

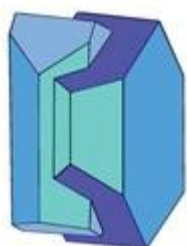
Tetrahedrite-(Hg), a new “old” member of the tetrahedrite group

CRISTIAN BIAGIONI^{1*}, JIŘÍ SEJKORA², SILVIA MUSETTI¹,
DALIBOR VELEBIL², and MARCO PASERO¹

¹*Dipartimento di Scienze della Terra, Università di Pisa, Via Santa Maria 53, 56126 Pisa, Italy*

²*Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193 00, Praha 9, Czech Republic*

*e-mail address: cristian.biagioni@unipi.it



Mineralogical Society

This is a 'preproof' accepted article for Mineralogical Magazine. This version may be subject to change during the production process.

DOI: 10.1180/mgm.2020.36

ABSTRACT

Tetrahedrite-(Hg), $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$, has been approved as a new mineral species using samples from Buca della Vena mine (hereafter BdV), Italy, Jedová hora (Jh), Czech Republic, and Rožňava (R), Slovakia. It occurs as anhedral grains or as tetrahedral crystals, black in color, with metallic luster. At BdV it is associated with cinnabar and chalcostibite in dolomite veins. At Jh, tetrahedrite-(Hg) is associated with baryte and chalcopyrite in quartz-siderite-dolomite veins; at R it is associated with quartz in siderite-quartz veins. Tetrahedrite-(Hg) is isotropic, greyish-white in color, with creamy tints. Minimum and maximum reflectance data for COM wavelengths in air (BdV sample) are [λ (nm): R (%)]: 470: 32.5; 546: 32.9; 589: 33.2; 650: 30.9. Chemical formulae of the studied samples, recalculated on the basis of 4 (As + Sb + Bi) atoms per formula unit, are: $(\text{Cu}_{9.44}\text{Ag}_{0.07})_{\Sigma 9.51}(\text{Hg}_{1.64}\text{Zn}_{0.36}\text{Fe}_{0.06})_{\Sigma 2.06}\text{Sb}_4(\text{S}_{12.69}\text{Se}_{0.01})_{\Sigma 12.70}$ (BdV), $\text{Cu}_{9.69}(\text{Hg}_{1.75}\text{Fe}_{0.25}\text{Zn}_{0.06})_{\Sigma 2.06}(\text{Sb}_{3.94}\text{As}_{0.06})\text{S}_{12.87}$ (Jh), and $(\text{Cu}_{9.76}\text{Ag}_{0.04})_{\Sigma 9.80}(\text{Hg}_{1.83}\text{Fe}_{0.15}\text{Zn}_{0.10})_{\Sigma 2.08}(\text{Sb}_{3.17}\text{As}_{0.58}\text{Bi}_{0.25})\text{S}_{13.01}$ (R). Tetrahedrite-(Hg) is cubic, $I\bar{4}3m$, with $a = 10.5057(8)$ Å, $V = 1159.5(3)$ Å³, $Z = 2$ (BdV). Unit-cell parameters for the other two samples are $a = 10.4939(1)$ Å, $V = 1155.61(5)$ Å³ (Jh) and $a = 10.4725(1)$ Å, $V = 1148.55(6)$ Å³ (R). The crystal structure of tetrahedrite-(Hg) has been refined by single-crystal X-ray diffraction data to a final $R_1 = 0.019$ on the basis of 335 reflections with $F_o > 4\sigma(F_o)$ and 20 refined parameters. Tetrahedrite-(Hg) is isotopic with other members of the tetrahedrite group. Mercury is hosted at the tetrahedrally coordinated $M(1)$ site, along with minor Zn and Fe. The occurrence of Hg at this position agrees both with the relatively large $M(1)$ –S(1) bond distance (2.393 Å) and the refined site scattering. Previous occurrences of mercurian tetrahedrite and tetrahedrite-(Hg) are reviewed, and its relations with other Hg sulfosalts are discussed.

Keywords: tetrahedrite-(Hg); new mineral; sulfosalt; copper; mercury; antimony; crystal structure.

Introduction

Tetrahedrite group minerals are the most common sulfosalts in different kinds of hydrothermal ore deposits. They form a complex isotopic series, with formula $M^{(2)}A_6^{M(1)}(B_4C_2)^{X(3)}D_4^{S(1)}Y_{12}^{S(2)}Z$, characterized by homo- and heterovalent substitutions, representing an interesting link between mineralogy and ore geochemistry (Biagioni *et al.*, 2020).

Within the tetrahedrite group, five different series have been identified: tetrahedrite, tennantite, freibergite, hakite, and giraudite series. Other unassigned members (e.g., rozhdstvenskayaite, goldfieldite) belong to this group. Biagioni *et al.* (2020), on the basis of literature data, defined thirty-two potential end-member compositions within the tetrahedrite group; among them, eleven can be considered as valid species, whereas the remaining phases have to be officially approved by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association (IMA-CNMNC).

The most common mineral species within the tetrahedrite group belong to the tetrahedrite and tennantite series, characterized by $B = Cu$, $D = Sb$, $Y = S$, and $B = Cu$, $D = As$, $Y = S$, respectively. Within these two series, the only approved species have $C = Zn$ and Fe , i.e., tetrahedrite-(Fe), tetrahedrite-(Zn), tennantite-(Fe), and tennantite-(Zn). However, the critical examination of available literature reveals that other tetrahedrite and tennantite series minerals, characterized by different C constituents, have been reported. Among them, tetrahedrite having $C = Hg$, i.e., mercurian tetrahedrite, is widely known, sometimes referred to with the term “schwazite” (e.g., Arlt and Diamond, 1998). Likely, the more complete description of “schwazite” is that reported by Karanović *et al.* (2003) using a specimen from Dragodol, Donja Trešnjica district, Serbia. However, their chemical data, collected using energy dispersive spectrometry (EDS) mode, were of low quality, contrasting with the goodness of their crystallographic data. Foit and Hughes (2004) studied the structural variations of a solid solution between tetrahedrite-(Zn) and tetrahedrite-(Hg) from the Spring Creek Claims, Harney County, Oregon, U.S.A.; the Hg-richest sample has chemical composition $Cu_6(Cu_{4.08}Hg_{1.15}Zn_{0.67}Fe_{0.03}Co_{0.01})_{\Sigma 5.94}(Sb_{2.64}As_{1.36})_{\Sigma 4.00}S_{13}$. In either case, type material could not be located.

Tetrahedrite-(Hg) was identified also at the Buca della Vena mine, Apuan Alps, Tuscany, Italy, and its occurrence and crystal-chemistry has been recently characterized. In addition to other two well-characterized occurrences from the Jedová hora deposit, Czech Republic, and the Rožňava ore field, Slovakia, these new data allowed the submission of a formal proposal to the IMA-CNMNC, in order to give an official certificate of birth to tetrahedrite-(Hg). The mineral and its name have been approved (IMA 2019-003). Holotype material is deposited in the mineralogical collections of the Museo di Storia Naturale, Università di Pisa, Via Roma 79, Calci (Pisa), Italy, catalogue number 19895. Both cotype samples are deposited in the mineralogical collection of the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic, catalogue numbers: P1N 9961 (Jedová hill) and P1N 33538 (Rožňava).

In this paper, the description of tetrahedrite-(Hg) is given, along with a brief history of previous studies on this mineral species.

Occurrence and physical properties

Tetrahedrite-(Hg) was found in the pyrite ± baryte ± iron-oxide ore deposit of Buca della Vena mine (latitude 43°59'55''N, longitude 10°18'37''E), Stazzema, Apuan Alps, Lucca Province, Tuscany, Italy. The ore bodies are located at the contact between a metavolcanic-metasiliciclastic sequence belonging to the Paleozoic basement of the Apuane Unit and the Triassic metadolostone of the Grezzoni Formation (Benvenuti *et al.*, 1986). Their textural and mineralogical features are affected by the greenschist facies metamorphism of Alpine age characterizing all the deposits of the southern Apuan Alps (e.g., D'Orazio *et al.*, 2017). Ore bodies have a simple primary mineralogy, basically formed by baryte, magnetite, hematite, and pyrite. However, the Buca della Vena mine is renowned among mineralogists and mineral collectors for several very rare mineral species here described since the end of the 1970s. Among them, twelve have this mine as their type locality: allanite-(La), apuanite, bohusslavite, dessauite-(Y), mapiquiroite, marrucciite, oxycalcioroméite, pellouxite, pillaitite, rouxelite, scainiite, and versiliaite. Tetrahedrite-(Hg) is the thirteenth new mineral species found at this locality.

Tetrahedrite-(Hg) was identified in samples collected in an exploitation void known, among mineral collectors, as the Sala del Castello. Here, a meter-sized metadolostone lens occurs embedded in microcrystalline baryte+iron-oxides and it is cut by several sets of veins and fractures. Tetrahedrite-(Hg) occurs as anhedral grains or equant crystals, up to 0.2 mm in size (Fig. 1a), black in color and with black streak. Luster is metallic. The Mohs hardness may be close to 3½-4, in agreement with other members of the tetrahedrite group and with the sample of mercurian tetrahedrite from Moschellandsberg (Germany), having a Vickers Hardness of 236-277 kg/mm² (Criddle and Stanley, 1993). Tetrahedrite-(Hg) is brittle, with an indistinct cleavage and a conchoidal fracture. Density was not measured, owing to the small amount of available material; on the basis of the empirical formula and the single-crystal unit-cell parameters, the calculated density is 5.326 g/cm³.

