



Article

Argentotetrahedrite-(Zn), $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, a new member of the tetrahedrite group

Jiří Sejkora^{1*} , Cristian Biagioni², Martin Števková^{3,1} , Thomas Raber⁴, Philippe Roth⁵ and Luboš Vrtiška¹

¹Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193 00, Praha 9, Czech Republic; ²Dipartimento di Scienze della Terra, Università di Pisa, Via Santa Maria 53, 56126 Pisa, Italy; ³Earth Science Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 840 05 Bratislava, Slovak Republic; ⁴FGL (Forschungsgemeinschaft Lenggenbach), Edith-Stein-Str. 9, D-79110 Freiburg, Germany; and ⁵FGL (Forschungsgemeinschaft Lenggenbach), Swiss Seismological Service, ETH Zurich, Sonneggstr. 5, 8092 Zurich, Switzerland

Abstract

Argentotetrahedrite-(Zn), $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, has been approved as a new mineral species by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) using samples from Kremnica, Slovak Republic (hereafter KR), and Lenggenbach, Switzerland (LE). Additionally, it was also identified at the small deposit of Zvěstov (Stříbrnice), Czech Republic (ZV). At the Slovak locality, it occurs as anhedral grains up to 0.1 mm in size, steel-grey in colour, with a metallic lustre, in association with ‘argentotennantite-(Fe)’ and tiny chalcopyrite grains in quartz gangue. At Lenggenbach, it was found as domains of tristetrahedral crystal of tetrahedrite-(Zn), up to 1 mm in size, associated with dolomite. At Zvěstov, it occurs as irregular aggregates, up to 0.2 mm in size, partly rimmed by kenoargentotetrahedrite-(Fe). Argentotetrahedrite-(Zn) is isotropic, grey in colour, with blue-greenish tints. Reflectance data for COM wavelengths in air (KR sample) are [λ (nm), R (%)]: 470, 30.1; 546, 29.8; 589, 29.8; and 650, 28.3. Chemical formulae of the samples studied, recalculated on the basis of $\Sigma\text{Me} = 16$ apfu (atoms per formula unit), are: $(\text{Ag}_{3.27}\text{Cu}_{2.69})_{\Sigma 5.96}[\text{Cu}_{4.00}(\text{Zn}_{1.69}\text{Fe}_{0.23}\text{Cu}_{0.05}\text{Cd}_{0.02}\text{Hg}_{0.01})_{\Sigma 2.00}](\text{Sb}_{3.86}\text{As}_{0.17})_{\Sigma 4.03}\text{S}_{12.73}$ (KR), $(\text{Ag}_{3.17}\text{Cu}_{2.79})_{\Sigma 5.96}[\text{Cu}_{4.00}(\text{Zn}_{1.55}\text{Cd}_{0.23}\text{Fe}_{0.16}\text{Cu}_{0.05}\text{Hg}_{0.01})_{\Sigma 2.00}](\text{Sb}_{3.71}\text{As}_{0.32})_{\Sigma 4.03}\text{S}_{12.77}$ (LE) and $(\text{Ag}_{3.27}\text{Cu}_{2.67})_{\Sigma 5.94}[\text{Cu}_{4.00}(\text{Zn}_{1.39}\text{Fe}_{0.50}\text{Cu}_{0.07}\text{Cd}_{0.03}\text{Hg}_{0.01})_{\Sigma 2.00}](\text{Sb}_{4.03}\text{As}_{0.04})_{\Sigma 4.07}\text{S}_{13.08}$ (ZV). Argentotetrahedrite-(Zn) is cubic, $\bar{I}43m$, with $a = 10.5505(10)$ Å, $V = 1174.4(3)$ Å³ and $Z = 2$ (KR); $a = 10.5155(13)$ Å and $V = 1162.8(4)$ Å³ (LE); and $a = 10.5663(12)$ Å and $V = 1179.7$ Å³ (ZV). The crystal structure of argentotetrahedrite-(Zn) has been refined by single-crystal X-ray diffraction data to a final $R_1 = 0.035$ on the basis of 327 unique reflections with $F_o > 4\sigma(F_o)$ and 22 refined parameters (sample KR). Argentotetrahedrite-(Zn) is isotypic with other members of the tetrahedrite group. The structural relationship between argentotetrahedrite-(Zn) and other members of the freibergite series are discussed and previous findings of this species are briefly reviewed.

Keywords: argentotetrahedrite-(Zn), new mineral, sulfosalt, copper, silver, antimony, crystal structure

(Received 14 January 2022; accepted 27 February 2022; Accepted Manuscript published online: 7 March 2022; Associate Editor: Ian Terence Graham)

Introduction

Tetrahedrite-group minerals are the most common sulfosalts in many hydrothermal ore deposits. These chalcogenides form a complex isotypic series, with the general structural formula $M^{(2)}A_6^{M(1)}(B_4C_2)^{X(3)}D_4^{S(1)}Y_{12}^{S(2)}Z$, where $A = \text{Cu}^+$, Ag^+ , \square (vacancy) and $(\text{Ag}_6)^{4+}$ cluster; $B = \text{Cu}^+$ and Ag^+ ; $C = \text{Zn}^{2+}$, Fe^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Cu^+ and Fe^{3+} ; $D = \text{Sb}^{3+}$, As^{3+} , Bi^{3+} and Te^{4+} ; $Y = \text{S}^{2-}$ and Se^{2-} ; and $Z = \text{S}^{2-}$, Se^{2-} and \square (Biagioni *et al.*, 2020a). Thus, tetrahedrite-group minerals are characterised by different homo- and heterovalent substitutions and represent an interesting link between mineralogy and ore geochemistry. The classification and nomenclature of the tetrahedrite-group minerals, in keeping with the current rules from the International Mineralogical Association (IMA), was recently published by Biagioni *et al.* (2020a).

Silver-rich members with 3 to 6 Ag atoms per formula unit (apfu) (A-constituent, freibergite/arsenofreibergite series) have been known for a long time. Indeed, ‘freibergite’ was first described from the Hab Acht Mine near Freiberg, Saxony, Germany by Weissenbach (1831) and named by Kenngott (1853). Currently IMA-accepted minerals belonging to the freibergite series are argentotetrahedrite-(Fe) (Welch *et al.*, 2018), argentotetrahedrite-(Hg) (Wu *et al.*, 2021), argentotetrahedrite-(Zn) (this paper), kenoargentotetrahedrite-(Fe) (the former freibergite – Welch *et al.*, 2018; Biagioni *et al.*, 2020a) and kenoargentotetrahedrite-(Zn) (Qu *et al.*, 2021). The arsenofreibergite series comprises fewer species, being currently represented only by argentotennantite-(Zn) (Spiridonov *et al.*, 1986; Biagioni *et al.*, 2020a) and kenoargentotennantite-(Fe) (Biagioni *et al.*, 2020b).

The most common C-constituent in minerals of the freibergite series is Fe (Riley, 1974; Patrick and Hall, 1983; Peterson and Miller, 1986; Johnson *et al.*, 1986; Welch *et al.*, 2018; Biagioni *et al.*, 2020a) but some Zn-dominant chemical compositions have been reported previously (see a brief review below). Patrick and Hall (1983) studied Ag substitution into synthetic

*Author for correspondence: Jiří Sejkora, Email: jiri.sejkora@nm.cz

Cite this article: Sejkora J., Biagioni C., Števková M., Raber T., Roth P. and Vrtiška L. (2022) Argentotetrahedrite-(Zn), $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, a new member of the tetrahedrite group. *Mineralogical Magazine* 86, 319–330. <https://doi.org/10.1180/mgm.2022.21>

Zn-, Cd-, and Fe-bearing tetrahedrites and for Zn members found that the maximum Ag content was 4.7 apfu.

The recent findings of mineral specimens corresponding to argentotetrahedrite-(Zn) at the Kremnica deposit, Slovak Republic, in the Lengenbach quarry, Switzerland, and the Zvěstov deposit, Czech Republic, allowed the submission of a formal proposal to the IMA Commission on New Minerals, Nomenclature and Classification, in order to give an official definition of argentotetrahedrite-(Zn). The mineral and its name (symbol Attr-Zn) have been approved (IMA2020-069, Sejkora *et al.*, 2021a). Holotype material of argentotetrahedrite-(Zn) from Kremnica and type material from Zvěstov are deposited in the collections of the Department of Mineralogy and Petrology, National Museum in Prague, Cirkusová 1740, 19300 Praha 9, Czech Republic, under the catalogue number P1P 51/2020 and 70/2021, respectively. The crystals used for the single-crystal X-ray diffraction study, along with cotype material from Lengenbach, are kept in the mineralogical collection of the Museo di Storia Naturale of the Università di Pisa, Via Roma 79, Calci (PI), under catalogue number 19922 (Kremnica), 19923 (Lengenbach) and 19939 (Zvěstov).

Occurrence and physical properties

Argentotetrahedrite-(Zn) was found at three different localities: the Kremnica Au–Ag epithermal deposit, Žiar nad Hronom Co., Banská Bystrica Region, Slovak Republic (type locality; 48°42′44″N, 18°54′7″E); the Lengenbach quarry, Imfeld, Binn Valley, Canton Valais, Switzerland (co-type locality; 46°21′54″N, 8°13′15″E); and the small deposit of Zvěstov (Stříbrnice), central Bohemia region, Czech Republic (co-type locality; 49°38′39.069″N, 14°47′51.993″E).

