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Olivenite and cornwallite from the Podlipa copper deposit near Ľubietová, Slovakia

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Abstract

An interesting occurrence of olivenite and cornwallite was recently discovered in cavities of quartz at the Podlipa copper deposit near Ľubietová, Slovakia. Olivenite occurs as olive to pale green sprays or radial aggregates consisting of individual acicular crystals up to 5 mm long. Its refined unit-cell parameters (for the monoclinic space group $P2_1/n$) are: *a* 8.6192(13) Å, *b* 8.2300(11) Å, *c* 5.9349(8) Å, *α* 90.055(12)° and *V* 420.99(7) Å^3. Studied olivenite shows intense chemical zoning caused by strong variation of As and P contents. Most of the zones are corresponding to olivenite (with P content ranging between 0.02 to 0.39 *apfu*), but darker zones or domains of As-rich libethenite (with As content ranging between 0.18 to 0.24 *apfu*) were occasionally observed. Cornwallite forms dark green massive fillings between olivenite crystals or microcrystalline botryoidal crusts. The refined unit-cell parameters (for the monoclinic space group $P2_1/c$) of botryoidal cornwallite from the Podlipa deposit are: *a* 4.6112(2) Å, *b* 5.7698(3) Å, *c* 17.4167(11) Å, *β* 92.009(5)° and *V* 463.10(3) Å^3. The two compositional types of cornwallite were distinguished. The first type is represented by relatively homogenous aggregates with only minor contents of P (from 0.04 to 0.22 *apfu*). The second type occurs as polycrystalline fillings with strong chemical zoning and has much more significant variation of As and P contents, representing solid-solution series between P-rich cornwallite (with 1.41 *apfu* of As and 0.59 *apfu* of P) and As-rich pseudomalachite (with 1.37 *apfu* of P and 0.63 *apfu* of As).

Key words: *olivenite, cornwallite-pseudomalachite series, supergene minerals, X-ray powder data, chemical composition, Podlipa deposit, Ľubietová, Slovakia*

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Introduction

Unusual specimen with olive green acicular to thin-tabular crystals of As-rich libethenite to P-rich olivenite was first described from the Podlipa deposit by Števko et al. (2017). Detailed sampling of this piece was not possible at that time, as it was in private collection and its owner allowed us sample only the external parts of the aggregates to prevent the damage of this unique specimen. This piece was recently purchased by the first author (MŠ) and careful systematic sampling of all morphological types of supergene minerals was conducted.

Both olivenite and minerals of the cornwallite-pseudomalachite series were discovered in this sample and the results of their detailed mineralogical study are presented in this short paper.

Location and geological setting

The Podlipa copper deposit is located 1.5 km east of Ľubietová village on the steep southern slopes of Vysoká hill (995.6 m a.s.l.), around 17 km east of Banská Bystrica town, Banská Bystrica Region, Slovakia. The main workings and extensive dumps are situated in Zelená valley, with Rainer mining field located about 400 meters northwest, in a side valley. Studied sample with olivenite and cornwallite was collected at the dump of Horný Johan adit by Jozef Gajdoš in 2006. GPS coordinates of the place where the studied sample was collected are: 48.747960° N and 19.385314° E, 662 m a.s.l.

The ore mineralization at the Podlipa copper deposit is developed as stockwork of randomly distributed hydrothermal veins with variable trends and dip directions hosted in Permian metasandstones, conglomerates and shales of the Predajná Formation, which belongs to the Ľubietová Group. The Ľubietová Group is representing basal part of the North Veporic crystalline basement cover (Bergfest 1951; Vozárová, Vozár 1988; Polák et al. 2003; Slavkay et al. 2004). The primary ore mineralization at the Podlipa deposit is rather simple. Chalcopyrite is dominant ore mineral accompanied by minor amount of pyrite and minerals of the tetrahedrite-tennantite series. Other ore minerals such as arsenopyrite, bismuthinite, cassiterite, cinnabar, cobaltite, galena, gold, kupčíkite, matildite(?) or siegenite are rare. The dominant gangue minerals are quartz, siderite, ankerite to Fe-rich dolomite and minor are calcite and schorl (Hauerová et al. 1989; Slavkay et al. 2004, Michňová et al. 2008; Luptáková et al. 2012; Luptáková et al. 2016). The Podlipa deposit is famous for a well developed supergene zone dominated by copper phosphates and carbonates. It is the type locality of libethenite (Breithaupt 1823) and mrázekite (Řídkošil et al. 1992; Effenberger et al. 1994). The most common supergene minerals are pseudomalachite, malachite, libethenite, cuprite, native copper, hematite, goethite and Mn oxides. Other

Fig. 1 *Olive green radial aggregates and sprays of olivenite crystals; field of view is 8 mm; photo by L. Hrdlovič.*

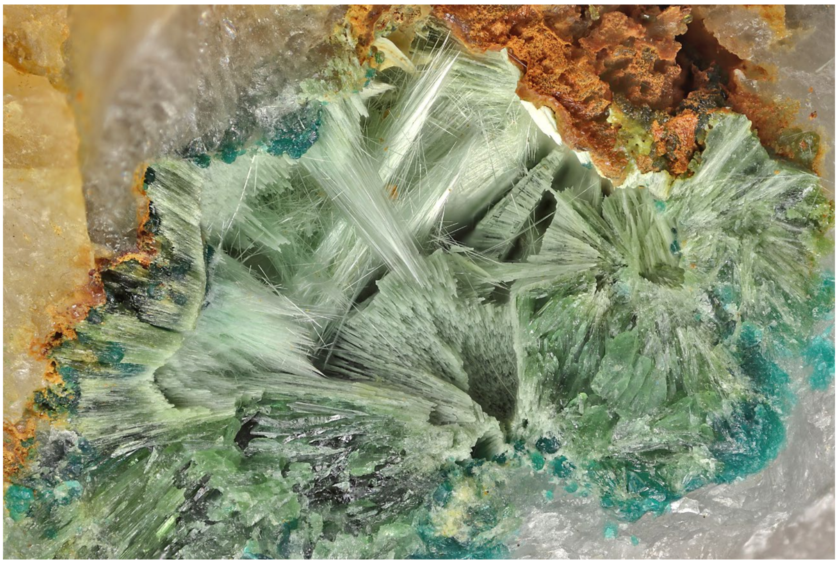


Fig. 2 *Pale to olive green aggregates of olivenite crystals associated with dark green cornwallite; field of view is 5.6 mm; photo by L. Hrdlovič.*

