderite, ankerite-dolomite)-quartz vein filling with baryte and abundant chalcopyrite and tetrahedrite is typical for the upper parts of the veins. In contrast, Ni-Co-As minerals are prevailing ore minerals in the deeper parts of the veins (Halahyiová-Andrusovová 1959, 1964b; Grecula et al. 1995). The dominant gangue minerals are carbonates, mainly Fe-rich dolomite to ankerite and siderite with quartz and minor tourmaline. Gersdorffite and arsenopyrite are the most frequent ore minerals, accompanied by minor pyrite, cobaltite, nickelskutterudite-skutterudite, nickeline, millerite, rammelsbergite, safflorite, ullmannite, löllingite, chalcopyrite, tetrahedrite group minerals, Bi sulfosalts and hematite (Halahyiová-Andrusovová 1959; Kiefer et al. 2017, 2020; Števkó and Sejkora 2020). The two adits in the Dionýz mining field (Dionýz adit and the short adit above, where the samples with dobšínáite were collected) explored one of the short hydrothermal ore veins developed at the southern margin of the Zemberg-Terézia vein system.

Dobšínáite was found in a relatively dry area of the mine in assemblage with other Ca and Co phases. This supergene post-mining assemblage was found growing on the surface of loose fragments of vein filling containing

calcite-dolomite-quartz matrix with rich impregnations of safflorite and Co-rich arsenopyrite. Dobšínáite is closely associated with phaunouxite, picropharmacolite, erythrite-hörnésite, gypsum and aragonite. Rauenthalite is also present in this assemblage but never in direct association with dobšínáite. The supergene assemblage with dobšínáite was formed by oxidation of primary Co and As-bearing ore minerals (safflorite, arsenopyrite) in a Ca enriched environment (abundant calcite in the matrix) under the relatively dry conditions (Števkó et al. *unpublished data*).

3. Appearance and physical properties

Dobšínáite occurs as clusters or polycrystalline aggregates up to 1–4 mm in size consisting of densely intergrown, slightly rounded thin platy crystals up to 0.1 mm in size (Figs 1 and 2), usually the thickness of individual crystals does not exceed 10 μm . It has a white to pink color depending on the Co content; the holotype is white, locally with a light pink/violet tint. The pink variety seems to be more coarse crystalline than the white variety. Its aggregates are opaque to translucent; individual crystals or tiny fragments are translucent to transparent. It has a white streak and a vitreous luster. It does not fluoresce under either short- or long-wave ultraviolet light. Cleavage on {010} is good, the Mohs hardness is ~ 3 (scratch tests), and the mineral is brittle with an uneven fracture. The density $D_{\text{calc}} = 3.395 \text{ g/cm}^3$ was calculated on the basis of the empirical formula and unit-cell volume refined from powder data; for the ideal formula, we obtained $3.405 \text{ g}\cdot\text{cm}^{-3}$.

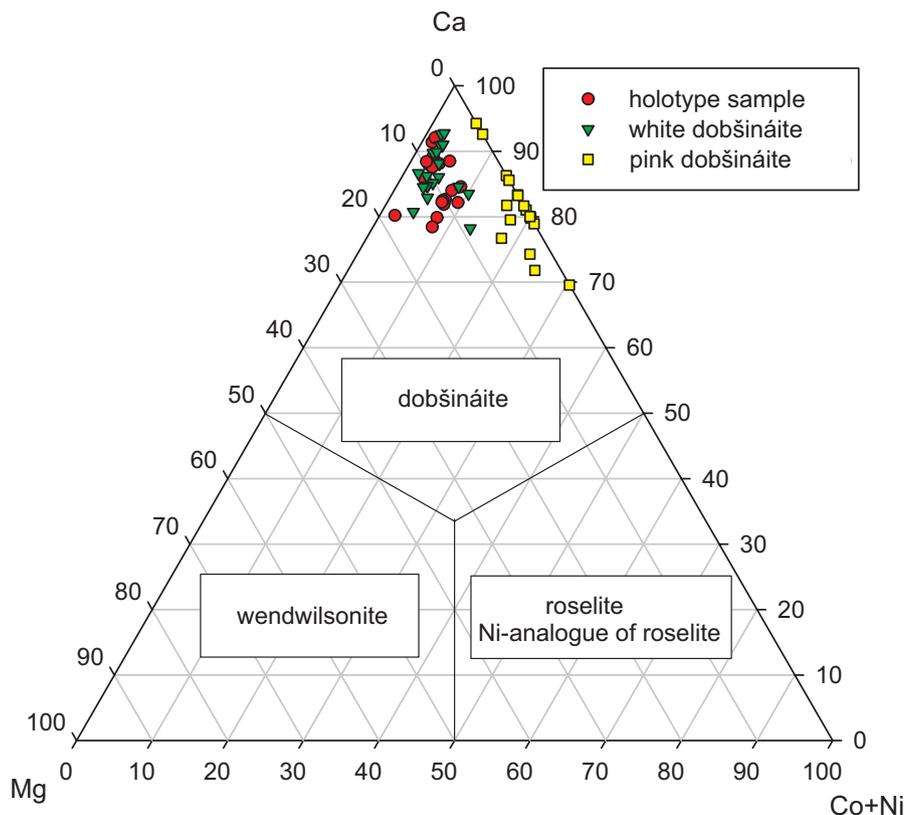
Dobšínáite is optically biaxial negative, with $\alpha' = 1.601(2)$ and $\gamma' = 1.629(2)$ (measured at 589 nm),

$2V_{\text{meas.}} = 60^\circ$ ($\pm 20^\circ$). Crystals and aggregates are formed of parallel intergrowths and bent fine elongated domains. Extinction has an undulatory character and is parallel to the elongation or with a minimum angle. The character of the sample hampers a more precise characterization. Dispersion is weak ($r > v$), and dobšínáite exhibits no noticeable pleochroism. The Gladstone-Dale compatibility index $1-(K_p/K_c)$ calculated from incomplete optical data is 0.003 for the empirical formula and unit-cell parameters from X-ray powder diffraction pattern, indicating superior compatibility (Mandarino 1981).

