

## The tetrahedrite group: Nomenclature and classification

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### ABSTRACT

The classification of the tetrahedrite group minerals in keeping with the current IMA-accepted nomenclature is discussed. Tetrahedrite isotypes are cubic, with space group symmetry  $I\bar{4}3m$ . The general structural formula of minerals belonging to this group can be written as  $M^{(2)}A_6M^{(1)}(B_4C_2)^{X(3)}D_4S^{(1)}Y_{12}S^{(2)}Z$ , where  $A = Cu^+, Ag^+, \square$  (vacancy), and  $(Ag_6)^{4+}$  clusters;  $B = Cu^+$ , and  $Ag^+$ ;  $C = Zn^{2+}$ ,  $Fe^{2+}$ ,  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Cu^+$ , and  $Fe^{3+}$ ;  $D = Sb^{3+}$ ,  $As^{3+}$ ,  $Bi^{3+}$ , and  $Te^{4+}$ ;  $Y = S^{2-}$  and  $Se^{2-}$ ; and  $Z = S^{2-}$ ,  $Se^{2-}$ , and  $\square$ . The occurrence of both  $Me^+$  and  $Me^{2+}$  cations at the  $M(1)$  site, in a 4:2 atomic ratio, is a case of valency-imposed double site-occupancy. Consequently, different combinations of B and C constituents should be regarded as separate mineral species. The tetrahedrite group is divided into five different series on the basis of the A, B, D, and Y constituents, i.e., the tetrahedrite, tennantite, freibergite, hakite, and giraudite series. The nature of the dominant C constituent (the so-called “charge-compensating constituent”) is made explicit using a hyphenated suffix between parentheses. Rozhdestvenskayaite, arsenofreibergite, and goldfieldite could be the names of three other series. Eleven minerals belonging to the tetrahedrite group are considered as valid species: argentotennantite-(Zn), argentotetrahedrite-(Fe), kenoargentotetrahedrite-(Fe), giraudite-(Zn), goldfieldite, hakite-(Hg), rozhdestvenskayaite-(Zn), tennantite-(Fe), tennantite-(Zn), tetrahedrite-(Fe), and tetrahedrite-(Zn). Furthermore, annivite is formally discredited. Minerals corresponding to different end-member compositions should be approved as new mineral species by the IMA-CNMNC following the submission of regular proposals. The nomenclature and classification system of the tetrahedrite group, approved by the IMA-CNMNC, allows the full description of the chemical variability of the tetrahedrite minerals and it is able to convey important chemical information not only to mineralogists but also to ore geologists and industry professionals.

**Keywords:** Tetrahedrite group, sulfosalts, nomenclature, classification

### INTRODUCTION

Minerals of the “tetrahedrite group” are the most common sulfosalts in many types of hydrothermal ore deposits and represent one of the most complex isotopic series among sulfides, owing to the potential occurrence of multiple homo- and heterovalent substitutions (Moëlo et al. 2008).

This chemical variability results in several mineral species so far accepted and reported in the official IMA-CNMNC List of Mineral Names. Notwithstanding this wide chemical variability, the classification of the tetrahedrite group minerals was still based on the *Report of the Sulfosalt sub-committee of IMA Commission on Ore Mineralogy* (IMA-COM) (Moëlo et al. 2008), and an up-to-date classification, based upon the ongoing rules recommended by the IMA Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC), was lack-

ing. Indeed, a classification and nomenclature for members of the tetrahedrite group should account for and describe the full chemical variability of these sulfosalts, thus providing information pertinent not only to mineral systematics but also to ore mineralogy. The aim of this report, based on the voting proposal IMA 18-K “*Nomenclature and classification of the tetrahedrite group*,” approved by the IMA-CNMNC in April 2019, is to fill this gap, rationalizing and updating the classification of the tetrahedrite group.

### CRYSTAL-CHEMISTRY OF THE TETRAHEDRITE GROUP MINERALS

#### Crystal structure

The crystal structure of tetrahedrite was first determined by Machatschki (1928a, 1928b), who assumed the ideal composition  $Cu_3SbS_3$ . Some years later, Pauling and Neuman (1934) concluded that the formula  $Cu_{12}Sb_4S_{13}$  was in closer agreement with available chemical data. They proposed a crystal structure

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derived from a sphalerite-type substructure. However, a more detailed description of the structural arrangement of tetrahedrite was given 30 years later by Wuensch (1964). Tetrahedrite is cubic, with space group symmetry  $\bar{I}43m$ . Three independent cation sites and two anion sites occur (Fig. 1):

- $M(1)$  site, at the Wyckoff position  $12d$ , with atomic coordinates  $(\frac{1}{4}, \frac{1}{2}, 0)$ ;
- $M(2)$  site, at the Wyckoff position  $12e$ , with atomic coordinates  $(x, 0, 0)$ . There is clear evidence that this triangular site is split into two flat pyramidal sub-sites located at Wyckoff positions  $24g$  and atomic coordinates  $(x, x, z)$ , each with half occupancy (e.g., Andreasen et al. 2008; Welch et al. 2018);
- $X(3)$  site, at the Wyckoff position  $8c$ , with atomic coordinates  $(x, x, x)$ ;
- $S(1)$  site, at the Wyckoff position  $24g$ , with atomic coordinates  $(x, x, z)$ ;
- $S(2)$  site, at the Wyckoff position  $2a$ , with atomic coordinates  $(0, 0, 0)$ .

On this basis, the structural formula of minerals belonging to the tetrahedrite group can be written as  $M(2)_6M(1)_6X(3)_4S(1)_{12}S(2)_{12}$  ( $Z=2$ ). The crystal structure of tetrahedrite (and those of its isotypes) is an example of a sulfidic sodalite-like (SOD) framework, with cavities that can be described as Laves truncated tetrahedra (e.g., Johnson et al. 1988). The stoichiometric relationship with sodalite becomes obvious by rearranging the chemical formula to yield  $[\text{Cu}_{12}\text{Sb}_8\text{S}_8][\text{Cu}_{12}\text{S}_{24}]$ . Indeed, tetrahedrite is made up of a considerably collapsed sodalite-like framework of corner-connected  $M(1)S(1)_4$  tetrahedra with cages containing  $S(2)$ -centered  $M(2)_6$ -octahedra, encircled by four  $X(3)S(1)_3$  trigonal pyramids (e.g., Johnson et al. 1988; Depmeier 2005). The dual character of the tetrahedrite structure, i.e., its sodalite-like and sphalerite-omission derivative, explains many of its properties.

### Chemical variability

The crystal structure of tetrahedrite is flexible in a chemical sense, accommodating several cations of medium to small ionic radius and variable formal charge (from +1 to +4). The occur-

rence of vacancies or interstitial atoms have been confirmed through structural studies (e.g., Maske and Skinner 1971; Makovicky and Skinner 1979; Rozhdestvenskaya et al. 1993; Makovicky et al. 2005; Welch et al. 2018). The chemical variability encompasses anions too, with the substitution of S by Se, or with the occurrence of vacancies. For such a wide range of possible substitutions, tetrahedrite has been referred to as a “sulfide amphibole” (Sack and Loucks 1985).

The general structural formula of the tetrahedrite group minerals can best be defined as  $^{M(2)}A_6^{M(1)}(B_4C_2)^{X(3)}D_4^{S(1)}Y_{12}^{S(2)}Z$ , where the upper cases represent the following constituents:

A =  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\square$  (vacancy);  $(\text{Ag}_6)^{4+}$  clusters are also possible, coupled with Z vacancies (see below);

B =  $\text{Cu}^+$ ,  $\text{Ag}^+$ ;

C =  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Fe}^{3+}$ ;

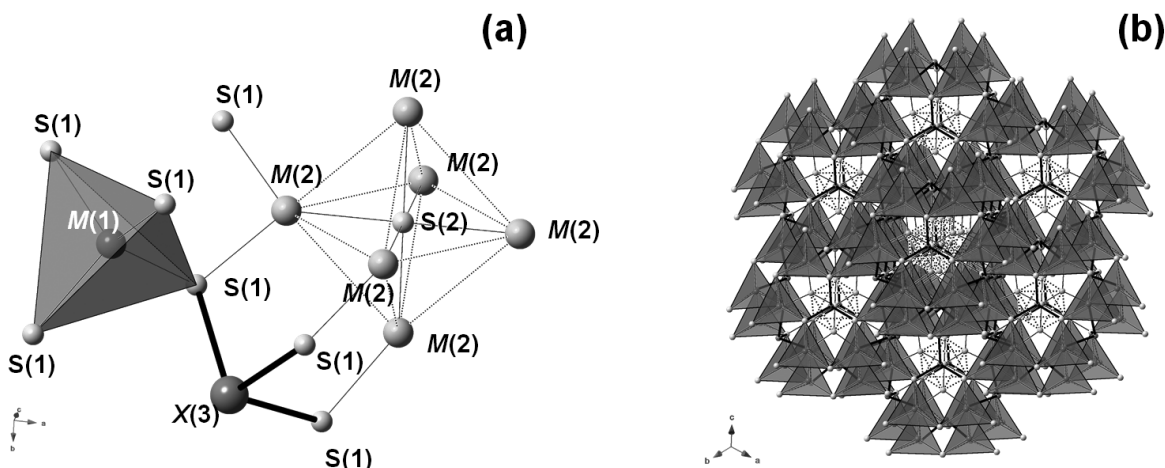
D =  $\text{Sb}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Te}^{4+}$ ;

Y =  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ;

Z =  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ,  $\square$ .

The crystal chemistry of the tetrahedrite group was first examined by Charlat and Lévy (1974). A more detailed investigation, based on 1294 microprobe analyses, was performed by Mozgova and Tsepin (1983). Similarly, Johnson et al. (1986) examined the compositional data of 1271 natural samples and 295 synthetic compounds. In all these samples, no more than 2 atoms per formula unit (apfu) of divalent metals ( $Me^{2+}$ ) occur and the sum of the monovalent metals ( $\text{Ag}^+ + \text{Cu}^+$ ) is usually about 10 apfu, with six of them hosted at the  $M(2)$  site and four at  $M(1)$ . The total number of anions is usually 13 ( $\text{S}^{2-} + \text{Se}^{2-}$ ) apfu, yielding 26 negative charges. As the sum of 10 monovalent cations ( $\text{Ag}^+ + \text{Cu}^+ = \text{A}$  and B constituents) and 4 trivalent cations ( $\text{Sb}^{3+} + \text{As}^{3+} + \text{Bi}^{3+} = \text{D}$  constituent) gives +22 charges, the excess of -4 charges is balanced by the accommodation of 2  $Me^{2+}$ -cations statistically distributed over the  $M(1)$  sites (C constituent). The latter acts as a “charge compensating cation” that fixes the (B:C) constituent atomic ratio to (4:2) in the general formula.