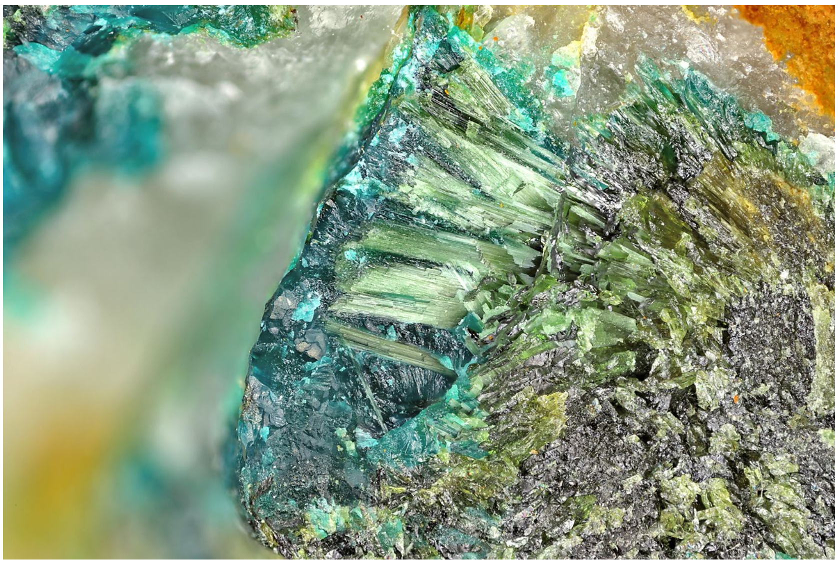


Fig. 3 *Aggregates of olivenite enclosed in dark green massive cornwallite; field of view is 5.6 mm; photo by L. Hrdlovič.*

supergene minerals such as acanthite, azurite, brochantite, covellite, chalcocite, cyanotrichite, gypsum, langite, ludjibaite, mrázekite, pharmacosiderite or reichenbachite are mostly rare (Čech, Láznička 1965; Figuschová 1977; Povondra, Řídkošil 1980; Řídkošil, Povondra 1982; Hyršl 1991; Řídkošil et al. 1992; Luptáková et al. 2012; Milovská et al. 2014; Števko et al. 2017; Majzlan et al. 2018). Števko et al. (2016) described from the Rainer mining field also occurrence of bismutite, corkite, kintoreite and petitjeanite.

Analytical methods

X-ray powder diffraction data of olivenite and cornwallite were recorded at room temperature using a Bruker D8 Advance diffractometer equipped with solid-state LynxEye detector and secondary monochromator producing CuK_{α} radiation (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic). The instrument was operating at 40 kV and 40 mA. To minimize the background, the powder samples were placed on the surface of a flat silicon wafer. The powder patterns were collected in the Bragg-Brentano geometry in the range 3 - 70° 2θ, step 0.01° and 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).

Chemical zoning, paragenetic and textural relationships of supergene minerals were studied in BSE mode using a JEOL JXA-8530FE electron microprobe (Earth Science Institute, Slovak Academy of Sciences, Banská Bystrica, Slovak Republic).

The quantitative chemical analyses of olivenite and cornwallite were performed using a Cameca SX100 electron microprobe (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic) operating in the wave-dispersive (WDS) mode (15 kV, 7 nA and 5 μm wide beam). The following standards and X-ray lines were used to minimize line overlaps: albite (Na*K*α), apatite (Ca*K*α, P*K*α), baryte (Ba*L*α), Bi (Bi*M*α), celestine (Sr*L*β, S*K*α), clinoclase (As*L*α), Co (Co*K*α), Cr_2O_3 (Cr*K*α), $CuFeS_2$ (Cu*K*α, S*K*α), diop-

Table 1 *X-ray powder diffraction data of olivenite from Lubietová - Podlipa*

$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*
5.951	43	5.952	1	1	0	2.4083	29	2.4080	0	-2	2	1.7714	2	1.7716	2	4	1
4.885	80	4.888	1	0	1	2.4043	21	2.4058	0	2	2	1.7434	20	1.7436	4	0	2
4.820	15	4.816	0	-1	1	2.3932	8	2.3931	1	-3	1	1.6922	15	1.6916	0	-4	2
4.809	47	4.812	0	1	1			2.3915	1	3	1	1.6876	12	1.6901	0	4	2
4.305	9	4.310	2	0	0	2.3412	37	2.3424	2	1	2	1.6549	6	1.6554	5	0	1
4.202	52	4.204	1	-1	1	2.3144	9	2.3142	2	3	0	1.6492	14	1.6499	3	-3	2
		4.201	1	1	1	2.1549	5	2.1548	4	0	0			1.6489	3	3	2
4.115	13	4.115	0	2	0	2.0019	6	2.0018	3	1	2	1.6297	5	1.6292	4	3	1
3.815	60	3.818	2	1	0	1.9674	7	1.9669	4	-1	1	1.6234	25	1.6230	5	-1	1
3.711	12	3.713	1	2	0	1.9612	3	1.9624	1	-3	2			1.6228	5	1	1
2.974	100	2.976	2	2	0			1.9607	1	3	2	1.6097	4	1.6104	3	-4	1
2.966	59	2.967	0	0	2	1.9283	5	1.9282	1	0	3			1.6097	3	4	1
2.712	28	2.713	3	1	0	1.9225	4	1.9239	0	-1	3	1.6059	23	1.6058	4	-2	2
2.659	36	2.656	1	-1	2			1.9231	0	1	3	1.5985	9	1.5981	3	1	3
2.654	64	2.655	1	1	2	1.8974	3	1.8969	1	-4	1	1.5790	5	1.5782	1	-3	3
2.614	82	2.614	1	3	0	1.8955	11	1.8958	1	4	1	1.5755	23	1.5746	2	-4	2
2.585	29	2.586	3	0	1	1.8822	12	1.8821	3	-3	1			1.5734	2	4	2
2.4905	19	2.4911	0	-3	1			1.8813	3	3	1	1.5596	17	1.5603	1	-5	1
		2.4893	0	3	1	1.8780	9	1.8777	1	-1	3			1.5596	1	5	1
2.4666	58	2.4674	3	-1	1	1.8446	4	1.8455	3	-2	2	1.4880	27	1.4881	4	4	0
		2.4668	3	1	1			1.8445	3	2	2	1.4840	34	1.4837	0	0	4
2.4443	25	2.4441	2	0	2	1.8259	4	1.8256	2	-3	2						

