

Příbramite, CuSbSe_2 , the Se-analogue of chalcostibite, a new mineral from Příbram, Czech Republic

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Abstract: The new mineral příbramite was found on the dump of shaft No. 16, one of the mines in the Příbram uranium and base-metal district, central Bohemia, Czech Republic. Příbramite is associated with antimonselite, permingerite, dzharkenite, ferroselite, hakite, tetrahedrite, chaméanite, giraudite, a new Hg-, Sb-, Cu selenide, a new Sb-, Cu selenide and uraninite in a calcite-dominant gangue. The new mineral occurs as columnar crystals up to $60 \times 12 \mu\text{m}$ (in the section), growing together in aggregates up to $150 \mu\text{m}$ across in the calcite gangue. Příbramite crystals form intergrowths and replace older permingerite; antimonselite crystals were observed in close association as well. Příbramite is brittle, is lead grey in colour, and has a metallic lustre. Mohs hardness is *ca.* 3–4; the calculated density is 5.884 g cm^{-3} . In reflected light příbramite is grey with a yellowish hue, birefractance is medium, and pleochroism is weak with grey tints. Anisotropy is strong with grey to brownish rotation tints. Internal reflections were not observed. The empirical formula, based on electron-microprobe analyses, is $\text{Cu}_{1.00}(\text{Sb}_{1.02}\text{As}_{0.01})_{1.03}(\text{Se}_{1.81}\text{S}_{0.15})_{1.96}$. The ideal formula is CuSbSe_2 , which requires Cu 18.52, Sb 35.47 and Se 46.01, total 100.00 wt%. Additional elements as Fe, Pb, Tl and Hg were found in small concentrations above detection limits. Příbramite is orthorhombic, *Pnma*, $a = 6.3042(15)$, $b = 3.980(1)$, $c = 14.989(4) \text{ \AA}$, with $V = 376.09(2) \text{ \AA}^3$ and $Z = 4$. The strongest reflections of the calculated powder X-ray diffraction pattern [d , Å (hkl)] are: 3.152(40) (2 0 0), 3.113(100) (0 1 3), 3.085(40) (2 0 1), 3.395(63) (0 1 5), 1.9900(38) (0 2 0), 1.8442(42) (3 1 1) and 1.8329(33) (3 0 4). According to single-crystal X-ray diffraction data ($R_{\text{obs}} = 0.0480$), příbramite is unequivocally isostructural with chalcostibite and emplectite. The structure of příbramite contains one Cu, one Sb and two Se sites (last mentioned is occupied both by Se and S atoms). It is built up from square Sb pyramids linked to form chains of SbSe_2 along b and CuSe_4 tetrahedra forming chains of CuSe_3 parallel to b . These two types of infinite chains are then linked to form sheets that are stacked perpendicular to c . The effect of the larger Se atom, compared with S, is well reflected by the increased unit-cell volume of příbramite ($V_{\text{příbramite}} \sim 380 \text{ \AA}^3$) compared with that of chalcostibite ($V_{\text{chalcostibite}} \sim 330 \text{ \AA}^3$). Příbramite is named after the type locality, the Příbram uranium and base-metal district.

Key-words: příbramite; new mineral; Se-analogue of chalcostibite; copper antimony selenide; selenide minerals; crystal structure; uranium deposit; Příbram; Czech Republic.

1. Introduction

Příbramite, the selenium analogue of chalcostibite, was found among a very rich selenide assemblage at the abandoned complex uranium and base-metal ore district Příbram, Czech Republic, during an extensive research programme focused on selenide mineralization of the Bohemian Massif (Sejkora *et al.*, 2011, 2012, 2014; Škácha, 2015; Škácha *et al.*, 2014, 2015, 2016; Sejkora & Škácha, 2015a and b).

Chalcostibite, CuSbS_2 , is a locally relatively common sulphosalt, typical for some Sb-rich base-metal deposits. It forms a complete solid solution with emplectite (CuBiS_2) (Razmara *et al.*, 1997). The Se-analogue of emplectite, grundmannite (CuBiSe_2), has been described recently (Förster *et al.*, 2016a). An unnamed mineral corresponding

to příbramite has been mentioned previously from the U–Se-bearing calcite veins of the U–Hg–Mo polymetallic deposit in Guizhou province, China (the exact locality was not given in the original description). Chen *et al.* (1995) published its chemical composition, microhardness and reflectance data.

Příbramite is named after its type locality, the Příbram uranium and base-metal ore district. ‘Ř’ in the name příbramite is pronounced as a raised alveolar non-sonorant trill. The name příbramite was used as a synonym for several minerals in the 19th and 20th centuries, *e.g.*, cronstedtite (Ponfíkl, 1828), goethite (Dana, 1944) and Cd-rich sphalerite (Glocker, 1831). These obsolete names have not been used for more than 70 years.

The new mineral and the name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association

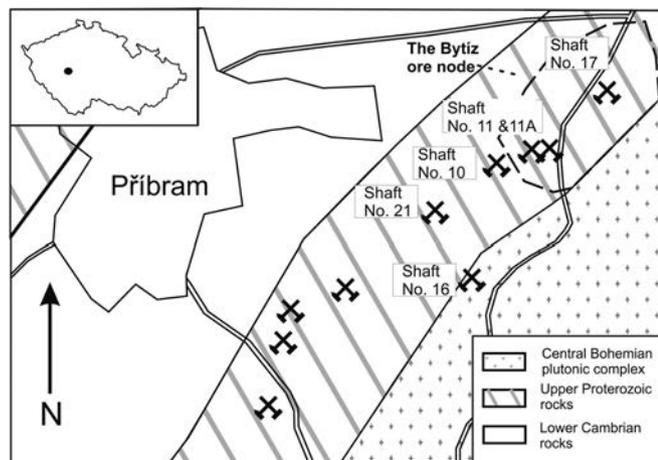


Fig. 1. Schematic geological map of part of the Příbram uranium and base-metal district.