In reflected light, tetrahedrite-(Hg) is isotropic. It is greyish-white, with creamy tints. Internal reflections were not observed. Reflectance values, measured in air using a spectrophotometer MSP400 Tidas at Leica microscope, with a 100 × objective, are given in Table 1 and shown in Figure 2.

Tetrahedrite-(Hg) is associated with cinnabar, as small µm-sized equant deep red crystals, and chalcocite, as striated tabular prismatic crystals, up to 0.2 mm in length, in vugs of dolomite veins. It is worth noting that other Hg-minerals have been identified at the same occurrence: coloradoite (Dini and Orlandi, 1995), rouxelite (Orlandi *et al.*, 2005), marrucciite (Orlandi *et al.*, 2007), tiemannite and metacinnabar (Biagioni and Orlandi, 2009). The crystallization of tetrahedrite-(Hg) is related to the circulation of hydrothermal fluids during the Tertiary Alpine tectono-metamorphic events.

During this study, in addition to the sample from the Buca della Vena mine, two other samples were examined. Tetrahedrite-(Hg) was identified from the Jedová hora deposit (49°47'31"N, 13°53'13"E), Hořovice, Central Bohemian Region, Czech Republic (Fig. 1b), and from the Rožňava ore field (48°40'37"N, 20°32'29"E), Košice Region, Slovakia (Fig. 1c). Sample from the Jedová hora deposit (vertical fissures with hydrothermal mineralization - quartz, siderite, dolomite, pyrite, baryte, cinnabar, and tetrahedrite-(Hg) - intersected two stratiform bodies of iron ores - siderite, hematite) is represented by groups of imperfect

crystals of tetrahedrite-(Hg) up to 4 mm in size on baryte, in association with chalcopyrite (sample $8 \times 4.5 \times 2.5$ cm). Sample from the Rožňava ore field probably came from upper part of Mária vein (hydrothermal siderite - quartz vein with chalcopyrite, pyrite, and tetrahedrite with various Hg contents) and it is represented by massive tetrahedrite-(Hg) aggregates up to 10 cm in association with quartz (sample $11 \times 6 \times 7$ cm). It is worth noting that tetrahedrite group minerals from the Rožňava ore field are typically Hg-poor. However, the studied sample came to the museum in 1941 from the well-known and careful scientist Radim Nováček (1905–1942), who studied this sample publishing his results (Nováček, 1942) (see Figure S1, available as Supplementary Material). Optical properties of both samples are similar to those reported for the Italian type material and the reflectance values are given in Table 1 and shown in Figure 2.

Chemical data

Quantitative chemical analyses were carried out using a Cameca SX 100 electron microprobe at the National Museum of Prague (Czech Republic). Experimental conditions were: WDS mode, accelerating voltage 25 kV, beam current 20 nA, beam diameter 1 μ m. Standards (element, emission line) were: pyrite (Fe $K\alpha$), chalcopyrite (Cu $K\alpha$, S $K\alpha$), ZnS (Zn $K\alpha$), NiAs (As $L\alpha$), Ag metal (Ag $L\alpha$), Sb₂S₃ (Sb $L\alpha$), PbSe (Se $L\alpha$), HgTe (Hg $M\alpha$), and Bi₂Se₃ (Bi $M\alpha$). Matrix correction by PAP software (Pouchou and Pichoir, 1985) was applied to the data. Chemical data for tetrahedrite-(Hg) from Buca della Vena mine, along with samples from Jedová hora and Slovakia, are given in Table 2. The empirical formula of tetrahedrite-(Hg), based on (As + Sb + Bi) = 4 atoms per formula unit (apfu), are:

- i) Buca della Vena: $(\text{Cu}_{9.44}\text{Ag}_{0.07})_{\Sigma 9.51}(\text{Hg}_{1.64}\text{Zn}_{0.36}\text{Fe}_{0.06})_{\Sigma 2.06}\text{Sb}_4(\text{S}_{12.69}\text{Se}_{0.01})_{\Sigma 12.70}$;
- ii) Jedová hora: $\text{Cu}_{9.69}(\text{Hg}_{1.75}\text{Fe}_{0.25}\text{Zn}_{0.06})_{\Sigma 2.06}(\text{Sb}_{3.94}\text{As}_{0.06})\text{S}_{12.87}$;
- iii) Rožňava: $(\text{Cu}_{9.76}\text{Ag}_{0.04})_{\Sigma 9.80}(\text{Hg}_{1.83}\text{Fe}_{0.15}\text{Zn}_{0.10})_{\Sigma 2.08}(\text{Sb}_{3.17}\text{As}_{0.58}\text{Bi}_{0.25})\text{S}_{13.01}$.

Taking into account the partitioning of Cu and Ag between A and B constituents, the chemical formulae can be rewritten as:

- i) Buca della Vena: $(\text{Cu}_{5.50}\text{Ag}_{0.07})_{\Sigma 5.57}(\text{Cu}_{3.94}\text{Hg}_{1.64}\text{Zn}_{0.36}\text{Fe}_{0.06})_{\Sigma 6.00}\text{Sb}_4(\text{S}_{12.69}\text{Se}_{0.01})_{\Sigma 12.70}$;
- ii) Jedová hora: $\text{Cu}_{5.75}(\text{Cu}_{3.94}\text{Hg}_{1.75}\text{Fe}_{0.25}\text{Zn}_{0.06})_{\Sigma 6.00}(\text{Sb}_{3.94}\text{As}_{0.06})\text{S}_{12.87}$;
- iii) Rožňava: $(\text{Cu}_{5.84}\text{Ag}_{0.04})_{\Sigma 5.88}(\text{Cu}_{3.92}\text{Hg}_{1.83}\text{Fe}_{0.15}\text{Zn}_{0.10})_{\Sigma 6.00}(\text{Sb}_{3.17}\text{As}_{0.58}\text{Bi}_{0.25})\text{S}_{13.01}$.

The studied specimens show a deficit of (Cu + Ag) (up to 0.43 apfu in the sample from Buca della Vena mine), and two samples also a slight S deficit (up to 0.30 apfu). The deficit of (Cu+Ag) is discussed below.

The end-member formula of tetrahedrite-(Hg) is $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$ ($Z = 2$), corresponding to (in wt%): Cu 32.75, Hg 20.67, Sb 25.10, S 21.48, total 100.00.

X-ray Crystallography

X-ray powder diffraction pattern of tetrahedrite-(Hg) from the Buca della Vena mine (Table 3) was collected using a 114.6 mm Gandolfi camera and Ni-filtered Cu $K\alpha$ radiation (Department of Earth Sciences, University of Pisa, Italy). Unit-cell parameters were refined on the basis of 18 unequivocally indexed reflections using the software UnitCell (Holland and Redfern, 1997): $a = 10.5072(6)$ Å, $V = 1160.0(2)$ Å³. X-ray powder diffraction data of both cotype samples were recorded using a Bruker D8 Advance diffractometer equipped with

solid-state LynxEye detector and secondary monochromator producing Cu $K\alpha$ radiation housed at the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic. The instrument was operating at 40 kV and 40 mA. In order 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 $3\text{--}75^\circ 2\theta$, step 0.01° and counting time of 20 s per step (total duration of experiment was ca. 3 days). The positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function of the ZDS program package (Ondruš, 1993) and the unit-cell parameters were refined by the least-squares program of Burnham (1962). Unit-cell parameters, refined from X-ray powder diffraction data given in Table 3, are $a = 10.4939(1) \text{ \AA}$, $V = 1155.61(5) \text{ \AA}^3$ for the sample from Jedová hora (Czech Republic) and $a = 10.4725(1) \text{ \AA}$, $V = 1148.55(6) \text{ \AA}^3$ for the sample from Rožňava (Slovakia).

For the refinement of the crystal structure, X-ray diffraction intensity data were collected on tetrahedrite-(Hg) from Buca della Vena mine using a Bruker Smart Breeze diffractometer (50 kV, 30 mA) equipped with a Photon II CCD detector and graphite-monochromatized Mo $K\alpha$ radiation. The detector-to-crystal distance was set at 50 mm. Data were collected using ω scan mode in 0.5° slices, with an exposure time of 10 s per frame, and they were corrected for Lorentz and polarization factors as well as for absorption using the software package Apex3 (Bruker AXS Inc., 2016). The refined unit-cell parameter is $a = 10.5057(8) \text{ \AA}$, $V = 1159.5(3) \text{ \AA}^3$; space group $I\text{-}43m$. The crystal structure of tetrahedrite-(Hg) was refined using Shelxl-2018 (Sheldrick, 2015) starting from the structural model of tetrahedrite given by Johnson and Burnham (1985). The occurrence of racemic twin was modelled, with a ratio between the two components of 94(3):6(3). The following neutral scattering curves, taken from the *International Tables for Crystallography* (Wilson, 1992) were used: Cu at $M(2)$, Cu vs Hg at $M(1)$, Sb at $X(3)$, S at $S(1)$ and $S(2)$ sites. The anisotropic structural model converged to $R_1 = 0.0190$ for 335 reflections with $F_o > 4\sigma(F_o)$ and 20 refined parameters. Details of data collection and refinement are given in Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 5. Table 6 reports selected bond distances. Finally, Table 7 gives the bond-valence calculations obtained using the bond-valence parameters of Brese and O’Keeffe (1991).