“Unsubstituted” tetrahedrite-tennantite (i.e., without metals other than Cu and Ag) is known, both as synthetic as well as



**FIGURE 1.** The cation and anion sites occurring in tetrahedrite group minerals (a) and the three-dimensional sodalite-like framework (b). Incorporation of  $X(3)S(1)_3$  pyramids is connected with the collapse of the sodalite motif.

natural samples (e.g., Makovicky et al. 2005); the apparent excess of negative charges could be compensated by the presence of  $\text{Cu}^{2+}$  (Patrick et al. 1993).

Maske and Skinner (1971) identified Cu excess in synthetic tennantite,  $\text{Cu}_{12+x}\text{As}_4\text{S}_{13}$ , with  $0 < x < 1.72$ . The  $x$  value increased up to 1.99, when As was partly replaced by Sb (Luce et al. 1977). According to Makovicky and Skinner (1979), synthetic tetrahedrite  $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$  ( $x$  varies continuously between less than 0.1 and 1.9) exsolves, below 120 °C, to a composition close to  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  ( $a = 10.32$  Å) and to a Cu-excess composition, close to  $\text{Cu}_{14-x}\text{Sb}_4\text{S}_{13}$  ( $x$  approximately equal to 0.2;  $a = 10.45$  Å). The Cu-excess variety could be more common than previously thought, but, as stressed by Lind and Makovicky (1982), during electron-microprobe analysis a “loss” of Cu over 12 apfu was observed, both in synthetic as well as natural samples of tetrahedrite and tennantite. The only current way to detect the Cu-excess is through X-ray diffraction. In Cu-excess tennantite (Makovicky et al. 2005), the distribution of excess Cu involves and partly splits the  $M(2)$  site, whereas in Cu-excess synthetic tetrahedrite (Makovicky and Skinner 1979) the diffusion paths involve and indirectly interconnect the 2/3-occupied  $M(1)$  sites.

Recently, tetrahedrite compounds were recognized as interesting materials owing to their thermoelectric properties (e.g., Chetty et al. 2015a) that led to numerous studies in the fields of solid-state chemistry and physics.

#### NOMENCLATURE OF THE TETRAHEDRITE GROUP MINERALS: STATE-OF-THE-ART

Ten different mineral species belonging to the tetrahedrite group have been so far recognized in the official IMA-CNMNC List of Mineral Names (Table 1). In the following, we will briefly report the main features of these 10 species within the tetrahedrite group.

##### Annivite

Annivite was considered the Bi-dominant analog of tetrahedrite and tennantite, although it was reported as “questionable” in the official IMA-CNMNC List of Mineral Names. Indeed, the chemical analysis of holotype annivite from the Anniviers Valley (Switzerland–Fellenberg 1854) leads to the following empirical formula:  $(\text{Cu}_{9.93}\text{Fe}_{1.22}\text{Zn}_{0.55})_{\Sigma 11.70}(\text{As}_{2.60}\text{Sb}_{1.28}\text{Bi}_{0.42})_{\Sigma 4.30}\text{S}_{13.15}$ , which corresponds to tennantite. Moreover, Breskovska and Tarkian (1994), through the examination of 214 analyses of natural members of the tetrahedrite group, found a maximum Bi content of 1.69 apfu. If we retroactively assume that annivite is the mineral with  $\text{Bi}^{3+}$  as the dominant D cation, natural compounds

with that composition have undoubtedly been reported (e.g., Bortnikov et al. 1979; Kieft and Eriksson 1984; Spiridonov et al. 1986b; Gołębiewska et al. 2012; Velebil and Sejkora 2018). However, these data are not supported by any X-ray diffraction study. Synthetic Bi-bearing tetrahedrite and tennantite were synthesized by Klünder et al. (2003) who found up to 1 Bi apfu at 450 and 520 °C.

##### Argentotennantite

Argentotennantite was first described by Spiridonov et al. (1986a) from the polymetallic Kvarstoviy Gorki deposit (Kazakhstan) as small grains up to 0.1 mm. Its unit-cell parameter is  $a = 10.583(4)$  Å. At the type locality, argentotennantite is associated with other members of the tetrahedrite group. The empirical formula of the holotype material is  $(\text{Ag}_{5.67}\text{Cu}_{0.33})_{\Sigma 6.00}(\text{Cu}_{4.15}\text{Zn}_{1.52}\text{Fe}_{0.37}\text{Pb}_{0.01}\text{Cd}_{0.01})_{\Sigma 6.06}(\text{As}_{2.14}\text{Sb}_{1.89})_{\Sigma 4.03}\text{S}_{12.90}$ , which leads to the end-member formula  $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$ . The crystal structure of argentotennantite is currently unsolved.

Števkó et al. (2018) reported electron microprobe data of minerals belonging to the tetrahedrite group from the Kremnica Au–Ag epithermal deposit (Slovak Republic). Among them was argentotennantite, having Fe as the dominant C constituent.

##### Argentotetrahedrite

Argentotetrahedrite was first described by Spiridonov et al. (1986b) as the Sb-rich derivative of argentotennantite, on the basis of electron microprobe analysis only (no X-ray data). Later, Zhdanov et al. (1992) reported chemistry and unit-cell parameter of a Cu-free Ag-end-member, but no formal proposal was submitted to the then IMA-CNMNC. Moëlo et al. (2008) reported this species as a member of the tetrahedrite isotypic series, with chemical composition  $\text{Ag}_{10}(\text{Fe},\text{Zn})_2\text{Sb}_4\text{S}_{13}$ . They pointed out that a redefinition through a formal proposal to the CNMNC was highly desirable. Finally, using new compositional and structural data for a sample from the Keno Hill Ag–Pb–Zn deposit, Yukon (Canada), having  $\text{Fe} > \text{Zn}$ , Welch et al. (2018) redefined argentotetrahedrite as the Sb counterpart of argentotennantite, with the simplified formula  $\text{Ag}_6\text{Cu}_4(\text{Fe},\text{Zn})_2\text{Sb}_4\text{S}_{13}$ . Crystal-structure analysis confirmed that all Ag is ordered at the  $M(2)$  site.

Foigt and Ulbricht (2001) reported a sample from the O’Keefe claims, Harney County, Oregon (U.S.A.) having 5.78 Ag apfu and Hg dominant over Zn and Fe, which leads to the end-member composition  $\text{Ag}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$ . Atanasov (1975) gave 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 gave the chemi-

**TABLE 1.** Mineral species belonging to the tetrahedrite group, following the Official IMA-CNMNC List of Mineral Names (January 2019)

Species	Chemical formula	IMA status	IMA number	Type locality
Annivite	$\text{Cu}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2](\text{Bi},\text{Sb},\text{As})_4\text{S}_{13}$	Q	2008 s.p.	Anniviers Valley, Switzerland
Argentotennantite	$\text{Ag}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2]\text{As}_4\text{S}_{13}$	A	1985-026	Kvarstoviy Gorki deposit, Kazakhstan
Argentotetrahedrite	$\text{Ag}_6\text{Cu}_4(\text{Fe},\text{Zn})_2\text{Sb}_4\text{S}_{13}$	A	2016-093	Keno Hill, Yukon, Canada
Freibergite	$\text{Ag}_6[\text{Cu}_4\text{Fe}_2]\text{Sb}_4\text{S}_{12}$	G	1853	Freiberg, Saxony, Germany
Giraudite	$\text{Cu}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2]\text{As}_4\text{Se}_{13}$	A	1980-089	Chaméane U deposit, France
Goldfieldite	$\text{Cu}_{10}\text{Te}_2\text{S}_{13}$	Rd	1998 s.p.	Mohawk mine, Goldfield, Nevada, USA
Hakite	$\text{Cu}_6[\text{Cu}_4\text{Hg}_2]\text{Sb}_4\text{S}_{13}$	A	1970-019	Předbořice, Bohemia, Czech Republic
Rozhdestvenskayaite	$\text{Ag}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$	A	2016-094	Moctezuma mine, Sonora, Mexico
Tennantite	$\text{Cu}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2]\text{As}_4\text{S}_{13}$	G	1819	Cornwall, United Kingdom
Tetrahedrite	$\text{Cu}_6[\text{Cu}_4(\text{Fe},\text{Zn})_2]\text{Sb}_4\text{S}_{13}$	A	1962 s.p.	unknown

Note: A = approved; G = grandfathered; Q = questionable; Rd = redefined; s.p. = special procedure.

cal 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 the  $M(1)$  and  $M(2)$  sites, the possible dominance of Ag at  $M(2)$  results, i.e.,  $M(2)(\text{Ag}_{2.96}\text{Cu}_{2.88})_{\Sigma 5.84}$ . The classification of this sample, without structural data, is uncertain: it may be considered either as the Ag-rich variety of  $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$  or as argentotetrahedrite with Hg as the dominant divalent cation, i.e.,  $\text{Ag}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$ .

Finally, Repstock et al. (2016) reported 6.66 Ag apfu and 1.45 Cd apfu in a sample from the Mavrokoryfi deposit (Greece), thus having end-member formula  $\text{Ag}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$ .

### Freibergite

Kenngott (1853) first used the name freibergite to indicate an Ag-rich tetrahedrite from Freiberg, Saxony (Germany). The type locality is actually the Hab Acht Mine (later part of the Beschert Glück Mine), Zug near Freiberg, Saxony, where it was first described by Weissenbach (1831) with an analysis of Heinrich Rose. This analysis can be recalculated, on the basis of  $\text{Sb} = 4$  apfu, to  $\text{Ag}_{5.74}\text{Cu}_{4.61}\text{Fe}_{2.12}\text{Zn}_{0.30}\text{Sb}_{4.00}\text{S}_{13.06}$ .