(IMA 2015-127). The cotype material (two polished sections) is deposited in the Mineralogical collection of the Department of Mineralogy and Petrology of the National Museum, Prague, Czech Republic (catalogue number P1P 15/2015) and in the mineralogical collection of the Mining Museum Příbram, Příbram, Czech Republic, under the catalogue number 1/2016.

2. Occurrence

The Příbram ore area (central Bohemia, Czech Republic) is known for the deposits of base-metals as well as for uranium ores. It could be divided into two main ore districts: the base-metal Březové Hory ore district and the complex U and base-metal Příbram district. The complex U and base-metal ore district Příbram represent the largest accumulation of vein-type hydrothermal U ores in the Czech Republic and is comparable to world-class deposits of this type (Fig. 1). The hydrothermal U mineralization of late Variscan age is bonded to a 1–2 km wide and almost 25 km long zone formed by a strongly tectonized series of Upper Proterozoic rocks along the contact with granitoids of the Central Bohemian Pluton (Ettler *et al.*, 2010). More than 2500 carbonate veins were prospected there; the U mineralization occurred in 1641 veins, base-metal mineralization in 35 veins and finally monomineralic silver mineralization in 19 veins. The main U-ore was represented by colomorph uraninite (pitchblende) and by antraxolite (organic compound containing U). Haematitization is typical for the carbonate veins containing uraninite. The total production of 48,432 t of pure U metal represented 49% of Czechoslovak production since 1945; the parallel extraction of base-metals and silver from veins produced more than 6000 t Pb, 2400 t Zn and 28 t Ag (Litochleb *et al.*, 2003). The Příbram uranium and base-metal district can be sub-divided into several ore deposits (also called ore nodes) – among them the most important were Bytíz, Háje and Brod. Selenides occurs in the Bytíz ore deposit in the carbonate–sulphidic mineralization stage closely linked to the uraninite of the previous carbonate–uraninite stage.

The first selenide found there – clausthalite – was mentioned by Růžička (1986); subsequently, eight selenides were found during a study of the museum's specimen by Litochleb *et al.* (2004). Since 2005, the first author (PŠ) has found many specimens of a selenide-containing gangue in the dump material of shafts # 16, #11A and #9. The collected material contains a very interesting and rich selenide assemblage (Škácha & Sejkora, 2007; Škácha, 2015; Škácha *et al.*, 2009, 2010, 2014, 2015, 2016), including a new mineral, here described as příbramite.

Two hand-sized samples with příbramite were found in mine dump material of shaft #16 (49.67°33.028' N, 14.05°89.919' E), located in the Háje deposit in particular. Shaft #16 opened mainly the middle and deeper parts of the vein system of the deposits Háje, Bytíz and Jerusalem (from 500 m down to a depth of 1800 m below the surface). The majority of the selenide-bearing material probably came from the ore deposit Bytíz, which provided 52% of the U net-production of the entire district. The Se–U mineralization is of low-temperature hydrothermal origin and is bound to a calcite vein with a thickness varying from tens of centimetres to several metres. The main ore is represented by uraninite, whereas younger antraxolite predominates in deeper parts of the deposit.

Příbramite appears in two different mineral associations. The first one includes antimonselite (Sb_2Se_3), dzharkenite (FeSe_2), ferroselite (FeSe_2), tiemannite, hakite ($\text{Cu}_6[\text{Cu}_4\text{Hg}_2]\text{Sb}_4\text{Se}_{13}$), tetrahedrite, uraninite and a new Hg–Cu–Sb selenide in calcite gangue (Type I). The second one contains, in addition to příbramite, an unnamed Sb–Cu selenide (IMA 2016-044), chaméanite ($\text{Cu,Fe}_4\text{As}(\text{Se,S})_4$), bukovite $\text{Tl}_2(\text{Cu,Fe})_4\text{Se}_4$, eskebornite, giraudite ($\text{Cu}_6[\text{Cu}_4(\text{Fe,Zn})_2]\text{As}_4\text{Se}_{13}$), umangite, hakite and tetrahedrite in calcite gangue (Type II). In another sample, Se-rich chalcostibite was found (Škácha *et al.*, 2015) as aggregates up to 3 mm across consisting of up to 50 μm large crystals in association with antimonselite, hakite, Se-rich tetrahedrite and chalcopyrite.