Results and discussion

Crystal structure description

The crystal structure of tetrahedrite-(Hg) agrees with the general features of the members of the tetrahedrite isotypic group. It can be described as a collapsed sodalite-like framework of corner-sharing $M(1)$ -centered tetrahedra, with cages hosting $S(2)$ -centered $M(2)$ -octahedra and four $X(3)S(1)_3$ trigonal pyramids (e.g., Johnson *et al.*, 1988).

In the studied sample, the triangularly coordinated $M(2)$ site has an average bond distance of 2.262 \AA . Refined site scattering, as well as the calculated bond-valence sum (BVS) of 1.02 valence units (v.u.), agree with the full occupancy at this position by Cu. However, electron microprobe analysis suggest the occurrence of minor vacancy (0.43 apfu). This may due to some analytical problems, such as the migration of Cu under the electron beam. However, this phenomenon was reported only for Cu-excess tetrahedrites, both natural and synthetic (e.g., Lind and Makovicky, 1982). If minor vacancy is real, this may be coupled

with the partial oxidation of Cu^+ to Cu^{2+} at the $M(1)$ site, giving an excess of divalent metals, as observed in pošepnýite (Škácha *et al.*, 2020). It is not unlikely that such a minor amount of vacancy could be overlooked, because the overestimated site scattering (29 electrons vs. 27.1 electrons, as calculated from chemical data) would be partially masked by the relatively large U_{eq} value due to the positional disorder affecting the $M(2)$ site, that is actually split into two flat pyramidal sub-sites, as previously reported by other authors (e.g., Andreasen *et al.*, 2008; Welch *et al.*, 2018). The splitting of this position did not improve significantly the crystal structure refinement of tetrahedrite-(Hg) and consequently an unsplit model was preferred.

The tetrahedrally coordinated $M(1)$ site has an average bond distance of 2.391 Å. Assuming the site population ($\text{Cu}_{0.66}\text{Hg}_{0.28}\text{Zn}_{0.05}\text{Fe}_{0.01}$), based on chemical data, the theoretical bond distance at $M(1)$ is 2.393 Å, as obtained using the atomic radii proposed by Johnson *et al.* (1988). The refined site scattering (44.3 electrons per site) is in accord with the site scattering calculated from the site population (43.0 electrons). Bond-valence sums show an overbonding at $M(1)$. This is an usual feature agreeing with previous studies on sulfosalts having tetrahedrally coordinated Hg (e.g., arsiccioite, $\text{AgHg}_2\text{TlAs}_2\text{S}_6$ – Biagioni *et al.*, 2014c) and it is possibly due to the inaccuracy of the bond parameters for the Hg–S pair or to a small shift of the S positions when the $M(1)$ site is occupied by Hg.

The $X(3)$ site has an average bond distance of 2.447 Å, fully consistent with a pure Sb occupancy, as indicated by the BVS of 3.03 v.u.

$S(1)$ site is four-fold coordinated, being bonded to two $M(1)$, one $M(2)$, and one $X(3)$. Its BVS is 2.16 v.u. $S(2)$ is octahedrally coordinated by atoms hosted at $M(2)$ sites, with BVS of 2.16 v.u. No hints of vacancies at $S(2)$ were observed during the structure refinement.

Relationships between geometrical features and chemistry

Several authors proposed some relationships between chemistry and geometrical features of tetrahedrite group minerals (e.g., Charlat and Lévy, 1975; Mozgova and Tsepina, 1983; Johnson *et al.*, 1987; Makovicky and Karup-Møller, 1994). Johnson *et al.* (1987) proposed a relation between the unit-cell parameter and chemistry: a (Å) = $10.379 + 0.082(\text{Ag}) - 0.01(\text{Ag}^2) - 0.009(\text{Cu}^*) + 0.066(\text{Hg}) - 0.038(\text{As}) + 0.144(\text{Bi})$, where $\text{Cu}^* = 2.0 - (\text{Fe} + \text{Zn} + \text{Hg} + \text{Cd})$ and the coefficient of the Hg term is corrected according to Di Benedetto *et al.* (2002). As the sum of Fe, Zn, and Hg is slightly larger than 2 apfu in all the three studied samples, the term Cu^* was neglected. Applying such a relation to the three studied samples, the unit-cell parameters $a = 10.493$, 10.492 , and 10.518 Å can be calculated for tetrahedrite-(Hg) from Buca della Vena, Jedová hora, and Rožňava, respectively. These values have to be compared with the observed ones, i.e., $a = 10.506$ Å (Buca della Vena), 10.494 Å (Jedová hora), and 10.472 Å (Rožňava).

The three studied samples have different compositions of the tetrahedral $M(1)$ site. Indeed, whereas among divalent constituents the main Hg substituent in the sample from Buca della Vena is Zn^{2+} [$\text{Zn}/(\text{Fe} + \text{Zn} + \text{Hg}) = 0.17$], with negligible Fe (less than 0.10 apfu), the samples from Jedová hora and Rožňava have $\text{Fe} > \text{Zn}$ [$\text{Zn}/(\text{Fe} + \text{Zn} + \text{Hg}) = 0.03$ and 0.05 , respectively]. For this reason, the relationship between the unit-cell parameter and the Zn and Hg content proposed by Karup-Møller and Makovicky (2004) can be applied to the sample from Buca della Vena: a (Å) = $0.0293 \text{ Zn (apfu)} + 0.096 \text{ Hg (apfu)} + 10.3245$. The calculated

value, 10.492 Å, is close to the value obtained through the relationship of Johnson *et al.* (1987), and slightly smaller than the observed value (10.506 Å).

Taking into account the crystal radii proposed by Johnson *et al.* (1988) and the site population given above, the M(1)–S(1) bond distance in the sample from Buca della Vena should be 2.393 Å, in perfect agreement with the observed value, 2.393 Å. Moreover, Foit and Hughes (2004) proposed a linear relationship between Hg content and the M(1)–S(1) bond distance. According to their relation, the M(1)–S(1) distance in tetrahedrite-(Hg) from Buca della Vena mine should be 2.385 Å, slightly shorter than the observed value, likely as a consequence of the occurrence of minor Zn and Fe replacing Cu. The observed value is comparable with the M(1)–S(1) distance reported by Karanović *et al.* (2004) in tetrahedrite-(Hg) from Dragodol (Serbia), 2.382 Å, and in the only Hg-dominant sample studied by Foit and Hughes (2004), 2.371 Å. These values are definitely longer than those reported in tetrahedrite-(Fe) and tetrahedrite-(Zn) (e.g., 2.342 Å – Wuensch, 1964).

Previous findings of tetrahedrite-(Hg): a short review

The occurrence of mercurian tetrahedrite, in some cases corresponding to tetrahedrite-(Hg), has been known since the 19th Century (e.g., Breithaupt, 1816, in Palache *et al.*, 1951; Kersten, 1843; Rath, 1855). Mercurian tetrahedrite is widely known with the term “schwazite” (sometimes misspelled as “schwartzite”), from the locality Schwaz, Tyrol, Austria. Indeed, Weidenbusch (1849) reported the analysis of a tetrahedrite group mineral from this locality having 15.9 wt% Hg and corresponding to the formula $\text{Cu}_{9.9}\text{Hg}_{1.4}\text{Fe}_{0.7}\text{Zn}_{0.4}\text{Sb}_{3.2}\text{S}_{13}$. The name “schwazite” was first introduced by Kenngott (1853). Arlt and Diamond (1998) reviewed the previous occurrences of “schwazite”, showing that none of the authors involved in the study of “schwazite” from Schwaz, following Weidenbusch (1849), found Hg content higher than 5.4 wt%. Moreover, they reported new chemical data, finding up to 9.4 wt% Hg, corresponding to 0.82 Hg apfu. Therefore, at Schwaz there are no samples having Hg as dominant divalent cation (Arlt and Diamond, 1998), discrediting the name “schwazite” (Biagioni *et al.*, 2020).

Several other occurrences of mercurian tetrahedrite are known. Mozgova *et al.* (1979) reviewed the occurrences of Hg-bearing tetrahedrites, identifying four possible kinds of occurrence. They listed i) cinnabar deposits, ii) Hg-Sb deposits, iii) Hg tetrahedrite-tennantite deposits, and iv) low-Hg tetrahedrites in Sb-W, Pb-Ag, and Au deposits. Moreover, Mozgova and Tsepın (1983) reported a dozen deposits where chemical analyses of tetrahedrite- and tennantite-series minerals gave Hg more than 18 wt% (up to 21.8 wt%) and (Fe+Zn) are less than 1 wt%. However, not all of the Hg-bearing tetrahedrite samples reported in literature can be classified as tetrahedrite-(Hg). For instance, Atanasov (1975) reported electron-microprobe and X-ray powder diffraction data of a sample from the Chiprovtsi Pb-Ag deposit, Western Stara-Planina mountains, Bulgaria. The average of three spot analyses gives the chemical formula $\text{Cu}_{6.88}\text{Ag}_{2.96}(\text{Hg}_{1.83}\text{Zn}_{0.17})_{\Sigma 2.00}(\text{Sb}_{3.36}\text{As}_{0.71})_{\Sigma 4.07}\text{S}_{13.09}$. It is worth noting that if Cu is partitioned between M(1) and M(2), the possible dominance of Ag at M(2) results, *i.e.*, $(\text{Ag}_{2.96}\text{Cu}_{2.88})_{\Sigma 5.84}$. The classification of this sample, without further data, is uncertain, being classifiable either as an Ag-rich variety of tetrahedrite-(Hg) or as argentotetrahedrite-(Hg). Some true tetrahedrite-(Hg) can be found in literature. Criddle and Stanley (1993) reported optical data for a sample of tetrahedrite-(Hg) from Moschellandsberg, Rhineland-Palatinate,

Germany, having chemical composition $\text{Cu}_{9.97}(\text{Hg}_{1.73}\text{Fe}_{0.17})_{\Sigma 1.90}\text{Sb}_{4.12}\text{S}_{13.64}$. Foit and Ulbricht (2001) recorded up to 2.02 Hg apfu in samples from the epithermal deposits of the Steens and Pueblo mountains, Harney County, Oregon, USA, whereas Grammatikopoulos *et al.* (2005) measured up to 1.97 Hg apfu in Ag-bearing samples from the Eskay Creek deposit, British Columbia, Canada. Velebil (2014) described the occurrence of tetrahedrite-(Hg) from some Czech and Slovak ore deposits, *i.e.*, the Jedová hora deposit (1.46 - 1.73 apfu Hg) from the Czech Republic, and Rudňany (1.47 - 1.79 apfu Hg), Rožňava (1.65 apfu Hg) and Nižná Slaná (1.07 - 1.39 apfu Hg), all in the Slovak Republic.