The definition of freibergite is much debated, often being confused with both Ag-rich tetrahedrite and argentotetrahedrite. Indeed, Kalbskopf (1972) studied Ag-rich tetrahedrite (with ca. 13 wt% Ag) and not freibergite; however, this study first suggested the preferential occurrence of Ag at the triangular coordinated  $M(2)$  site. Similarly, freibergite from Keno Hill, Yukon (Canada), examined by Peterson and Miller (1986), was actually argentotetrahedrite, as recently redefined by Welch et al. (2018).

Since the pioneering study of Riley (1974), several authors (e.g., Samusikov et al. 1988; Balitskaya et al. 1989) reported that an increase in the Ag content of freibergite is coupled with a decrease in the  $a$ -parameter and an increase in the amount of vacancy at the  $S(2)$  site. However, the Ag-for-Cu substitution in the tennantite-tetrahedrite pair actually results in a linear increase of the  $a$ -parameter, and only when Ag content exceeds ca. 23 wt% (~4 apfu) does the abnormal trend in the behavior of the  $a$ -parameter, typical of freibergite, occur.

The crystal structure of freibergite was reported by Rozhdestvenskaya et al. (1993). At the  $M(2)$  site, Cu is mainly or completely substituted by Ag; at the same time, the  $S(2)$  site, having octahedral coordination, is progressively emptied, allowing the formation of  $(\text{Ag}_6)^{4+}$  octahedral clusters. Thus, the ideal formula of freibergite is  $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{12}$ , and as such, it is a distinct species from argentotetrahedrite. Moëlo et al. (2008) reported the idealized formula  $(\text{Ag}_{4+2x}\text{Cu}_{2-2x})[(\text{Cu},\text{Ag})_4(\text{Fe},\text{Zn})_2]_{\Sigma 6}\text{Sb}_4\text{S}_{12}\text{S}_{1-x}$  ( $0 < x < 1$ ). The boundary between freibergite and Ag-rich tetrahedrite is unknown, and further studies are required.

Welch et al. (2018) refined the structure of freibergite with (Fe,Zn) as divalent cations and the octahedral cluster nearly fully occupied by Ag. The  $S(2)$  site refined to zero occupancy (i.e., vacant). Charge-balance was rationalized by invoking intermetallic bonding in the  $M(2)(\text{Ag}_6)$  group, having a formal charge of +4, as has been shown for synthetic organometallic compounds (e.g., Kikukawa et al. 2013).

### Giraudite

Giraudite was described by Johan et al. (1982) from the Chaméane uranium deposit, Puy-de-Dôme, Auvergne (France) as the As-analog of hakite. It occurs as grains up to 400  $\mu\text{m}$  in size. Three

sets of chemical data are given in the type description, corresponding to the empirical formulas  $(\text{Cu}_{5.32}\text{Ag}_{0.68})_{\Sigma 6.00}(\text{Cu}_4^+\text{Zn}_{1.16}\text{Cu}_{0.72}^{2+}\text{Hg}_{0.08}\text{Fe}_{0.04})_{\Sigma 6.00}(\text{As}_{2.20}\text{Sb}_{1.76})_{\Sigma 3.96}\text{Se}_{11.04}\text{S}_{2.00}$ ,  $(\text{Cu}_{5.24}\text{Ag}_{0.76})_{\Sigma 6.00}(\text{Cu}_4^+\text{Zn}_{1.12}\text{Cu}_{0.84}^{2+}\text{Fe}_{0.08}\text{Hg}_{0.04})_{\Sigma 6.08}(\text{As}_{2.16}\text{Sb}_{1.88})_{\Sigma 4.04}\text{Se}_{11.08}\text{S}_{1.80}$ , and  $(\text{Cu}_{5.68}\text{Ag}_{0.32})_{\Sigma 6.00}(\text{Cu}_4^+\text{Zn}_{1.00}\text{Cu}_{0.92}^{2+}\text{Hg}_{0.04})_{\Sigma 6.00}(\text{As}_{2.60}\text{Sb}_{1.28})_{\Sigma 3.88}\text{Se}_{10.52}\text{S}_{2.64}$ . Formally,  $\text{Cu}^{2+}$  occurs in giraudite. The end-member formula is  $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{Se}_{13}$ . Its crystal structure has not been solved yet.

Förster et al. (2002) described a complete substitution series between giraudite and hakite from the Niederschlema-Alberoda uranium deposit, Erzgebirge (Germany). Indeed, they did not describe giraudite (i.e., the Zn-rich pole) but a mercurian giraudite, ideally  $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{As}_4\text{Se}_{13}$ ; one spot analysis corresponded to a cuprian giraudite, having formally  $\text{Cu}^{2+}$  as dominant divalent C constituent. Moreover, Förster and Rhede (2004) reported an extensive substitution series between giraudite and tennantite, involving the  $\text{Se}^{2-}$ - $\text{S}^{2-}$  substitution. These authors gave chemical data corresponding to Fe- and  $\text{Cu}^{2+}$ -terms, ideally  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{Se}_{13}$  and  $\text{Cu}_6(\text{Cu}_4\text{Cu}_2^{2+})\text{As}_4\text{Se}_{13}$ , respectively. Hg- and Cu-dominant giraudites were also recently described from the Příbram uranium and base-metal district (Czech Republic) by Škácha et al. (2017).

### Goldfieldite

Goldfieldite was first identified by Sharwood (1907) and later reported in the mineralogical literature by Ransome (1909) from the Mohawk mine, Goldfield, Nevada (U.S.A.). Its nature was debated, as discussed by Thompson (1946), who additionally proved it to be a member of the tetrahedrite group. Kato and Sakurai (1970) and Kalbskopf (1974) realized that Te does not substitute for S but behaves like As and Sb in the tennantite-tetrahedrite series. Kase (1986) proposed that the substitution of  $\text{Te}^{4+}$  for trivalent As and Sb is compensated by an increase in monovalent Cu (and minor Ag) from 10 to 12 apfu at the expense of divalent elements (e.g., Fe, Zn). This substitution is valid up to 2 Te apfu; for higher Te contents, the charge balance of goldfieldite is maintained through the formation of vacancies at the  $M(2)$  trigonally coordinated site, usually occupied by monovalent cations (e.g., Dmitrieva et al. 1987). The partial occupancy of the  $M(2)$  site was confirmed by Pohl et al. (1996) who refined, through the Rietveld technique, the crystal structure of Se-bearing goldfieldite from the Ozernoya deposit, central Kamchatka (Russia), and concluded that Se is preferentially hosted at the  $S(1)$  site.

Trudu and Knittel (1998) gave an extensive description and discussion of the crystal chemistry and mineralogy of goldfieldite, whereas Makovicky and Karup-Møller (2017) synthesized phases along the tetrahedrite-goldfieldite and tennantite-goldfieldite joins to study their solid solution, refining the data of Kase (1986).

The highest amount of Te was reported by Repstock et al. (2016), who found 3.71–3.77 apfu in goldfieldite samples from Rhodope Mountains (Greece), with a sum of Cu and substituting cations of 10.59 apfu.

Kato and Sakurai (1970) and Spiridonov et al. (1984) suggested that the name goldfieldite should be applied to members of the tetrahedrite solid solution with Te as the most abundant semimetal; such an approach was also followed by Trudu and Knittel (1998). On the contrary, Dmitrieva et al. (1987) suggested

that the mineral can be named goldfieldite only when Te content is greater than the sum of all other semimetals. The nomenclature of goldfieldite will be discussed below.

### Hakite

Hakite was first described by Johan and Kvaček (1971) from Předbořice, Central Bohemia region (Czech Republic), as anhedral grains up to 300  $\mu\text{m}$  in size. The studied material showed variable Se:S atomic ratios, ranging between the empirical compositions  $\text{Cu}_6(\text{Cu}_{4.08}\text{Hg}_{1.83})_{\Sigma 5.91}(\text{Sb}_{3.05}\text{As}_{1.03})_{\Sigma 4.08}(\text{Se}_{10.35}\text{S}_{2.62})_{\Sigma 12.97}$  and  $\text{Cu}_6(\text{Cu}_{4.22}\text{Hg}_{1.73})_{\Sigma 5.95}(\text{Sb}_{3.83}\text{As}_{0.22})_{\Sigma 4.05}\text{Se}_{11.90}$ . These two compositions correspond to unit-cell parameters  $a = 10.83(1)$  and  $10.88(1)$  Å, respectively. Johan and Kvaček (1971) proposed the existence of a substitution series between hakite and tetrahedrite. From the same locality, Brodin (1981) reported the occurrence of Ag-bearing hakite; however, the recalculation of its chemical formula shows that Cu is still the dominant cation at the  $M(2)$  site.

Förster et al. (2002) described a complete substitution series between hakite and mercurian giraudite from the Niederschlema-Alberoda uranium deposit, Erzgebirge (Germany). The sum (Se+S) varies between 13.00 and 13.10 apfu.

Škácha et al. (2016) described hakite from Příbram, Central Bohemia (Czech Republic), and stressed the occurrence of different compositions characterized by the dominance of  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ , or  $\text{Cd}^{2+}$ . They indicated these different compositions as “Hg-hakite,” “Zn-hakite,” and “Cd-hakite,” ideally  $\text{Cu}_6(\text{Cu}_x\text{Hg}_y)\text{Sb}_4\text{Se}_{13}$ ,  $\text{Cu}_6(\text{Cu}_x\text{Zn}_y)\text{Sb}_4\text{Se}_{13}$ , and  $\text{Cu}_6(\text{Cu}_x\text{Cd}_y)\text{Sb}_4\text{Se}_{13}$ , respectively. The crystal structure of “Hg-hakite” was solved through electron diffraction tomography, confirming the isotopic relations with tetrahedrite and the occurrence of  $\text{Hg}^{2+}$  at the  $M(1)$  site. Later, Škácha et al. (2017) described also Fe- and Cu-dominant hakite samples from the same occurrence on the base of electron microprobe data.