3. Physical and optical properties

Příbramite forms subhedral blade-shaped crystals up to $60 \times 13 \mu\text{m}$ (Fig. 2), growing together in aggregates up to $150 \mu\text{m}$ across (Type I); it partly replaced earlier permingeatite. In close association, antimonselite crystals were also observed (Fig. 2). Příbramite was also found (Type II) as anhedral grains up to $15 \mu\text{m}$ in size growing with the new Sb–Cu selenide (IMA 2016-044). Příbramite is lead grey in colour. The mineral is opaque in transmitted light and has a metallic lustre. No cleavage and fracture were observed, the tenacity is brittle. The calculated density ($Z=4$) for the empirical formula is 5.884 g cm^{-3} . Mohs hardness is assumed at 3–4 by analogy with chalcostibite. In reflected light, příbramite is grey with a yellowish hue and medium bireflectance. Pleochroism is weak, showing grey tints. Anisotropy under crossed polarizers is strong (Fig. 2), with grey to brownish rotation

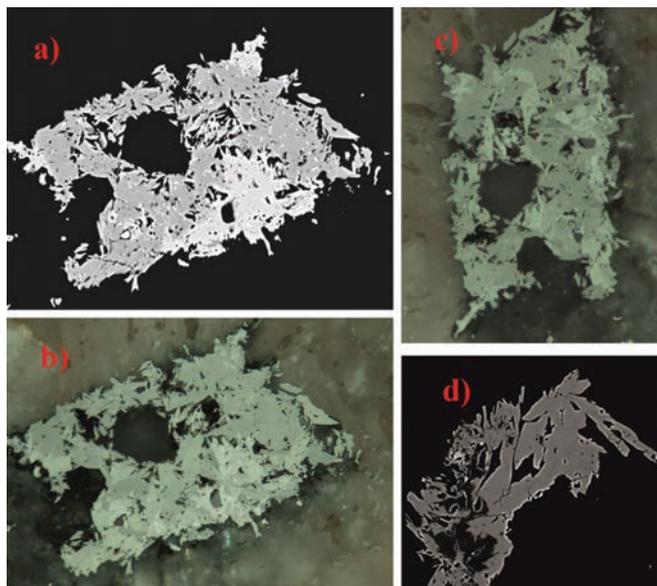


Fig. 2. (a) Backscattered-electron (BSE) image of aggregate (ca. 120 μm across) of příbramite (grey) and antimonselite (white) crystals in calcite gangue; (b) and (c) reflected-light image, partly crossed polarizers (different extinction); under crossed polars, příbramite is strongly anisotropic with grey to brownish rotation tints; (d) příbramite crystal aggregate (light) used for the single-crystal study. Dark areas are formed by older permingeatite. BSE image. Horizontal field 170 μm , picture by J. Sejkora, P. Škácha.

tints. Internal reflections were not observed. Reflectance percentages for the four COM wavelengths (R_{min} and R_{max}) for příbramite from Příbram are: 39.8/44.8 (470 nm), 40.4/46.2 (546 nm), 40.4/46.5 (589 nm) and 38.9/44.8 (650 nm). The reflectance values for příbramite from Příbram are given in Table 1 and are compared with data of chalcostibite in Fig. 3.

4. Chemical composition

Chemical analyses ($n=53$) were performed using a Cameca SX100 electron microprobe (National Museum, Prague) operating in wavelength-dispersive mode (25 kV, 20 nA and 2 μm wide beam). Analytical data are given in Table 2 and representative analyses are given in Table 3. The following standards and X-ray lines were used to minimize line overlaps: Ag ($\text{AgL}\alpha$), Au ($\text{AuM}\alpha$), Bi ($\text{BiM}\beta$), CdTe ($\text{CdL}\alpha$), Co ($\text{CoK}\alpha$), chalcopyrite ($\text{CuK}\alpha$), FeS₂ ($\text{FeK}\alpha$, $\text{SK}\alpha$), HgTe ($\text{HgM}\alpha$), NiAs ($\text{NiK}\alpha$, $\text{AsL}\alpha$), PbS ($\text{PbM}\alpha$), PbSe ($\text{SeL}\alpha$), PbTe ($\text{TeL}\alpha$), Sb₂S₃ ($\text{SbL}\alpha$), Tl(BrI) ($\text{TlL}\alpha$) and ZnS ($\text{ZnK}\alpha$). Peak counting times were 20 s for all elements, and one half of the peak time for each background. Other elements, such as Ag, Au, Bi, Cd, Co, Ni, Te and Zn, were found to be below the detection limits (0.02–0.05 wt%). Raw intensities were converted to the concentrations of elements using the automatic ‘PAP’ (Pouchou & Pichoir, 1985) matrix-correction software.

The chemical composition of příbramite from both associations is very similar and corresponds very well with the formula CuSbSe₂ derived from the crystal-structure

Table 1. Reflectance values (WTiC standard in air, Zeiss 370; spectrophotometer MSP400 Tidas at Leica microscope, objective 50 \times) are as follows (data are plotted in Fig. 3 together with published reflectance data of chalcostibite).

$R_{\text{min}}/R_{\text{max}}$	λ (nm)	$R_{\text{min}}/R_{\text{max}}$	λ (nm)
39.6/42.1	400	40.6/46.4	560
39.9/43.1	420	40.5/46.6	580
39.9/43.9	440	40.4/46.5	589 (COM)
39.9/44.6	460	40.2/46.4	600
39.8/44.8	470 (COM)	39.8/45.9	620
39.8/44.9	480	39.2/45.2	640
39.9/45.2	500	38.9/44.8	650 (COM)
40.1/45.6	520	38.5/44.3	660
40.4/46.0	540	38.1/43.6	680
40.4/46.2	546 (COM)	37.4/42.8	700