The first crystallographic study was reported by Kalbskopf (1971) who proposed that Hg occurs at the tetrahedral position in mercurian tetrahedrite from Rožňava, ČSSR (right Rožňava, now Slovak Republic). However, no quantitative chemical data and atomic coordinates were given. The crystal structure of tetrahedrite-(Hg) was solved by Kaplunnik *et al.* (1980). Unfortunately, some very important details were misinterpreted or missing. Indeed, the refinement was performed using an incorrect 12 S apfu model, and the $M(1)$ – $S(1)$ distance (2.354 Å) agrees with the 1.02 Hg apfu content reported in their electron microprobe analysis, whereas a content of 1.6 Hg apfu on the basis of the a unit-cell parameter and the refined site occupancy was given. Karanović *et al.* (2003) reported the crystal structure investigation of “schwazite” from Dragodol, Donja Trešnjica district, Serbia. Electron microprobe data (EDS mode) gave the formula $\text{Cu}_{9.28}\text{Hg}_{1.64}\text{Zn}_{0.76}\text{Fe}_{0.02}\text{As}_{0.17}\text{Sb}_{4.19}\text{S}_{13}$ [$Ev(\%) = +4.6$]. This formula can be recalculated to $\text{Cu}_{8.57}\text{Hg}_{1.52}\text{Zn}_{0.70}\text{Fe}_{0.02}\text{Sb}_{3.87}\text{As}_{0.13}\text{S}_{12.00}$, on the basis of $(\text{Sb}+\text{As}) = 4$ apfu. The poor quality of chemical data contrasts with the high quality of structural data [$R_1 = 0.0148$ for 165 reflections with $F_o > 4\sigma(F_o)$], confirming the occurrence of Hg at the tetrahedral $M(1)$ site. Further structural data on mercurian tetrahedrite [actually a solid solution between tetrahedrite-(Zn) and tetrahedrite-(Hg)] were given by Foit and Hughes (2004), who studied the structural variations in mercurian tetrahedrite from the Spring Creek Claims. The Hg-richest sample, corresponding to tetrahedrite-(Hg), has composition $\text{Cu}_6(\text{Cu}_{4.08}\text{Hg}_{1.15}\text{Zn}_{0.67}\text{Fe}_{0.03}\text{Co}_{0.01})_{\Sigma 5.94}(\text{Sb}_{2.64}\text{As}_{1.36})_{\Sigma 4.00}\text{S}_{13}$. Synthetic Hg-rich tetrahedrites (up to 2 apfu Hg) were studied by Johnson (1991), who reported X-ray powder diffraction data and a unit-cell parameter $a = 10.5071(1)$ Å, and by Karup-Møller and Makovicky (2003, 2004), who examined mercurian tetrahedrite and the solid solution between zincian and mercurian tetrahedrite.

Tetrahedrite-(Hg) and related phases

As described above, the crystal structure of tetrahedrite-(Hg) is formed by a three-dimensional framework composed by $M(1)S(1)_4$ tetrahedra connected through corner sharing, delimiting cavities that can be described as truncated tetrahedra, the so-called Laves polyhedra. In this cavities, Z-centered $M(2)_6$ -octahedra are hosted, encircled by four XY_3 trigonal pyramids. The structural formula of tetrahedrite-(Hg) can thus be written as $[\text{Cu}_6\text{Sb}_4\text{S}][(\text{Cu}_4\text{Hg}_2)\text{S}_{12}]$ ($Z = 2$). Tetrahedrite-(Hg) has isotypic relationships with the hypothetical end-member “tenantite-(Hg)”. This phase has actually been found in nature (e.g., Mozgova *et al.*, 1978; Mozgova and Tsepina, 1983). Mozgova *et al.* (1978) reported “tenantite-(Hg)” from the ore deposit of Kulpolnei, Čukotka, Russia. The chemical formula, recalculated on the basis of three analyses (No. 2, 3-1, and 4 of Table 1 in Mozgova *et al.*, 1978), corresponds to $\text{Cu}_{5.68}(\text{Cu}_{4.11}\text{Hg}_{1.82}\text{Zn}_{0.05}\text{Fe}_{0.02})(\text{As}_{3.90}\text{Sb}_{0.10})\text{S}_{13.07}$. “Tenantite-(Hg)”

has unit-cell parameter $a = 10.34 \text{ \AA}$; the a parameter, shorter than that of tetrahedrite-(Hg), is in keeping with the As-to-Sb substitution and agrees with the value calculated applying the relation of Johnson *et al.* (1987), i.e., $a = 10.35 \text{ \AA}$.

Two other groups of phases share similar topologies with tetrahedrite group minerals, with some important differences: the galkhaite and routhierite groups. The galkhaite group (“galkhaites”) is currently formed by three different species: galkhaite, $(\text{Hg}_5\text{Cu})\text{CsAs}_4\text{S}_{12}$ (e.g., Biagioni *et al.*, 2014a), vorontsovitte $(\text{Hg}_5\text{Cu})\text{TlAs}_4\text{S}_{12}$, and ferrovorontsovitte, $(\text{Fe}_5\text{Cu})\text{TlAs}_4\text{S}_{12}$ (Kasatkin *et al.*, 2018). These minerals are cubic, $I-43m$, and have the same tetrahedral tetrahedrite-like framework, with $(\text{Hg,Cu})\text{S}_4$ or $(\text{Fe,Cu})\text{S}_4$ tetrahedra and AsS_3 trigonal pyramids. The difference lies in the occupancy of the Laves polyhedra: whereas $\text{ZM}(2)_6$ octahedra occur in tetrahedrite group minerals (Fig. 3a), galkhaite group compounds show Cs or Tl at the center of the truncated tetrahedra, in twelve-fold coordination (Fig. 3b). Taking into account such a crystal-chemistry, the structural formula of galkhaite can be written as $[\text{CsAs}_4][(\text{Hg}_5\text{Cu})\text{S}_{12}]$.

Mercury is an important constituent also in the routhierite group minerals (hereafter routhierites). In these phases, the occurrence of two distinct kinds of tetrahedral sites, showing different occupancies, lowers the symmetry to $I-42m$. Among the currently five known mineral species, two contain essential Hg: routhierite, $\text{CuHg}_2\text{TlAs}_2\text{S}_6$ (Bindi, 2008; Biagioni *et al.*, 2014b), and arsiccioite, $\text{AgHg}_2\text{TlAs}_2\text{S}_6$ (Biagioni *et al.*, 2014a). Doubling the formula of routhierite, one obtains $\text{Cu}_2\text{Hg}_4\text{Tl}_2\text{As}_4\text{S}_{12}$ ($Z = 2$), that can be written as $[\text{Tl}_2\text{As}_4][\text{Cu}_2\text{Hg}_4\text{S}_{12}]$, discriminating the composition of the tetrahedral framework and the content of the distorted Laves polyhedron (Fig. 3c).

Passing from tetrahedrite-(Hg) to routhierites and then to galkhaites, the content of Hg in the tetrahedral framework increases, from 2 apfu to 5 apfu. The excess of positive charges is balanced by decreasing the charges hosted in the cavities, replacing six Cu^+ atoms with one Tl_2 dimer in routhierites and one large monovalent ion (Cs or Tl) in galkhaites. It seems likely that the tetrahedrite-like tetrahedral framework may be able to adapt to the variable ore geochemistry, allowing the incorporation of variable amounts of divalent elements (Hg, Zn, Fe) in tetrahedrite group minerals as well as favouring the crystallization of peculiar mineral phases like galkhaites and routhierites in environments characterized by the occurrence of large monovalent cations like Tl^+ and Cs^+ .

Conclusions

This study permitted the characterization of tetrahedrite-(Hg) as a specific mineral species belonging to the tetrahedrite group, in accordance with the nomenclature rules defined by Biagioni *et al.* (2020). It confirms the structural plasticity of the tetrahedrite structure, favouring the incorporation of a wide range of monovalent and divalent cations typical of hydrothermal ore deposits.

Acknowledgements

CB and MP acknowledge financial support from the Ministero dell'Istruzione, dell'Università e della Ricerca through the project PRIN 2017 “TEOREM – deciphering geological processes using Terrestrial and Extraterrestrial ORE Minerals”, prot.