Finally, Karup-Møller and Makovicky (1999) synthesized a sample having 1.8 Fe apfu, leading to the end-member composition  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{Se}_{13}$ , as well as fully Zn substituted  $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{Se}_{13}$ . The  $\text{Cu}_6\text{Cu}_6\text{Sb}_4\text{Se}_{13}$  composition resulted in the orthorhombic phase  $\text{Cu}_3\text{SbSe}_3$  and not in tetrahedrite-like structure.

### Rozhdestvenskayaite

Silver hyper-rich tetrahedrite varieties, with  $\text{Ag} > 8$  apfu and increased  $a$ -parameter, were first described by Russian authors. Zhdanov et al. (1992) described a Cu-free, Fe-rich sample of Ag-rich tetrahedrite from the deposit of Hachakchansk (up to 54.2 wt% Ag, corresponding to 10.74 Ag apfu on the basis of 29 apfu;  $a = 10.92$  Å). Later, Samusikov and Gamyarin (1994) presented an almost Ag-pure sample (52 wt% Ag, with only 0.7 wt% Cu;  $a = 10.90$  Å) from Yakutia (Russia) and named it “tarynite” from the locality. Unfortunately, no official proposal was submitted to the then IMA-CNMMN by these authors.

Finally, rozhdestvenskayaite, ideally  $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$ , was recently described as a new tetrahedrite group mineral by Welch et al. (2018). The type locality is the Moctezuma mine (Bambolla mine), Sonora (Mexico).

Foit and Ulbricht (2001) documented samples corresponding to rozhdestvenskayaite from the O’Keefe claims, Oregon (U.S.A.) in which Hg is the dominant divalent cation, thus cor-

responding to the end-member composition  $\text{Ag}_6(\text{Ag}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$ .

Ixer and Stanley (1983) analyzed a tetrahedrite group grain of composition  $(\text{Ag}_{8.18}\text{Cu}_{1.91}\text{Zn}_{1.44}\text{Fe}_{0.49}\text{Pb}_{0.17}\text{Cd}_{0.16})_{\Sigma 12.35}(\text{As}_{2.22}\text{Sb}_{1.93})_{\Sigma 4.15}\text{S}_{12.5}$  in which Ag could be dominant at both  $M(2)$  and  $M(1)$  sites, and  $\text{As} > \text{Sb}$  at  $X(3)$ , but close to  $^{S(2)}(\text{S}_{0.5}\square_{0.5})$  boundary. Consequently, it could be either the As-analog of rozhdestvenskayaite or the As-analog of freibergite (if  $^{S(2)}\square > 0.5$ ). The As-analog of rozhdestvenskayaite was also possibly reported from the Manson Lode, Ulu Sokor gold-base metal deposit, Kelantan (Malaysia) (Gan 1980).

### Tennantite

Tennantite was first described by the two brothers W. Phillips (1819) and R. Phillips (1819) from Cornwall (England, U.K.). Even if no accurate quantitative chemical data are available, the latter author reported that Cu, Fe, As, and S are the elements occurring in the studied material. Consequently, it could be that the original tennantite was close to the ideal composition  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$ .

Makovicky et al. (2003) observed  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{n+}$  with intermediate valence ( $+2 < n < +3$ ) in synthetic Fe-bearing tennantite through Mössbauer spectroscopy. Tennantite with a low Fe content contains  $\text{Fe}^{3+}$ , whereas  $\text{Fe}^{2+}$  appears at higher Fe contents, becoming the dominant valence state at Fe content larger than 1 apfu (in Cu-excess samples) and 1.4 apfu in stoichiometric samples. The occurrence of charge-transfer phenomena (manifested as “intermediate valence iron”) was reported (Makovicky et al. 2003). In every case, the sum of the aggregate charge of the C-cations is +4; this sum is produced by  $2\text{Cu}^{2+} \rightarrow \text{Cu}^{+} + \text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+}$  combinations, in a continuous process of exchange, with a possible share of  $\text{Cu}^{2+} + \text{Fe}^{2+}$ .

After the structural model proposed by Pauling and Neuman (1934), the crystal structure of tennantite was refined by Wuensch et al. (1966) using a crystal of the variety known as “binnite” from the Lengenbach quarry, Binn Valley (Switzerland). Chemical data suggested a composition corresponding to the end-member  $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$ . Zincian tennantite was reported under the name *Kupferblende* by Plattner (1846) from the Prophet Jonas Mine, Zug near Freiberg, Saxony (Germany). This mineral was named erythroconite (*Erythroconit*) by Glocker (1847).

As shown by several studies (e.g., George et al. 2017), the most common end-member compositions of tennantite have either Fe or Zn as the dominant divalent cation. A Cu-rich tennantite from the Huaron polymetallic ore deposit (Central Peru) gave the formula  $(\text{Cu}_{5.97}\text{Ag}_{0.03})_{\Sigma 6.00}(\text{Cu}_{5.63}\text{Fe}_{0.37})_{\Sigma 6.00}(\text{As}_{3.28}\text{Sb}_{0.38})_{\Sigma 3.66}\text{S}_{13}$  (basis: 12 Me atoms) (Thouvenin 1983; Marcoux et al. 1994). Despite a weak As- and Sb-deficit, this analysis clearly points to a  $\text{Cu}^{2+}$  dominant C-cation at the  $M(1)$  site. A sample of tennantite with dominant  $\text{Mn}^{2+}$  (up to 1.53 apfu) was reported by Burkart-Baumann (1984) from the Quiruvilca deposit (Peru).

Natural Cu-excess tennantite has been reported by Makovicky et al. (2005) from the Farallon Negro mining district, Province of Catamarca (Argentina). The occurrence of this particular composition is likely related to the crystallization of tennantite from late hydrothermal solutions devoid of ubiquitous Fe, Zn, and other divalent elements.

Finally, Mozgova et al. (1979) reported the occurrence of tennantite having 2 Hg apfu, thus corresponding to the end-member  $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{As}_4\text{S}_{13}$ .

## Tetrahedrite

Tetrahedrite is a grandfathered species. The name “tetrahedrite” was introduced by Haidinger (1845) in agreement with the common tetrahedral form shown by its crystals. Previously, tetrahedrite was known with different names, for instance *fahlerz*, *weissgiltigerz*, *gray ore*, or *panabase*. Haidinger (1845) reported the occurrence of Fe and Zn in tetrahedrite. Indeed, these two constituents are the most common divalent cations (e.g., George et al. 2017). For instance, Bechi (1863) described the end-member  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$  from the Frigido mine, Apuan Alps, Tuscany (Italy), indicating it with the discredited name *coppite*. The speciation of Fe in tetrahedrite has been studied by several authors (e.g., Makovicky et al. 1990, 2003; Andreasen et al. 2008; Nasonova et al. 2016). Spectroscopic Mössbauer studies indicated that along the join  $\text{Cu}_{12+x}(\text{Sb,As})_4\text{S}_{13}$ – $\text{Cu}_{10}\text{Fe}_2(\text{Sb,As})_4\text{S}_{13}$ , the replacement of Cu by Fe starts by incorporation of  $\text{Fe}^{3+}$ , which is the only type of Fe present in  $\text{Cu}_6(\text{Cu}_{5.5}\text{Fe}_{0.5})(\text{Sb,As})_4\text{S}_{13}$ . Then,  $\text{Fe}^{2+}$  starts to be incorporated, together with the gradual reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , up to the composition  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)(\text{Sb,As})_4\text{S}_{13}$  (Makovicky et al. 1990, 2003).

The crystal structure of tetrahedrite was refined by Wuensch (1964) using a sample from Horhausen, Westerwald (Germany); only old chemical data (dating back to the end of 19th and beginning of 20th Century) were given, corresponding to phases having Cu or Zn as dominant C-cation at *M*(1). Consequently, the actual chemical composition of the studied specimen is not known. The occurrence of tetrahedrite samples having  $\text{Cu}^{2+}$  as the dominating C-cation is known in the literature. For instance, Repstock et al. (2016) documented Cu contents up to 11.78 apfu in specimens from Northern Greece, corresponding to the ideal composition  $\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{Sb}_4\text{S}_{13}$ . The compositions  $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$  (minor *x*) are commonly obtained in synthetic runs.

In addition to Fe, Zn, and Cu as dominant divalent cations, many other elements have been reported as C-constituents. Weidenbusch (1849) reported the analysis of a tetrahedrite group mineral from Schwaz, Tyrol (Austria), having 15.9 wt% Hg and corresponding to the formula  $\text{Cu}_{9.9}\text{Hg}_{1.4}\text{Fe}_{0.7}\text{Zn}_{0.4}\text{Sb}_{3.2}\text{S}_{13}$ . Later, Kenngott (1853) introduced the name “schwazite” to indicate mercurian tetrahedrite. Actually, Arlt and Diamond (1998) proved that no samples with Hg as dominant C constituent occur at Schwaz. Several other occurrences of mercurian tetrahedrite have been reported: Foit and Ulbricht (2001) recorded up to 2.02 Hg apfu in samples from the epithermal ore deposits of Harney County, Oregon (U.S.A.), in agreement with the end-member composition  $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$ , that was obtained in synthetic samples by Karup-Møller and Makovicky (2003). Karanović et al. (2003) reported the crystal structure of mercurian tetrahedrite from Dragodol, Donja Trešnjica district (Serbia), confirming the results of Kalbskopf (1971) who proposed the incorporation of Hg at the *M*(1) site. Other structural investigations on mercurian tetrahedrite were reported by Kaplunnik et al. (1980), who assumed a wrong structural model with 12 S apfu, and by Foit and Hughes (2004) for samples up to 1.23 Hg apfu from the Harney County, Oregon (U.S.A.). Velebil (2014), on the basis of electron microprobe analysis and X-ray powder diffraction, described Hg-dominant tetrahedrite (1.46–1.73 Hg apfu) from Jedová hora deposit (Czech Republic) and from Rudňany (1.47–1.79 Hg apfu), Rožňava (1.65 Hg apfu), and Nižná Slaná

(1.07–1.39 Hg apfu), all in the Slovak Republic.