Table 2 *Unit-cell parameters of olivenite*

occurrence	reference	SG	*a* [Å]	*b* [Å]	*c* [Å]	*α* [°]	*V* [Å³]
Podlipa	this paper	$P2_1/n$	8.6192(13)	8.2300(11)	5.9349(8)	90.055(12)	420.99(7)
Majuba Hill	Li et al. (2008)	$P2_1/n$	8.5844(3)	8.2084(3)	5.9258(2)	90.130(2)	417.56(3)
Cornwall	Burns, Hawthorne (1995)	$P2_1/n$	8.5894(2)	8.2073(2)	5.9285(1)	90.088(3)	417.90
Krupka	Sejkora et al. (2015)	*Pnnm*	8.6300(8)	8.2405(8)	5.8384(7)		422.31(5)
Farbište	Števko et al. (2011)	*Pnnm*	8.6080(7)	8.2151(7)	5.9193(5)		418.59(6)
Farbište	Števko et al. (2011)	*Pnnm*	8.6111(7)	8.2189(7)	5.9209(5)		419.05(3)
Cornwall	Burns, Hawthorne (1995)	*Pnnm*	8.5894(2)	8.2076(2)	5.9286(1)		417.9
Gelnica	Sejkora et al. (2001)	*Pnnm*	8.633(2)	8.245(2)	5.940(1)		422.8(1)

SG: ortorhombic (*Pnnm*) or monoclinic ($P2_1/n$) space group

Table 3 *Representative quantitative chemical analyses of olivenite and As-rich libethenite from the Podlipa copper deposit (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Oli	Oli	Oli	Oli	Oli	Oli	Oli	Oli	Oli	Oli	Oli	Oli	Lib	Lib	Lib
CuO	56.30	56.10	57.43	57.17	58.19	57.24	57.34	61.39	60.79	56.92	61.59	60.91	63.00	62.72	63.33
Fe_2O_3	0.00	0.14	0.00	0.00	0.23	0.21	0.19	0.00	0.00	0.41	0.00	0.10	0.00	0.00	0.00
Al_2O_3	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.41
Sb_2O_3	0.15	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00
SiO_2	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As_2O_5	40.55	39.63	39.71	38.72	32.73	34.78	34.70	28.01	29.63	39.32	27.13	29.10	10.58	8.78	8.13
P_2O_5	0.68	0.51	0.66	0.92	6.71	4.03	4.85	10.34	9.17	1.32	10.71	9.68	20.40	22.07	22.58
SO_3	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
total	97.76	96.50	98.07	96.88	97.86	96.26	97.08	99.74	99.59	98.12	99.43	99.79	94.07	93.57	94.45
Cu^{2+}	1.947	1.999	2.009	2.049	1.928	2.002	1.947	1.982	1.975	1.978	2.001	1.965	2.087	2.035	2.047
Fe^{3+}	0.000	0.005	0.000	0.000	0.008	0.007	0.006	0.000	0.000	0.014	0.000	0.003	0.000	0.000	0.000
Al^{3+}	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.021
Σ	1.952	2.004	2.009	2.049	1.936	2.009	1.953	1.982	1.975	1.992	2.001	1.969	2.092	2.035	2.068
Sb^{3+}	0.003	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000
Si^{4+}	0.000	0.000	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
As^{5+}	0.971	0.977	0.962	0.961	0.751	0.842	0.815	0.626	0.666	0.946	0.610	0.650	0.243	0.197	0.182
P^{5+}	0.026	0.020	0.026	0.037	0.249	0.158	0.185	0.374	0.334	0.051	0.390	0.350	0.757	0.803	0.818
S^{6+}	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Σ	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
OH^-	0.910	1.015	1.031	1.100	0.880	1.026	0.913	0.964	0.949	1.001	1.002	0.940	1.188	1.071	1.156

calculated empirical formulae are based on sum of (Sb+Si+As+P+S)=1 *apfu* side (Mg*K*α), halite (Cl*K*α), hematite (Fe*K*α), LiF (F*K*α), Ni (Ni*K*α), PbSe (Se*L*β), PbTe (Te*L*α), rhodonite (Mn*K*α), sanidine (Al*K*α, K*K*α, Si*K*α), Sb_2S_3 (Sb*L*α), scheelite (W*L*α), vanadinite (V*K*α), wulfenite (Pb*M*α, Mo*L*α) and ZnO (Zn*K*α). Contents of the above-listed elements, which are not included in the tables, were analysed quantitatively, but their contents were below the detection limit (ca. 0.03 - 0.05 wt. % for individual elements). Raw intensities were converted to the concentrations of elements using automatic "PAP" matrix-correction procedure (Pouchou, Pichoir 1985).

Results

Olivenite occurs in cavities of milky quartz as olive to pale green acicular crystals up to 5 mm long with vitreous to silky lustre. Individual crystals are frequently grouped to sprays or radial aggregates (Fig. 1, 2) and are often included in aggregates of minerals of the cornwallite-pseudomalachite series (Fig. 3).

The experimental powder data set of olivenite from the Podlipa deposit given in Table 1 agrees well with the X-ray pattern calculated from the single-crystal data of olivenite from Majuba Hill (Li et al. 2008). The refined unit-cell parameters of olivenite from Ľubietová - Podlipa are compared in Table 2 with published data.

Representative WDS analyses of olivenite from Ľubietová - Podlipa as well as calculated empirical formulae are shown in Table 3 (all 58 analyses are available in supplementary file). Studied olivenite from the Pod-