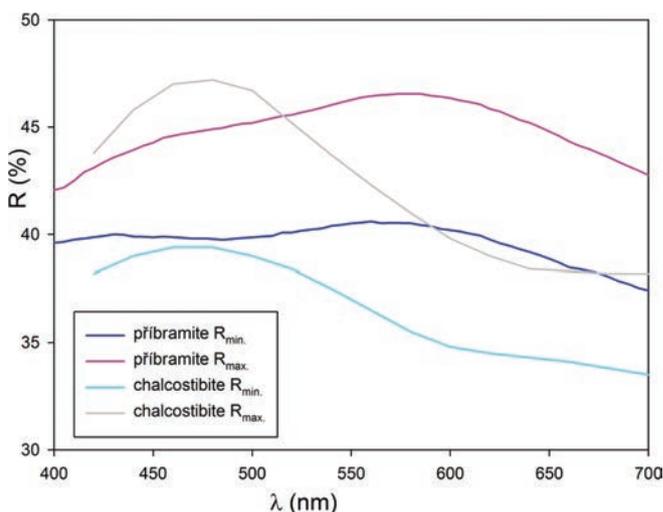


Fig. 3. Reflectivity curves for příbramite and chalcostibite (Picot & Johan, 1982).

study. Only weak Sb–As substitution was observed; a similar trend was found in another Cu–Sb selenide from Příbram, permingeatite (Škácha *et al.*, 2014). In contrast, an extensive Se–S substitution was determined for the studied příbramite and Se-rich chalcostibite (Fig. 4).

The empirical formula of příbramite calculated on the basis of 4 atoms per formula unit (*apfu*) is Cu_{1.00}(Sb_{1.02}As_{0.01})_{1.03}(Se_{1.81}S_{0.15})_{1.96}. The ideal formula is CuSbSe₂, which requires Cu 18.52, Sb 35.47 and Se 46.01, total 100.00 wt%. The first recorded occurrence of a phase corresponding to příbramite (Chen *et al.*, 1995) from Guizhou province (China) shows higher Hg content (0.008–0.077 *apfu*), and smaller (up to 0.04 *apfu*) As, S, Ni and Fe contents.

5. X-ray diffraction data

The paucity of příbramite did not allow us to collect a powder X-ray diffraction pattern. Therefore, calculated powder diffraction data are given in Table 4.

Table 2. Chemical data (wt%) for přibramite ($n = 53$).

Constituent	Wt%	Range	Stand. dev.	Probe standard
Ag	0.00	0.00–0.07	0.01	Ag
Fe	0.07	0.00–0.54	0.13	FeS ₂
Pb	0.02	0.00–0.23	0.04	PbS
Tl	0.02	0.00–0.60	0.08	Tl(BrI)
Hg	0.09	0.00–0.45	0.13	HgS
Cu	18.75	16.11–20.38	0.76	CuFeS ₂
Sb	36.75	33.62–39.49	1.08	Sb ₂ S ₃
As	0.28	0.00–1.34	0.30	NiAs
Se	42.21	37.80–44.39	1.31	PbSe
S	1.45	0.64–3.49	0.60	FeS ₂
Total	99.86			

Table 3. Representative analyses (wt%) for přibramite.

	1	2	3	4	5	6	7	8	9	10	China*
Ag	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.05	0.00	0.00
Fe	0.10	0.00	0.21	0.09	0.21	0.00	0.11	0.27	0.00	0.40	0.05
Pb	0.00	0.00	0.00	0.00	0.00	0.23	0.07	0.07	0.16	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Tl	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.60	0.00
Hg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.65
Cu	19.40	19.32	19.21	19.24	19.68	19.41	19.70	20.02	20.00	20.38	17.42
Sb	35.26	36.23	35.97	36.07	37.74	33.91	36.19	35.50	36.02	35.63	34.08
As	0.73	0.00	0.30	0.13	0.00	1.34	0.62	0.51	0.76	0.59	0.58
Se	44.24	44.39	44.33	43.47	39.12	43.17	41.87	39.97	40.12	37.80	45.80
S	0.85	0.88	0.92	1.30	3.49	0.91	1.36	2.26	2.30	3.26	0.11
Total	100.58	100.82	100.94	100.31	100.28	99.01	99.93	98.62	99.41	98.66	99.71
Ag	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.002	0.000	0.000
Fe	0.006	0.000	0.012	0.005	0.012	0.000	0.007	0.016	0.000	0.024	0.003
Pb	0.000	0.000	0.000	0.000	0.000	0.004	0.001	0.001	0.003	0.000	0.000
Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Tl	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.010	0.000
Hg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.028
Cu	1.023	1.021	1.011	1.015	1.009	1.037	1.042	1.054	1.048	1.059	0.950
ΣM	1.029	1.021	1.023	1.020	1.022	1.043	1.050	1.071	1.053	1.093	0.982
Sb	0.971	0.999	0.988	0.993	1.010	0.945	0.999	0.976	0.985	0.966	0.970
As	0.033	0.000	0.013	0.006	0.000	0.061	0.028	0.023	0.034	0.026	0.027
ΣSb + As	1.004	0.999	1.001	0.999	1.010	1.006	1.027	0.999	1.019	0.992	0.997
Se	1.878	1.888	1.878	1.845	1.614	1.856	1.781	1.694	1.691	1.580	2.009
S	0.089	0.092	0.096	0.136	0.354	0.096	0.143	0.236	0.239	0.335	0.012
ΣSe + S	1.967	1.980	1.974	1.981	1.968	1.952	1.924	1.930	1.930	1.915	2.021

1–10 representative analyses of Přibramite from Přibram; 1–5 Type I, 6–10 Type II.

* Přibramite from China, Gizhou province, mean of 12 analyses.