4. Chemical composition

Initial chemical analyses of dobšínáite were collected utilizing Cameca SX-100 electron microprobe (Masaryk University, Brno) during a routine investigation of the secondary arsenate mineral assemblage from Dobšíná. Subsequently, a more systematic chemical characterization of dobšínáite was performed by a Cameca SX-100 electron microprobe (National Museum, Prague) operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 4 nA, and a beam diameter of 20 μm . The following lines and standards were used: K_α : diopside (Mg), fluorapatite (P), rhodonite (Mn), wollastonite (Ca), Co (Co), Ni (Ni), celestine (S), and L_α : clinoclase (As). Peak counting times (CT) were 20 s, CT for each background was one-half of the peak time. The raw intensities were converted to the concentrations automatically using *PAP* (Pouchou and Pichoir 1985) matrix-correction software. Other elements, such as Al, Cu, Fe, Si, V and Zn were found to be below the detection limits (0.03–0.08 wt. %). Water content could not be analyzed directly because of the minute amount of material available and was calculated

Fig. 3 Ternary graph of occupation of Co+Ni vs. Ca vs. Mg (atom. unit) in the octahedral *M* position of dobšínáite from Dobšíná; data for holotype sample are compared with white and pink dobšínáite aggregates from other samples.



Tab. 1 Chemical data (in wt. %) for holotype sample of dobšínáite

constituent	mean	range	stand. dev. (σ)
CaO	36.74	35.88–37.81	0.65
MgO	0.89	0.58–1.65	0.26
CoO	0.51	0.10–0.84	0.24
NiO	0.37	0.08–0.70	0.23
As ₂ O ₅	52.75	51.96–53.58	0.41
P ₂ O ₅	0.03	0.00–0.16	0.05
SO ₃	0.18	0.06–0.28	0.05
H ₂ O*	8.31		
total	99.78		

H₂O* – content calculated on the basis of 2 H₂O from the ideal composition of roselite group minerals

on the basis of 2 H₂O (from the ideal composition of roselite group minerals).

Table 1 gives the chemical composition of the holotype sample of dobšínáite (mean of nineteen determinations). The empirical formula of dobšínáite based on 10 O atoms per formula unit is Ca₂(Ca_{0.84}Mg_{0.10}Co_{0.03}Ni_{0.02})_{Σ0.99}[(AsO₄)_{1.99}(SO₄)_{0.01}]_{Σ2.00}·2H₂O. The simplified formula is Ca₂(Ca,Mg)(AsO₄)₂·2H₂O, and the ideal end-member formula is Ca₂Ca(AsO₄)₂·2H₂O, which requires CaO 38.75, As₂O₅ 52.94, H₂O 8.30, total 100.00 wt. %.

In other samples, besides white ones, pink aggregates with increased Co (up to 3.66 wt. % CoO,

Tab. 2 Representative analyses (wt. %) of dobšínáite

	holotype				white				pink					
CaO	35.88	36.07	36.83	37.38	34.53	34.72	35.23	36.21	33.91	34.56	35.88	36.47	36.76	37.26
MgO	1.65	0.75	0.64	0.90	0.67	1.14	1.01	0.41	0.00	0.25	0.00	0.00	0.00	0.00
CoO	0.26	0.84	0.84	0.27	1.46	0.42	0.51	0.19	3.66	3.04	2.58	2.37	1.81	0.59
NiO	0.09	0.70	0.63	0.10	0.38	0.17	0.26	0.16	0.79	0.64	0.39	0.46	0.42	0.35
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.17	0.22	0.00
As ₂ O ₅	51.96	53.02	52.79	52.54	52.65	52.75	51.35	51.54	53.59	52.17	52.72	52.98	53.30	52.50
P ₂ O ₅	0.03	0.00	0.08	0.00	0.41	0.45	0.53	0.45	0.00	0.00	0.14	0.00	0.19	0.08
SO ₃	0.23	0.13	0.14	0.15	0.30	0.18	0.20	0.12	0.20	0.20	0.22	0.15	0.19	0.08
H ₂ O*	8.20	8.34	8.33	8.27	8.43	8.42	8.23	8.22	8.45	8.22	8.35	8.34	8.45	8.27
total	98.29	99.85	100.28	99.61	98.83	98.25	97.32	97.30	100.60	99.08	100.48	100.94	101.34	99.13
Ca	2.810	2.778	2.842	2.904	2.633	2.648	2.751	2.830	2.580	2.700	2.761	2.810	2.796	2.895
Mg	0.180	0.080	0.069	0.097	0.071	0.121	0.110	0.045	0.000	0.027	0.000	0.000	0.000	0.000
Co	0.015	0.048	0.049	0.016	0.083	0.024	0.030	0.011	0.208	0.178	0.149	0.137	0.103	0.034
Ni	0.005	0.040	0.036	0.006	0.022	0.010	0.015	0.009	0.045	0.038	0.023	0.027	0.024	0.020
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.010	0.013	0.000
As	1.986	1.993	1.988	1.992	1.959	1.963	1.956	1.966	1.989	1.989	1.980	1.992	1.978	1.991
P	0.002	0.000	0.005	0.000	0.025	0.027	0.033	0.028	0.000	0.000	0.009	0.000	0.011	0.005
S	0.013	0.007	0.008	0.008	0.016	0.010	0.011	0.007	0.011	0.011	0.012	0.008	0.010	0.004
H ₂ O	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