Many authors reported the occurrence of Cd contents up to 2 apfu, e.g., 1.92 apfu indicated by Patrick (1978) at Tyndrum (Scotland, U.K.). Voudouris et al. (2011) reported 1.97 Cd apfu from the Evia Island (Greece) and Jia et al. (1988) gave 1.85 Cd apfu in a sample from Xitieshan (China). Consequently,  $\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$  is another potential natural end-member composition. Jia et al. (1988) actually gave the empirical formula  $(\text{Cu}_{6.95}\text{Ag}_{3.03})_{\Sigma 9.98}(\text{Cd}_{1.85}\text{Zn}_{0.15}\text{Fe}_{0.15})_{\Sigma 2.15}(\text{Sb}_{4.19}\text{As}_{0.25})_{\Sigma 4.44}\text{S}_{13}$ ; taking into account the partitioning of Ag at the *M*(2) site, this formula could represent an intermediate composition between a hypothetical end-member  $\text{Ag}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$  and  $\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$ .

Basu et al. (1984) described an Mn-rich tetrahedrite (up to 1.71 Mn apfu) in the Rajpura-Dariba polymetallic deposit (India). Dobbe (1992) analyzed tetrahedrite from Bergslagen (Sweden), having Mn dominating over both Cd and Fe, leading to the end-member composition  $\text{Cu}_6(\text{Cu}_4\text{Mn}_2)\text{Sb}_4\text{S}_{13}$ . Makovicky and Karup-Møller (1994) synthesized tetrahedrite containing up to 1.91 Mn apfu. The crystal structure of a synthetic tetrahedrite with 1.4 Mn apfu was solved by Chetty et al. (2015b).

Finally, Vavelidis and Melfos (1997) documented tetrahedrite from the Maronia area (Greece), where Pb dominated over both Fe and Zn and assumed that Pb is hosted at the tetrahedral *M*(1) site, implying the occurrence of a potential end-member  $\text{Cu}_6(\text{Cu}_4\text{Pb}_2)\text{Sb}_4\text{S}_{13}$ . However, Makovicky and Karup-Møller (1994) observed a maximum Pb content during their syntheses of 0.45 apfu; moreover, there is still much uncertainty on these results and the occurrence of very fine exsolution of Pb-rich phases cannot be excluded. Finally, even if Pb enters the crystal structure of tetrahedrite, its oxidation state is currently unknown. Indeed,  $\text{Pb}^{2+}$  is too large and displays a different coordination environment, making its presence in tetrahedrite unlikely. Lead could occur as  $\text{Pb}^{4+}$ , as could Ge and Sn. In this case, its crystal-chemical role has to be understood.

Although undocumented in nature, Makovicky and Karup-Møller (1994) synthesized tetrahedrite compositions having both 2 Co and 2 Ni apfu. Barbier et al. (2015) gave the crystal structure of a synthetic tetrahedrite with 1.6 Ni apfu. Natural analogs are unknown, however, even if D’Achiardi (1881) reported a Ni-bearing tetrahedrite from the Frigido mine, Apuan Alps, Tuscany (Italy), naming it “*frigidite*.” More recent studies indicated that this sample was actually an intergrowth of tetrahedrite [approximated formula  $\text{Cu}_6(\text{Cu}_4\text{Fe}_{1.5}\text{Zn}_{0.5})\text{Sb}_4\text{S}_{13}$ ] and Ni-bearing minerals (Carrozzini et al. 1991).

Minor gold (up to ~1 wt%) is known in tetrahedrite and goldfieldite (Mozgova and Tsepín 1983). The same authors also described Sn-bearing tetrahedrite (up to ~3 wt%). Tin contents up to 0.96 apfu were obtained in synthetic tetrahedrite by Hansen et al. (2003).

## APPLYING THE IMA RECOMMENDATIONS TO THE TETRAHEDRITE GROUP

### Nomenclature rules

The occurrence of  $\text{Me}^+$  and  $\text{Me}^{2+}$  cations at the *M*(1) site of the minerals of the tetrahedrite group is a case of valency-imposed double-site occupancy (Hatert and Burke 2008). Consequently, samples having different pairs of B and C constituents should be regarded as separate mineral species. Since divalent metals

are preferentially allocated at the  $M(1)$  site, the nomenclature system for the tetrahedrite isotopic series may be applied solely using chemical data, in accord with the main requirement for a practical nomenclature system (Hatert and Burke 2008). In agreement with Mills et al. (2009), the following nomenclature and classification are recommended.

(1) A member of the tetrahedrite group is a sulfosalt having a considerably collapsed sodalite-like framework compatible with the general structural formula  $M^{(2)}A_6M^{(1)}(B_4C_2)X^{(3)}D_4S^{(1)}Y_{12}S^{(2)}Z$ .

(2) Each different combination of dominant constituents  $M^{(1)}B$ ,  $X^{(3)}D$ , and  $S^{(1)}Y$  deserves a distinct root-name:

B = Cu, D = Sb, Y = S: tetrahedrite;

B = Cu, D = As, Y = S: tennantite;

B = Cu, D = Sb, Y = Se: hakite;

B = Cu, D = As, Y = Se: giraudite;

B = Ag, D = Sb, Y = S: rozhdestvenskayaite;

B = Cu, D = Te, Y = S: goldfieldite

(3) Each distinct mineral species within the tetrahedrite group must have a hyphenated suffix between parentheses, indicating the dominant  $M^{(1)}C$  constituent (the charge compensating constituent), e.g., tetrahedrite-(Fe) for  $Cu_6(Cu_4Fe_2)Sb_4S_{13}$ .

(4) Depending on the  $Cu^+/Ag^+$  ratio, if two minerals have  $M^{(1)}B = Cu$  and the same dominant constituent at  $X^{(3)}D$  and  $S^{(1)}Y$ , they will be assigned the same root-name. The adjectival prefix “argento” will be added to the root-name if  $M^{(2)}Ag > M^{(2)}Cu$  (no prefix when  $M^{(2)}Cu > M^{(2)}Ag$ ). Minerals with  $M^{(1)}B = Ag$  deserve a different root-name.

(5) The chemical composition of every member of the tetrahedrite group should be expressed by an end-member formula as defined by Hawthorne (2002), i.e., an end-member composition must be fixed, it must be compatible with the crystal structure, and it may have more than one type of cation or anion at only one site if required by the electroneutrality principle. Note that an end-member is an algebraic and chemical construct that is important to determine its thermodynamic properties, regardless of whether the end-member exists as a stable mineral (Henry et al. 2011).

(6) The established tetrahedrite group can be divided into series, on the basis of the combination of  $M^{(2)}A$ ,  $M^{(1)}B$ ,  $X^{(3)}D$ , and  $S^{(1)}Y$  constituents. Due to the ambiguities in the end-member composition of tetrahedrite group minerals, in which poor attention has been paid to the dominant charge compensating cation, and aiming at having minimum impact into the current nomenclature, unsuffixed names—such as “tetrahedrite” or “tennantite”—from now on will become series names. As the name freibergite has been applied to phases having composition  $Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$  (Moëlo et al. 2008), we suggest using this name as a series name to indicate different Ag-rich members of the tetrahedrite group. The proposed series are as follow:

Tetrahedrite series: A = Cu, B = Cu, D = Sb, Y = S

Tennantite series: A = Cu, B = Cu, D = As, Y = S

Freibergite series: A = Ag, B = Cu, D = Sb, Y = S

Hakite series: A = Cu, B = Cu, D = Sb, Y = Se

Giraudite series: A = Cu, B = Cu, D = As, Y = Se

Rozhdestvenskayaite could be the name of a series of tetrahedrite group minerals having B = Ag. Goldfieldite (B = Cu, D = Te,

Y = S) is an unassigned member, in agreement with Mills et al. (2009). Argentotennantite-(Zn) is another unassigned member of the tetrahedrite group. Taking into account the likely occurrence of the Fe-analog of argentotennantite-(Zn), the “arsenofreibergite series” could be proposed as the As-analog of the freibergite series.

(7) In the freibergite series, Ag at the  $M(2)$  site can occur either as trigonally coordinated cations [argentotetrahedrite,  $Ag_6(Cu_4Fe_2)Sb_4S_{13}$ ; Welch et al. (2018)] or as discrete  $(Ag_6)^{4+}$  clusters, characterized by Ag–Ag bonds coupled with vacancy at the S(2) site. The latter leads to the end-member formula  $(Ag_6)(Cu_4Fe_2)Sb_4S_{12}\square$  (Rozhdestvenskaya et al. 1993; Welch et al. 2018) for which the prefix “keno” (from the Greek word κενός, meaning empty) is proposed on the root-name argentotetrahedrite to indicate the strict relation between the S(2) vacant site and the peculiar  $(Ag_6)^{4+}$  cluster in the freibergite series.

### Freibergite: Status and relations with other Ag-rich members of the tetrahedrite group

The name freibergite has usually referred to a grandfathered mineral, having chemical composition  $Ag_6[Cu_4Fe_2]Sb_4S_{12}$  (official IMA-CNMNC List of Mineral Names, updated January 2019). However, its definition is not straightforward and several authors confused freibergite with Ag-rich tetrahedrite or the recently approved species argentotetrahedrite, e.g., Kalbskopf (1972), Peterson and Miller (1986). Indeed, Moëlo et al. (2008) reported freibergite as  $Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$ . A chronological review of the crystal-chemical studies performed on Ag-rich members of the tetrahedrite group can help in clarifying the status of the different Ag-rich phases.

From the beginning of the 1970s to the end of the 1980s, the research focus was devoted to the study of the relationships between chemistry and unit-cell parameter, as well as to the understanding of the Ag speciation in the crystal structure of tetrahedrite. Petruk (1971) examined some Ag-bearing tetrahedrites from some Canadian Ag-As ores, finding quite the same unit-cell parameter ( $a \sim 10.49 \text{ \AA}$ ) for Ag  $\sim 2.9$  and 5.4 apfu. The lack of samples with intermediate Ag content inhibits observation of the increase, followed by the decrease, of the unit-cell parameter. Shimada and Hirowatari (1972), using natural samples, established the variation of the unit-cell parameter with increasing Ag content. Kalbskopf (1972) first suggested the preferential occurrence of Ag at the  $M(2)$  site. Two years later, Riley (1974) revealed the specific “freibergite trend” using natural samples, i.e., a decrease of the unit-cell parameter with increasing Ag content. Charlat and Lévy (1975) proposed a relation between Ag content and unit-cell parameter similar to that observed by Shimada and Hirowatari (1972); the samples with the highest Ag content (3.41 apfu) have  $a = 10.535 \text{ \AA}$ . Moreover, Sugaki et al. (1975) experimentally established the increase of the unit-cell parameter with Ag content, up to 4.2 apfu. Patrick and Hall (1983), following Hall (1972), experimentally determined the increase of the unit-cell parameter with the Ag content, using synthetic tetrahedrite. The largest  $a$  value (10.927  $\text{\AA}$ ) was measured on a Cd-tetrahedrite having 7.02 Ag apfu. Finally, the structural results obtained by Kalbskopf (1972) were confirmed by Johnson and Burnham (1985), Peterson and Miller (1986), and Charnock et al. (1988).