The Kremnica (Slovak Republic) occurrence

The Kremnica Au–Ag epithermal deposit is located close to Kremnica town, in the northern part of the Central Slovakian Volcanic Field, which is represented by the remnants of a large Miocene andesite stratovolcano (Lexa *et al.*, 1998). The deposit is characterised by a low-sulfidation epithermal vein system with Au–Ag–Sb mineralisation developed on marginal faults in the eastern part of the Kremnica resurgent horst. Two principal vein systems can be distinguished: (1) 1st vein system, which is located NW of Kremnica town, is dominated by a first-order listric fault, intruded by rhyolite dykes and (2) 2nd vein system, which extends underneath the town of Kremnica and is represented by a large-scale complementary vein system with 40 veins in the hanging wall of the listric fault (Böhmer, 1966; Kraus *et al.*, 1999; Lexa and Bartalský, 1999; Koděra *et al.*, 2007). The sample with argentotetrahedrite-(Zn) was collected from the hydrothermal quartz–dolomite vein, situated at the hanging wall of the 1st stibnite vein in the crosscut P-102, Václav-south adit, in the central part of the 1st vein system (area of Šturec). This thin (from 3 to 20 cm wide) NE–SW trending vein exhibits a brecciated to drusy structure, with white to grey cavernous or drusy quartz and yellow dolomite as principal gangue minerals. Macroscopic aggregates of older common sulfides (sphalerite, pyrite and minor chalcopyrite) up to 5 mm as well as late-stage Ag-sulfosalts (mainly miargyrite, pyrrargyrite and proustite) up to 2 mm are scattered locally in both quartz and dolomite. A Se-enriched association of ore minerals from this vein was studied in detail by Števkó *et al.* (2018) with Au–Ag alloys, uytnebogaardtite, minerals of the galena–clausthalite

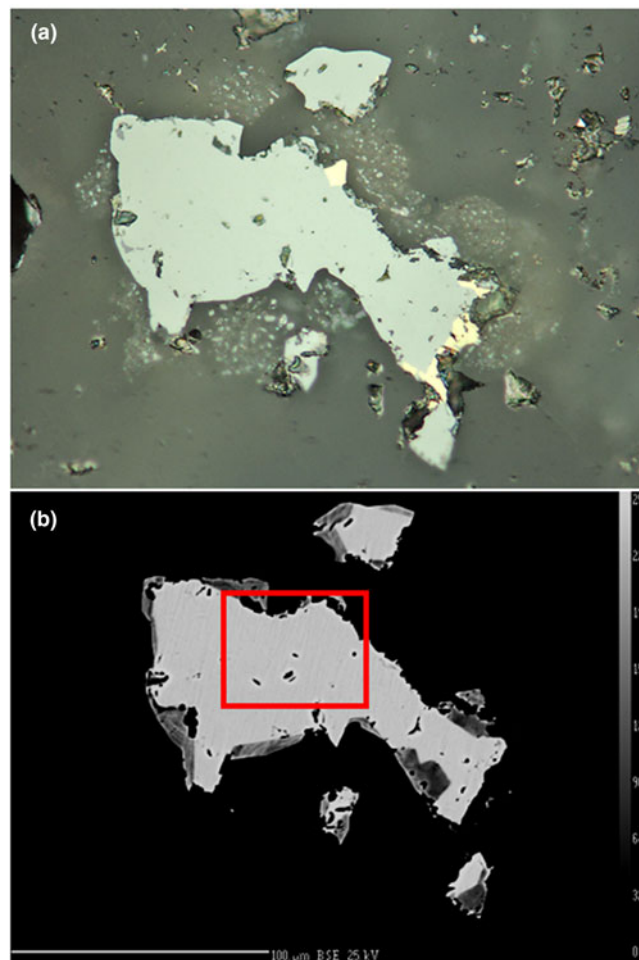


Fig. 1. Argentotetrahedrite-(Zn), anhedral grains up to 0.1 mm in length as seen in reflected light microscopy (a) and back-scattered electrons (b). The darker rims in (b) have a composition corresponding to the potential end-member argentotennantite-(Fe). The red box indicates the area where the grain used for single-crystal X-ray diffraction was extracted. Holotype material from Kremnica, Slovak Republic, catalogue number P1P 51/2020.

and of the acanthite–naumannite series, diaphorite, miargyrite, pyrrargyrite–proustite, members of the polybasite group, various minerals of the tetrahedrite group and andorite branch (quatrondorite, senandorite, Ag-excess fizélyite), freieslebenite as well as Pb–Sb sulfosalts (scainiite, robinsonite and plagionite) being identified.

At Kremnica, argentotetrahedrite-(Zn) occurs as anhedral grains, up to 0.1 mm in size (Fig. 1), steel-grey in colour, tarnished to black and with a black streak. Lustre is metallic. The Mohs hardness may be close to 3½–4, in agreement with other members of the tetrahedrite group. Argentotetrahedrite-(Zn) 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 5.089 g/cm³. In reflected light, argentotetrahedrite-(Zn) is isotropic. It is grey, with blue-greenish tints. Internal reflections were not observed. Reflectance values, measured in air using a spectrophotometer MSP400 Tidas at Leica microscope, with a 50 × objective, are given in Table 1 and shown in Fig. 2.

Table 1. Reflectance data for argentotetrahedrite-(Zn) from Kremnica, Lengenbach, and Zvěstov.*

λ (nm)	R (%)			λ (nm)	R (%)		
	Kremnica	Lengenbach	Zvěstov		Kremnica	Lengenbach	Zvěstov
400	31.0	30.6	30.7	560	29.9	29.7	29.9
420	31.0	30.5	30.7	580	29.8	29.6	29.9
440	30.7	30.3	30.4	589	29.8	29.6	29.8
460	30.3	29.8	30.1	600	29.6	29.4	29.7
470	30.1	29.6	30.0	620	29.3	29.0	29.4
480	30.0	29.6	29.8	640	28.7	28.4	28.9
500	29.8	29.5	29.7	650	28.3	28.0	28.5
520	29.8	29.6	29.7	660	28.0	27.6	28.2
540	29.8	29.6	29.8	680	27.2	26.9	27.6
546	29.8	29.6	29.8	700	26.6	26.2	27.0

*The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

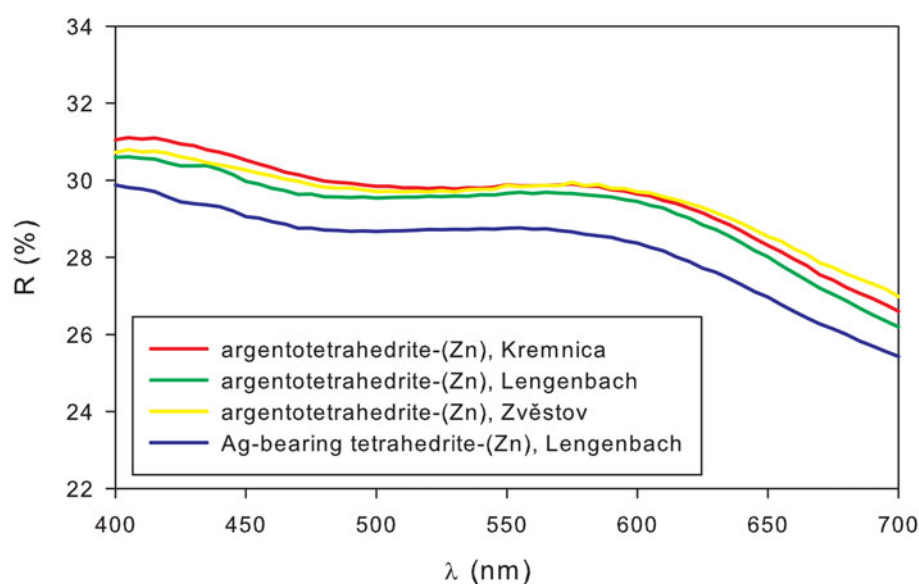


Fig. 2. Reflectance curves for argentotetrahedrite-(Zn) from Kremnica, Lengenbach and Zvěstov compared with the curve for Ag-bearing tetrahedrite-(Zn) from Lengenbach.

Argentotetrahedrite-(Zn) is directly associated with thin earlier rims of the not-yet approved end-member 'argentotennantite-(Fe)' and tiny chalcopyrite grains. Its crystallisation is related to the activity of hydrothermal fluids during an early stage of the formation of the Kremnica Au–Ag epithermal deposit.

The Lengenbach (Switzerland) occurrence

The Lengenbach quarry exploits a Triassic metadolostone overlying the gneiss basement, at the northern front of the Monte Leone Nappe, in the Penninic domain of the Alps. The rocks were metamorphosed up to upper greenschist – lower amphibolite-facies conditions. The mineralisation occurs in the uppermost part of a 240 metre thick metadolostone sequence, 180 to 200 metres above its base, close to the contact with the overlying Jurassic to Lower Cretaceous *Bündnerschiefer*. Graeser *et al.* (2008) distinguished five major, bedding-parallel zones. Argentotetrahedrite-(Zn) occurs in the Ag-rich, realgar-poor 'Zone 0', which also hosts the so-called jordanite–galena paragenesis with other rare Ag-minerals (e.g. marrite, quadratite, proustite, xanthoconite and hatchite). The Lengenbach quarry is the type locality for 46 new mineral species; a review of its mineralogy is given in Roth *et al.* (2014).

At Lengenbach, argentotetrahedrite-(Zn) forms domains within a tetratetrahedral crystal of Ag-bearing tetrahedrite-(Zn), with composition $(\text{Cu}_{3.12}\text{Ag}_{2.89})_{\Sigma 6.01}(\text{Cu}_{4.03}\text{Zn}_{1.56}\text{Cd}_{0.22}\text{Fe}_{0.17}\text{Hg}_{0.02})_{\Sigma 6.00}(\text{Sb}_{2.64}\text{As}_{1.36})_{\Sigma 4.00}\text{S}_{12.97}$, 1 mm in size associated with dolomite (Fig. 3). Its optical properties are similar to those reported for the Kremnica type material and the reflectance values are given in Table 1 and shown in Fig. 2. The crystallisation of argentotetrahedrite-(Zn) is related to the activity of hydrothermal fluids during the tectono-metamorphic Alpine events. Probably, it formed as a consequence of increasing Ag and Sb activities in the hydrothermal fluids during the late-stage evolution of the Lengenbach ore deposit and the consequent partial replacement of earlier Ag-bearing tetrahedrite-(Zn).