H₂O* – content calculated on the basis of 2 H₂O from the ideal composition of roselite group minerals

0.21 *apfu*) and Ni contents (up to 0.79 wt. % NiO, 0.05 *apfu*) were observed; this composition also corresponds very well to dobšínáite (Fig. 3). The representative analyses for all dobšínáite samples are given in Tab. 2.

5. Crystallography

Attempts to obtain single-crystal X-ray data (Rigaku SuperNova single-crystal diffractometer with Atlas S2 CCD detector) were unsuccessful due to the nature of the studied material; it is formed by multiple intergrowths of sub-microscopic domains.

X-ray powder diffraction data of dobšínáite (Tab. 3) were recorded at room temperature using a Bruker D8

Advance diffractometer equipped with a solid-state Lynx-Eye detector and secondary monochromator producing CuK α radiation housed at the Department of Mineralogy and Petrology, National Museum, Prague. The instrument was operated at 40 kV and 40 mA. To minimize the background, the powdered samples were placed (without any liquid) on the surface of a flat silicon wafer. The powder pattern was collected in the Bragg–Brentano geometry in the range 3–70° 2 θ , step 0.01°, and a counting time of 20 s per step (total duration of the experiment was ca. 30 hours). The positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function of the ZDS program package (Ondruš 1993). The unit-cell parameters were refined by the least-squares program of Burnham (1962) for monoclinic space group $P2_1/c$ (#14) as follows: $a = 5.990(2)$, $b = 13.013(4)$, $c =$

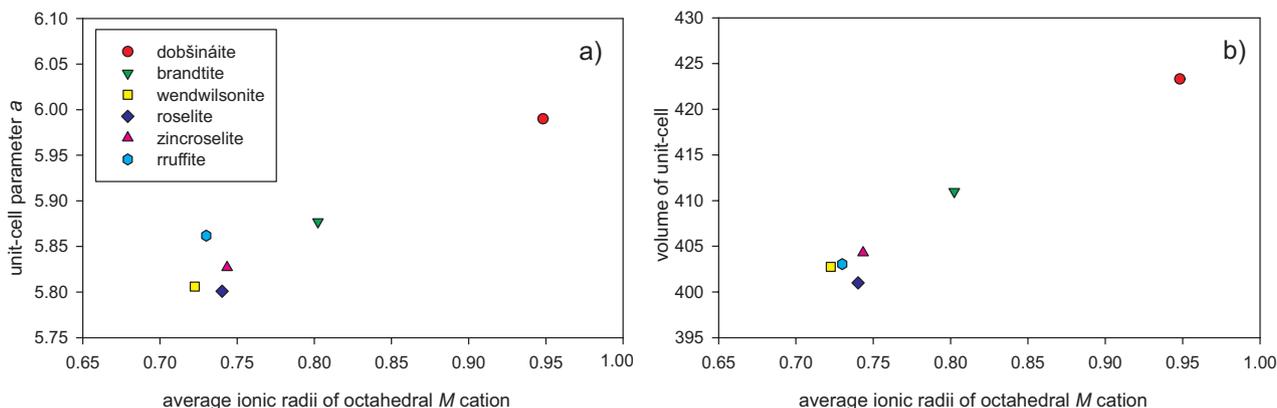


Fig. 4 Correlations of average ionic radii of octahedral *M* cation [Å] (Tab. 3) and unit-cell parameters (a [Å] and V [Å³]) in the crystal structure of the roselite group members.

Tab. 3 Powder diffraction data (d in Å) of dobšínáite; the strongest diffractions are given in bold

$I_{obs.}$	$d_{obs.}$	$d_{calc.}$	$I_{calc.}^*$	h	k	l
24	6.484	6.506	18	0	2	0
37	5.197	5.207	40	1	1	0
33	5.002	5.012	21	0	1	1
22	4.458	4.461	14	1	1	-1
25	3.831	3.836	22	1	2	-1
38	3.443	3.448	33	1	3	0
66	3.385	3.389	53	0	3	1
33	3.309	3.309	18	1	1	1
77	3.249	3.253	40	0	4	0
42	3.201	3.203	35	1	3	-1
100	3.026	3.028	100	1	2	1
28	2.854	2.855	36	2	1	-1
60	2.822	2.823	41	1	0	-2
8	2.713	2.716	8	0	0	2
30	2.665	2.669	34	2	2	-1
3	2.3781	2.3764	6	2	3	0
5	2.3456	2.3470	5	0	5	1
19	2.2819	2.2823	19	1	5	-1
33	2.1327	2.1320	31	1	4	-2
6	2.0804	2.0794	6	1	2	2
6	2.0263	2.0262	4	1	6	0
4	1.9584	1.9582	5	1	3	2
7	1.9461	1.9448	5	2	5	-1
8	1.9186	1.9178	9	2	4	-2
11	1.9097	1.9077	8	3	2	-1
6	1.8798	1.8790	6	0	5	2
4	1.8721	1.8740	9	3	1	0
18	1.8317	1.8318	25	1	6	1
27	1.7443	1.7442	23	0	2	3
6	1.7428	1.7425	14	2	6	-1
10	1.7364	1.7355	14	3	3	0
6	1.6963	{ 1.6962	3	2	1	2
		{ 1.6947	3	0	6	2

$I_{calc.}^*$ – intensities were calculated using the software PowderCell 2.3 (Kraus and Nolze 1996) on the basis of the structural model (brandtite – Herwig and Hawthorne 2006 – with Ca replacing for Mg).