Starting from the mid-1980s, some nomenclature issues were discussed by several authors. Spiridonov (1985) introduced the name “argentotetrahedrite” for phases having  $\text{Ag} > \text{Cu}$  and  $\text{Sb} > \text{As}$ , on a theoretical basis. The Commission on Ore Microscopy of the IMA published the *Quantitative Data File for Ore Minerals* (Criddle and Stanley 1986), reporting data for a sample of “freibergite” from the Himmelsfürst mine, Saxony (Germany), with 4.5 Ag apfu, 12.03 S apfu, and  $a = 10.50 \text{ \AA}$ . Argentotennantite was defined by Spiridonov et al. (1986a) on the basis of  $\text{Ag} > \text{Cu}$  and  $\text{As} > \text{Sb}$ . In the same study, two analyses of “argentotetrahedrite” were given (Ag range 5.05–6.74 apfu) as well as four analyses of “freibergite” (Ag range: 3.2–4.9 apfu;  $\text{S} \approx 13$  apfu).

Between the end of the 1980s and the mid-1990s, Russian authors were particularly active in studying the crystal chemistry of Ag-rich members of the tetrahedrite group. Samusikov et al. (1988) confirmed the decrease of the unit-cell parameter with increasing Ag content (over 22 wt%, corresponding to 4.5 Ag apfu). They noted correlatively the S deficiency, forming vacancy, and proposed a regrouping of threefold coordinated Ag atoms to explain the unit-cell contraction. Balitskaya et al. (1989) presented similar results, in samples within the range 3.53–8.75 Ag apfu, summarizing all the published results in a diagram  $a$  (Å) vs. Ag (apfu). Interestingly, one sample of the “freibergite trend” had Ag contents close to 9 apfu, i.e., some three atoms over the  $(\text{Ag}_6)^{4+}$  cluster. Figure 2, showing the relations between the Ag content and the unit-cell parameter of the studied samples, is based on this work. The diagram has been completed taking into account all papers published up to now, presenting both chemical data and unit-cell parameters, since the first electron microprobe analysis of tetrahedrite (Springer 1969). Note that the first electron microprobe data of tennantite were given three years earlier by Wuensch et al. (1966).

Rozhdestvenskaya et al. (1989) presented the crystallographic results of four samples of the tetrahedrite-“freibergite” series. In the Ag-richest sample (5.87 Ag apfu), “Ag–Ag distance equals that in metallic Ag”, and the authors proposed the formation of “octahedral Ag-cluster [...] around S2-site”. The details of the crystal structure of “freibergite,” with almost empty S(2) site, were then published

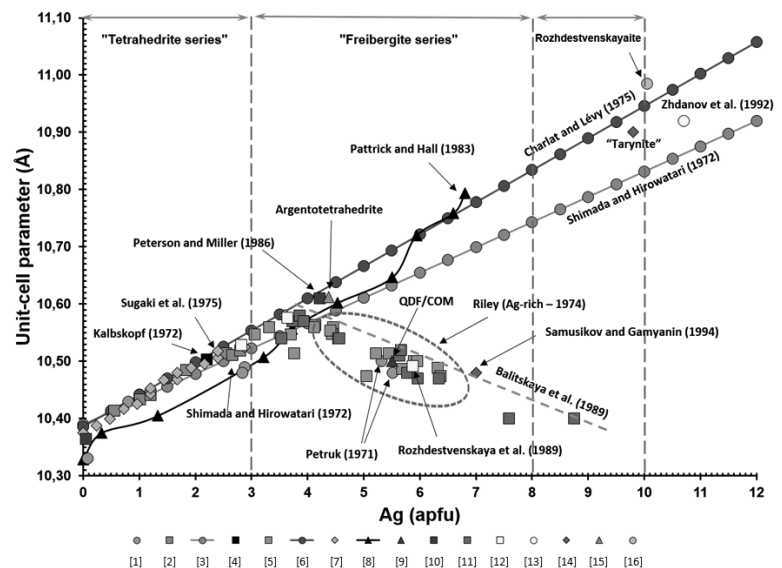
four years later (Rozhdestvenskaya et al. 1993). Around the same period, Zhdanov et al. (1992) and Samusikov and Gamyaniin (1994) described Cu-free/poor samples of Ag-rich tetrahedrite, with Ag content exceeding the 8 apfu limit. In the sample studied by Zhdanov et al. (1992), Fe is dominant over Zn (0.94 vs. 0.81 apfu, respectively;  $\text{Hg} = 0.2$  apfu). In addition, Samusikov and Gamyaniin (1994) proposed a nomenclature of the Ag-rich tetrahedrites, with a distinction between “tarynite” ( $\text{Ag} > 8$  apfu) and “Cu-tarynite” ( $\text{Ag} < 8$  apfu) on the increasing  $a$  trend, on the one hand, and, on the other hand, between hypothetical “freibergite” ( $\text{Ag} > 8$  apfu) and “Cu-freibergite” ( $\text{Ag} < 8$  apfu) on the decreasing  $a$  trend. The sample with 8.75 Ag apfu (and  $a = 10.34 \text{ \AA}$ ) of Balitskaya et al. (1989) plots in the field of this so-called “freibergite,” and may correspond potentially to a new mineral species:  $\text{Ag} > \text{Cu}$ , with Fe and Zn at the  $M(1)$  site.

After more than 20 years, Welch et al. (2018) defined, after IMA-CNMNC approval, the new species rozhdestvenskayaite and argentotetrahedrite. The former has Zn dominant over Fe, contrary to the sample studied by Zhdanov et al. (1992). Moreover, they confirmed and improved the results of Rozhdestvenskaya et al. (1989, 1993) for freibergite.

Rozhdestvenskaya et al. (1993) and Welch et al. (2018) demonstrated that freibergite has homeotypic relations with the other members of the tetrahedrite group, with the  $(\text{Ag}_6)^{4+}$  cluster replacing the S(2)-centered  $\text{Ag}_6$  octahedron (Fig. 3), according to the substitution mechanism  $6^{M(2)}\text{Ag}^{+} + \text{S}(2)\text{S}^{2-} = \text{M}(2)(\text{Ag}_6)^{4+} + \text{S}(2)\square$ . These data are in agreement with EXAFS analysis performed by Charnock et al. (1988) on a sample containing ca. 31 wt% Ag. They showed the occurrence of a first shell of S atoms at 2.55 Å and a second shell, interpreted as due to Sb atoms (but likely due to Ag atoms), at 2.75 Å. In addition, the number of S atoms coordinating Ag is 1.8, to be compared to 2.8 in a sample poor in Ag, in agreement with the Ag-cluster model.

Consequently, freibergite and argentotetrahedrite are two different mineral species, forming an anion-omission homeotypic series, with the latter being a sulfide and the former a sulfide-alloy compound or a subsulfide (see Moëlo et al. 2008). However,

**FIGURE 2.** Relations between the unit-cell parameter  $a$  (Å) and the Ag content (apfu). Dashed vertical lines indicate the boundaries between the tetrahedrite and freibergite series and between the freibergite and the rozhdestvenskayaite series. References: [1] Petruk (1971); [2,3] Shimada and Hirowatari (1972); [4] Kalbskopf (1972); [5] Riley (1974); [6] Charlat and Lévy (1975); [7] Sugaki et al. (1975); [8] Patrick and Hall (1983); [9] Criddle and Stanley (1986); [10] Peterson and Miller (1986); [11] Balitskaya et al. (1989); [12] Rozhdestvenskaya et al. (1989); [13] Zhdanov et al. (1992); [14] Samusikov and Gamyaniin (1994); [15, 16] Welch et al. (2018).





the current S determination by routine EPMA seems to be usually insufficient to reliably quantify the number of vacancies at the S(2) site and thus the presence of  $(\text{Ag}_6)^{4+}$  clusters. Specific structural information on the M(2) and S(2) sites is therefore required to distinguish these two mineral species.

Taking into account the widespread use of the term freibergite, it should be used to indicate the members of the anion-omission homeotypic series  $\text{Ag}_6(\text{Cu}_4\text{Me}_2)\text{Sb}_4\text{S}_{13-x}$  with end-member compositions corresponding to  $x = 0$  [argentotetrahedrite-(Me),  $\text{Ag}_6(\text{Cu}_4\text{Me}_2)\text{Sb}_4\text{S}_{13}$ ] and  $x = 1$  [kenoargentotetrahedrite-(Me),  $\text{Ag}_6(\text{Cu}_4\text{Me}_2)\text{Sb}_4\text{S}_{12}$ ]. The use of the historical name “freibergite” as a series name is in keeping with the IMA-CNMNC guidelines for suffixes and prefixes (Hatert et al. 2013), suggesting that when historical names cannot be associated to unambiguously characterized type materials [as stated above this name was used for phases with composition  $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13-x}$ ; Moëlo et al. 2008], the name may need to be discredited as a species name but retained as a group (in our case as a series) name.

Taking into account the recently defined species argentotetrahedrite and rozhdestvenskayaite, the following boundaries between Ag-members of the tetrahedrite group could be defined (Fig. 2):

- (1)  $3 < \text{Ag} < 8$  apfu,  $0.5 < \text{S}^{(2)} < 1.0 =$  argentotetrahedrite;
- (2)  $3 < \text{Ag} < 8$  apfu,  $0.0 < \text{S}^{(2)} < 0.5 =$  kenoargentotetrahedrite;
- (3)  $8 < \text{Ag} < 10$  apfu,  $0.5 < \text{S}^{(2)} < 1.0 =$  rozhdestvenskayaite.