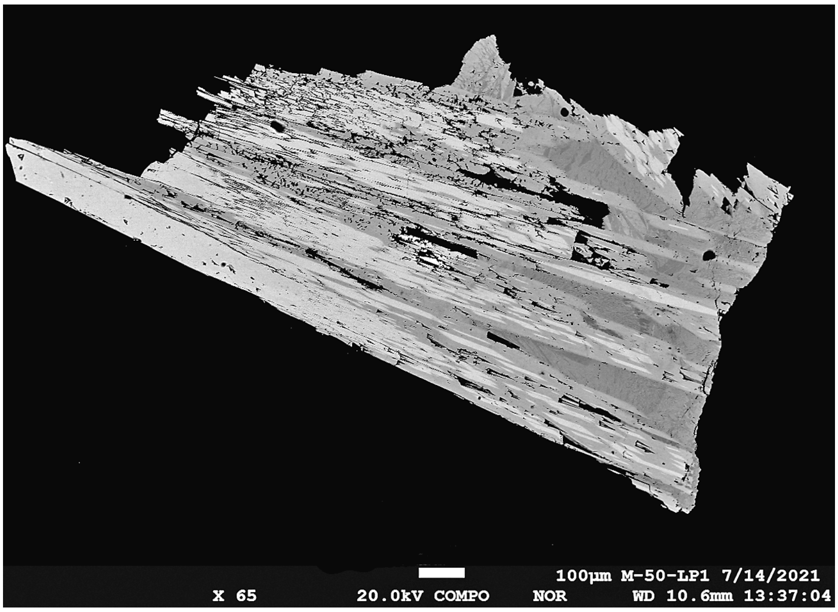


Fig. 4 *Zonal acicular crystals of olivenite (very light grey to grey) with minerals of cornwallite-pseudomalachite series (darker grey zonal fillings); BSE image by T. Mikuš.*

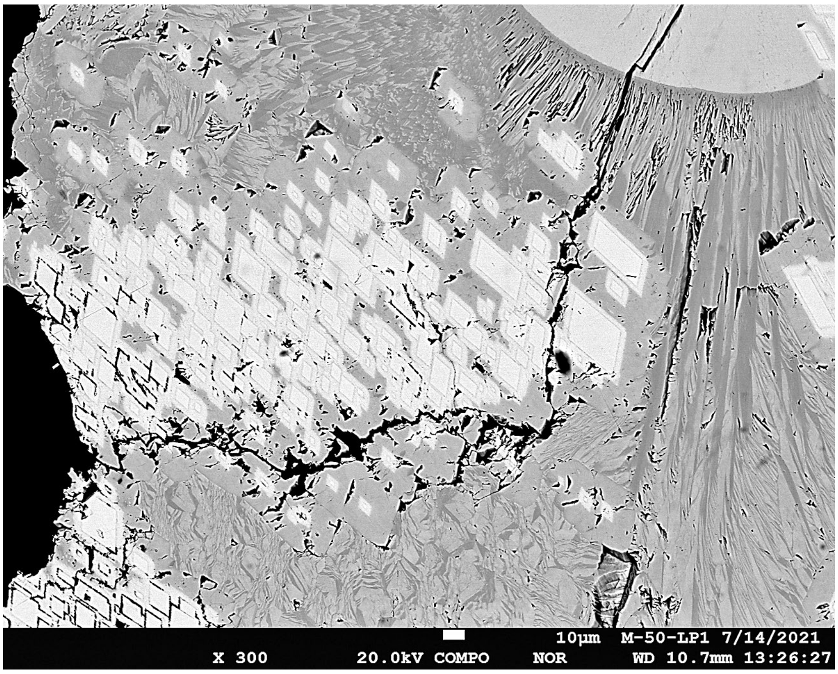


Fig. 5 *Cross-sections of acicular zonal crystals of olivenite (white with light grey outer zone) enclosed in minerals of the cornwallite-pseudomalachite series (homogenous botryoidal aggregate in the upper right corner as well as light to dark grey zonal mass); BSE image by T. Mikuš.*

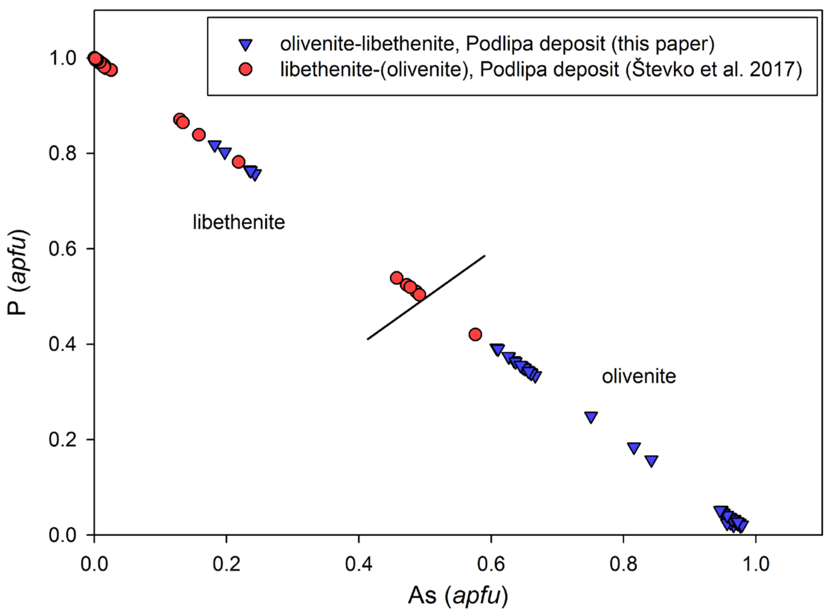


Fig. 6 *Variation of As and P content in olivenite and As-rich libethenite from the Podlipa deposit.*

Table 4 *X-ray powder diffraction data of cornwallite from Lubietová - Podlipa*

$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*
8.703	2	8.703	0	0	2	2.4950	13	2.4948	1	0	-6	1.8779	8	1.8780	0	3	2
5.479	12	5.477	0	1	1	2.4692	29	2.4692	1	1	5	1.8339	3	1.8337	0	1	9
4.813	23	4.809	0	1	2	2.4155	85	2.4153	1	2	1	1.8252	2	1.8256	0	3	3
4.608	100	4.608	1	0	0	2.3657	15	2.3656	1	2	-2	1.8007	8	1.8004	2	2	0
4.094	2	4.091	0	1	3	2.3430	33	2.3428	1	2	2	1.7969	4	1.7971	2	1	5
3.545	86	3.545	1	1	-1	2.3041	41	2.3042	2	0	0	1.7727	18	1.7727	2	2	-2
3.508	44	3.507	1	1	1	2.2833	8	2.2835	0	1	7	1.7596	2	1.7599	1	2	-7
3.361	8	3.360	1	1	-2	2.2294	2	2.2294	1	1	6	1.7534	6	1.7536	2	2	2
3.296	7	3.296	1	1	2	2.2211	5	2.2213	0	2	5	1.7440	5	1.7437	1	3	-2
3.221	43	3.221	1	0	-4	2.1760	6	2.1757	0	0	8	1.7329	7	1.7330	2	2	-3
3.110	33	3.110	1	0	4	2.1491	1	2.1489	1	2	-4	1.6831	5	1.6834	0	3	5
3.097	15	3.098	1	1	-3	2.1399	2	2.1399	2	1	0	1.6485	15	1.6487	2	1	-7
3.023	47	3.023	1	1	3	2.1325	1	2.1323	2	1	-1			1.6478	2	2	4
2.981	3	2.981	0	1	5	2.1150	7	2.1150	1	2	4	1.6172	3	1.6174	2	2	-5
2.902	3	2.901	0	0	6	2.0628	6	2.0625	2	1	2	1.6104	2	1.6107	1	2	8
2.885	17	2.885	0	2	0	2.0291	2	2.0292	2	1	-3	1.5965	3	1.5965	2	1	7
2.738	25	2.738	0	2	2	2.0072	3	2.0074	2	0	4	1.5813	10	1.5816	2	2	5
2.583	10	2.583	0	2	3	1.8840	3	1.8835	0	2	7	1.5547	5	1.5550	2	0	8
2.538	13	2.538	1	1	-5												