5.726(2) Å, $\beta = 108.47(3)^\circ$, $V = 423.3(3)$ Å³ and $Z = 2$. The $a:b:c$ ratio calculated from unit-cell parameters is 0.4603:1:0.4400.

The well-known crystal structure of As-dominant members of the roselite group ($\text{Ca}_2M^{2+}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$) is characterized by isolated $\text{MO}_4(\text{H}_2\text{O})_2$ octahedra that are linked by corner-sharing with AsO_4 tetrahedra to form the kröhnkite-type chains parallel to the c axis. These chains are linked together by the large Ca cations and hydrogen bonding (Hawthorne and Ferguson 1977; Keller et al. 2004; Herwig and Hawthorne 2006; Kolitsch and Fleck 2006; Yang et al. 2011). The values of unit-cell parameters (especially a and V) positively correlate with the octahedral M cation's average ionic radii (Fig. 4).

6. Raman spectroscopy

The Raman spectrum of dobšínáite (Fig. 5) was obtained employing a Horiba Labram HR Evolution spectrometer (Masaryk University, Brno). This dispersive, edge-filter-based system is equipped with an Olympus BX 41 optical microscope, a diffraction grating with 600 grooves per millimeter, and a Peltier-cooled, Si-based charge-coupled device (CCD) detector. The 633 nm He-Ne laser with the beam power of 5 mW at the sample surface was selected for spectra acquisition to minimize analytical artifacts. Raman signal was collected in the range of 50–4000 cm^{-1} with a 100× objective (NA 0.9) and the system being operated in the confocal mode; beam diameter was ~ 1 μm and the depth resolution ~ 2 μm . No visual damage to the analyzed surface was observed at these conditions after the excitation. For wavenumber calibration, the Rayleigh line and low-pressure Ne-discharge lamp emissions were used. The wavenumber accuracy was ~ 0.5 cm^{-1} , and the spectral resolution was ~ 2 cm^{-1} . Band fitting was done after appropriate background correction, assuming combined Lorentzian-Gaussian band shapes using the Voigt function (PeakFit; Jandel Scientific Software).

The main bands observed are (in wavenumbers): 3358, 3170, 2960, 863, 828, 724, 474, 447, 416, 366, 333, 295, 196, 171, 125, 106, 81 and 53 cm^{-1} . Weak broad Raman bands with maxima at 3358, 3170 and 2960 cm^{-1} are assigned to the ν OH stretching vibrations of structurally distinct differently hydrogen-bonded water molecules. The most prominent very strong Raman band at 828 cm^{-1} with a shoulder at 863 cm^{-1} is attributed to overlapping ν_1 (AsO_4)³⁻ symmetric stretching and ν_3 (AsO_4)³⁻ antisymmetric stretching vibrations. A weak shoulder band at 724 cm^{-1} can be connected to the libration of H_2O molecules. Raman bands 474, 447 and 416 cm^{-1} are attributed with the ν_4 (AsO_4)³⁻ bending vibrations. Raman bands at 366, 333 and 295 cm^{-1} are related to the ν_2 (AsO_4)³⁻ bending vibrations and those below 200 cm^{-1} to the lattice modes (Vansant et al. 1973; Yang et al. 2011; Sejkora et al. 2020). In the area of ν_1 and ν_3 (AsO_4)³⁻ vibrations (1000–700 cm^{-1}), the Raman spectrum of dobšínáite is close to other As-dominant members of the roselite group and distinctly differs from those of As-dominant members of the fairfieldite group (Fig. 6).

7. Comparison with related minerals

Dobšínáite is a Ca- and As-dominant member of the roselite group, Strunz class 8.CG.10, Dana class 40.2.3. A comparison of selected data for As-dominant members of this group is given in Tab. 4. An unambiguous determination of dobšínáite as a member of the roselite group