Kenoargentotetrahedrite is the S-deficient homeotype of argentotetrahedrite, with localized Ag–Ag bonds. These two phases belong to the freibergite series; a clear determination between them seems to be possible only through single-crystal X-ray diffraction studies. On the basis of published data in the 1980s, sample no. BM88668 from the Natural History Museum, London, may be taken as a neotype for the redefinition of kenoargentotetrahedrite [now “kenoargentotetrahedrite-(Fe)”]:

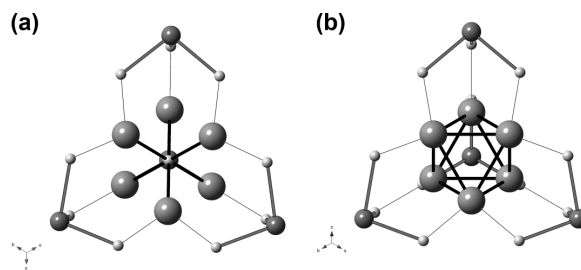
(1) Card no. 118 of the QDF/COM of the IMA (second issue, 1986) gives the locality Himmelsfürst, Freiberg district, Saxony (Germany), the reflectance data, the unit-cell parameter ( $a = 10.50$  Å, J.G. Francis), and the chemical composition (unpublished data from Criddle and Stanley 1986). The formula, based on  $\Sigma \text{Me} = 12$  apfu, is:  $(\text{Ag}_{8.51}\text{Cu}_{4.52})_{\Sigma 10.03}(\text{Fe}_{1.68}\text{Zn}_{0.29})_{\Sigma 1.97}(\text{Sb}_{4.09}\text{As}_{0.01})_{\Sigma 4.10}\text{S}_{12.03}$ ;

(2) In this same sample, the EXAFS spectroscopic study by Charnock et al. (1988) was performed, validating the occurrence of  $(\text{Ag}_6)^{4+}$  clusters.

In addition, the sample studied by Welch et al. (2018) can be considered as co-neotype material.

#### Goldfieldite: End-member formula and relations with tellurian tetrahedrites

The actual definition of goldfieldite has been debated. According to some authors (e.g., Kato and Sakurai 1970; Spiridonov et al. 1984; Trudu and Knittel 1998), the name goldfieldite should be applied to members of the tetrahedrite group having Te as the dominant D constituent, i.e.,  $\text{Te} > \text{Sb}$  and  $\text{Te} > \text{As}$  and  $\text{Te} > \text{Bi}$ . Another approach was followed by Dmitrieva et al. (1987), who suggested that a tetrahedrite group mineral can be named goldfieldite only when Te is more abundant than the sum of all the other semimetals, i.e.,  $\text{Te} > (\text{Sb} + \text{As} + \text{Bi})$ . This latter ap-



**FIGURE 3.** Details of the coordination of the M(2) site in argentotetrahedrite (a) and “freibergite” (b). In the former, Ag–Ag distances are 3.24 Å and S(2) is occupied, whereas in the latter the Ag–Ag distances are 2.84 Å, in agreement with Ag–Ag bonds in native silver, and S(2) site is vacant. Crystallographic data after Welch et al. (2018). Symbols: circles indicate M(2), X(3), and S(1) and S(2) sites.

proach agrees with the dominant-valency rule, an extension of the dominant-constituent rule that considers a group of atoms with the same valency as a single constituent (Hatert and Burke 2008).

Makovicky and Karup-Møller (2017) discussed the substitution mechanisms involved in the Fe-bearing tetrahedrite/tennantite–goldfieldite substitutional series. As pointed out by previous authors (e.g., Kase 1986), the accommodation of  $\text{Te}^{4+}$  in the tetrahedrite-type structure is coupled with an increase in content of  $\text{Cu}^+$  (and minor  $\text{Ag}^+$ ) from 10 to 12 apfu, according to the substitution  $(\text{Sb,As})^{3+} + \text{Me}^{2+} = \text{Te}^{4+} + \text{Cu}^+$ , where  $\text{Me} = (\text{Fe, Zn} \dots)$ . This substitution is valid up to 2 Te apfu. For higher Te contents, the charge balance is achieved through the formation of vacancies at M(2), according to the substitution mechanism  $(\text{Sb,As})^{3+} + \text{Cu}^+ = \text{Te}^{4+} + \square$ . In synthetic Fe-bearing phases, however, this latter mechanism can be considered an oversimplification because the incomplete elimination of Fe for compositions with more than 2 Te apfu is compensated by the early onset of Cu vacancies at M(2) (Makovicky and Karup-Møller 2017).

In the tennantite/tetrahedrite–goldfieldite field, the following end-member compositions can be proposed:

- (1) tennantite-(Me),  $\text{Cu}_6(\text{Cu}_4\text{Me}_2)\text{As}_4\text{S}_{13}$  and tetrahedrite-(Me),  $\text{Cu}_6(\text{Cu}_4\text{Me}_2)\text{Sb}_4\text{S}_{13}$ , where Me is a divalent constituent;
- (2)  $\text{Cu}_6\text{Cu}_6(\text{As}_2\text{Te}_2)\text{S}_{13}$  and  $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$ ;
- (3) goldfieldite,  $(\text{Cu}_4\square_2)\text{Cu}_6\text{Te}_4\text{S}_{13}$ .

In accord with Hawthorne (2002), the intermediate compositions  $\text{Cu}_6\text{Cu}_6(\text{As}_2\text{Te}_2)\text{S}_{13}$  and  $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$  are end-member formulas as they cannot be obtained as a linear combination of tetrahedrite/tennantite and goldfieldite end-member formulas. Even if Makovicky and Karup-Møller (2017) predict a miscibility gap on the tetrahedrite–goldfieldite join, the  $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$  can be considered as a potential phase.

Although the data reported by Ransome (1909) indicate that goldfieldite might correspond to a phase having an Sb:Te atomic ratio close to 1, that is, close to the end-member composition  $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$ , Trudu and Knittel (1998) recommended this name to “those compositions of the tetrahedrite<sub>ss</sub> that contain more than 3 apfu of Te.” Following this recommendation, Moëlo et al. (2008) reported the formula  $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$  for goldfieldite.

To avoid further confusion, the name goldfieldite is maintained for the species consistent with the end-member

composition  $(\text{Cu}_4\Box_2)\text{Cu}_6\text{Te}_4\text{S}_{13}$  and new names have to be assigned to the end-member compositions  $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$  and  $\text{Cu}_6\text{Cu}_6(\text{As}_2\text{Te}_2)\text{S}_{13}$ . The names “stibiogoldfieldite” and “arsenogoldfieldite” could be applied to these two potential new mineral species.

In the tetrahedrite/tennantite–goldfieldite series, the following boundaries should be applied:

- (1) tetrahedrite/tennantite, with  $0 < \text{Te (apfu)} < 1$ ;
- (2) new names, with  $1 < \text{Te (apfu)} < 3$ . Two different names should be applied, taking into account the dominant trivalent constituent;
- (3) goldfieldite, with  $3 < \text{Te (apfu)} < 4$ .

Natural occurrences of goldfieldite up to 3.77 Te apfu and phases corresponding to the end-member formulas  $\text{Cu}_6\text{Cu}_6(\text{As}_2\text{Te}_2)\text{S}_{13}$  and  $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$  are known in the literature (Spiridonov and Okrugin 1985; Kase 1986; Knittel 1989; Shimizu and Stanley 1991; Voudouris 2006; Spiridonov et al. 2014; Repstock et al. 2016).

### Discreditation of annivite

Annivite is discredited for the following reasons: (1) annivite is an ill-defined species, listed as a questionable species in the current official IMA-CNMNC List of Mineral Names, (2) the holotype annivite is certainly not a  $\text{Bi}^{3+}$ -dominant end-member, and (3) X-ray diffraction studies confirming that a species with appropriate composition actually belongs to the tetrahedrite group have not been carried out yet. Re-validation of the mineral and name on the basis of samples with  $\text{Bi} > \text{Sb}$  and  $\text{Bi} > \text{As}$  should be done by submitting a formal proposal to the IMA-CNMNC.

### Valid mineral species in the tetrahedrite group and type materials

Thirty-two potential natural end-member compositions are given in the literature (Table 2). Among these, only 11 mineral species can be considered as valid. The remaining phases need to follow the usual procedure for the approval as valid mineral species by the IMA-CNMNC.

In the following, valid tetrahedrite group minerals, their type locality, and essential references are reported.

**Argentotennantite-(Zn).** Argentotennantite-(Zn),  $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$ , is renamed after “argentotennantite.” Type locality is the Kvarstiovoye Gorki deposit, Aksu, Stepnyak, Enbekshilder, Akmola (Kazakhstan). Type material is preserved in the Fersman mineralogical museum, Moscow (Russia). Reference: Spiridonov et al. (1986a).

**Argentotetrahedrite-(Fe).** Argentotetrahedrite-(Fe),  $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$ , is renamed after “argentotetrahedrite.” Type locality is Keno Hill, Mayo mining district, Yukon (Canada). Type material is preserved in the Miller Museum collection, University of Western Ontario (Canada), under catalog number M8224. References: Peterson and Miller (1986); Welch et al. (2018).

**Kenoargentotetrahedrite-(Fe).** Kenoargentotetrahedrite-(Fe),  $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{12}\Box$ , is renamed after “freibergite.” Type localities are the Hab Acht Mine (later part of the Beschert Glück Mine), Zug near Freiberg, Saxony (Germany) and Himmelsfürst, Freiberg, Saxony (Germany). Neotype materials can be con-

sidered the specimen number 2289Sa kept in the Senckenberg Museum Collection, Frankfurt (Germany), and studied by Welch et al. (2018), and the specimen number BM88668 of the Natural History Museum (London, U.K.), studied by the *Commission on Ore Microscopy of the IMA* (Criddle and Stanley 1986). References: Criddle and Stanley (1986); Welch et al. (2018).

**Giraudite-(Zn).** Giraudite-(Zn),  $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{Se}_{13}$ , is renamed after “giraudite.” Type locality is the Chaméane uranium deposit, Chaméane, Puy-de-Dôme, Auvergne-Rhône-Alpes (France). Type material is deposited in the mineralogical collections of Écoles de Mines of Paris (France). Reference: Johan et al. (1982).