A $0.029 \times 0.022 \times 0.013$ mm large single-crystal of přibramite extracted from the polished section was examined using a Rigaku (Oxford Diffraction) SuperNova single-crystal diffractometer with Atlas S2 CCD detector utilizing MoK α radiation provided by the micro-focus X-ray tube and monochromatized by primary mirror optics. The ω rotational scans (frame width 1.0° , counting time 400 s) were adopted for the acquisition of the three-dimensional intensity data. From a total of 1076 reflections, 484 were independent and 342 classified as unique and observed with $I > 3\sigma(I)$. Corrections for

background, Lorentz effects and polarization were applied during the data reduction using the CrysAlis package supplied by Rigaku. The correction for absorption was done in Jana2006 (Petříček *et al.*, 2014) using Gaussian integration ($\mu = 31.20 \text{ mm}^{-1}$). The structure of přibramite was solved independently from earlier structure determinations of structurally related compounds by the charge-flipping algorithm implemented in the SHELXT programme (Sheldrick, 2015). Systematic absences and intensity statistics clearly indicated the centrosymmetric space-group $Pnma$, in line with previous structure

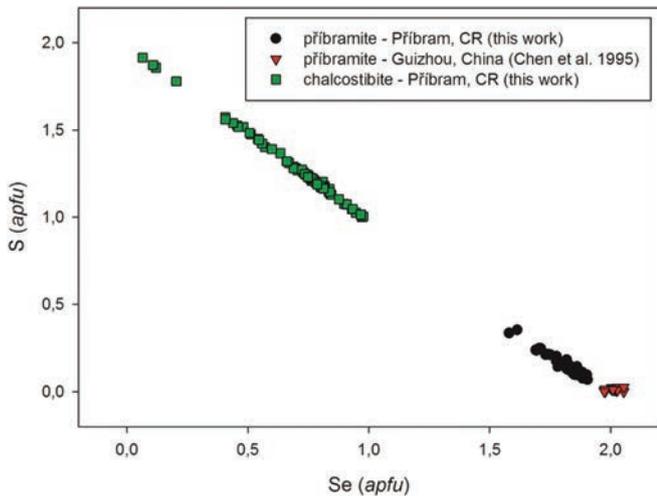


Fig. 4. Plot of Se and S contents (apfu) of přibramite and Se-rich chalcostibite from Příbram and of přibramite from Guizhou (China).

determinations of chalcostibite and emplectite (Kyono & Kimata, 2005) and a synthetic CuSbSe₂ (Imamov *et al.*, 1964; Zhou *et al.*, 2009; Baker *et al.*, 2015). The solution provided a complete structure, which was subsequently refined by full-matrix least-squares using Jana2006 (Petříček *et al.*, 2014) based on F^2 . All atoms were refined with anisotropic atomic displacement parameters. In line with the results from electron microprobe, the S atoms were introduced into the refinement to be substituting at the Se1 and Se2 sites. The refinement of the occupancies returned quite reasonable values similar to those obtained from the microprobe study. Refinement for 27 parameters converged smoothly to the final $R=0.0480$, $wR=0.0850$ for 342 observed reflections with $GOF=1.33$. Details of data collection, crystallographic data and refinement are given in Table 5. Atom coordinates, displacement parameters and tentative bond–valence sums are listed in Table 6; selected interatomic distances are provided in Table 7. The comparison among the known synthetic analogues of přibramite, utilizing the COMPSTRU utility within the BILBAO crystallographic server (Tasci *et al.*, 2012) is given in Table 8.

Based on the current crystal-structure study, we conclude that přibramite is unequivocally isostructural with chalcostibite, emplectite and grundmannite. The structure of přibramite (Fig. 5) contains one Cu, one Sb and two Se sites occupied both by Se and S atoms. According to structure studies on chalcostibite, emplectite (Portheine & Nowacki, 1975; Razmara *et al.*, 1997; Kyono & Kimata, 2005) and grundmannite (Förster *et al.*, 2016a), these structures contain square pyramids of Sb (or Bi) linked to form chains of SbS₂ (or BiS₂) composition along b and CuS₄ tetrahedra forming chains of CuS₃ composition parallel to b . These two types of infinite chains are then linked to form sheets that are stacked perpendicular to c . In case of přibramite, the chalcogen sites are dominantly occupied by Se; therefore, there are SbSe₅ square

Table 4. Calculated X-ray powder diffraction data for přibramite.