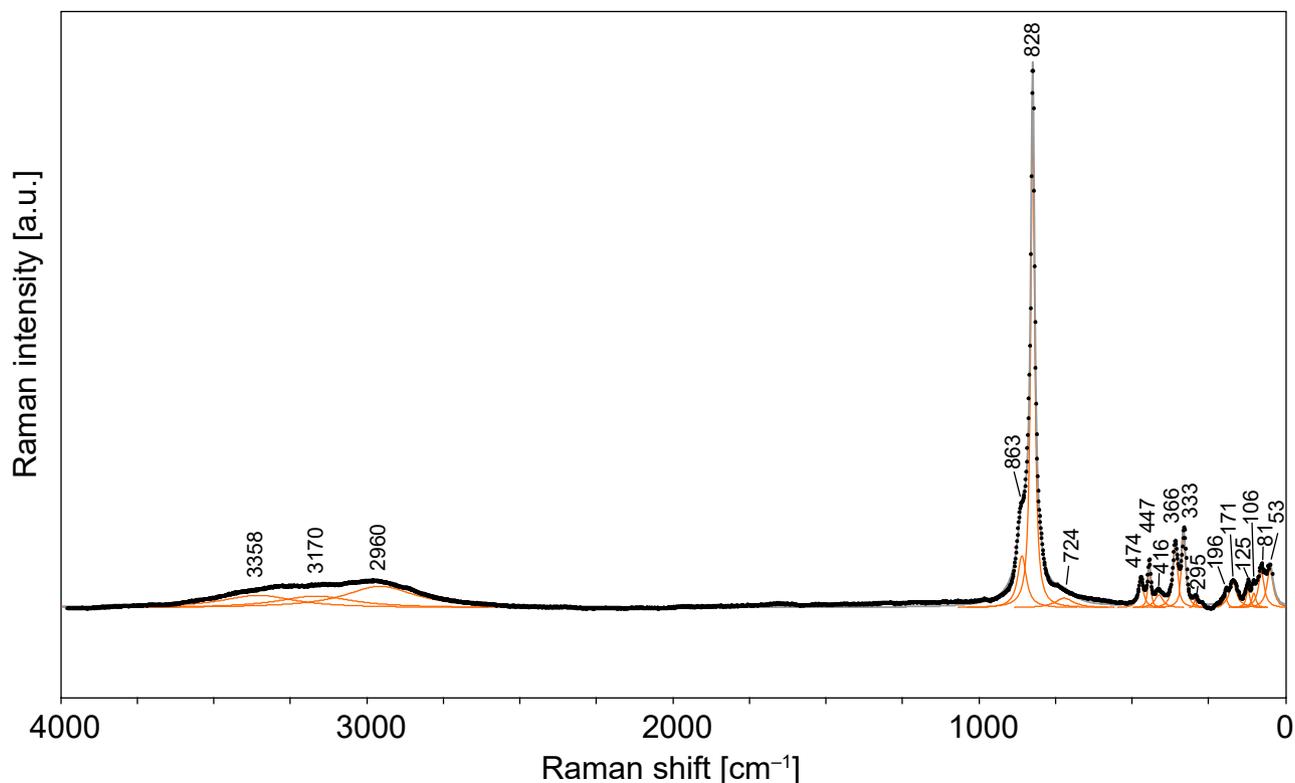


Fig. 5 Raman spectrum of dobšínáite (full-range).

is based on its chemical composition (stoichiometry), X-ray powder diffraction data and Raman spectroscopy.

A mineral phase corresponding to dobšínáite was described in 1953 by Evgeniy I. Nefedov from Tuvinskaya deposit, Tuva Autonomous Republic, Russia. Nefedov provided an empirical formula $\text{Ca}_2(\text{Ca},\text{Mg})(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, some structural, optical and physical data; however, a chemical analysis is missing. Nefedov (1953) named

this mineral belovite and assigned it to the roselite group mainly based on similarities of general formula and inaccurate structural information. Borodin and Kazakova (1954) described a Sr, REE, Na-bearing member of the apatite supergroup and named it belovite, too. To reduce the confusion, belovite of Nefedov was then used to be called arsenate-belovite. Subsequent reinvestigation of belovite original material of Nefedov (Yakhontova and

Tab. 4 Comparison of the properties for As-dominant members of the roselite group

	dobšínáite	brandtite	wendwilsonite	roselite	zincroselite	ruffite
M_{ideal}	Ca	Mn	Mg	Co	Zn	Cu
M_{meas}	$\text{Ca}_{0.84}\text{Mg}_{0.10}\text{Co}_{0.03}\text{Ni}_{0.02}$	$\text{Mn}_{0.88}\text{Mg}_{0.10}\text{Fe}_{0.01}$	$\text{Mg}_{0.90}\text{Co}_{0.10}$	$\text{Co}_{0.52}\text{Mg}_{0.49}$	$\text{Zn}_{0.90}\text{Mg}_{0.05}\text{Mn}_{0.05}$	$\text{Cu}_{1.01}$
SG	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	5.990(2)	5.877(1)	5.806(1)	5.801(1)	5.827(1)	5.8618(2)
b (Å)	13.013(4)	12.957(2)	12.923(3)	12.898(3)	12.899(3)	12.7854(5)
c (Å)	5.726(2)	5.675(1)	5.628(1)	5.617(1)	5.646(1)	5.7025(2)
β (°)	108.47(3)	108.00(3)	107.49(3)	107.42(2)	107.69(3)	109.425(2)
V (Å ³)	423.3(3)	411.0	402.75(14)	401.0	404.3	403.05(3)
Z	2	2	2	2	2	2
AIR (Å)	0.948	0.802	0.723	0.740	0.743	0.730
optical	biaxial –	biaxial +	biaxial –	biaxial +	biaxial +	biaxial –
α	α' 1.658	1.707–1.709	1.694(3)	1.694–1.725	1.703(3)	1.725(1)
β		1.711	1.703(3)	1.704–1.703	1.710(4)	1.734(1)
γ	γ' 1.670	1.722–1.727	1.713(3)	1.719–1.735	1.720(3)	1.740(1)
	[1]	[2]	[3]	[4]	[5]	[6]

SG – space group; AIR – average ionic radii of octahedral M cation (Shannon 1976); optical data are taken from Anthony et al. (2000) and Yang et al. (2011); [1] this proposal; [2] Herwig and Hawthorne (2006); [3] Kolitsch and Fleck (2006); [4] Hawthorne and Ferguson (1977); [5] Keller et al. (2004); [6] Yang et al. (2011)

Sidorenko 1956; Pierrot 1964) revealed that its chemical composition is richer in Mg and corresponds to $\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, and it is a triclinic member of a beta-roselite group. Hence, this material corresponds to mineral talmessite, described in 1960 by Bariand and Herpin (1960) from the Talmessi deposit, Iran.