2017AK8C32. This work was also supported (JS, DV) financially by the Ministry of Culture of the Czech Republic (long-term project DKRVO 2019-2023/1.II.b National Museum, 00023272). The comments of Yves Moëlo and two anonymous reviewer were greatly appreciated, helping us in improving the paper.

Prepublished Article

References

- Andreasen, J.W., Makovicky, E., Lebeck, B. and Karup-Møller, S. (2008) The role of iron in tetrahedrite and tennantite determined by Rietveld refinement of neutron powder diffraction data. *Physics and Chemistry of Minerals*, **35**, 447–454.
- Arlt, T. and Diamond, L.W. (1998) Composition of tetrahedrite-tennantite and ‘schwazite’ in the Schwaz silver mines, North Tyrol, Austria. *Mineralogical Magazine*, **62**, 801–820.
- Atanasov, V.A. (1975) Argentinian mercurian tetrahedrite, a new variety, from the Chiprovtsi ore deposit, Western Stara-Planina mountains, Bulgaria. *Mineralogical Magazine*, **40**, 233–237.
- Benvenuti, M., Lattanzi, P., Tanelli, G. and Cortecchi, G. (1986) The Ba-Fe-pyrite deposit of Buca della Vena, Apuan Alps, Italy. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, **41**, 347–358.
- Biagioni, C. and Orlandi, P. (2009) Tiemannite e metacinabro della miniera Buca della Vena (Alpi Apuane). *Atti della Società Toscana di Scienze Naturali, Memorie*, **114**, 13–17.
- Biagioni, C., Bindi, L. and Zaccarini, F. (2014a) Crystal chemistry of mercury-sulfosalts – galkhaite, $(\text{Hg}_{5+x}\text{Cu}_{1-x})\text{Cs}_{1-x}\text{As}_4\text{S}_{12}$ ($x \approx 0$): crystal structure and revision of the chemical formula. *Canadian Mineralogist*, **52**, 873–882.
- Biagioni, C., Bonaccorsi, E., Moëlo, Y. and Orlandi, P. (2014b) Mercury-arsenic sulfosalts from Apuan Alps (Tuscany, Italy). I. Routhierite, $(\text{Cu}_{0.8}\text{Ag}_{0.2})\text{Hg}_2\text{Tl}(\text{As}_{1.4}\text{Sb}_{0.6})_{\Sigma=2}\text{S}_6$, from Monte Arsiccio mine: occurrence and crystal structure. *Mineralogical Magazine*, **78**, 101–117.
- Biagioni, C., Bonaccorsi, E., Moëlo, Y., Orlandi, P., Bindi, L., D’Orazio, M. and Vezzoni, S. (2014c) Mercury-arsenic sulfosalts from the Apuan Alps (Tuscany, Italy). II. Arsiccioite, $\text{AgHg}_2\text{TlAs}_2\text{S}_6$, a new mineral from the Monte Arsiccio mine: occurrence, crystal structure and crystal chemistry of the routhierite isotopic series. *Mineralogical Magazine*, **78**, 101–117.
- Biagioni, C., George, L.L., Cook, N.J., Makovicky, E., Moëlo, Y., Pasero, M., Sejkora, J., Stanley, C.J., Welch, M.D. and Bosi, F. (2020) The tetrahedrite group: Nomenclature and classification. *American Mineralogist*, **105**, 109–122.
- Bindi, L. (2008) Routhierite, $\text{Tl}(\text{Cu},\text{Ag})(\text{Hg},\text{Zn})_2(\text{As},\text{Sb})_2\text{S}_6$. *Acta Crystallographica*, **C64**, i95–i96.
- Breese, N.E. and O’Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Bruker, AXS Inc. (2016) APEX 3. Bruker Advanced X-ray Solutions, Madison, Wisconsin, USA.
- Burnham, C. W. (1962) Lattice constant refinement. *Carnegie Institute Washington Yearbook* **61**, 132–135.
- Charlat, M. and Lévy, C. (1975) Influence des principales substitutions sur le paramètre cristallin dans la série tennantite-tétraédrite. *Bulletin de la Société française de Minéralogie et de Cristallographie*, **98**, 152–158.
- Criddle, A.J. and Stanley, C.J. (1993) Quantitative Data File for Ore Minerals (Third Issue). Chapman & Hall, London, 635 p.

- Di Benedetto, F., Bernardini, G.P., Borrini, D., Emiliani, C., Cipriani, C., Danti, C., Caneschi, A., Gatteschi, D. and Romanelli, M. (2002) Crystal chemistry of tetrahedrite solid solution: EPR and magnetic investigations. *Canadian Mineralogist*, **40**, 837–847.
- Dini, A. and Orlandi, P. (1995) Coloradoite (HgTe), from Buca della Vena mine, Apuan Alps, Tuscany, Italy. *Atti della Società Toscana di Scienze Naturali, Memorie*, **102**, 47–50.
- D’Orazio, M., Biagioni, C., Dini, A. and Vezzoni, S. (2017) Thallium-rich pyrite ores from the Apuan Alps, Tuscany, Italy: constraints for their origin and environmental concerns. *Mineralium Deposita*, **52**, 687–707.
- Foit, F.F.Jr. and Hughes, J.M. (2004) Structural variations in mercurian tetrahedrite. *American Mineralogist*, **89**, 159–163.
- Foit, F.F.Jr. and Ulbricht, M.E. (2001) Compositional variation in mercurian tetrahedrite-tennantite from the epithermal deposits of the Steens and Pueblo Mountains, Harney County, Oregon. *The Canadian Mineralogist*, **39**, 819–830.
- Grammatikopoulos, T., Roth, T. and Valeyev, O. (2005) Compositional variation in Hg-Ag-rich tetrahedrite from the polymetallic Eskay Creek deposit, British Columbia, Canada. *Neues Jahrbuch für Mineralogie Abhandlungen*, **181**, 281–292.
- Holland, T.J.B. and Redfern, S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*, **61**, 65–77.
- Johnson, N.E. (1991) X-ray powder diffraction data for synthetic varieties of tetrahedrite. *Powder Diffraction*, **6**, 43–47.
- Johnson, M.L. and Burnham, C.W. (1985) Crystal structure refinement of an arsenic-bearing argentian tetrahedrite. *American Mineralogist*, **70**, 165–170.
- Johnson, N.E., Craig, J.R. and Rimstidt, J.D. (1987) Effect of substitutions on the cell dimension of tetrahedrite. *Canadian Mineralogist*, **25**, 237–244.
- Johnson, N.E., Craig, J.R. and Rimstidt, J.D. (1988) Crystal chemistry of tetrahedrite. *American Mineralogist*, **73**, 389–397.
- Kalbskopf, R. (1971) Die Koordination des Quecksilbers in Schwazit. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **16**, 173–175.
- Kaplunnik, L.N., Pobedinskaya, E.A. and Belov, N.V. (1980) Crystal structure of schwazite, $(\text{Cu}_{4.4}\text{Hg}_{1.6})\text{Cu}_6\text{Sb}_4\text{S}_{12}$. *Soviet Physics Crystallography*, **25**, 508–509 (in Russian).
- Karanović, L., Cvetković, L., Poleti, D., Balić-Žunić, T. and Makovicky, E. (2003) Structural and optical properties of schwazite from Dragodol (Serbia). *Neues Jahrbuch für Mineralogie Monatshefte*, **2003**, 503–520.
- Karup-Møller, S. and Makovicky, E. (2003) Exploratory studies of element substitutions in synthetic tetrahedrite. Part V. Mercurian tetrahedrite. *Neues Jahrbuch für Mineralogie Abhandlungen*, **179**, 73–83.
- Karup-Møller, S. and Makovicky, E. (2004) Exploratory studies of the solubility of minor elements in tetrahedrite. VI. Zinc and the combined zinc-mercury and iron-mercury substitutions. *Neues Jahrbuch für Mineralogie Monatshefte*, **2004**, 508–524.
- Kasatkin, A.V., Nestola, F., Agakhanov, A.A., Škoda, R., Karpenko, V.Y., Tsyganko, M.V. and Plášil, J. (2018) Vorontsovite, $(\text{Hg}_5\text{Cu})_{\Sigma 6}\text{TlAs}_4\text{S}_{12}$, and ferrovorontsovite, $(\text{Fe}_5\text{Cu})_{\Sigma 6}\text{TlAs}_4\text{S}_{12}$: the Tl- and Tl-Fe analogues of galkhaite from the Vorontsovskoe gold deposit, Northern Urals, Russia. *Minerals*, **8**, 185.