h	k	l	d (Å)	I_{rel} (%)	h	k	l	d (Å)	I_{rel} (%)
0	0	2	7.4945	13.0	2	0	8	1.6106	8.3
1	0	2	4.8244	3.9	1	0	9	1.6102	3.2
1	0	3	3.9157	4.4	1	2	5	1.6034	4.8
0	1	1	3.8467	6.1	2	2	3	1.5947	6.1
0	0	4	3.7473	18.9	4	0	2	1.5423	0.9
1	1	1	3.2837	28.8	0	1	9	1.5364	0.5
1	0	4	3.2212	20.3	1	2	6	1.5111	8.3
2	0	0	3.1521	40.1	4	0	3	1.5030	1.0
0	1	3	3.1130	100.0	2	1	8	1.4930	0.5
2	0	1	3.0846	40.4	1	1	9	1.4927	13.1
1	1	2	3.0701	30.0	3	1	6	1.4910	1.2
2	0	2	2.9056	4.7	2	0	9	1.4725	2.9
1	1	3	2.7913	10.3	4	1	0	1.4653	0.9
1	0	5	2.7073	12.2	1	0	10	1.4582	0.6
2	0	3	2.6659	14.9	4	0	4	1.4528	0.9
1	1	4	2.5039	2.5	4	1	2	1.4381	1.6
2	1	0	2.4710	1.4	3	2	2	1.4188	0.5
2	1	1	2.4381	0.6	3	1	7	1.4035	4.0
0	1	5	2.3945	63.1	3	0	8	1.3985	2.8
2	1	2	2.3467	24.0	4	0	5	1.3950	0.8
1	0	6	2.3225	16.1	1	1	10	1.3692	1.3
2	1	3	2.2149	21.9	0	2	8	1.3641	9.3
3	0	1	2.0810	0.7	2	0	10	1.3536	2.3
2	1	4	2.0629	1.2	3	2	4	1.3482	23.0
3	0	2	2.0234	0.7	1	2	8	1.3333	1.1
1	1	6	2.0059	0.6	4	1	5	1.3165	1.8
0	2	0	1.9900	38.2	3	0	9	1.3052	2.8
0	2	2	1.9234	0.9	3	2	5	1.3016	1.7
2	1	5	1.9067	30.0	1	3	1	1.2934	1.6
0	1	7	1.8857	11.5	0	3	3	1.2822	6.4
0	0	8	1.8736	13.6	2	1	10	1.2816	0.5
3	1	1	1.8442	42.0	1	3	2	1.2792	2.0
1	2	2	1.8396	0.7	4	1	6	1.2639	0.9
3	0	4	1.8329	33.0	1	1	11	1.2630	4.6
1	1	7	1.8066	4.2	1	3	3	1.2565	1.1
3	1	2	1.8037	2.5	5	0	1	1.2564	1.5
1	0	8	1.7960	1.4	2	2	8	1.2519	6.9
1	2	3	1.7740	0.9	1	2	9	1.2518	2.7
2	0	7	1.7712	0.5	0	0	12	1.2491	1.5
0	2	4	1.7575	4.2	3	1	9	1.2402	8.4
2	1	6	1.7568	26.4	1	0	12	1.2253	2.8
3	1	3	1.7417	5.5	5	0	3	1.2225	1.0
3	0	5	1.7207	2.1	4	2	2	1.2190	0.9
1	2	4	1.6930	6.0	0	3	5	1.2132	6.8
2	2	0	1.6827	12.2	4	1	7	1.2093	4.8
2	2	1	1.6722	12.8	2	3	2	1.2068	2.8
3	1	4	1.6648	3.3	4	0	8	1.2061	0.7
2	2	2	1.6418	1.8	4	2	3	1.1994	1.0
1	1	8	1.6370	0.6					

Note: calculated diffraction pattern obtained with the atom coordinates reported in Table 6 (only reflection with $I_{rel} \geq 0.5$ are listed).

pyramids and CuSe₄ tetrahedra. An effect of the Se atom, which has a larger ionic radius than S, is well reflected by the increased unit-cell volume (about $\sim 380 \text{ \AA}^3$ in the case of přibramite and $\sim 330 \text{ \AA}^3$ in the case of chalcostibite). This is caused by the larger interatomic distances in the Cu–Se and Sb–Se bond-pairs compared with Cu–S and Sb–S (Table 7). From the comparison of “similarity”

Table 5. Summary of data collection conditions and refinement parameters for přibramite.

Structural formula	CuSb(Se _{1.92} S _{0.08}) ₂
<i>a</i> , <i>b</i> , <i>c</i> [Å]	6.3042(15), 3.980(1), 14.989(4)
<i>V</i> [Å ³]	376.09(2)
<i>Z</i>	4
Space group	<i>Pnma</i>
<i>D</i> _{calc} (g cm ⁻³)	5.996
Temperature	296 K
Wavelength	MoKα, 0.71073 Å
Crystal dimensions	0.029 × 0.022 × 0.013 mm
Collection mode	ω scans to fill a Ewald sphere
Limiting θ angles	3.51–28.43°
Limiting Miller indices	−8 ≤ <i>h</i> ≤ 7, −5 ≤ <i>k</i> ≤ 2, −19 ≤ <i>l</i> ≤ 8
No. of reflections	1076
No. of unique reflections	484
No. of observed reflections (criterion)	342 [<i>I</i> > 3σ(<i>I</i>)]
Absorption correction (mm ⁻¹), method	31.20, Gaussian
<i>T</i> _{min} / <i>T</i> _{max}	0.625/0.799
<i>R</i> _{int}	0.0437
<i>F</i> ₀₀₀	586
Parameters, constraints, restraints	27, 12, 0
<i>R</i> , <i>wR</i> (obs)	0.0480, 0.0850
<i>R</i> , <i>wR</i> (all)	0.0715, 0.0950
GOF (obs, all)	1.33, 1.24
Weighting scheme, weights	σ, 1/(σ ² (<i>F</i>) + 0.0004 <i>F</i> ²)
Δρ _{min} , Δρ _{max} (e Å ⁻³)	−2.69, 2.53

Table 6. Atom positions, displacement parameters (Å²) and bond–valence (BV) sums for přibramite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>BV</i>	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ¹²	<i>U</i> ¹³	<i>U</i> ²³
Sb	0.22467 (19)	0.75	0.56005 (9)	0.0159 (4)	2.587 (8)	0.0089 (7)	0.0187 (8)	0.0202 (7)	0	−0.0018 (6)	0
Se1/S1	1.1264 (3)	0.25	0.67451 (12)	0.0130 (6)	2.016 (5)	0.0084 (10)	0.0149 (11)	0.0156 (11)	0	0.0003 (8)	0
Se2/S2	0.6238 (3)	0.75	0.59467 (13)	0.0146 (7)	1.582 (7)	0.0084 (11)	0.0140 (12)	0.0214 (12)	0	−0.0008 (8)	0
Cu	0.7443 (4)	0.25	0.67081 (17)	0.0238 (9)	0.983 (3)	0.0169 (15)	0.0258 (15)	0.0286 (15)	0	0.0006 (11)	0

Refined occupational factors for Se1/S1 and Se2/S2 atoms are 0.975 (14)/0.025 (14) and 0.945 (14)/0.055 (14), respectively.