The Zvěstov (Czech Republic) occurrence

Argentotetrahedrite-(Zn) was also identified in samples collected from the mine dump in the southern part of the abandoned small deposit of Zvěstov (Stříbrnice), which is located 1200 m NNE from the village of Zvěstov. This deposit located 10 km SW of Vlašim, central Bohemia region, Czech Republic, is one of the small ore occurrences connected with the Blanice Graben, which represents an ~200 km long NNE–SSW trending

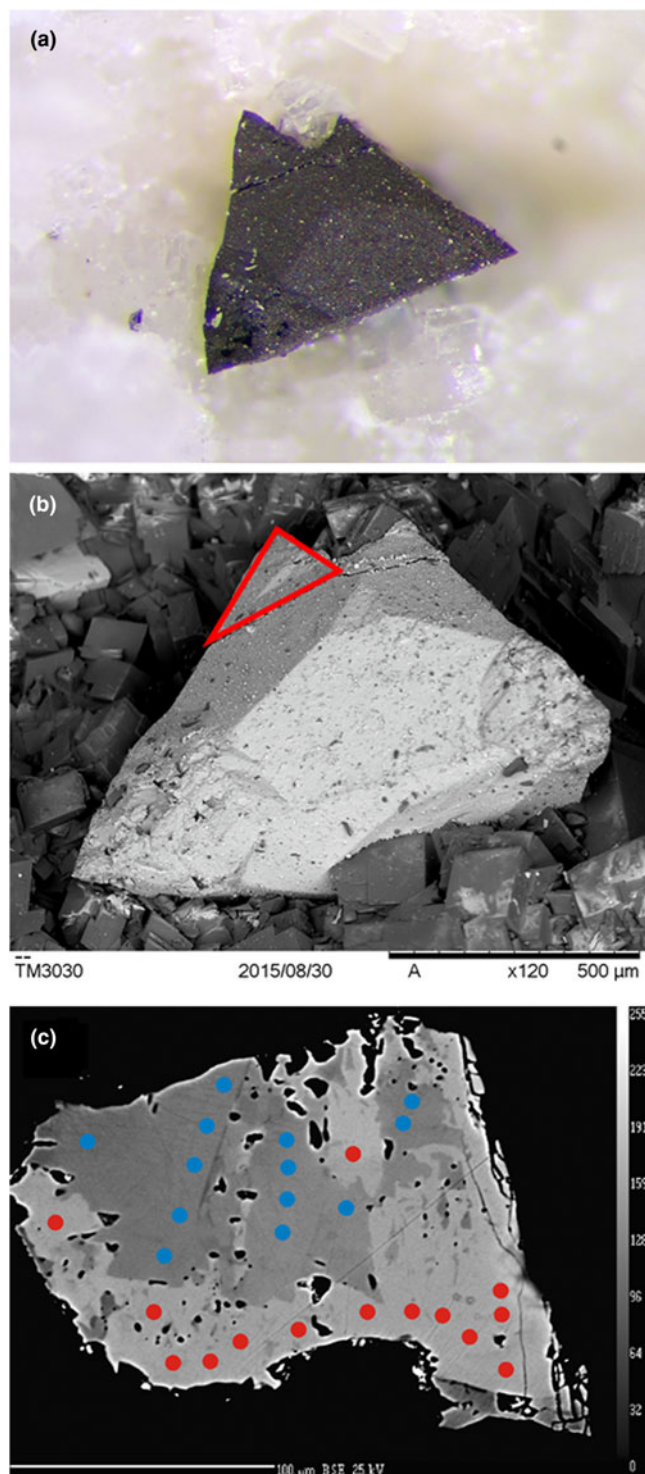


Fig. 3. Argentotetrahedrite-(Zn) from Lengenbach. (a) Tristetrahedral crystal, 1 mm in size, with dolomite. Collection H. Geuer, photo T. Raber. (b) Back-scattered electron (BSE) image of the same crystal. The red line indicates the grain selected for single-crystal X-ray diffraction study. (c) BSE image showing the chemical zoning of the grain used for the structural study. Red and blue circles indicate argentotetrahedrite-(Zn) and tetrahedrite-(Zn) spot analyses, respectively.

crustal-scale brittle tectonic zone in the Moldanubian Unit, with minimal sinistral movement of ~ 17 km (Zachariáš and Hübst, 2012). The deposit consists of an irregular hydrothermal vein system ~ 1300 m long, with thickness ~ 20 –50 cm and a vertical

extent (verified by a prospect borehole) of ~ 60 m (Nouza, 1988). There are no written records about the historical mining of this deposit (Velebil, 2004). A fragment of a ceramic mug found in the studied mine dump was dated to the turn of the 15th and 16th centuries (Velebil *et al.*, 2016). Exploration was last carried-out here in the years 1956–1957 (Nouza, 1988). The quartz + baryte veins of the Zvěstov deposit host grains of galena, sphalerite, chalcopyrite, pyrite, arsenopyrite and minerals of the tetrahedrite group (Nouza, 1988; Velebil *et al.*, 2016); it is also the type locality of the new member of the tetrahedrite group zvěstovite-(Zn), $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$ (Sejkora *et al.*, 2021b).

At Zvěstov, argentotetrahedrite-(Zn) forms irregular aggregates (Fig. 4) up to 200 μm in size, partly rimmed and replaced by younger kenoargentotetrahedrite-(Fe) with average empirical formula $(\text{Ag}_{5.36}\text{Cu}_{4.60})_{\Sigma 9.96}(\text{Fe}_{1.52}\text{Zn}_{0.41})_{\Sigma 1.93}(\text{Sb}_{4.01}\text{As}_{0.11})_{\Sigma 4.12}\text{S}_{12.23}$. Its optical properties are similar to those reported for the Kremnica type material and the reflectance values are given in Table 1 and shown in Fig. 2. Its crystallisation is related to the activity of Variscan hydrothermal fluids; samples are partly supergene altered.

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: wavelength dispersive spectroscopy mode, accelerating voltage = 25 kV, beam current = 20 nA and beam diameter = 1 μm . Standards (element, emission line) were: pyrite ($\text{FeK}\alpha$), chalcopyrite ($\text{CuK}\alpha$ and $\text{SK}\alpha$), ZnS ($\text{ZnK}\alpha$), NiAs ($\text{AsL}\beta$), Ag metal ($\text{AgL}\alpha$), Sb_2S_3 ($\text{SbL}\alpha$), PbSe ($\text{SeL}\alpha$), HgTe ($\text{HgM}\alpha$) and Bi_2Se_3 ($\text{BiM}\alpha$). Peak counting times were 20 s for all elements, and 10 s for each background. Bismuth and Se were found to be below the detection limits (0.02–0.05 wt.%). Matrix correction by PAP software (Pouchou and Pichoir, 1985) was applied to the data.

There are several different approaches to calculate the chemical formula of the tetrahedrite-group minerals; due to possible vacancies at the S(2) site in the Ag-rich members the best approaches are (Biagioni *et al.*, 2020a; Sejkora *et al.* 2021b): (1) normalisation on the basis of $\Sigma\text{Me} = 16$ apfu, assuming that no vacancies occur at M(2), M(1) and X(3); or (2) normalisation on the basis of $(\text{As} + \text{Sb}) = 4$ apfu, taking into account that previous studies (e.g. Johnson *et al.*, 1986) revealed that negligible variations with respect to the ideal number of X(3) atoms occur. The results of our study indicate that only very minor vacancies possibly occur at M(2), M(1) and X(3) sites and therefore the first approach was selected for calculation.

Chemical data for the holotype grain of argentotetrahedrite-(Zn) from Kremnica are given in Table 2 and give the following formula: $\text{Cu}_{6.74}\text{Ag}_{3.27}\text{Zn}_{1.69}\text{Fe}_{0.23}\text{Cd}_{0.02}\text{Hg}_{0.01}(\text{Sb}_{3.86}\text{As}_{0.17})_{\Sigma 4.03}\text{S}_{12.73}$; taking into account the results of the crystal structure refinement (see below), the crystal-chemical formula can be written as $(\text{Ag}_{3.27}\text{Cu}_{2.69})_{\Sigma 5.96}[\text{Cu}_{4.00}(\text{Zn}_{1.69}\text{Fe}_{0.23}\text{Cu}_{0.05}\text{Cd}_{0.02}\text{Hg}_{0.01})_{\Sigma 2.00}]_{\Sigma 6.00}(\text{Sb}_{3.86}\text{As}_{0.17})_{\Sigma 4.03}\text{S}_{12.73}$. The end-member formula of argentotetrahedrite-(Zn) is $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$ ($Z = 2$), corresponding to (in wt.%) Cu 13.13, Ag 33.43, Zn 7.65, Sb 25.16, S 21.53, total 100.00.

The chemical compositions for other samples (Kremnica grain 2, Lengenbach, Zvěstov) are given in Tables 2 and 3 and presented in Fig. 5. The Ag contents for all samples studied are found to lie in the range 3.10–3.54 apfu and do not correlate with S contents (Fig. 5a), whereas the positive correlation between Sb and Ag is indistinct (Fig. 5b); a similar situation was described for Ag-rich

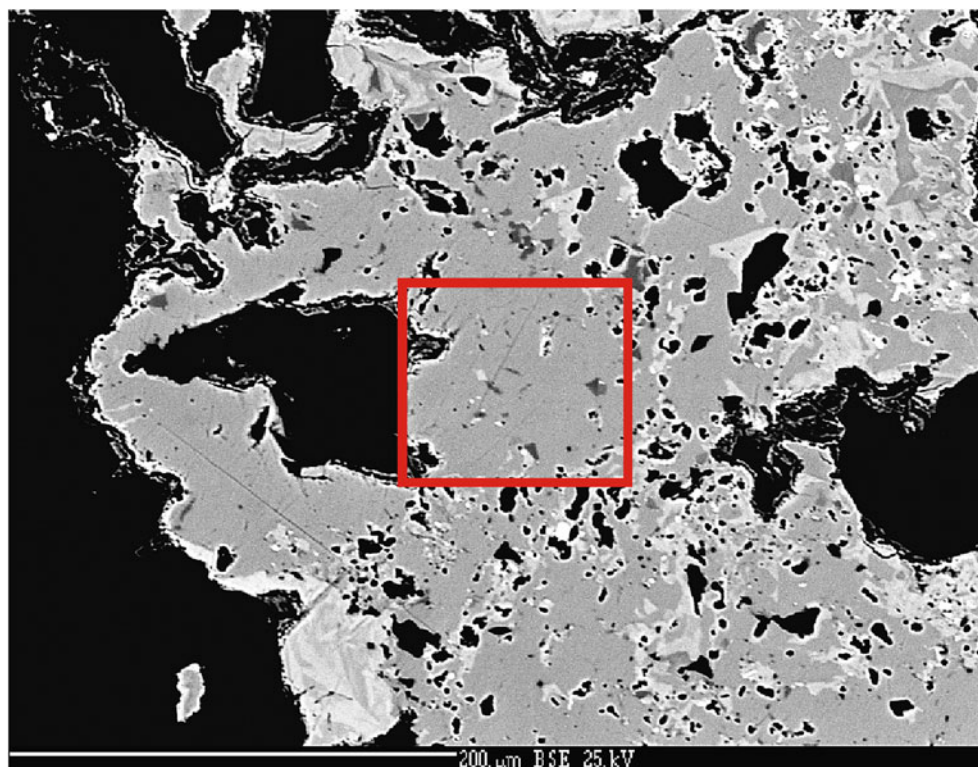


Fig. 4. Argentotetrahedrite-(Zn) from Zvěstov, Czech Republic. Aggregates up to 0.1 mm in size as seen in the BSE image. The lighter rims have a composition corresponding to kenoargentotetrahedrite-(Fe). The red box indicates the area where the grain used for single-crystal X-ray diffraction was extracted.