Synthetic $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been prepared experimentally by Nelson and Haring (1937). The authors determined its relatively narrow stability field in the $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$ system and performed an X-ray study; however, it is difficult to acquire more structural details from the photograph of the diffraction pattern they provided in the publication. A synthetic analog of dobšináite was synthesized by Guérin (Pierrot 1964). The X-ray powder diffraction data of this material, published by Pierrot (1964), are similar to those of dobšináite from Dobšiná, but also contain reflections at 11.7 Å and 6.1 Å, which were probably caused by the presence of impurities in Guérin's phase, e.g., a synthetic analog of phaunouxite. The solubility of $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ in water was studied by Chukhlantsev (1956) and Mahapatra et al. (1984). Unfortunately, both studies lack any structural information. There are many experimental works focused on the system $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$ at various T-X conditions (Pearce and Avens 1937; Nishimura and Robins 1998; Bothe and Brown 1999; Zhu et al. 2006; Raičević et al. 2007; Hernandez-Barcenas et al. 2017, etc.), however $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ is usually missing among the precipitated solid phases which indicates specific conditions are necessary for dobšináite formation.

Acknowledgments. The reviewers, Juraj Majzlan and Nicolas Meisser, same as handling editor Jiří Zachariáš, are thanked for a lot of their constructive comments. This work was supported financially by the Ministry of Culture of the Czech Republic (long-term project DKRVO 2019-2023/1.II.c National Museum, 00023272) for JS, MŠ, ZD and its institutional support of long-term conceptual development of research institutions (ref. MK000094862) for JT and EV and the MUNI/A/1594/2020 research project of Masaryk University for RŠ and SH.

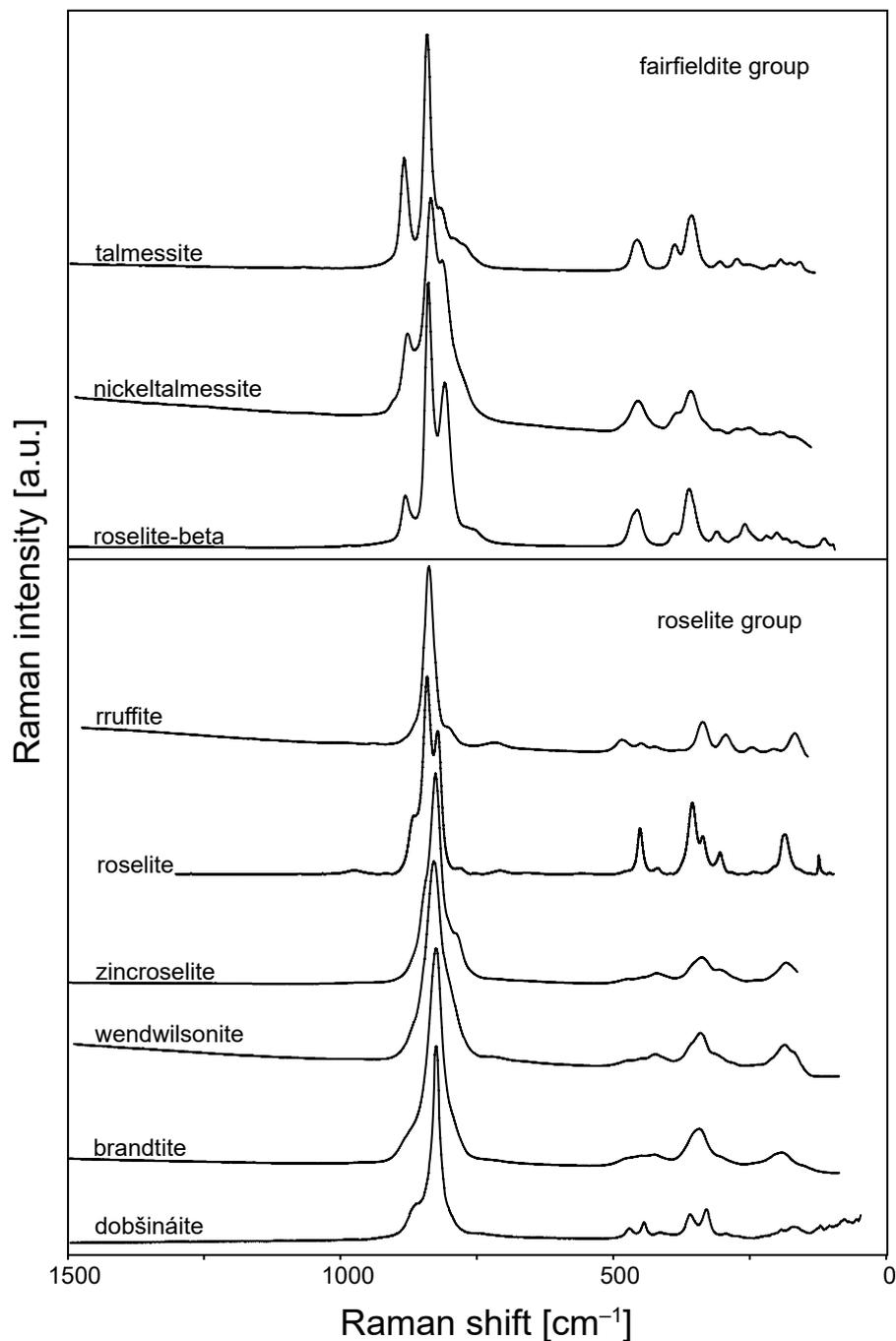


Fig. 6 Raman spectra of dobšináite and those of As-dominant members of roselite (monoclinic) and fairfieldite (triclinic) group from the RRUFF project for comparison. The spectra of the figure are shown with a vertical offset for more clarity.