Table 7. Interatomic distances (Å) in přibramite, chalcostibite and emplectite.

Přibramite			Chalcostibite*			Emplectite*		
Sb–Se1/S1 ⁱ	2.6996 (15)		Sb–S1 ⁱ	2.567 (2)		Bi–S1 ⁱ	2.648 (4)	
Sb–Se1/S1 ⁱⁱ	2.6996 (15)		Sb–S1 ⁱⁱ	2.567 (2)		Bi–S1 ⁱⁱ	2.648 (4)	
Sb–Se2/S2	2.569 (2)		Sb–S2	2.427 (3)		Bi–S2	2.528 (7)	
Sb–Se2/S2 ⁱⁱⁱ	3.2020 (16)		Sb–S2 ⁱⁱⁱ	3.115 (2)		Bi–S2 ⁱⁱⁱ	3.153 (5)	
Sb–Se2/S2 ^{iv}	3.2020 (16)		Sb–S2 ^{iv}	3.115 (2)		Bi–S2 ^{iv}	3.153 (5)	
Cu–Se1/S1	2.409 (3)		Cu–S1	2.297 (4)		Cu–S1	2.303 (7)	
Cu–Se1/S1 ^v	2.435 (3)		Cu–S1 ^v	2.316 (4)		Cu–S1 ^v	2.318 (7)	
Cu–Se2/S2	2.4163 (19)		Cu–S2	2.331 (2)		Cu–S2	2.345 (4)	
Cu–Se2/S2 ^{vi}	2.4163 (19)		Cu–S2 ^{vi}			Cu–S2 ^{vi}		

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*−1, *y*+1, *z*; (iii) −*x*+1, *y*−1/2, −*z*+1; (iv) −*x*+1, *y*+1/2, −*z*+1; (v) *x*+1/2, −*y*+1/2, −*z*+3/2; (vi) *x*, *y*+1, *z*.

* Data from Kyono & Kimata (2005).

Table 8. Measures of similarity of přibramite and synthetic CuSbSe₂ phases.

Reference	<i>d</i> _{av}	Δ	<i>S</i>
CuSbSe ₂ (Imamov <i>et al.</i> , 1964)	0.085	0.032	0.0092
CuSbSe ₂ (Zhout <i>et al.</i> , 2009)	0.004	0.002	0.0007
CuSbSe ₂ (Baker <i>et al.</i> , 2015)	0.030	0.008	0.0004

Measures defined after: Orobengoa *et al.* (2009) (*d*_{av}); Bergerhoff *et al.* (1999) (Δ) and Capillas *et al.* (2007) (*S*).

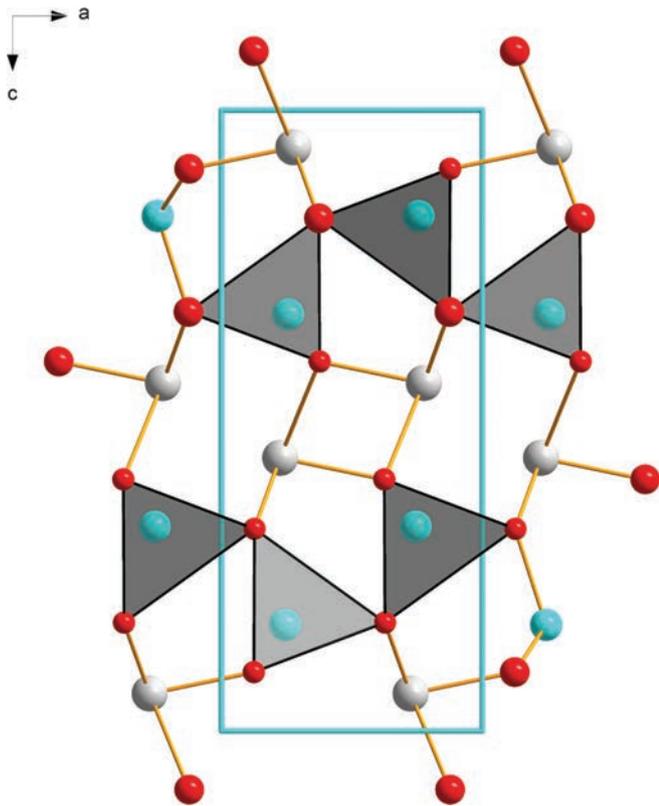


Fig. 5. Crystal structure of přibramite viewed along *b* showing Cu (Se/S)₄ tetrahedra (grey) and Sb – (Se/S) bonds. In the space between the Sb atoms the lone electron pair is localized. Unit-cell edges are highlighted in blue thick line.

values provided in Table 8, it is clear that přibramite is unequivocally isostructural with synthetic CuSbSe₂ phases (Imamov *et al.*, 1964; Zhou *et al.*, 2009; Baker *et al.*, 2015).