tetrahedrites by Johnson *et al.* (1986). All samples studied have Zn as the dominant C-constituent (Fig. 5c). Samples from Kremnica and Lengenbach are Fe-poor, with contents in the range 0.11–0.34 apfu Fe. The sample from Zvěstov shows slightly higher Fe contents, in the wider range 0.21–0.74 apfu. Moreover, the Lengenbach sample contains 0.21–0.29 apfu Cd. The extent of SbAs_{-1} substitution in all samples is limited to 0.42 apfu As (Fig. 5d). The determined S contents in the range 12.57–13.30 apfu indicates only minor possible vacancies at the S(2) site, which is consistent with results of crystal structure refinements (see below). The chemical composition of the studied samples can be expressed by the following empirical formulae: Kremnica (grain 2) $(\text{Ag}_{3.50}\text{Cu}_{2.44})_{\Sigma 5.94}[\text{Cu}_{4.00}(\text{Zn}_{1.66}\text{Fe}_{0.27}\text{Cu}_{0.04}\text{Cd}_{0.02}\text{Hg}_{0.01})_{\Sigma 2.00}]_{\Sigma 6.00}(\text{Sb}_{3.88}\text{As}_{0.17})_{\Sigma 4.05}\text{S}_{12.70}$; Lengenbach $(\text{Ag}_{3.17}\text{Cu}_{2.79})_{\Sigma 5.96}[\text{Cu}_{4.00}(\text{Zn}_{1.55}\text{Cd}_{0.23}\text{Fe}_{0.16}\text{Cu}_{0.05}\text{Hg}_{0.01})_{\Sigma 2.00}]_{\Sigma 6.00}(\text{Sb}_{3.71}\text{As}_{0.32})_{\Sigma 4.03}\text{S}_{12.77}$

and Zvěstov $(\text{Ag}_{3.27}\text{Cu}_{2.67})_{\Sigma 5.94}[\text{Cu}_{4.00}(\text{Zn}_{1.39}\text{Fe}_{0.50}\text{Cu}_{0.07}\text{Cd}_{0.03}\text{Hg}_{0.01})_{\Sigma 2.00}]_{\Sigma 6.00}(\text{Sb}_{4.03}\text{As}_{0.04})_{\Sigma 4.07}\text{S}_{13.08}$.

X-ray crystallography

Powder X-ray diffraction data could not be collected, due to the paucity of available material. Consequently, powder X-ray diffraction data, given in Table 4, were calculated through the software *PowderCell 2.3* (Kraus and Nolze, 1996) using the structural model of holotype material from Kremnica discussed below.

Single-crystal X-ray diffraction studies were performed using a Bruker Apex II diffractometer equipped with an air-cooled CCD detector, and graphite-monochromatised $\text{MoK}\alpha$ radiation (Dipartimento di Scienze della Terra, Università di Pisa). The detector-to-crystal distance was 50 mm. The data were corrected

Table 2. Compositional data for argentotetrahedrite-(Zn) from Kremnica (holotype sample) and Lengenbach (cotype sample).

	Kremnica (n = 13)			Lengenbach (n = 14)			Standard
	wt.%	range	e.s.d.	wt.%	range	e.s.d.	
Cu	23.97	23.82–24.18	0.12	23.99	23.58–24.28	0.18	chalcopyrite
Ag	19.78	19.42–20.02	0.18	18.90	18.26–19.40	0.34	Ag
Fe	0.73	0.58–0.92	0.13	0.50	0.36–0.60	0.07	pyrite
Zn	6.20	5.94–6.46	0.19	5.58	5.25–5.88	0.14	ZnS
Cd	0.15	0.08–0.21	0.04	1.45	1.28–1.81	0.15	CdTe
Hg	0.06	0.00–0.25	0.10	0.13	0.00–0.33	0.09	HgTe
As	0.71	0.52–1.02	0.16	1.32	0.97–1.66	0.23	NiAs
Sb	26.33	25.72–26.71	0.29	24.97	24.24–25.63	0.42	Sb_2S_3
S	22.85	22.59–23.05	0.17	22.61	22.37–22.96	0.10	chalcopyrite
Total	100.78	100.23–101.36	0.39	99.44	98.26–100.31	0.65	

e.s.d. = estimated standard deviation.

Table 3. Compositional data for argentotetrahedrite-(Zn) from Kremnica (grain 2) and Zvěstov.

	Kremnica (n = 17)			Zvěstov (n = 93)			Standard
	wt.%	range	e.s.d.	wt.%	range	e.s.d.	
Cu	23.01	22.77–23.26	0.13	23.65	23.09–24.13	0.24	chalcopyrite
Ag	21.12	20.75–21.53	0.22	19.52	18.84–20.98	0.33	Ag
Fe	0.85	0.72–1.05	0.11	1.53	0.64–2.30	0.30	pyrite
Zn	6.05	5.84–6.22	0.11	5.03	4.29–6.40	0.36	ZnS
Cd	0.13	0.10–0.18	0.03	0.16	0.00–1.16	0.16	CdTe
Hg	0.08	0.00–0.25	0.09	0.08	0.00–0.64	0.15	HgTe
As	0.73	0.47–0.96	0.16	0.17	0.00–1.76	0.43	NiAs
Sb	26.42	25.91–26.79	0.26	27.09	24.49–27.75	0.73	Sb ₂ S ₃
S	22.76	22.46–22.99	0.13	23.17	22.60–23.76	0.20	chalcopyrite
Total	101.14	100.24–101.93	0.36	100.41	98.74–101.73	0.53	

e.s.d. = estimated standard deviation.

for Lorentz and polarisation factors and absorption using the software package *Apex3* (Bruker AXS Inc., 2016). The crystal structure of argentotetrahedrite-(Zn) was refined using *Shelxl-2018* (Sheldrick, 2015) starting from the atomic coordinates of argentotetrahedrite-(Fe) (Welch *et al.*, 2018). In all three refinements, the modelling of the racemic twin indicated that the structure had to be inverted, and the difference-Fourier maps indicated the splitting of the *M*(2) site. Since electron microprobe data did not suggest any vacancy or cation excess at the *M*(2) site, the sum of the site occupancy factors (s.o.f.) at *M*(2a) and *M*(2b) was constrained to the full occupancy. The following neutral scattering curves, taken from the *International Tables for Crystallography* (Wilson, 1992) were initially used: Ag vs □ at *M*(2a), Cu vs □ at *M*(2b), Cu at *M*(1), As vs Sb at *X*(3), S at *S*(1) and *S*(2) sites.

Details of the crystal structure refinement of the three samples studied are described below and reported in Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 6. Table 7 reports selected bond distances. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Kremnica (Slovak Republic)

A prismatic fragment of argentotetrahedrite-(Zn) from Kremnica, 50 µm × 40 µm × 35 µm in size, was extracted from the polished section analysed using electron microprobe (Fig. 1). Data were collected using the φ scan mode, in 0.5° slices, with an exposure time

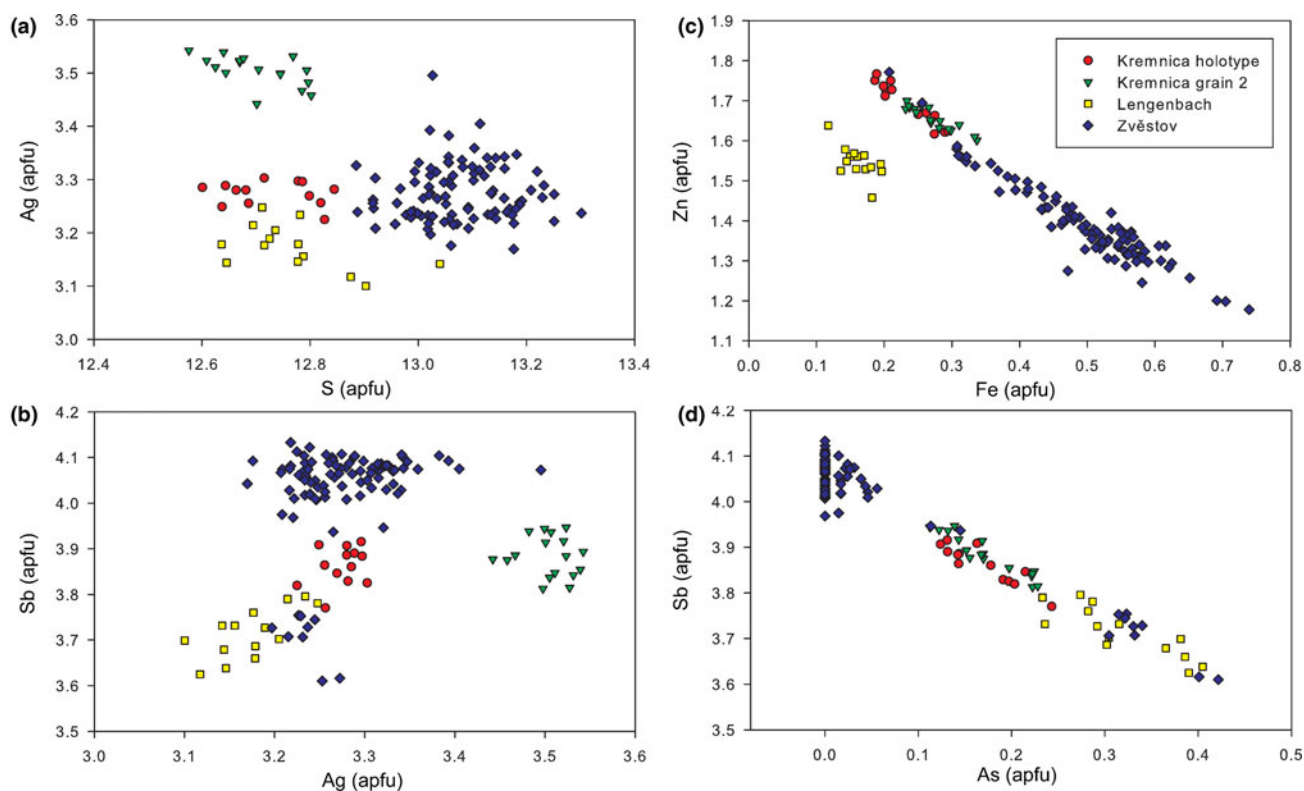
**Fig. 5** Chemical relationships (in apfu) between Ag vs S (a), Sb vs Ag (b), Zn vs Fe (c) and Sb vs As (d) in argentotetrahedrite-(Zn) from Kremnica, Lengenbach and Zvěstov.