References

- ANTHONY JW, BIDEAUX RA, BLADH KW, NICHOLS MC (2000) Handbook of Mineralogy, Vol. IV, Arsenates, Phosphates, Vanadates. Mineral Data Publishing, Tucson, Arizona 680 pp.
- BARIAND P, HERPIN P (1960) Un arséniate de calcium et de magnésium, isomorphe de la β rosélite. Bull Soc franç Minéral Cristallogr 83: 118–121
- BORODIN LS, KAZAKOVA ME (1954) Belovite-(Ce): a new mineral from an alkaline pegmatite. Dokl Akad Nauk SSSR 96: 613–616
- BOTHE JR JV, BROWN PW (1999) The stabilities of calcium arsenates at $23 \pm 1^\circ\text{C}$. J Hazard Mater 69(2): 197–207
- BURNHAM CW (1962) Lattice constant refinement. Carnegie Institute Washington Yearbook 61: 132–135
- CHUKHLANTSEV VG (1956) The solubility products of a number of arsenates. J Anal Chem USSR, 11: 565
- GRECULA P, ABONYI A, ABONYIOVÁ M, ANTAŠ J, BARTALSKÝ B, BARTALSKÝ J, DIANIŠKA I, ĎUĐA R, GARGULÁK M, GAZDAČKO Ľ, HUDÁČEK J, KOBULSKÝ J, LÖRINCZ L, MACKO J, NÁVESŇÁK D, NÉMETH Z, NOVOTNÝ L, RADVANEC M, ROJKOVIČ I, ROZLOŽNÍK L, VARČEK C, ZLOCHA Z (1995) Mineral deposits of the Slovak Ore Mountains, Vol 1. Geocomplex, Bratislava, 1–834
- HALAHYJOVÁ-ANDRUSOVÁ G (1959) Mineralogical a paragenetic study of the ore deposits around Dobšiná. Manuscript, ŠGÚDŠ-Geofond, Bratislava, 1–140 (in Slovak)
- HALAHYJOVÁ-ANDRUSOVÁ G (1964a) About the genesis of the ore veins near Dobšiná. Geol Práce Správy 33: 53–69 (in Slovak)
- HALAHYJOVÁ-ANDRUSOVÁ G (1964b) About the structures of Ni–Co–Fe sulfarsenides and arsenides from Dobšiná. Geol Sbor Slov Akad Vied 15: 87–91 (in Slovak)
- HAWTHORNE FC, FERGUSON RB (1977) The crystal structure of rosélite. Canad Mineral 15: 36–42
- HERNANDEZ-BARCENAS G, CASTILLO F, AVALOS-BORJA M, MARTINEZ-VILLEGAS NV (2017) Synthesis of calcium arsenates (guerinite, haidingerite and pharmacolite) morphologically similar to those found in contaminated soils. Rev Inter Contam Ambient 33(1): 153–163
- HERWIG S, HAWTHORNE FC (2006) The topology of hydrogen bonding in brandtite, collinsite and fairfieldite. Canad Mineral 44: 1181–1196
- KELLER P, LISSNER F, SCHLEID T (2004) The crystal structures of zincrosélite and gaitite: Two natural polymorphs of $\text{Ca}_2\text{Zn}[\text{AsO}_4]_2 \cdot 2\text{H}_2\text{O}$ from Tsumeb, Namibia. Eur J Mineral 16: 353–359
- KIEFER S, MAJZLAN J, CHOVAN M, ŠTEVKO M (2017) Mineral compositions and phase relations of the complex sulfarsenides and arsenides from Dobšiná (Western Carpathians, Slovakia). Ore Geol Rev 80: 894–908
- KIEFER S, ŠTEVKO M, VOJTKO R, OZDÍN D, GERDES A, CREASER RA, SZCZERBA M, MAJZLAN J (2020) Geochronological constraints on the carbonate-sulfarsenide veins in Dobšiná, Slovakia: U/Pb ages of hydrothermal carbonates, Re/Os age of gersdorffite, and K/Ar ages of fuchsite. J Geosci 65(4): 229–247
- KOLITSCH U, FLECK M (2006) Third update on compounds with krohnkite-type chains: the crystal structure of wendwilsonite $[\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}]$ and the new triclinic structure types of synthetic $\text{AgSc}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{Cu}(\text{Cr}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (M = Rb, Cs). Eur J Mineral 18: 471–482
- KRAUS W, NOLZE G (1996) POWDER CELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. J Appl Crystallogr 29: 301–303
- MAHAPATRA PP, MAHAPATRA LM, NANDA CN (1984) Dissolution of $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ in the system $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$ at 35, 40, 45 and 50°C and the related thermodynamic data. Thermochim Acta 76(3): 301–309
- MANDARINO JA (1981) The Gladstone–Dale relationship: Part IV. The compatibility concept and its application. Canad Mineral 19: 441–450
- NEFEDOV EI (1953) Report on new minerals discovered by him. In: Mokievsky VA: The scientific session of the Federov institute together with the All-Union Mineralogical Society. Zap Vsesojuz Mineral Obšč 82 (4): 311–317 (in Russian)
- NELSON OA, HARING MM (1937) Calcium Arsenates. An Investigation into the Three-Component System Calcium Oxide-Arsenic Oxide-Water. J Amer Chem Soc 59(11): 2216–2223
- NISHIMURA T, ROBINS RG (1998) A re-evaluation of the solubility and stability regions of calcium arsenites and calcium arsenates in aqueous solution at 25°C . Mineral Process Extr Metall Rev 18(3–4): 283–308
- ONDRUŠ P (1993) A computer program for analysis of X-ray powder diffraction patterns. Materials Science Forum, EPDIC-2, Enchede, 133–136, 297–300
- PEARCE GW, AVENS AW (1937) Further Phase Rule Studies of the Calcium Arsenates. J Amer Chem Soc 59(7): 1258–1261
- PIERROT R (1964) Contribution à la minéralogie des arsénites calciques et calcomagnésiens naturels. Bull Minéral 87(2): 169–211
- PLUMHOFF AM, PLÁŠIL J, DACHS E, BENISEK A, SEJKORA J, ŠTEVKO M, RUMSEY MS, MAJZLAN J (2020) Thermodynamic properties, crystal structure and phase relations of pushcharovskite $[\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O}) \cdot 0.5\text{H}_2\text{O}]$, geminite $[\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O})]$ and lironite $[\text{Cu}_2\text{Al}(\text{AsO}_4)(\text{OH})_4 \cdot 4\text{H}_2\text{O}]$. Eur J Mineral 32(3): 285–304
- POUCHOU JL, PICHOU F (1985) “PAP” ($\phi\rho Z$) procedure for improved quantitative microanalysis. In: ARMSTRONG JT (ed) Microbeam Analysis. San Francisco Press, San Francisco, 104–106