6. Relationship to the known species

As already mentioned, přibramite is a selenium analogue of chalcostibite. It is a new member of the emplectite isotypic series (Močlo *et al.*, 2008) along with emplectite, chalcostibite and grundmannite. Comparative data for members of the emplectite series are given in Table 9. A chemically identical unnamed mineral phase was previously reported from China (Chen *et al.*, 1995), but this phase has never been submitted to the IMA approval process.

The synthetic analogue of chalcostibite has been prepared by solvothermal reaction by Zhou *et al.* (2009). A sealed tube containing Cu, Sb, Se, H₂O and dap was heated at 160 °C for 10 days. The structural behaviour of synthetic CuSbSe₂ at high pressure (up to 80 GPa) was studied by Baker *et al.* (2015), who observed a structural transformation from the ambient orthorhombic structure to a triclinic-type structure with space group *P1* in the range 8–10 GPa.

Table 9. Comparative data for the members of emplectite series and hansblockite.

	Přibramite	Přibramite	Přibramite	Chalcostibite	Emplectite	Grundmannite	Hansblockite
Locality Reference	Přibram, CZ This work	Guizhou province, China Chen <i>et al.</i> (1995)	Synt. Zhou <i>et al.</i> (2009)	Synt. Razmara <i>et al.</i> (1997)	Synt. Razmara <i>et al.</i> (1997)	El Dragón, BOL Förster <i>et al.</i> (2016a)	El Dragón, BOL Förster <i>et al.</i> (2016b)
Ideal composition	CuSbSe ₂	CuSbSe ₂	CuSbSe ₂	CuSbSe ₂	CuBiSe ₂	CuBiSe ₂	(Cu,Hg)(Bi,Pb)Se ₂
Empirical composition	(Cu _{1.03} Fe _{0.01}) _{1.04} (Sb _{0.98} As _{0.03}) _{1.01} (Se _{1.78} S _{0.18}) _{1.96}	(Cu _{0.95} Hg _{0.03}) _{0.98} (Sb _{0.97} As _{0.03}) _{1.00} (Se _{2.01} S _{0.01}) _{2.02}	CuSbSe ₂	CuSbSe ₂	Cu _{0.99} (Bi _{0.91} Pb _{0.02}) _{0.93} Se _{2.08}	(Cu _{0.68} Hg _{0.27} Ag _{0.03} Ni _{0.01}) _{0.99} (Bi _{0.69} Pb _{0.31}) _{1.00} Se _{2.01}	
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>P2₁/c</i>
<i>a</i> [Å]	6.3042 (15)	6.299 (2)	6.0160 (1)	6.1413 (5)	6.6362 (5)	6.853 (1)	6.853 (1)
<i>b</i>	3.980 (1)	3.9734 (14)	3.7968 (6)	3.9191 (5)	4.2581 (3)	7.635 (1)	7.635 (1)
<i>c</i>	14.989 (4)	15.005 (5)	14.499 (3)	14.524 (2)	15.3691 (9)	7.264 (1)	7.264 (1)
β (°)	90	90	90	90	90	97.68 (1)	97.68 (1)
<i>V</i>	376.09 (2)	375.5 (2)	331.176 (7)	349.588 (5)	434.04 (2)	376.66 (9)	376.66 (9)
<i>Z</i>	4	4	4	4	4	4	4
Strongest lines in powder pattern*	3.152/40 3.113/100 3.085/40 2.395/63 1.844/42	3.150/40 3.111/100 3.082/40 2.395/65 1.842/42	3.135/100 3.105/78 3.008/62 2.986/95 2.305/58	3.221/100 3.126/78 3.071/71 3.046/95 2.334/53	3.490/49 3.318/57 3.275/100 2.492/41 2.331/45	3.97/90 3.100/40 2.986/100 2.808/50 2.620/50	

* Calculated from the structure data.

7. Remarks to origin of the selenium mineralization

The new selenide, přibramite, is part of an extraordinary diverse Se mineralization in Příbram, which is – with 22 known selenide species (Škácha, 2015) – one of the richest selenide localities in the world. One of the main reasons for the species diversity of the studied Se mineralization is the crystallization of a part of selenides from late hydrothermal solutions containing remobilized Sb, As, Cu, Hg, Ag and Fe.

Crystallization of the first selenides started after formation of collomorph uraninite (pitchblende), with Pb and Hg selenides (clausthalite and tiemannite) and eucairite. This event was followed by a Cu–Se mineralization represented by berzelianite, umangite, klockmannite, athabascaite and bellidoite. Minerals of the tetrahedrite group (hakite and giraudite) are younger than Cu selenides in most cases. Přibramite is the result of the youngest mobilization processes together with antimonselite, hakite, chaméanite and other selenides. The temperature of this hydrothermal solution was about 100 °C, according to the presence of umangite in the association. It is in accordance with the homogenization temperatures of the fluid inclusions determined in the Příbram uranium district (Žák & Dobeš, 1991). Considering the absence of krut'aite in the association and according to the phase diagram for the temperature of 100 °C (Simon *et al.*, 1997), we can expect the origin of the Se mineralization below the stability field of krut'aite, *i.e.* at $\log f_{\text{Se}_2} < -12$.

The presence of selenides is typical for most of the Czech hydrothermal U vein-type deposits of Permo–Carboniferous age developed in various geological environments. Therefore, we conclude that the selenium is derived from the primary hydrothermal solutions, not from the surroundings rocks through mobilization.

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