- Kenngott, G.A. (1853) Das Mohs'sche Mineralsystem, dem gegenwärtigen Standpuncte der Wissenschaft gemäss bearbeitet. Wien.
- Kersten, C. (1843) Untersuchung eines quecksilberhaltigen Fahlerzes von Val di Castello in Toscana. *Annalen der Physik*, **135**, 131–135.
- Kraus, W. and Nolze, G. (1996) POWDER CELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *Journal of Applied Crystallography*, **29**, 301–303.
- Lind, I.L. and Makovicky, E. (1982) Phase relations in the system Cu–Sb–S at 200°C, 10⁸ Pa by hydrothermal synthesis. Microprobe analyses of tetrahedrite—a warning. *Neues Jahrbuch für Mineralogie Abhandlungen*, **145**, 134–156.
- Makovicky, E. and Karup-Møller, S. (1994) Exploratory studies on substitution of minor elements in synthetic tetrahedrite. Part I. Substitution by Fe, Zn, Co, Ni, Mn, Cr, V and Pb Unit-cell parameter changes on substitution and the structural role of “Cu²⁺”. *Neues Jahrbuch für Mineralogie, Abhandlungen*, **167**, 89–123.
- Mozgova, N.N. and Tsepin, A.I. (1983) Fahlores. Nauka, Moscow, 280 p. (in Russian).
- Mozgova, N.N., Tsepin, A.I. and Ozerova, N.N. (1978) About arseniferous schwazite. *Doklady Akademii Nauk SSSR*, **239**, 439–442 (in Russian).
- Mozgova, N.N., Tsepin, A.I., Ozerova, N.N., Bortnikov, N.S., and Tronieva, N.V. (1979) Mercuriferous grey copper ores. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, **108**, 437–452 (in Russian).
- Nováček, R. (1942) Slovak mercury tetrahedrites. *Zprávy Geologického ústavu pro Čechy a Moravu*, **18**, 107–110 (in Czech).
- Ondruš, P. (1993) A computer program for analysis of X-ray powder diffraction patterns. *Materials Science Forum, EPDIC-2, Enchede*, **133-136**, 297–300.
- Orlandi, P., Meerschaut, A., Moëlo, Y., Palvadeau, P. and Léone, P. (2005) Lead-antimony sulfosalts from Tuscany (Italy). VIII. Rouxelite, Cu₂HgPb₂₂Sb₂₈S₆₄(O,S)₂, a new sulfosalt from Buca della Vena mine, Apuan Alps: definition and crystal structure. *The Canadian Mineralogist*, **43**, 919–933.
- Orlandi, P., Moëlo, Y., Campostrini, I. and Meerschaut, A. (2007) Lead-antimony sulfosalts from Tuscany (Italy). IX. Marrucciite, Hg₃Pb₁₆Sb₁₈S₄₆, a new sulfosalt from Buca della Vena mine, Apuan Alps: Definition and crystal structure. *European Journal of Mineralogy*, **19**, 267–279.
- Palache, C. Berman, H. and Frondel, C. (1951): The system of Mineralogy of James Dwing Dana and Edward Salisbury Dana, Yale University 1837–1892, Volume II. John Wiley and Sons Inc., New York, 7th edition revised and enlarged, 1124, 532–534.
- Pouchou, J.L., and Pichoir, F. (1985) “PAP” (jρZ) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, San Francisco.
- Rath, G. (1855) Ueber ein quecksilberreiches Fahlerz von Kotterbach (nahe bei Poratsch) in Oberungarn. *Annalen der Physik*, **172**, 322–330.
- Sheldrick, G.M. (2015) Crystal Structure Refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.

- Škácha, P., Sejkora, J., Plášil, J. and Makovický, E. (2020) Pošepnýite, IMA 2018-121a. In: CNMNC Newsletter 54. *European Journal of Mineralogy*, **32**, <https://doi.org/10.5194/ejm-32-275-2020>.
- Velebil, D. (2014) A contribution to knowledge of chemistry of mercurian tetrahedrites: localities Jedová hora (Czech Republic), Rudňany, Rožňava, Nižná Slaná, Slovinky (Slovakia) and Maškara (Bosnia and Herzegovina). *Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze*, **22**, 131–143. (in Czech).
- Weidenbusch, H. (1849) Analyse des quecksilberhaltigen Fahlerzes von Schwatz in Tyrol. *Annalen der Physik*, **152**, 86–88.
- Welch, M.D., Stanley, C.J., Spratt, J. and Mills, S.J. (2018) Rozhdestvenskayaite $\text{Ag}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$ and argentotetrahedrite $\text{Ag}_6\text{Cu}_4(\text{Fe}^{2+}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$: two Ag-dominant members of the tetrahedrite group. *European Journal of Mineralogy*, **30**, 1163–1172.
- Wilson, A.J.C. (1992) International Tables for Crystallography. Volume C. Kluwer, Dordrecht.
- Wuensch, B.J. (1964) The crystal structure of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. *Zeitschrift für Kristallographie*, **119**, 437–453.

Table captions

Table 1. Reflectance data of tetrahedrite-(Hg) from Buca della Vena, Jedová hora, and Rožňava. For sake of comparison, literature data are reported.

Table 2. Chemical data for tetrahedrite-(Hg) from Buca della Vena, Jedová hora, and Rožňava.

Table 3. Observed and calculated X-ray powder diffraction data for tetrahedrite-(Hg) from Buca della Vena. Intensity and d_{hkl} were calculated using the software *PowderCell2.3* (Kraus and Nolze, 1996) on the basis of the structural model given in Table 5. Only reflections with $I_{calc} > 2$ are listed, if not observed. The eight strongest reflections are given in bold. Observed intensities were visually estimated (vs = very strong; m = medium; mw = medium-weak; w = weak; vw = very weak). For sake of comparison, the observed X-ray powder diffraction patterns of samples from Jedová hora and Rožňava are given.

Table 4. Summary of crystal data and parameters describing data collection and refinement for tetrahedrite-(Hg).

Table 5. Sites, Wyckoff positions, site occupancy factors (s.o.f.), fractional atom coordinates and isotropic (*) or equivalent isotropic displacement parameters (\AA^2) for tetrahedrite-(Hg).

Table 6. Selected bond distances (\AA) for tetrahedrite-(Hg).

Table 7. Bond-valence sums (in valence unit) for tetrahedrite-(Hg).

Figure captions

Type material of tetrahedrite-(Hg). (a) Tetrahedral crystals up to 0.2 mm, with dolomite. Buca della Vena mine, Apuan Alps, Tuscany, Italy. (b) Aggregates up to 4 mm with baryte. Field of view: 5 cm. Jedová hora deposit, Czech Republic. (c) Massive aggregate with quartz. Size: $11 \times 6 \times 7$ cm. Rožňava ore field, Slovakia.

Fig. 2. Reflectance curves for tetrahedrite-(Hg) in air. For sake of comparison, the reflectance curves of type material from Buca della Vena, cotype samples from Jedová hora and Rožňava, and literature data are shown.

Fig. 3. Structural fragments of the crystal structure of tetrahedrite group (a), galkhaite group (b), and routhierite group minerals (c), organized around the Laves polyhedra, showing their topological relationships. Polyhedra: grey = $M(1)$ site in tetrahedrites, (Hg/Fe,Cu) site in galkhaites, and the $M(2)$ site in routhierites; green = $M(1)$ site in routhierites. Circles: green = $M(2)$ site in tetrahedrites; orange = $X(3)$ site in tetrahedrites; dark violet = As sites in galkhaites and routhierites; violet = (Cs/Tl) site in galkhaites; grey = Tl site in routhierites; yellow = S sites.

Supplementary figure caption

Fig. S1. (a) Front and back of the historical label accompanying the specimen of tetrahedrite-(Hg) from the Rožňava ore field, Slovakia (specimen PIN 33538), and (b) its entry in the inventory book (highlighted in the yellow box).

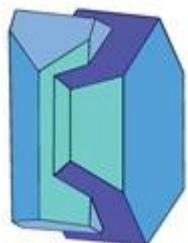
Table 1. Reflectance data of tetrahedrite-(Hg) from Buca della Vena, Jedová hora, and Rožňava. For sake of comparison, literature data are reported.

	Buca della Vena mine (this work)	Jedová hora (this work)	Rožňava (this work)	Moschellandsberg (Criddle and Stanley, 1993)	Dragodol (Karanović <i>et al.</i> , 2003)
λ (nm)	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>	<i>R</i>
400	34.2	33.8	33.6	33.3	31.0
420	34.0	33.5	33.2	32.9	30.6
440	33.5	33.1	32.9	32.5	30.4
460	32.8	32.8	32.5	32.3	30.4
470	32.5				
480	32.3	32.4	32.0	32.0	30.6
500	32.2	32.2	31.7	32.1	31.2
520	32.4	32.3	31.8	32.4	31.8
540	32.8	32.6	32.1	32.8	32.6
546	32.9				
560	33.2	33.0	32.4	33.2	33.2
580	33.3	33.2	32.5	33.2	33.4
589	33.2				
600	33.0	33.2	32.5	32.9	33.1
620	32.4	32.7	32.2	32.3	32.6
640	31.5	32.1	31.6	31.4	31.7
650	30.9				
660	30.4	31.1	30.9	30.6	30.6
680	29.5	30.4	30.2	29.9	29.4
700	28.8	29.7	29.5	29.3	28.0

Note: the four COM values measured for the type material from Buca della Vena mine are shown in bold.

Table 2. Chemical data for tetrahedrite-(Hg) from Buca della Vena, Jedová hora, and Rožňava.