- RAIČEVIĆ S, STANIĆ V, KALUDJEROVIĆ-RADOIČIĆ T (2007) Theoretical assessment of calcium arsenates stability: Application in the treatment of arsenic contaminated waste. *Mater Sci Forum* 555: 131–136
- ROZLOŽNÍK L (1959) Tectonic conditions of the ore deposits around Dobšiná. *Acta Geol Geogr Univ Comen, Geol* 2: 167–175 (in Slovak)
- ROZLOŽNÍK L (1965) An analysis of the structural and metallogenetic elements between Dobšiná and Mlynky. *Sbor Geol vied, Záp Karp* 4: 29–93 (in Slovak).
- SEJKORA J, ŘÍDKOŠIL T, ŠREIN V (1999) Zálesiite, a new mineral of the mixite group, from Zálesí, Rychlebské hory Mts., Czech Republic. *Neu Jb Mineral, Abh* 175(2): 105–124
- SEJKORA J, HAWTHORNE FC, COOPER MA, GRICE JD, VAJDAK J, JAMBOR JL (2009) Burgessite, $\text{Co}_2(\text{H}_2\text{O})_4[\text{AsO}_3(\text{OH})]_2 \cdot \text{H}_2\text{O}$, a new arsenate mineral species from the Keeley mine, South Lorrain township, Ontario, Canada. *Canad Mineral* 47(1): 159–164
- SEJKORA J, PLÁŠIL J, KAMPF AR (2018) Honzaite, $(\text{Ni}, \text{Co})_2(\text{AsO}_3\text{OH})_2(\text{H}_2\text{O})_5$, a new Ni-dominant analogue of burgessite, from Jáchymov, Czech Republic. *Eur J Mineral* 30(5): 989–997
- SEJKORA J, PLÁŠIL J, ČEJKA J, DOLNÍČEK Z, PAVLÍČEK R (2020) Molecular structure of the arsenate mineral chongite from Jáchymov – a vibrational spectroscopy study. *J Geosci* 65: 111–120
- SHANNON RD (1976) Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr A* 32: 751–767
- STECIUK G, SEJKORA J, ČEJKA J, PLÁŠIL J, HLOUŠEK J (2021) Krupičkaite, $\text{Cu}_6[\text{AsO}_3(\text{OH})]_6 \cdot 8\text{H}_2\text{O}$, a new copper arsenate mineral from Jáchymov (Czech Republic). *J Geosci* 66: 37–50
- ŠTEVKO M, SEJKORA J (2020) Sb-enriched association of Ni arsenides and sulfarsenides from the Zemberg-Terézia vein system near Dobšiná (Western Carpathians, Slovak Republic). *Bull Mineral Petrolog* 28: 105–115
- VANSANT FK, VAN DER VEKEN BJ, DESSEYN HD (1973) Vibrational analysis of arsenic and its anions I. Description of the Raman spectra. *J Molecul Struct* 15: 425–437
- YAKHONTOVA LK, SIDORENKO GA (1956) The new mineral arsenate-belovite. *Zap Vsesojuz Mineral Obšč SSSR* 85: 297–302 (in Russian)
- YANG H, JENKINS RA, DOWNS RT, EVANS SH, TAIT KT (2011) Rruffite, $\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new member of the roselite group, from Tierra Amarilla, Chile. *Canad Mineral* 49: 877–884
- ZHU YN, ZHANG XH, XIE QL, WANG DQ, CHENG GW (2006) Solubility and stability of calcium arsenates at 25 °C. *Water Air Soil Pollut* 169(1): 221–238