Table 4. Calculated powder X-ray diffraction data for argentotetrahedrite-(Zn).*

I_{calc}	d_{calc}	hkl	I_{calc}	d_{calc}	hkl
24	7.460	1 1 0	6	1.926	5 2 1
1	4.307	2 1 1	35	1.865	4 4 0
2	3.730	2 2 0	3	1.809	4 3 3
1	3.336	3 1 0	1	1.712	5 3 2
100	3.046	2 2 2	1	1.712	6 1 1
6	2.820	3 2 1	1	1.668	6 2 0
23	2.638	4 0 0	1	1.628	5 4 1
2	2.487	3 3 0	18	1.591	6 2 2
6	2.487	4 1 1	1	1.556	6 3 1
1	2.359	4 2 0	2	1.523	4 4 4
6	2.249	3 3 2	1	1.492	5 5 0
6	2.069	5 1 0	1	1.492	7 1 0
5	2.069	4 3 1			

*Intensity and d_{hkl} were calculated using the software *PowderCell2.3* (Kraus and Nolze, 1996) on the basis of the structural model of the Kremnica sample given in Table 6. Only reflections with $I_{\text{calc}} > 1$ are listed. The five strongest reflections are given in bold.

of 45 s per frame. Unit-cell parameters are $a = 10.5505(10)$ Å, $V = 1174.4(3)$ Å³ and space group $\bar{I}43m$. Several cycles of isotropic refinement converged to $R_1 = 0.0797$, confirming the correctness of the structural model. However, a residual maximum of $ca. 5 e^-/\text{Å}^3$ suggested that the $M(2)$ site was actually split into two subpositions, namely $M(2a)$ and $M(2b)$. After the addition of the split positions, the isotropic refinement converged to $R_1 = 0.0410$. The anisotropic structural model converged to $R_1 = 0.0351$ for 327 unique reflections with $F_o > 4\sigma(F_o)$ and 22 refined parameters.

Lengenbach (Switzerland)

A fragment, $200 \mu\text{m} \times 120 \mu\text{m} \times 90 \mu\text{m}$, of the tristetrahedral individual shown in Figs 3a and 3b was used for the intensity

data collection. As shown in Fig. 3c, argentotetrahedrite-(Zn) from Lengenbach is associated closely with Ag-bearing tetrahedrite-(Zn). As the crystal studied through single-crystal X-ray diffraction was chemically inhomogeneous, the results of the crystal structure refinement are probably a weighted average of the two domains. Unit-cell parameters of the Lengenbach sample are $a = 10.5155(13)$ Å, $V = 1162.8(4)$ Å³ and space group $\bar{I}43m$. Several cycles of isotropic refinement converged to $R_1 = 0.1085$, showing a residual maximum of $ca. 6 e^-/\text{Å}^3$ around $M(2)$; a second maximum was observed close to $M(1)$. After the addition of the split positions, the isotropic refinement converged to $R_1 = 0.0516$, lowered to 0.0378 refining the s.o.f. at $M(1)$, using the scattering curves of Cu vs Cd. The anisotropic structural model converged to $R_1 = 0.0297$ for 385 unique reflections with $F_o > 4\sigma(F_o)$ and 23 refined parameters.

Zvěstov (Czech Republic)

A tabular fragment of argentotetrahedrite-(Zn), $ca. 50 \mu\text{m} \times 50 \mu\text{m} \times 30 \mu\text{m}$, was extracted from the polished section prepared on the sample from Zvěstov. Unit-cell parameters of this sample are $a = 10.5663(12)$ Å, $V = 1179.7(4)$ Å³ and space group $\bar{I}43m$. Several cycles of isotropic refinement converged to $R_1 = 0.0859$, showing a residual maximum of $ca. 5 e^-/\text{Å}^3$ around $M(2)$. After the addition of the split positions, the isotropic refinement converged to $R_1 = 0.0477$. The $X(3)$ site was found to be occupied by Sb only. The anisotropic structural model converged to $R_1 = 0.0381$ for 379 reflections with $F_o > 4\sigma(F_o)$ and 22 refined parameters.

Table 5. Summary of crystal data and parameters describing data collection and refinement for argentotetrahedrite-(Zn).

	Kremnica	Lengenbach	Zvěstov
Crystal data			
Crystal size (mm)	0.050 x 0.040 x 0.035	0.200 x 0.120 x 0.090	0.050 x 0.050 x 0.030
Cell setting, space group	Cubic, $\bar{I}43m$	Cubic, $\bar{I}43m$	Cubic, $\bar{I}43m$
a (Å)	10.5505(10)	10.5155(13)	10.5663(12)
V (Å ³)	1174.4(3)	1162.8(4)	1179.7(4)
Z	2	2	2
Data collection and refinement			
Radiation, wavelength (Å)	MoK α , $\lambda = 0.71073$	MoK α , $\lambda = 0.71073$	MoK α , $\lambda = 0.71073$
Temperature (K)	293(2)	293(2)	293(2)
$2\theta_{\text{max}}$ (°)	64.36	62.85	62.51
Measured reflections	2123	1751	1621
Unique reflections	358	388	384
Reflections with $F_o > 4\sigma(F_o)$	327	385	370
R_{int}	0.0485	0.0242	0.0388
$R\sigma$	0.0361	0.0213	0.0323
Range of h, k, l	$-13 \leq h \leq 8$, $-13 \leq k \leq 13$, $-13 \leq l \leq 10$	$-15 \leq h \leq 10$, $-12 \leq k \leq 9$, $-10 \leq l \leq 14$	$-11 \leq h \leq 11$, $-15 \leq k \leq 5$, $-12 \leq l \leq 12$
$R [F_o > 4\sigma(F_o)]$	0.0351	0.0297	0.0381
R (all data)	0.0418	0.0301	0.0399
wR (on F_o^2)	0.0537	0.0692	0.0812
Goof	1.163	1.282	1.245
Absolute structure parameter ²	0.01(8)	0.00(8)	0.07(10)
Number of least-squares parameters	22	23	22
Maximum and minimum residual peak ($e^- \text{Å}^{-3}$)	1.31 [at 0.70 Å from S(2)] -1.73 [at 0.00 Å from S(2)]	1.36 [at 0.52 Å from S(2)] -1.11 [at 0.68 Å from M(2)]	1.69 [at 0.59 Å from S(2)] -1.95 [at 0.00 Å from S(2)]

¹ $w = 1/[\sigma^2(F_o) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. KR: $a = 0$, $b = 10.6938$; LE: $a = 0$, $b = 17.9923$; ZV: $a = 0$, $b = 28.1692$.

²Flack (1983)

Table 6. Atoms, Wyckoff positions, site occupancy factors (s.o.f.), atom coordinates, equivalent isotropic displacement parameters (\AA^2), and refined (obs) and calculated (calc) site scattering for argentotetrahedrite-(Zn).

	Site	Wyckoff position	s.o.f.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
Kremnica	<i>M</i> (2a)	12e	Ag _{0.52(3)}	0.7822(6)	0	0	0.039(4)
	<i>M</i> (2b)	24g	Cu _{0.240(16)}	0.7876(14)	-0.0298(17)	0.0298(17)	0.039(4)
	<i>M</i> (1)	12d	Cu _{1.00}	3/4	1/2	0	0.0200(7)
	<i>X</i> (3)	8c	Sb _{0.95(3)} As _{0.05(3)}	0.73169(7)	0.73169(7)	0.73169(7)	0.0148(4)
	<i>S</i> (1)	24g	S _{1.00}	0.8795(2)	0.8795(2)	0.6336(3)	0.0163(6)
	<i>S</i> (2)	2a	S _{1.00}	0	0	0	0.134(11)
Lengenbach	<i>M</i> (2a)	12e	Ag _{0.54(3)}	0.7820(4)	0	0	0.042(3)
	<i>M</i> (2b)	24g	Cu _{0.228(14)}	0.7908(12)	-0.0357(12)	0.0357(12)	0.042(3)
	<i>M</i> (1)	12d	Cu _{0.96(3)} Cd _{0.04(3)}	3/4	1/2	0	0.0196(7)
	<i>X</i> (3)	8c	Sb _{0.76(3)} As _{0.24(3)}	0.73334(6)	0.73334(6)	0.73334(6)	0.0172(3)
	<i>S</i> (1)	24g	S _{1.00}	0.87914(17)	0.87914(17)	0.6362(2)	0.0170(6)
	<i>S</i> (2)	2a	S _{1.00}	0	0	0	0.126(10)
Zvěstov	<i>M</i> (2a)	12e	Ag _{0.67(4)}	0.7862(11)	0	0	0.057(5)
	<i>M</i> (2b)	24g	Cu _{0.164(18)}	0.787(4)	-0.024(7)	0.024(7)	0.057(5)
	<i>M</i> (1)	12d	Cu _{1.00}	3/4	1/2	0	0.0193(7)
	<i>X</i> (3)	8c	Sb _{1.00}	0.73143(8)	0.73143(8)	0.73143(8)	0.0160(4)
	<i>S</i> (1)	24g	S _{1.00}	0.8791(2)	0.8791(2)	0.6335(3)	0.0158(6)
	<i>S</i> (2)	2a	S _{1.00}	0	0	0	0.144(16)

Note: s.o.f. are used to model the site scattering, giving the MAN_{REF} reported in Table 8.

Results and discussion

Crystal structure description

The crystal structure of argentotetrahedrite-(Zn) agrees with the general features of the members of the tetrahedrite isotypic group, i.e. a collapsed sodalite-like framework formed by corner-sharing *M*(1)*S*(1)₄ tetrahedra with cages hosting *S*(2)-centred *M*(2)-octahedra, surrounded by four *X*(3)*S*(1)₃ trigonal pyramids (e.g. Johnson *et al.*, 1988).