Element	Buca della Vena mine (n = 33)			Jedová hora (n = 29)			Rožňava (n = 26)		
	wt%	range	e.s.d.	wt%	range	e.s.d.	wt%	range	e.s.d.
Cu	32.22	31.53 – 32.62	0.28	32.99	32.18 – 34.26	0.53	32.83	32.44 – 33.28	0.25
Ag	0.40	0.36 – 0.44	0.02	0.01	0.00 – 0.07	0.02	0.22	0.18 – 0.27	0.02
Fe	0.18	0.15 – 0.21	0.01	0.76	0.23 – 1.92	0.42	0.45	0.29 – 0.82	0.15
Zn	1.25	0.51 – 1.63	0.31	0.24	0.10 – 0.67	0.14	0.33	0.15 – 0.52	0.10
Hg	17.68	16.37 – 20.06	0.91	18.77	13.77 – 22.70	2.27	19.42	17.85 – 20.96	1.07
As	-	-	-	0.25	0.00 – 0.88	0.25	2.31	2.16 – 2.55	0.10
Sb	26.17	25.73 – 26.42	0.17	25.69	24.04 – 26.93	0.73	20.43	20.14 – 20.76	0.18
Bi	-	-	-	-	-	-	2.74	2.51 – 3.02	0.13
S	21.86	21.58 – 22.09	0.14	22.10	21.59 – 22.89	0.32	22.09	21.73 – 22.49	0.19
Se	0.05	0.00 – 0.13	0.05	-	-	-	-	-	-
Total	99.81	99.34 – 100.20	0.23	100.81	99.59 – 101.99	0.66	100.82	99.60 – 101.46	0.53
apfu (As + Bi + Sb = 4)	apfu	range	e.s.d.	apfu	range	e.s.d.	apfu	range	e.s.d.
Cu	9.44	9.34 – 9.54	0.05	9.69	9.61 – 9.77	0.05	9.76	9.61 – 9.85	0.05
Ag	0.07	0.06 – 0.08	0.00	0.00	0.00 – 0.01	0.00	0.04	0.03 – 0.05	0.00
Fe	0.06	0.05 – 0.07	0.00	0.25	0.08 – 0.62	0.14	0.15	0.10 – 0.28	0.05
Zn	0.36	0.15 – 0.46	0.09	0.07	0.03 – 0.19	0.04	0.10	0.04 – 0.15	0.03
Hg	1.64	1.51 – 1.89	0.10	1.75	1.23 – 2.18	0.24	1.83	1.66 – 2.01	0.11
As	-	-	-	0.06	0.00 – 0.22	0.06	0.58	0.55 – 0.64	0.02
Sb	4.00	-	-	3.94	3.78 – 4.00	0.06	3.17	3.12 – 3.21	0.03
Bi	-	-	-	-	-	-	0.25	0.23 – 0.27	0.01
S	12.69	12.60 – 12.80	0.05	12.87	12.65 – 13.07	0.10	13.01	12.85 – 13.16	0.07



Mineralogical Society

This is a 'preproof' accepted article for Mineralogical Magazine. This version may be subject to change during the production process.

DOI: 10.1180/mgm.2020.36

Se	0.01	0.00 – 0.03	0.01	-	-	-			
<i>Ev</i> (%)	+0.8	0.0 – 1.6	0.4	+0.4	-0.9 – 2.1	0.9	-0.3	-1.8 – 1.1	0.8

Note: $Ev(\%) = [\Sigma(\text{val}+) - \Sigma(\text{val}-)] \times 100 / \Sigma(\text{val}-)$; Fe assumed as Fe^{2+} . e.s.d. = estimated standard deviation.

Prepublished Article

Table 3. Observed and calculated X-ray powder diffraction data for tetrahedrite-(Hg) from Buca della Vena. Intensity and d_{hkl} were calculated using the software *PowderCell2.3* (Kraus and Nolze, 1996) on the basis of the structural model given in Table 5. Only reflections with $I_{calc} > 2$ are listed, if not observed. The eight strongest reflections are given in bold. Observed intensities were visually estimated (vs = very strong; m = medium; mw = medium-weak; w = weak; vw = very weak). For sake of comparison, the observed X-ray powder diffraction patterns of samples from Jedová hora and Rožňava are given.

Buca della Vena					Jedová hora		Rožňava	
I_{obs}	d_{obs}	I_{calc}	d_{calc}	hkl	I_{obs}	d_{obs}	I_{obs}	d_{obs}
-	-	0.5	7.428	1 1 0	0.4	7.422	0.3	7.411
vw	5.25	0.7	5.253	2 0 0	1.3	5.248	0.9	5.237
w	4.29	8	4.289	2 1 1	6.3	4.285	5.6	4.276
w	3.716	4	3.714	2 2 0	5.2	3.711	4.6	3.703
vs	3.035	100	3.033	2 2 2	100.0	3.030	100.0	3.023
w	2.806	8	2.808	3 2 1	7.4	2.805	7.2	2.799
w	2.626	27	2.626	4 0 0	17.4	2.624	14.9	2.618
		3	2.476	3 3 0				
w	2.476	5	2.476	4 1 1	6.4	2.4735	6.5	2.4682
vw	2.349	1	2.349	4 2 0	1.2	2.3466	0.9	2.3416
vw	2.235	0.7	2.240	3 3 2	0.6	2.2370	0.7	2.2328
vw	2.147	0.7	2.144	4 2 2	-	-	-	-
w	2.062	6	2.060	4 3 1	6.1	2.0578	5.1	2.0537
w	1.920	7	1.918	5 2 1	5.9	1.9159	7.0	1.9121
m	1.860	40	1.857	4 4 0	32.5	1.8551	33.8	1.8513
vw	1.801	2	1.802	4 3 3	2.2	1.7996	2.8	1.7959
vw	1.751	0.4	1.751	4 4 2	-	-	-	-
		5	1.704	6 1 1				
w	1.706	2	1.704	5 3 2	4.9	1.7023	5.5	1.6988
vw	1.660	1	1.661	6 2 0	-	-	-	-
mw	1.584	24	1.584	6 2 2	13.4	1.5820	16.3	1.5787
vw	1.550	2	1.548	6 3 1	0.8	1.5472	0.9	1.5440
w	1.516	4	1.516	4 4 4	2.6	1.5147	4.2	1.5117
					1.5	1.4841	1.8	1.4811
					1.0	1.4281	1.1	1.4252

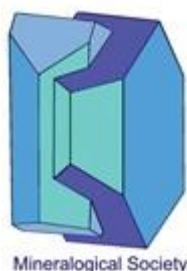


Table 4. Summary of crystal data and parameters describing data collection and refinement for tetrahedrite-(Hg).

Crystal data	
Crystal size (mm)	0.100 x 0.075 x 0.050
Cell setting, space group	Cubic, <i>I</i> -43 <i>m</i>
<i>a</i> (Å)	10.5057(8)
<i>V</i> (Å ³)	1159.5(3)
<i>Z</i>	2
Data collection and refinement	
Radiation, wavelength (Å)	Mo Kα, λ = 0.71073
Temperature (K)	293
2θ _{max} (°)	59.93
Measured reflections	2243
Unique reflections	348
Reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	335
<i>R</i> _{int}	0.0274
<i>R</i> σ	0.0396
Range of <i>h</i> , <i>k</i> , <i>l</i>	-14 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 11, -14 ≤ <i>l</i> ≤ 10
<i>R</i> [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.0190
<i>R</i> (all data)	0.0212
<i>wR</i> (on <i>F</i> _o ²)	0.0696
Goof	1.350
Number of least-squares parameters	20
Maximum and minimum residual peak (e Å ⁻³)	0.84 [at 0.85 Å from <i>M</i> (2)] -0.91 [at 1.06 Å from <i>X</i> (3)]

Table 5. Sites, Wyckoff positions, site occupancy factors (s.o.f.), fractional atom coordinates and isotropic (*) or equivalent isotropic displacement parameters (\AA^2) for tetrahedrite-(Hg).

Site	Wyckoff position	s.o.f.	x/a	y/b	z/c	U_{eq}
M(2)	12e	Cu _{1.00}	0	0	0.7866(4)	0.0547(11)
M(1)	12d	Cu _{0.70(1)} Hg _{0.30(1)}	1/4	1/2	0	0.0252(6)
X(3)	8c	Sb _{1.00}	0.26540(6)	0.26540(6)	0.26540(6)	0.0157(4)
S(1)	24g	S _{1.00}	0.1141(2)	0.1141(2)	0.3575(3)	0.0189(6)
S(2)	2a	S _{1.00}	0	0	0	0.0195(18)

Table 6. Selected bond distances (\AA) for tetrahedrite-(Hg).

M(1)	–S(1) ×4	2.3913(18)
M(2)	–S(2)	2.242(4)
	–S(1) ×2	2.272(4)
X(3)	–S(1) ×3	2.447(3)

Table 7. Bond-valence sums (in valence unit) for tetrahedrite-(Hg).

Site	M(1)	M(2)	X(3)	Σ anions	Theor.
S(1)	^{2x→} 0.41 ^{x4↓}	0.33 ^{x2↓}	1.01 ^{x3↓}	2.16	2.00
S(2)		^{6x→} 0.36		2.16	2.00
Σ cations	1.64	1.02	3.03		
Theor.	1.35	1.00	3.00		

Note: left and right superscripts indicate the number of equivalent bonds involving cations and anions, respectively.

Fig. 1. Type material of tetrahedrite-(Hg). (a) Tetrahedral crystals up to 0.2 mm, with dolomite. Buca della Vena mine, Apuan Alps, Tuscany, Italy. (b) Aggregates up to 4 mm with baryte. Field of view: 5 cm. Jedová hora deposit, Czech Republic. (c) Massive aggregate with quartz. Size: 11 × 6 × 7 cm. Rožňava ore field, Slovakia.