Table 5 *Unit-cell parameters of cornwallite (for monoclinic space group $P2_1/c$)*

occurrence	reference	*a* [Å]	*b* [Å]	*c* [Å]	*β* [°]	*V* [Å^3]
Lubietová - Podlipa, Slovakia	this paper	4.6112(2)	5.7698(3)	17.4167(11)	92.009(5)	463.10(3)
Farbište, Slovakia	Števko et al. (2011)	4.6051(2)	5.7591(5)	17.3854(3)	91.93(2)	460.9 (1)
Clara Mine, Germany	Arlt, Armbruster (1999)	4.600(2)	5.757(3)	17.380(6)	91.87(3)	460.04
Gelnica, Slovakia	Sejkora et al. (2001)	4.608(1)	5.765(1)	17.400(4)	92.01(1)	461.9(1)
Horní Slavkov, Czech Republic	Sejkora et al. (2006)	4.5685(4)	5.7708(4)	17.287(1)	93.02(2)	455.1

Table 6 *Representative quantitative chemical analyses of minerals of the cornwallite-pseudomalachite series from the Podlipa copper deposit (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Cnw-b	Cnw-b	Cnw-b	Cnw-b	Cnw-b	Cnw-b	Cnw-z	Cnw-z	Cnw-z	Cnw-z	Cnw-z	Cnw-z	Pmlc	Pmlc	Pmlc
CuO	59.49	60.04	60.33	60.46	59.72	60.58	64.51	62.85	64.17	62.46	63.22	63.28	63.68	65.27	66.16
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.36	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO_2	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As_2O_5	30.59	31.04	30.85	33.97	33.42	34.32	25.50	22.24	24.50	25.81	20.13	20.90	18.06	13.99	12.79
P_2O_5	2.35	2.18	1.91	0.54	0.92	0.44	7.53	9.15	8.32	6.74	10.88	10.29	12.16	14.78	17.08
SO_3	0.00	0.00	0.00	0.09	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00
total	92.43	93.26	93.09	95.06	94.17	95.51	97.54	94.24	97.09	95.01	94.23	94.71	93.97	94.40	96.03
Cu^{2+}	5.00	5.02	5.14	5.00	4.92	4.98	4.95	4.90	4.88	4.91	4.84	4.87	4.85	4.97	4.73
Fe^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Mn^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Al^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.00
Σ	5.00	5.02	5.14	5.00	4.92	4.98	4.95	4.90	4.89	4.91	4.84	4.89	4.85	5.02	4.73
Sb^{3+}	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si^{4+}	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As^{5+}	1.78	1.80	1.82	1.94	1.90	1.95	1.35	1.20	1.29	1.41	1.07	1.11	0.95	0.74	0.63
P^{5+}	0.22	0.20	0.18	0.05	0.08	0.04	0.65	0.80	0.71	0.59	0.93	0.89	1.04	1.26	1.37
S^{6+}	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Σ	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	2.00
OH^-	4.00	4.04	4.27	4.00	3.85	3.96	3.89	3.80	3.78	3.83	3.68	3.80	3.71	4.07	3.45

Calculated empirical formulae are based on sum of (Sb+Si+As+P+S)=2 *apfu;* Cnw-b - botryoidal (type 1), Cnw-z - zonal mass (type 2), Pmlc - As-rich pseudomalachite lipa deposit often shows relatively strong, oscillatory to sector chemical zoning in BSE (Figs. 4, 5). Except of dominant content of Cu only minor amounts of Fe (up to 0.04 *apfu*) and locally also Al (only up to 0.01 *apfu*) were detected. Chemical zoning observed in BSE is caused by strong variation of As and P contents (Fig. 6), ranging mostly between nearly end member olivenite containing only 0.02 *apfu* of P up to P-rich olivenite with 0.39 *apfu* of P. Dark, P-rich zones or domains were rarely also observed (Fig. 7) and are compositionally corresponding to As-rich libethenite with As content ranging between 0.18 to 0.24 *apfu*. Except of As and P minor content of Si (up to 0.01 *apfu*) is locally present in studied olivenite.

Cornwallite forms dark green massive fillings between crystals of olivenite (Fig. 3) or microcrystalline botryoidal aggregates (Fig. 8) in cavities of quartz.

The experimental powder data set of botryoidal cornwallite from the Podlipa deposit given in Table 4 is in good agreement with the X-ray pattern calculated from the single-crystal data of cornwallite from Clara mine (Arlt, Armbruster 1999). The refined unit-cell parameters of cornwallite from Ľubietová - Podlipa are compared in Table 5 with published data.

Representative quantitative chemical analyses as well as calculated empirical formulae of minerals of the cornwallite-pseudomalachite series from the Podlipa deposit are given in