In the three samples studied, the tetrahedrally coordinated *M*(1) site shows average distances ranging from 2.339 to 2.348 Å, the larger value being observed in argentotetrahedrite-(Zn) from the Lengenbach quarry, where minor Cd replaces Zn and Fe. Indeed, the crystal radius of Cd²⁺ in tetrahedral coordination is, according to Johnson *et al.* (1988), 0.84 Å, similar to that of Hg²⁺. In the samples from Kremnica and Zvěstov, the average bond distance agrees with those reported for other mixed (Cu,Zn,Fe) tetrahedral sites in tetrahedrite-group minerals (e.g. 2.342 Å – Wuensch, 1964). Taking into account the results of electron microprobe analyses and the mean atomic numbers (MAN) obtained during the crystal structure refinements (Table 8), the following site populations can be proposed for the *M*(1) site: (Cu_{4.00}Zn_{1.70}Fe_{0.25}Cu_{0.05}²⁺) (KR), (Cu_{4.00}Zn_{1.55}Cd_{0.25}Fe_{0.15}Cu_{0.05}²⁺) (LE), and (Cu_{4.00}Zn_{1.40}Fe_{0.50}Cu_{0.05}²⁺Cd_{0.05}) (ZV). There is a good agreement between refined MAN and those calculated on the basis of the proposed site populations.

Table 7. Selected bond distances (Å) for argentotetrahedrite-(Zn).

Site	Kremnica	Lengenbach	Zvěstov
<i>M</i> (1)– <i>S</i> (1)×4	2.3386(19)	2.3475(15)	2.342(2)
<i>M</i> (2a)– <i>S</i> (2)	2.298(7)	2.292(5)	2.259(12)
<i>M</i> (2a)– <i>S</i> (1)×2	2.386(5)	2.363(4)	2.422(9)
<i>M</i> (2b)– <i>S</i> (2)	2.284(17)	2.263(12)	2.28(5)
<i>M</i> (2b)– <i>S</i> (1)×2	2.464(9)	2.481(10)	2.45(3)
<i>X</i> (3)– <i>S</i> (1)×3	2.436(3)	2.397(2)	2.438(4)

Weighted bond-valence sums (Table 9) are 1.44 valence unit (vu) for all the studied samples, compared with a theoretical value of 1.33 vu. Such slight overbonding is a common feature for tetrahedrally coordinated cations in tetrahedrite-group minerals (Welch *et al.*, 2018).

The *M*(2) site is split in all the three specimens studied, in agreement with previous results (Welch *et al.*, 2018 and Sejkora *et al.*, 2021b) for rozhdestvenskayaite-(Zn) and zvěstovite-(Zn), respectively. Both sub-positions have a triangular coordination, with average bond distances ranging between 2.339 and 2.408 Å. These distances are shorter than those reported in rozhdestvenskayaite-(Zn) (2.43 and 2.53 Å for the two split positions – Welch *et al.*, 2018) and zvěstovite-(Zn) (2.39 and 2.57 Å – Sejkora *et al.*, 2021b), in agreement with the lower Ag content occurring in argentotetrahedrite-(Zn).

Shorter distances have been observed for the *M*(2a) positions (range of average distances: 2.339–2.367 Å), whereas *M*(2b) shows longer average distances, varying between 2.393 and 2.408 Å. For this reason, it is probable that Cu is preferentially hosted at *M*(2a), whereas the larger Ag⁺ cation may be hosted

Table 8. Refined mean atomic numbers (MAN – in electrons) and proposed site populations for cation sites in argentotetrahedrite-(Zn).

Site	MAN _{REF}	Proposed site population	MAN _{calc}
Kremnica			
<i>M</i> (2)	38.36	Ag _{3.25} Cu _{2.75}	38.75
<i>M</i> (1)	29.00	Cu _{4.00} Zn _{1.70} Fe _{0.25} Cu _{0.05} ²⁺	29.15
<i>X</i> (3)	50.10	Sb _{3.85} As _{0.15}	50.32
Lengenbach			
<i>M</i> (2)	38.72	Ag _{3.20} Cu _{2.80}	38.60
<i>M</i> (1)	29.76	Cu _{4.00} Zn _{1.55} Cd _{0.25} Fe _{0.15} Cu _{0.05} ²⁺	29.98
<i>X</i> (3)	46.68	Sb _{3.70} As _{0.30}	49.65
Zvěstov			
<i>M</i> (2)	41.06	Ag _{3.25} Cu _{2.75}	38.75
<i>M</i> (1)	29.00	Cu _{4.00} Zn _{1.40} Fe _{0.50} Cu _{0.05} ²⁺ Cd _{0.05}	29.14
<i>X</i> (3)	51.00	Sb _{3.90} As _{0.10}	50.55

Table 9. Weighted bond-valence sums (in vu) in argentotetrahedrite-(Zn).

	Site	M(1)	M(2a)	M(2b)	X(3)	Σanions	Theoretical
Kremnica	S(1)	2x→0.36 ^{x4}	0.24 ^{x2}	2x→0.06 ^{x2}	1.02 ^{x3}	2.10	2.00
	S(2)		6x→0.30	12x→0.10		3.00	2.00
	Σcations	1.44	0.78	0.22	3.06		
	Theoretical	1.33	0.70	0.15	3.00		
Lengenbach	S(1)	2x→0.36 ^{x4}	0.26 ^{x2}	2x→0.06 ^{x2}	1.07 ^{x3}	2.17	2.00
	S(2)		6x→0.32	12x→0.10		3.12	2.00
	Σcations	1.44	0.84	0.22	3.21		
	Theoretical	1.33	0.72	0.14	3.00		
Zvěstov	S(1)	2x→0.36 ^{x4}	0.29 ^{x2}	2x→0.03 ^{x2}	1.02 ^{x3}	2.11	2.00
	S(2)		6x→0.45	12x→0.05		3.30	2.00
	Σcations	1.44	1.03	0.11	3.06		
	Theoretical	1.33	0.85	0.08	3.00		

Note: bond-valence sums are calculated using the bond parameters of Brese and O'Keeffe (1991).

Table 10. Comparison of argentotetrahedrite-(Zn) samples and other members of the freibergite series.

	Argentotetrahedrite-(Zn)				Argentotetrahedrite-(Fe)	Kenoargentotetrahedrite-(Zn)	Kenoargentotetrahedrite-(Fe)
	Kremnica [1]	Lengenbach [1]	Zvěstov [1]	Yakutia [2]	Keno Hill [3]	Yindongpo [4]	Freiberg [3]
End-member formula	$M^{(2)}Ag_6^{M(1)}(Cu_4Zn_2)^{X(3)}Sb_4^{S(1)}S_{12}^{S(2)}S$				$M^{(2)}Ag_6^{M(1)}(Cu_4Fe_2)^{X(3)}Sb_4^{S(1)}S_{12}^{S(2)}S$	$M^{(2)}Ag_6^{M(1)}(Cu_4Zn_2)^{X(3)}Sb_4^{S(1)}S_{12}^{S(2)}\square$	$M^{(2)}Ag_6^{M(1)}(Cu_4Fe_2)^{X(3)}Sb_4^{S(1)}S_{12}^{S(2)}\square$
$M^{(2)}Ag/(Ag+Cu)$	0.54	0.53	0.54	0.60	0.73	0.63	0.90
$M^{(1)}Zn/(Zn+Fe+Me^{2+})$	0.84	0.78	0.70	0.66	0.26	0.54	0.13
$X^{(1)}Sb/(Sb+As)$	0.96	0.92	0.99	0.98	0.99	0.93	1.00
$Y+Z$ (apfu)	$S_{12.73}$	$S_{12.77}$	$S_{13.08}$	$S_{12.85}$	$S_{12.68}$	$S_{11.93}$	$S_{12.01}$
a (Å)	10.5505(10)	10.5155(13)	10.5663(12)	10.576(3)	10.6116(1)	10.4624(4)	10.4930(4)
V (Å ³)	1174.4(3)	1162.8(4)	1179.7	1182.9(1)	1194.92(2)	1145.23(13)	1155.31(8)
$M(2)-S(1)$ (Å)	2.386/2.464	2.363/2.481	2.422/2.45	2.431	2.437	n.p.	2.554
$M(2)-S(2)$ (Å)	2.298/2.284	2.292/2.263	2.259/2.28	2.249	2.291	n.p.	-
$M(1)-S(1)$ (Å)	2.339	2.348	2.342	2.346	2.344	n.p.	2.333
U_{eq} S(2) (Å ²)	0.134	0.126	0.144	0.108	0.121	-	-
V S(2) _{oct.} (Å ³)	16.2	16.1	15.3	15.2	16.0	n.p.	10.8

Me²⁺ = e.g. Cd, Hg. n.p. = not published.

[1] this work; [2] Rozhdestvenskaya *et al.* (1993); [3] Welch *et al.* (2018); [4] Qu *et al.* (2021).

at both sub-positions. Table 8 reports the mean atomic number for $M(2)$ sites [= $M(2a) + M(2b)$]. The agreement between refined and calculated MAN is usually good, the largest deviation being observed for the sample from Zvěstov. If Cu is assumed to be preferentially hosted at $M(2a)$, the following site populations may be proposed, taking into account the refined mean atomic numbers: $M(2a) = Cu_{0.46}Ag_{0.24}$, $M(2b) = Ag_{0.15}$ (KR); $M(2a) = Cu_{0.47}Ag_{0.25}$, $M(2b) = Ag_{0.14}$ (LE); and $M(2a) = Cu_{0.46}Ag_{0.39}$, $M(2b) = Ag_{0.075}$ (ZV). Using these hypothetical populations, weighted bond-valence sums have been calculated (Table 9), resulting in a general overbonding, as observed in other Ag-bearing tetrahedrite-group minerals (e.g. Sejkora *et al.*, 2021b). This is mainly due to the short $M(2)-S(2)$ distance, definitely shorter than the ideal $\langle Ag-S \rangle$ distance in three-fold coordination, i.e. 2.56 Å.

The $X(3)$ site shows the typical trigonal pyramidal coordination. Average bond distances range between 2.397 and 2.438 Å. Whereas the bond distance in samples from Kremnica and Zvěstov are very similar, due to similar $Sb/(As+Sb)$ atomic ratios, the distance observed in the sample from Lengenbach is distinctly shorter, owing to its larger As content. However, the results obtained for the Swiss samples agree with its inhomogeneous

nature. As described above, the sample from this locality actually comprises two phases, i.e. argentotetrahedrite-(Zn) and Ag-rich tetrahedrite-(Zn). The latter is As-richer than the former, whereas the site populations at the $M(1)$ site are similar in both phases. Whereas such an inhomogeneity was not observed in the refinement of the MAN at the $M(2)$ site, it can be observed considering the MAN at the $X(3)$ site (Table 8). Indeed, whereas electron microprobe analysis suggests an $Sb/(As+Sb)$ atomic ratio close to 0.92, the refined s.o.f. indicates a lower $Sb/(As+Sb)$ atomic ratio, i.e. 0.76. Such a value is in accordance with the ratio calculated on the basis of the observed bond distance, corresponding to a site having an ideal occupancy ($Sb_{0.72}As_{0.28}$). Taking into account the chemistry of argentotetrahedrite-(Zn) and Ag-rich tetrahedrite-(Zn), it is possible to estimate a ratio of 0.40/0.60 for the two phases in the grain studied. This ratio can help in explaining why such an inhomogeneity cannot be detected at the $M(2)$ site: indeed, the two phases have the ideal occupancy ($Ag_{0.53}Cu_{0.47}$) and ($Cu_{0.52}Ag_{0.48}$), respectively. The phase ratio indicated above results in the average composition ($Cu_{0.50}Ag_{0.50}$), corresponding to a MAN of 38.0 electrons, not dramatically different from the observed value, i.e., 38.72 electrons. Weighted bond-valence sums (Table 9) agree with the theoretical value. The largest

discrepancy is observed for the Lengenbach sample, probably due to the inhomogeneity just described.