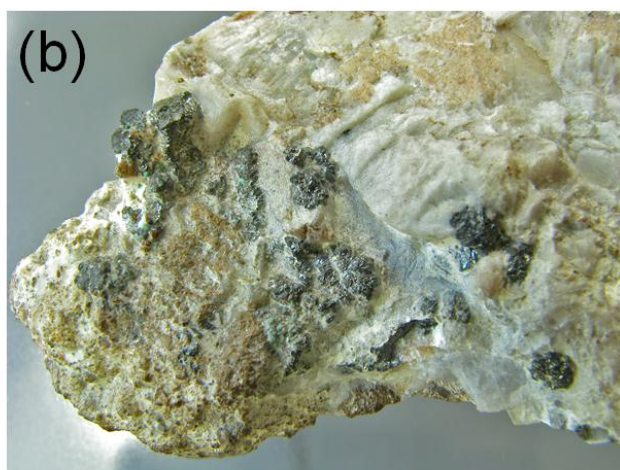
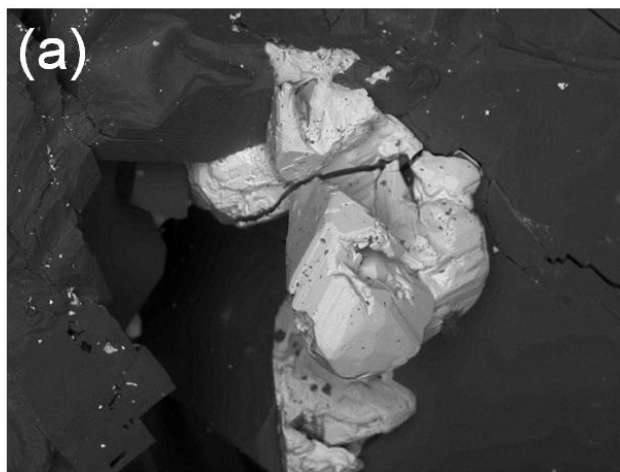


Fig. 2. Reflectance curves for tetrahedrite-(Hg) in air. For sake of comparison, the reflectance curves of type material from Buca della Vena, cotype samples from Jedová hora and Rožňava, and literature data are shown.

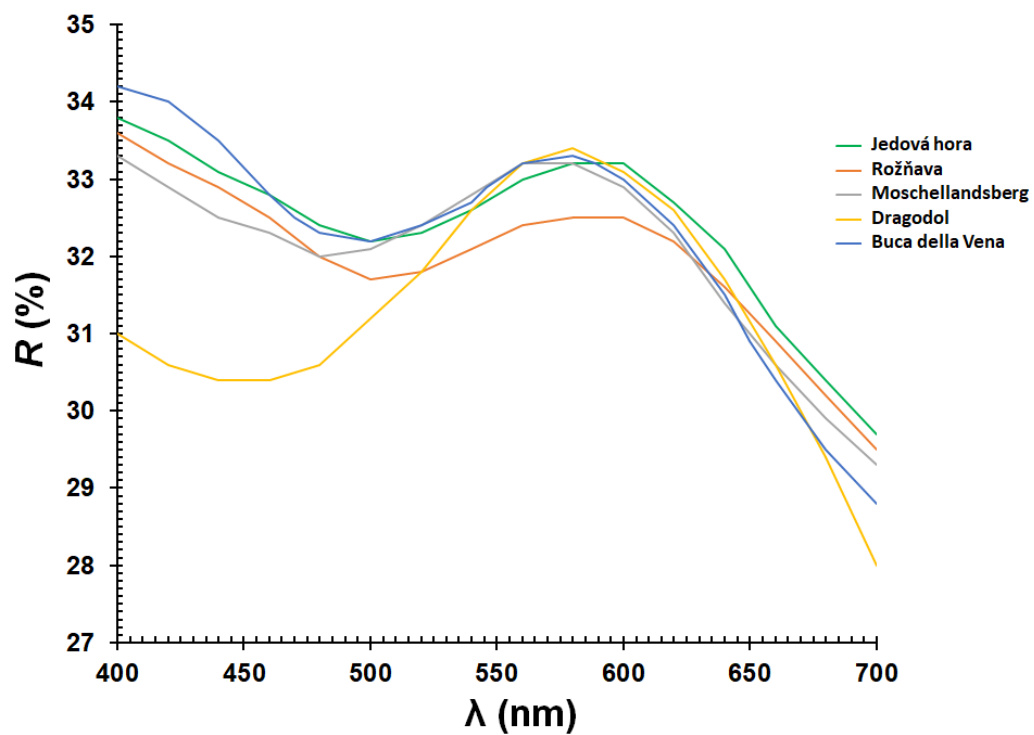


Fig. 3. Structural fragments of the crystal structure of tetrahedrite group (a), galkhaite group (b), and routhierite group minerals (c), organized around the Laves polyhedra, showing their topological relationships. Polyhedra: grey = $M(1)$ site in tetrahedrites, (Hg/Fe,Cu) site in galkhaites, and the $M(2)$ site in routhierites; green = $M(1)$ site in routhierites. Circles: green = $M(2)$ site in tetrahedrites; orange = $X(3)$ site in tetrahedrites; dark violet = As sites in galkhaites and routhierites; violet = (Cs/Tl) site in galkhaites; grey = Tl site in routhierites; yellow = S sites.

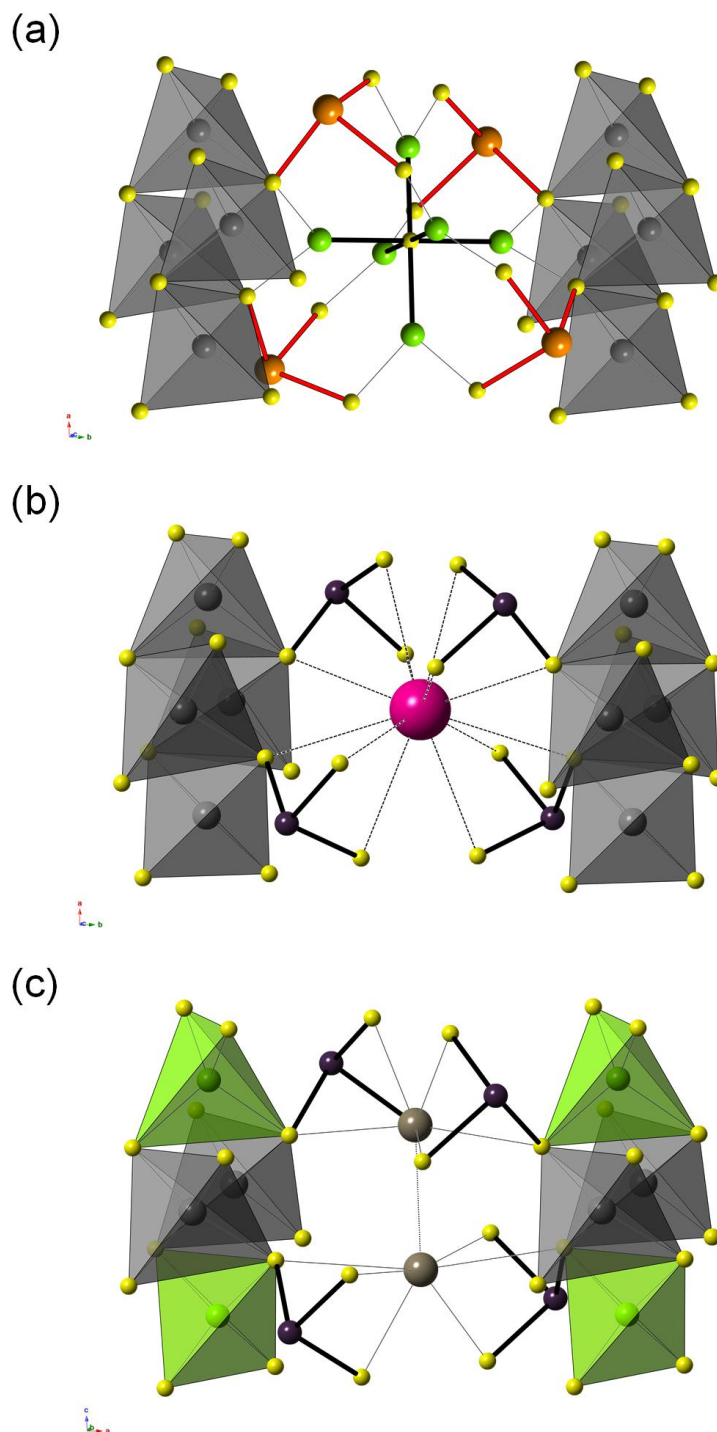
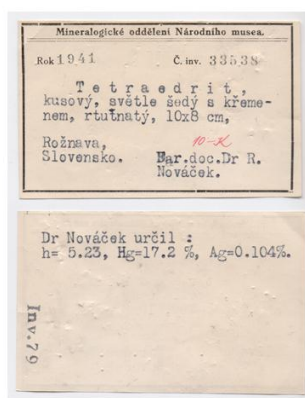


Fig. S1. (a) Front and back of the historical label accompanying the specimen of tetrahedrite-(Hg) from the Rožňava ore field, Slovakia (specimen PIN 33538), and (b) its entry in the inventory book (highlighted in the yellow box).

(a)



(b)

1941					
33535	Brehmit	ledvinité porcelán, ve starším prohnutí s kalcitem,	7.6 cm	Trávnice, ze Čáslavi, Brambora	5 - inv. 79 Katastrál Katastrál
33536	Albit	řidký kusový, světlý až šedý, křem,	6.4 cm	Mladobítce, ze Čáslavi, Čeňky	5 - inv. 79
33537	Chalcedon- kvarcín	šedolilý čirou až bílou, roztoučená kornice,	7.5 cm	Boškovice, ze Čáslavi, Čeňky	5 - inv. 79
33538	Tetradrit	kusový, světlý, šedý s křemem, rtuťnatý,	10.1 cm	Rožňava, Slovensko	10 - inv. 79 Katastrál Katastrál

Prepublished Article