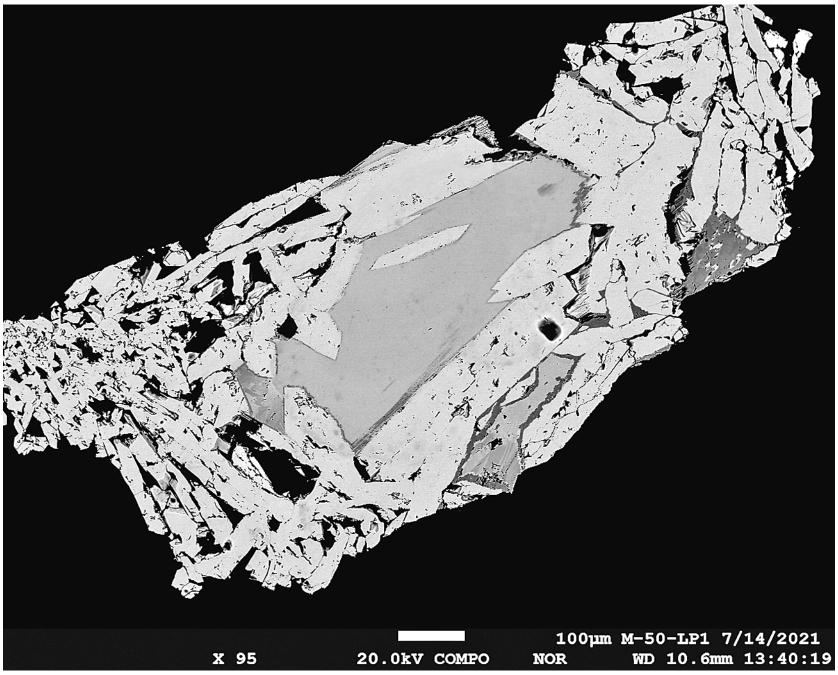


Fig. 7 *Group of homogenous olivenite crystals (white) with dark grey external domains represented by As-rich libethenite; light grey mass filling the space between olivenite crystals is cornwallite; BSE image by T. Mikuš.*

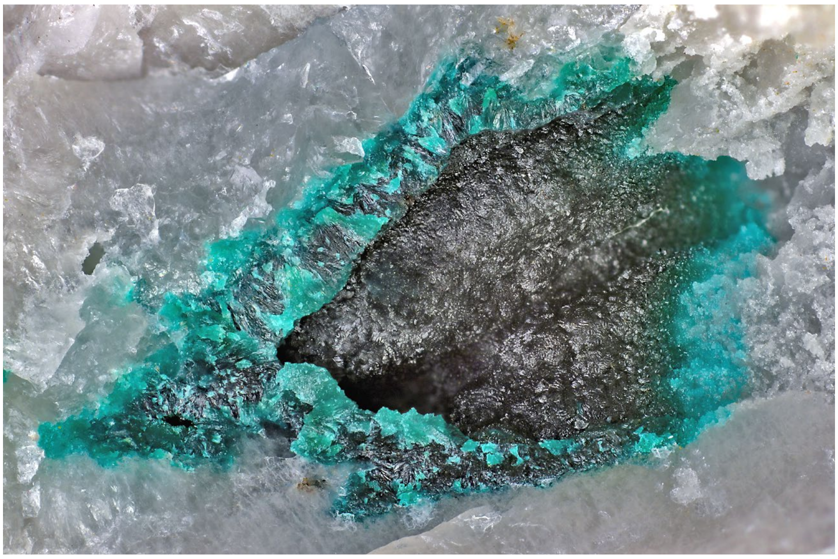


Fig. 8 *Dark green botryoidal aggregate of cornwallite with microcrystalline surface; field of view is 5.1 mm; photo by L. Hrdlovič.*

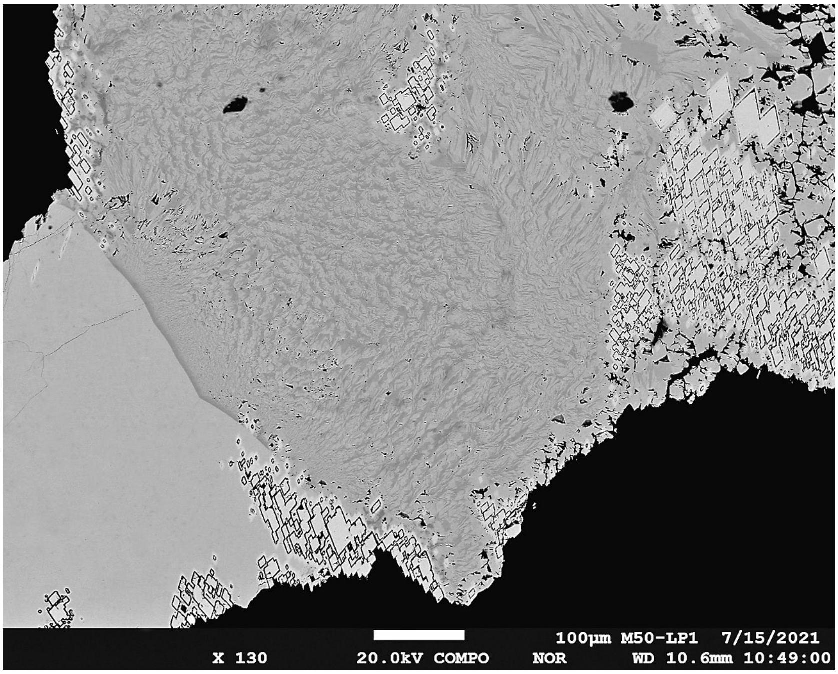
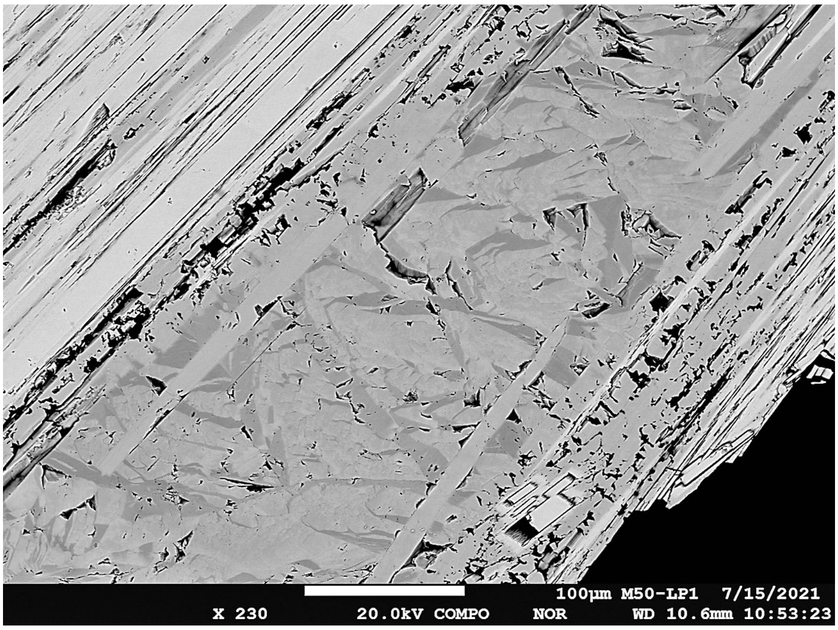