The S(1) site is coordinated tetrahedrally by two M(1) sites, one M(2) site [i.e. M(2a) or one of the two mutually-exclusive M(2b)] and one X(3) site. Its bond-valence sum ranges between 2.10 and 2.17 vu, in agreement with the occurrence of S²⁻. On the contrary, the S(2) site, octahedrally coordinated by the M(2) site, is severely overbonded, with values ranging between 3.00 and 3.30 vu, as observed in other Ag-rich tetrahedrite-group minerals (e.g. Sejkora *et al.*, 2021b). This is due to the short distance between M(2) and S(2); this kind of behaviour was described previously by Johnson *et al.* (1988), who stressed the aspherical nature of three-fold Ag. This feature, along with the high U_{eq} value shown by S(2) and the overbonding of the M(2) site, will be further discussed below.

Comparison between argentotetrahedrite-(Zn) and other members of the freibergite series

Argentotetrahedrite-(Zn) belongs to the freibergite series within the tetrahedrite group (Biagioni *et al.*, 2020a). It is the Zn-isotope of argentotetrahedrite-(Fe) (Welch *et al.*, 2018) and the Sb-isotope of argentotennantite-(Zn) (Spiridonov *et al.*, 1986).

Selected data for argentotetrahedrite-(Zn) samples and valid (Zn/Fe)-members of the freibergite series are compared in Table 10. The Ag/(Ag+Cu) atomic ratios range between 0.53 and 0.73 and these show a linear relationship with the unit-cell parameter a , the deviation from the linearity being due to different Sb/(Sb+As) ratios. For instance, the specimen from Lengenbach displays a shorter unit-cell parameter owing to the higher As content with respect to the specimens from Kremnica and Zvěstov with very similar Ag contents. In all the samples studied currently, Sb/(Sb+As) is > 0.90. Different Zn/(Zn+Fe+Me²⁺) ratios, where Me²⁺ are other divalent metals (e.g. Hg²⁺, Cd²⁺), do not significantly affect the unit-cell parameter. The same is true for the M(1)–S(1) bond distance, that varies between 2.339 and 2.348 Å, the longer distance probably being due to the partial replacement of Zn and Fe by Cd in the Lengenbach sample. In the M(2) polyhedron, the M(2)–S(1) distance is definitely longer and more sensitive to the Ag content than the M(2)–S(2) distance, in agreement with previous studies (e.g. Peterson and Miller, 1986; Welch *et al.*, 2018). The M(2)–S(2) distance is usually short, being in the range 2.25–2.30 Å; this short Ag–S contact results in the exceptional overbonding of the S atoms hosted at S(2), as shown in Table 9. This physically unrealistic value is probably the effect of S(2) disorder, in agreement with the high U_{eq} values, varying between 0.11 and 0.14 Å². A high U_{eq} value may be related to the incorrect refinement of the s.o.f., that is, more S than that actually present is assumed at the S(2) site, or to positional disorder. As electron microprobe data do not support the occurrence of significant vacancies (S contents ranging between 12.68 and 13.08 apfu in specimens of argentotetrahedrite-(Fe/Zn) reported in Table 10), the second hypothesis could be the correct one. This is in agreement with Peterson and Miller (1986), who suggested that in order to achieve longer Ag–S bonds, S should be located off site 2a. Indeed, in the crystal structure refinement of the three samples of argentotetrahedrite-(Zn) studied in this work, a residual maximum at position 8c (x, x, x), with $x = 0.0384, 0.0284$ and 0.0321 for samples from Kremnica, Lengenbach and Zvěstov, respectively, was found. The displacement of S(2), coupled with minor shifts in the positions of Ag and Cu atoms hosted at M(2), agreeing with the

high U_{eq} value and the split nature of this latter site, will probably be able to achieve a physically sound coordination for both Ag and S in the argentotetrahedrite structure.

The range of Ag/(Ag+Cu) atomic ratios for argentotetrahedrite-(Zn) overlaps partially with that of kenoargentotetrahedrite-(Fe) and kenoargentotetrahedrite-(Zn), 0.63–0.90 (Table 10). Actually, few crystallographic data are available for the keno-members of the freibergite series. What is clear is that a detectable contraction of the unit-cell parameter can be observed for these keno-phases. For instance, kenoargentotetrahedrite-(Zn), having an Ag/(Ag+Cu) atomic ratio of 0.63, has a unit-cell parameter $a = 10.4624(4)$ Å (Qu *et al.*, 2021), significantly shorter than that given by Rozhdestvenskaya *et al.* (1993) for argentotetrahedrite-(Zn) with Ag/(Ag+Cu) = 0.60, i.e. $a = 10.576(3)$ Å. This probably reflects the contraction of the S(2)-centred M(2)-octahedron. In the two keno-members of the freibergite series reported in Table 10, S ranges between 11.93 and 12.01 apfu, agreeing with the empty nature of S(2). Indeed, the volume of the M(2)-octahedron is 10.8 Å³ in kenoargentotetrahedrite-(Fe) (Welch *et al.*, 2018), to be compared with 15.2 and 16.2 Å³ (+ 40–50%) in argentotetrahedrite-(Zn/Fe). This seems to be a clear structural feature allowing for the distinction between argentotetrahedrite and kenoargentotetrahedrite.

Previous findings of argentotetrahedrite-(Zn): a brief review

Tetrahedrite-group minerals having chemical compositions corresponding to that of argentotetrahedrite-(Zn) have been reported previously. To the best of our knowledge, the first chemical data corresponding to argentotetrahedrite-(Zn) were reported by Ixer and Stanley (1983), who gave two analyses on samples from the Sark's Hope mine, Sark, Channel Islands, showing 3.6–3.9 Ag apfu and 1.4–1.7 Zn apfu. Later, in the 1990s, Li and Wang (1990) reported four analyses from the Dachang ore field, Guangxi, China, with 3.1–3.7 Ag apfu and 1.0–1.8 Zn apfu, whereas Rozhdestvenskaya *et al.* (1993) described the crystal structure investigation of 'freibergite' from eastern Yakutia, Russia. Electron microprobe data gave the formula $(\text{Ag}_{3.62}\text{Cu}_{6.37})_{\Sigma 9.99}(\text{Zn}_{1.33}\text{Fe}_{0.72})_{\Sigma 2.05}(\text{Sb}_{3.89}\text{As}_{0.07})_{\Sigma 3.96}\text{S}_{12.85}$, and their structural data [$a = 10.576(3)$ Å, $R_1 = 0.041$] represent the first determination of the crystal structure of argentotetrahedrite-(Zn). Filimonov and Spiridonov (2005) described members of the freibergite series from the Kvartsitovye Gorki deposit, central Kazakhstan, characterised by an unusual wide range of Ag contents (3.1–6.7 apfu) with 1.5–1.7 Zn apfu and S in the range 12.6–13.3 apfu. Recently, argentotetrahedrite-(Zn) was reported also from the Vyhne deposit, Slovak Republic (3.1–3.2 Ag, 1.6–1.9 Zn and 12.7–13.0 S apfu) by Vlasáč *et al.* (2021) and from the San Genaro mine, Peru (3.2–3.3 Ag, 1.5–1.9 Zn and 12.9–13.1 S apfu) by Velebil *et al.* (2021).

In addition to these occurrences, other Zn-dominant members of the freibergite series were reported from Silvermines, County Tipperary, Ireland (Zakrzewski, 1989), the Keno Hill district, Yukon, Canada (Lynch, 1989), and the Xinhua Pb–Zn deposit, China (Wang *et al.*, 2018). However, the chemical data given by these authors do not allow for an accurate classification of these samples. For instance, Zakrzewski (1989) reported seven chemical analyses of tetrahedrite-group minerals from Silvermines; among these, five have Ag contents ranging between 20.6 and 23.9 wt.%. This author recalculated the chemical data on the basis of 29 apfu, obtaining ΣMe in the range 16.29–16.49 apfu, with (Sb+As)

varying between 4.09 and 4.32 apfu. Normalising these analyses on the basis of $\Sigma\text{Me} = 16$ apfu or $(\text{Sb} + \text{As}) = 4$ apfu leads to chemical formulae that are intermediate between argentotetrahedrite-(Zn) and kenoargentotetrahedrite-(Zn). The lack of structural data, coupled with the uncertainty on the actual S content, do not allow for a straightforward classification at a species level, and thus these samples must be labelled as 'Zn-rich freibergite', using the series name.

Finally, synthetic analogues of argentotetrahedrite-(Zn) were studied by Patrick and Hall (1983), who reported a unit-cell parameter $a = 10.565$ Å for a sample with 3.6 Ag apfu, whereas samples with 4.49 and 4.70 Ag apfu showed unit-cell parameters $a = 10.620$ and 10.625 Å, respectively.

Conclusions

Following the approval of the new nomenclature of the tetrahedrite group (Biagioni *et al.*, 2020a), a renewed interest in this group of common sulfosalts has allowed for the definition of several new mineral species. Argentotetrahedrite-(Zn) is one of the latest additions to this group. In addition to the new mineral, new structural data have been collected, thereby improving our knowledge on the crystal chemistry of these chalcogenides. This is particularly important for Ag-bearing tetrahedrite-group minerals, whose actual definition was unclear up to the paper by Welch *et al.* (2018), who confirmed the results of Rozhdstvenskaya *et al.* (1989, 1993), pointing out the difference between 'freibergite' [now kenoargentotetrahedrite-(Fe)] and argentotetrahedrite-(Fe). Even if the distinction between argentotetrahedrites and their keno-counterpart is not always an easy task using only electron microprobe data, due to uncertainties in S determination, single-crystal X-ray diffraction data seem to allow for a distinction between them, with implications on the knowledge of ore-forming processes. Further studies on Ag-bearing members of the tetrahedrite group will be useful, not only for depicting a better picture of the chemical variability of tetrahedrite-group minerals, but also for achieving a better understanding of the crystal chemistry of Ag in these compounds.

Acknowledgements. The authors thank Zdeněk Dolníček (National Museum, Praha) for his help with the analytical work, Dalibor Velebil (National Museum, Praha) for useful information about the history and geology of the Zvěstov occurrence and Kai Qu (Tianjin Centre, China Geological Survey, Tianjin) for unpublished information on kenoargentotetrahedrite-(Zn). The helpful comments of an anonymous reviewer, Peter Leverett, Yves Moëlo, Associate Editor Ian Graham and Principal Editor Stuart Mills are greatly appreciated. The study was financially supported by the Ministry of Culture of the Czech Republic (long-term project DKRVO 2019–2023/1.II.d; National Museum, 00023272) for JS, MŠ and LV. CB acknowledges 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.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2022.21>

References

- Biagioni C., George L.G., Cook N.J., Makovicky E., Moëlo Y., Pasero M., Sejkora J., Stanley C.J., Welch M.D. and Bosi F. (2020a) The tetrahedrite group: Nomenclature and classification. *American Mineralogist*, **105**, 109–122.

- Biagioni C., Sejkora J., Moëlo Y., Makovicky E., Pasero M. and Dolníček Z. (2020b) Kenoargentotetrahedrite-(Fe), IMA 2020-062. In: CNMNC Newsletter 58. *Mineralogical Magazine*, **84**, 971–975.
- Böhmer M. (1966) Geology and mineral associations of gold-bearing veins in the central part of the Kremnica ore field. *Acta Geologica et Geographica Universitatis Comenianae, Geologica*, **11**, 5–123 [in Slovak].
- Brese 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.
- Filimonov S.V. and Spiridonov E.M. (2005) Fahlores from the Kvartsitovye Gorki hypabyssal gold antimonite deposit (north of central Kazakhstan). *New Data on Minerals*, **40**, 96–104.
- Flack H.D. (1983) On enantiomorph-polarity estimation. *Acta Crystallographica*, **A39**, 876–881.
- Graeser S., Cannon R., Drechsler E., Raber T. and Roth P. (2008) *Faszination Lengenbach Abbau-Forschung-Mineralien 1958–2008*. Kristallographik Verlag, Achberg, Germany [in German].
- Ixer R.A. and Stanley C.J. (1983) Silver mineralization at Sark's Hope mine, Sark, Channel Islands. *Mineralogical Magazine*, **47**, 539–545.
- Johnson N.E., Craig J.R. and Rimstidt J.D. (1986) Compositional trends in tetrahedrite. *The Canadian Mineralogist*, **24**, 385–397.
- Johnson N.E., Craig J.R. and Rimstidt J.D. (1988) Crystal chemistry of tetrahedrite. *American Mineralogist*, **73**, 389–397.
- Kenngott G.A. (1853) *Das Mohs'sche Mineralsystem, dem gegenwärtigen Standpunkte der Wissenschaft gemäss bearbeitet*. Gerold Verlag, Wien.
- Koděra P., Šucha V., Lexa J. and Fallick A.E. (2007) The Kremnica Au-Ag epithermal deposit: an example of laterally outflowing hydrothermal system? Pp. 173–176 in: *Digging Deeper* (Andrew *et al.*, editors). Proceedings of IX SGA Conference, Irish Association for Economic Geology.
- 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.
- Kraus I., Chernishev I.V., Šucha V., Kovalenker V.A., Lebedev V.A. and Šamajová E. (1999) Use of illite for K/Ar dating of hydrothermal precious and base metal mineralization in Central Slovak Neogene volcanic rocks. *Geologica Carpathica*, **50**, 353–364.
- Lexa J. and Bartalský B. (1999) Low-sulfidation epithermal gold at Kremnica. Pp. 265–273 in: *Epithermal mineralization of the Western Carpathians* (Molnár, F., Lexa, J. and Hedenquist, J.W., editors). Society of Economic Geologists, Guidebook Series, **31**. Littleton, Colorado, USA.
- Lexa J., Halouzka R., Havrila M., Hanzel L., Kubeš P., Liščák P. and Hojstříčková V. (1998) *Explanatory notes to the geological map of the Kremnické vrchy mountain range*. D. Štúr Institute of Geology, Bratislava, 1–308.
- Li X. and Wang G. (1990) Studies of the tetrahedrite-group minerals from Dachang ore field, Guangxi, China. *Acta Mineralogica Sinica*, **10**, 119–126 [in Chinese].
- Lynch J.G. (1989) Large-scale hydrothermal zoning reflected in the tetrahedrite-freibergite solid solution, Keno Hill Ag-Pb-Zn district, Yukon. *The Canadian Mineralogist*, **27**, 383–400.
- Nouza R. (1988) *Prognostic Evaluation of Ag-Pb-Zn Mineralization of the Blanice Graben*. Unpublished Dissertation Thesis, Faculty of Science, Charles University Prague, 143 pp. [in Czech].
- Patrick R.A.D. and Hall A.J. (1983) Silver substitution into synthetic zinc, cadmium, and iron tetrahedrites. *Mineralogical Magazine*, **47**, 441–451.
- Peterson R.C. and Miller I. (1986) Crystal structure and cation distribution in freibergite and tetrahedrite. *Mineralogical Magazine*, **50**, 717–721.
- Pouchou J.L. and Pichoir F. (1985) "PAP" (ϕρZ) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, San Francisco.
- Qu K., Sima X., Gu X., Sun W., Fan G., Hou Z., Ni P., Wang D., Yang Z. and Wang Y. (2021) Kenoargentotetrahedrite-(Zn), IMA 2020-075. CNMNC Newsletter 59; *Mineralogical Magazine*, **85**, 278–281, <https://doi.org/10.1180/mgm.2021.5>
- Riley J.F. (1974) The tetrahedrite-freibergite series, with reference to the Mount Isa Pb-Zn-Ag orebody. *Mineralium Deposita*, **9**, 117–124.
- Roth P., Raber T., Drechsler E. and Cannon R. (2014) The Lengenbach quarry, Binn Valley, Switzerland. *The Mineralogical Record*, **45**, 157–196.

- Rozhdestvenskaya I.V., Zayakina N.V. and Samusikov V.P. (1989) Crystal structure studies in the tetrahedrite-freibergite series. 12th *European Crystallographic Meeting, Moscow, USSR, August 20–29*. Collected abstracts, vol. 2, 145.
- Rozhdestvenskaya I.V., Zayakina N.V. and Samusikov V.P. (1993) Crystal structure features of minerals from a series of tetrahedrite-freibergite. *Mineralogiceskij Zhurnal*, **15**, 9–17 [in Russian].
- Sejkora J., Biagioni C., Števkó M., Raber T. and Roth P. (2021a) Argentotetrahedrite-(Zn). IMA 2020-069. CNMNC Newsletter 59. *Mineralogical Magazine*, **84**, 278–281, <https://doi.org/10.1180/mgm.2021.5>
- Sejkora J., Biagioni C., Vrtiška L. and Moělo Y. (2021b) Zvěstovite-(Zn), $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, a new tetrahedrite-group mineral from Zvěstov, Czech Republic. *Mineralogical Magazine*, **85**, 716–724.
- Sheldrick G.M. (2015) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.
- Spiridonov E.M., Sokolova N.G., Gapeev A.K., Dashevskaya D.M., Evstigneeva T.L., Chvileva T.N., Demidov V.G., Balashov E.P. and Shulga V.I. (1986) A new mineral – argentotennantite. *Doklady Akademii Nauk SSSR*, **290**, 206–210 [in Russian].
- Števkó M., Sejkora J., Dolníček Z. and Škákha P. (2018) Selenium-rich Ag-Au mineralization at the Kremnica Au-Ag epithermal deposit, Slovak Republic. *Minerals*, **8**, 572.
- Velebil D. (2004) The occurrence of base-metal ores at Zvěstov, SW of Vlašim. *Sborník semináře Stříbrná Jihlava 2004*, 160–162 [in Czech].
- Velebil D., Macek I. and Soumar J. (2016) A contribution to knowledge of chemistry of tetrahedrites from the Czech localities: Příbram, Obecnice, Zvěstov, Mníšek pod Brdy, Ratibořské Hory, Stará Vožice, Jáchymov, Kutná Hora and Stříbrná Skalice. *Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze*, **24**, 132–143 [in Czech].
- Velebil D., Hyršl J., Sejkora J. and Dolníček Z. (2021) Chemistry and classification of minerals of tetrahedrite group from deposits of Peru. *Bulletin Mineralogie Petrologie* **29**, 321–336 [in Czech].
- Vlasáč J., Chovan M., Vojtko R., Žitňan P. and Mikuš T. (2021) Mineralogy of the Au-Ag mineralization from the Finsterort and Anton vein system, Štiavnické vrchy Mts. (Slovakia). *Bulletin Mineralogie Petrologie* **29**, 255–269.
- Wang M., Zhang X., Guo X., Pi D. and Yang M. (2018) Silver-bearing minerals in the Xinhua hydrothermal vein-type Pb-Zn deposit, South China. *Mineralogy and Petrology*, **112**, 85–103.
- Weissenbach C.G.A. von (1831) Ueber die Gehalte der beym sächsischen Bergbau vorkommenden Silbererze. *Kalender für den Sächsischen Berg- und Hüttenmann auf das Jahr 1831*, 223–248.
- 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. (editor) (1992) *International Tables for Crystallography Volume C: Mathematical, Physical and Chemical Tables*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Wu P., Gu X., Qu K., Yang H. and Wang Y. (2021) Argentotetrahedrite-(Hg), IMA 2020-079. In: CNMNC Newsletter 59. *Mineralogical Magazine*, **85**, 278–281.
- Wuensch B.J. (1964) The crystal structure of tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. *Zeitschrift für Kristallographie*, **119**, 437–453.
- Zachariáš J. and Hübst T. (2012) Structural evolution of the Roudný gold deposit, Bohemian Massif: a combination of paleostress analysis and review of historical documents. *Journal of Geosciences*, **57**, 87–103.
- Zakrzewski M.A. (1989) Members of the freibergite-argentotennantite series and associated minerals from Silvermines, County Tipperary, Ireland. *Mineralogical Magazine*, **53**, 293–298.