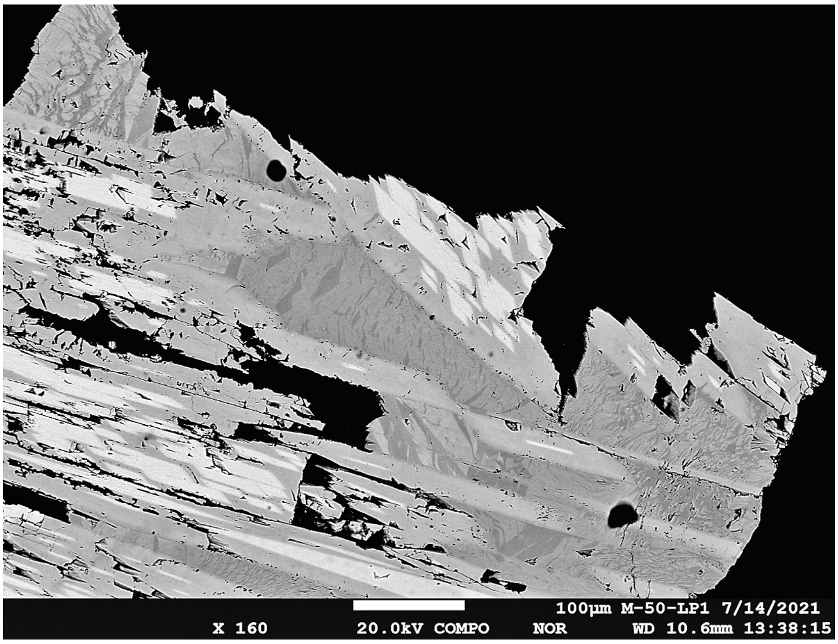
Fig. 9 *Homogenous botryoidal cornwallite (type 1, grey aggregate in the lower left corner) and zonal mass of minerals of cornwallite -pseudomalachite series (type 2, grey to dark grey); white euhedral crystals are olivenite; BSE image by T. Mikuš.*

Table 6 (all 52 analyses are available in supplementary file). The two compositional types of cornwallite were distinguished. The first type is represented by relatively homogenous botryoidal aggregates (Fig. 9), which contain only minor amounts of P (ranging between 0.04 to 0.22 *apfu*). The second type is represented by polycrystalline fillings and it shows strong irregular chemical zoning in BSE (Fig. 9, 10, 11). This zoning is caused by significant variation of As and P contents (Fig. 12), ranging compositionally from P-rich cornwallite (with 1.41 *apfu* of As and 0.59 *apfu* of P) up to As-rich pseudomalachite (with 1.37 *apfu* of P and 0.63 *apfu* of As). Except of Cu, As and P only minor amounts of Al (up to 0.04 *apfu*) as well as Fe, Mn, Sb and Si (all up to 0.01 *apfu*) were detected in studied samples of minerals of the cornwallite-pseudomalachite series.

Conclusions

A new occurrence of olivenite and cornwallite was discovered at the Podlipa copper deposit near Ľubietová, Slovakia. Both in olivenite as well as in minerals of the cornwallite-pseudomalachite series a wide compositional variability, caused by significant variation of As and P contents was documented. Studied association of minerals was formed by the weathering of primary ore minerals in supergene zone *in-situ* and the most probable source of arsenic at the Podlipa deposit were minerals of the tetrahedrite-tennantite series.





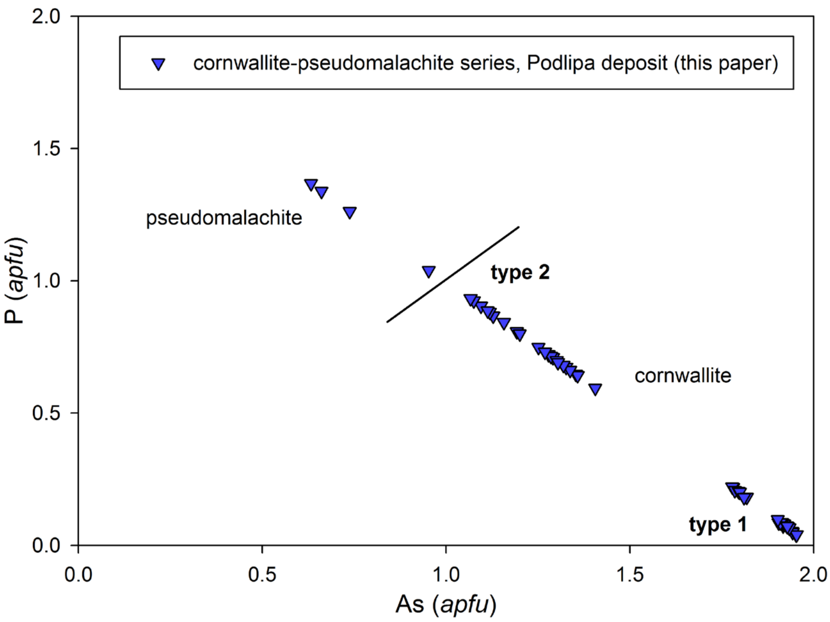


Fig. 10 *Detail on irregular chemical zoning of minerals of the cornwallite-pseudomalachite series (type 2, grey to dark grey); white to grey acicular crystals are olivenite; BSE image by T. Mikuš.*

Fig. 11 *Zonal masses of minerals of the cornwallite-pseudomalachite series (type 2, grey to dark grey) filling the space between zonal acicular crystals of olivenite (white to light grey); dark grey zones are corresponding to As-rich pseudomalachite; BSE image by T. Mikuš.*

Fig. 12 *Variation of As and P content in minerals of the cornwalllite-pseudomalachite series from the Podlipa deposit.*

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References

Arlt T, Armbruster T (1999) Single-crystal X-ray structure refinement of cornwallite, $Cu_5(AsO_4)_2(OH)_4$: A comparison with its polymorph cornubite and the PO_4 analogue pseudomalachite. N Jb Miner Mh 10: 468-480

Bergfest A (1951) Baníctvo v Ľubietovej na medenú rudu. MS, archív ŠGÚDŠ-Geofond, Bratislava, 1-42, 3668

Breithaupt A (1823) Vollständige Charakteristik des Mineral-System´s. 1-358, Arnoldische Buchhandlung, Dresden und Leipzig

Burnham CW (1962) Lattice constant refinement. Carnegie Institute Washington Yearbook 61: 132-135

Burns PC, Hawthorne FC (1995) Rietveld refinement of the crystal structure of olivenite: a twinned monoclinic structure. Can Mineral 33: 885-888

Čech F, Láznička P (1965) Cyanotrichit z ložiska měděných rud od Lubietové. Acta Univ Carol Geol 3: 149-155

Effenberger H, Krause W, Belendorff K, Bernhardt HJ, Medenbach O, Hybler J, Petříček V (1994) Revision of the crystal structure of mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$. Can Mineral 32(2): 365-372

Figuschová M (1977) Sekundárne minerály medi z Ľubietovej. In: Zborník referátov z konferencie Ložiskotvorné procesy Západných Karpát, Bratislava: 135-137

Hauerová J, Blaha M, Bartoň B, Linkešová M, Fodorová V, Makuša M, Pitoňák P, Spišiak J (1989) Ľubietová-Kolba, Záverečná správa úlohy: Surovina: Cu (Sb, Ag, Ni, Co, Bi, W), vyhľadávací prieskum, I. podetapa. MS, archív Geofond, Bratislava, 74660

Hyršl J (1991) Three polymorphs of $Cu_5(PO_4)_2(OH)_4$ from Ľubietová, Czechoslovakia. N Jb Miner Mh 6: 281-287

Li C, Yang H, Downs RT (2008) Redetermination of olivenite from an untwinned single-crystal. Acta Cryst E64: i60-i61

Luptáková J, Milovská S, Biroň A, Jeleň S, Andráš P (2012) Study of secondary minerals of abandoned Cu deposit Ľubietová-Podlipa (Slovakia). Acta Mineral Petrogr Abstr Ser 7: 80

Luptáková J, Milovská S, Jeleň S, Mikuš T, Milovský R, Biroň A (2016) Primary ore Cu mineralizitaion at the Ľubietová-Podlipa locality (Slovakia). AGEOS 8(2): 175-194

Majzlan J, Števko M, Chovan M, Luptáková J, Milovská S, Milovský R, Jeleň S, Sýkorová M, Pollok K, Göttlicher J, Kupka D (2018) Mineralogy and geochemistry of the copper-dominated neutral mine drainage at the Cu deposit Ľubietová-Podlipa (Slovakia). Appl Geochem 92: 59-70

Michňová J, Ozdín D, Bačík P (2008) Štúdium fluidných inklúzií a chemického zloženia turmalínov z hydrotermálneho ložiska Ľubietová. Bull mineral-petrolog Odd Nár Muz (Praha) 16(1): 100-108

Milovská S, Luptáková J, Jeleň S, Biroň A, Lazor P, Polák Ľ (2014) Manganese oxides and oxyhydroxides from Banská Štiavnica, Ľubietová and Selce (Central Slovakia). In: Proceedings of the international symposium CEMC 2014 (Skalský Dvůr): 101-102

Ondruš P (1993) A computer program for analysis of X-ray powder diffraction patterns. Materials Science Forum, EPDIC-2, Enchede, 133-136: 297-300

Polák M, Filo I, Havrila M, Bezák V, Kohút M, Kováč P, Vozár J, Mello J, Maglay J, Elečko M, Vozárová A, Olšavský M, Siman P, Buček S, Siráňová Z, Hók J, Rakús M, Lexa J, Šimon L, Pristaš J, Kubeš P, Zakovič M, Liščák P, Žáková E, Boorová D, Vaněková H (2003) Geologická mapa Starohorských vrchov, Čierťaže a severnej časti Zvolenskej kotliny. 1:50 000. Štátny geologický ústav Dionýza Štúra, Bratislava

Pouchou JL, Pichoir F (1985) “PAP” (φρZ) procedure for improved quantitative microanalysis. In: Microbeam Analysis (J. T. Armstrong, ed.). San Francisco Press, San Francisco: 104-106

Povondra P, Řídkošil T (1980) Brochantit z Piesků a Lubietové u Banské Bystrice. Acta Univ Carol Geol 1-2: 1-8

Řídkošil T, Povondra P (1982) The relation between posnjakite and langite. N Jb Miner Mh: 16-28

Řídkošil T, Šrein V, Fábry J, Hybler J, Maximov BA (1992) Mrázekite, $Bi_2Cu_3(OH)_2O_2(PO_4)_2{\cdot}2H_2O$, a new mineral species and its crystal structure. Can Mineral 30(1): 215-224

Sejkora J, Ďuďa R, Novotná M (2001) Minerály oxidační zóny žíly Krížová, Gelnica, Slovenské Rudohorie. Bull mineral-petrolog Odd Nár Muz 9: 121-139

Sejkora J, Ondruš P, Fikar M, Veselovský F, Mach Z, Gabašová A, Škoda R, Beran P (2006) Supergene minerals at the Huber stock and Schnöd stock deposits, Krásno ore district, the Slavkovský les area, Czech Republic. J Czech Geol Soc 51: 57-101

Sejkora J, Škácha P, Dvořák Z, Muzikant P (2015) Slavkovit z Preisselbergu, rudní revír Krupka (Česká republika) a jeho minerální asociace. Bull mineral-petrolog Odd Nár Muz (Praha) 23(1): 1-18

Slavkay M, Beňka J, Bezák V, Gargulák M, Hraško Ľ, Kováčik M, Petro M, Vozárová A, Hruškovič S, Knésl J, Knéslová A, Kusein M, Maťová V, Tulis J (2004) Ložiská nerastných surovín Slovenského rudohoria, Zväzok 2. 1-286, Štátny geologický ústav Dionýza Štúra, Bratislava

Števko M, Sejkora J, Bačík P (2011) Mineralogy and origin of supergene mineralization at the Farbiště ore occurrence near Poniky, central Slovakia. J Geosci 56: 273-298

Števko M, Sejkora J, Malíková R (2016) Nové údaje o supergénnych mineráloch z banského poľa Rainer, ložisko Ľubietová-Podlipa (Slovenská republika). Bull mineral-petrolog Odd Nár Muz (Praha) 24(1): 1-12

Števko M, Sejkora J, Súľovec Š (2017) Príspevok k chemickému zloženiu libethenitu z typovej lokality: ložisko Podlipa, Ľubietová (Slovenská republika). Bull Mineral Petrolog 25(2): 252-259

Vozárová A, Vozár J (1988) Late Paleozoic in the Western Carpathians. 1-314, Štátny geologický ústav Dionýza Štúra, Bratislava