**Goldfieldite.** Goldfieldite is defined as  $(\text{Cu}_4\Box_2)\text{Cu}_6\text{Te}_4\text{S}_{13}$ . Its type locality was given as Mohawk mine, Goldfield, Goldfield district, Esmeralda County, Nevada (U.S.A.). However, no information about type material is available, and its actual composition is doubtful. We strongly suggest proposing a formal redefinition of goldfieldite, indicating a new type locality and neotype material. References: Lévy (1967); Trudu and Knittel (1998).

**Hakite-(Hg).** Hakite-(Hg),  $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{Se}_{13}$ , is renamed after “hakite.” Type locality is Předbořice, Central Bohemia region (Czech Republic). Type material is kept in the collection of the mineralogical laboratory of the Charles University in Prague (Czech Republic), and in the mineralogical collection of the Écoles de Mines of Paris (France). Reference: Johan and Kvaček (1971).

**Rozhdestvenskayaite-(Zn).** Rozhdestvenskayaite-(Zn),  $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$ , is renamed after “rozhdestvenskayaite.” Type locality is the Moctezuma mine, Moctezuma, Sonora (Mexico). Type material is kept in the Natural History Museum (London, U.K.), under catalog number BM2016,120. Reference: Welch et al. (2018).

**Redefinition of tennantite and tetrahedrite.** Since the two grandfathered minerals tennantite and tetrahedrite have been historically known with both Zn- or Fe-dominance as the C-constituents, these two species are split into the pairs “tetrahedrite-(Fe) and tetrahedrite-(Zn)” and “tennantite-(Fe) and tennantite-(Zn).” Their end-member compositions are  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$ ,  $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$ ,  $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$ , and  $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$ , respectively. Their type localities and type materials are the following.

(1) Tennantite-(Fe) corresponds to the species described by W. Phillips (1819) and R. Phillips (1819) from Cornwall (England, U.K.). No type material is known.

(2) Tennantite-(Zn) has been known since the mid-19th Century, e.g., Plattner (1846) described zincian tennantite under the name *Kupferblende* from Freiberg, Saxony (Germany). Nine years later, Des Cloizeaux (1855) described zincian tennantite from Lengenbach, Binn Valley (Switzerland), under the name “*binnite*.” Since a sample of “*binnite*” was used by Wuensch et al. (1966) for the refinement of the crystal structure of tennantite-(Zn) [the Zn/(Zn+Fe) atomic ratio is 0.63], the type locality of tennantite-(Zn) can be considered to be Lengenbach, Binn Valley (Switzerland). Type material is the specimen L2120 from the collection of the Mineralogical Institute of the University of Bern (Switzerland).

(3) Tetrahedrite-(Fe): the first ferroan tetrahedrite is likely

**TABLE 2.** Nomenclature and classification of the tetrahedrite group minerals

Tetrahedrite series		Tetrahedrite group	
Tetrahedrite-(Fe)	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Fe)	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$
Tetrahedrite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$
Tetrahedrite-(Cd)	$\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Cu)	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{As}_4\text{S}_{13}$
Tetrahedrite-(Cu)	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Hg)	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{As}_4\text{S}_{13}$
Tetrahedrite-(Hg)	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Mn)	$\text{Cu}_6(\text{Cu}_4\text{Mn}_2)\text{As}_4\text{S}_{13}$
Tetrahedrite-(Mn)	$\text{Cu}_6(\text{Cu}_4\text{Mn}_2)\text{Sb}_4\text{S}_{13}$		
Freibergite series		Arsenofreibergite series	
Argentotetrahedrite-(Fe)	$\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$	Argentotennantite-(Zn)	$\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$
Kenoargentotetrahedrite-(Fe)	$\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{12}\square$	Argentotennantite-(Fe)	$\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$
Argentotetrahedrite-(Cd)	$\text{Ag}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$		
Argentotetrahedrite-(Hg)	$\text{Ag}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$		
Hakite series		Giraudite series	
Hakite-(Hg)	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{Se}_{13}$	Giraudite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{Se}_{13}$
Hakite-(Cd)	$\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{Se}_{13}$	Giraudite-(Cu)	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{As}_4\text{Se}_{13}$
Hakite-(Cu)	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{Sb}_4\text{Se}_{13}$	Giraudite-(Fe)	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{Se}_{13}$
Hakite-(Fe)	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{Se}_{13}$	Giraudite-(Hg)	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{As}_4\text{Se}_{13}$
Hakite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{Se}_{13}$		
Rozhdestvenskayaite series		Goldfieldite series	
Rozhdestvenskayaite-(Zn)	$\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$	Goldfieldite	$(\text{Cu}_4\square)_2\text{Cu}_6\text{Te}_4\text{S}_{13}$
Rozhdestvenskayaite-(Fe)	$\text{Ag}_6(\text{Ag}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$	"Stibiofieldite"	$\text{Cu}_6\text{Cu}_4(\text{Sb}_2\text{Te}_2)\text{S}_{13}$
Rozhdestvenskayaite-(Hg)	$\text{Ag}_6(\text{Ag}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$	"Arsenogoldfieldite"	$\text{Cu}_6\text{Cu}_4(\text{As}_2\text{Te}_2)\text{S}_{13}$

Note: Italicized names require official approval by the IMA-CNMNC.

"coppite" (Bechi, 1863). It corresponds to tetrahedrite-(Fe). Carrozzini et al. (1991) reexamined tetrahedrite from the Frigido mine, Apuan Alps, Tuscany (Italy) using samples from the University of Pisa and from the Pelloux collection. Type material can be considered the specimen 9964 of the Pelloux collection kept in the mineralogical collections of the Geomineralogical Department of the Bari University (Italy) and the specimen no.7936 belonging to the mineral collections of the Museo di Storia Naturale, Pisa University (Italy).

(4) Tetrahedrite-(Zn): Charlat and Lévy (1974, 1975, 1976) characterized samples of tetrahedrite (samples M11 and M12) from Horhausen, Westernwald, Rhineland (Germany). These samples have chemical formulas  $\text{Cu}_{10.08}\text{Zn}_{1.74}\text{Fe}_{0.18}\text{Sb}_{3.97}\text{As}_{0.09}\text{S}_{13.4}$  (M11) and  $\text{Cu}_{10.06}\text{Ag}_{0.06}\text{Zn}_{1.62}\text{Fe}_{0.27}\text{Sb}_{3.90}\text{As}_{0.06}\text{S}_{12.7}$  (M2), unit-cell parameter  $a = 10.383(2)$  Å for both samples, and reflectance spectra in the range 440–800 nm are given in Charlat and Lévy (1976). It is worth noting that the structure refinement of tetrahedrite reported by Wuensch (1964) was obtained using a sample from this German locality. We re-examined sample M11 of Charlat and Lévy (1974, 1975, 1976), refining its crystal structure to  $R_1 = 0.0144$  for 364 unique reflections with  $F_o > 4\sigma(F_o)$ . Unit-cell parameter is  $a = 10.3798(8)$  Å. The corresponding CIF is available as Supplementary Material<sup>1</sup>. This sample was deposited in the mineralogical collection of the Museo di Storia Naturale, Pisa University (Italy) (catalog number no.19910) and of the Musée de Minéralogie, Mines Paris-Tech (France) (catalog number no. 83693) as neotype material of tetrahedrite-(Zn). Co-neotype material can be considered the specimen of tetrahedrite-(Zn) from the Namex deposit, Huffman Township, western Abitibi Greenstone Belt, Ontario (Canada), characterized by McDonald et al. (in preparation) and kept in the Canadian Museum of Nature, Gatineau (Canada) under catalog number CMNMC 87261.

## IMPLICATIONS

The present nomenclature of the tetrahedrite group minerals is based on the end-member formula, a concept extremely useful

for unambiguously identifying and classifying complex mineral compositions (e.g., Hawthorne 2002). Moreover, it highlights the frequent occurrence of the "valency-imposed double site-occupancy" (Hatert and Burke 2008) in the sulfosalt realm. Consequently, it is fully consistent with the current nomenclature rules (e.g., Bosi et al. 2019).

Often the dominant divalent cation in tetrahedrite group minerals has been identified by the use of a prefix, e.g., Fe-tennantite and Zn-tennantite (Kemkin and Kemkina 2013), or using descriptors like "Zn-rich," "Fe-bearing," or "Ag-enriched" preceding the mineral name (e.g., Arlt and Diamond 1998; Foit and Ulbricht 2001; Förster and Rhede 2004; Gallego Hernández and Akasaka 2010; Gołębiewska et al. 2012; Plotinskaya et al. 2015; Škácha et al. 2016, 2017). Even when such terminology is well defined, inconsistent usages by different authors have inadvertently led to unnecessary complication in comparing different members of the tetrahedrite group. The reason that so many authors add compositional information to the tetrahedrite nomenclature is because such chemical information is very useful in the context of a wide range of mineralogical studies. Such a trend is likely to continue, especially as characterization of mineral species in terms of ore textures and electron microprobe data is increasingly complemented by quantitative trace element data that can provide additional constraints of value. Indeed, the wide compositional variations in the tetrahedrite isotopes reflect spatial and temporal changes in physico-chemical conditions during processes of ore formation (e.g., Sack and Loucks 1985; Sack and Ebel 1993; Förster and Rhede 2004; Staude et al. 2010; Catchpole et al. 2012; Gołębiewska et al. 2012; Plotinskaya et al. 2015; Repstock et al. 2016). Last but not least, tetrahedrite group minerals attract interest from the perspective of minerals processing and geometallurgy, as potential, often significant, hosts for both unwanted elements (particularly As, but also Cd and Hg) as well as potential by-products such as Ag and even Sb, Au, or Te.

Consequently, this new nomenclature system, allowing the full description of the chemical variability of the tetrahedrite

group minerals, would be able to convey important chemical information not only to geoscientists (crystallographers, mineralogists, petrologists, ore geologists, and so on) but also to industry professionals as well.

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### Endnote:

<sup>1</sup>Deposit item AM-20-17128, CIF. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to [http://www.minsocam.org/MSA/AmMin/TOC/2020/Jan2020\\_data/Jan2020\\_data.html](http://www.minsocam.org/MSA/AmMin/TOC/2020/Jan2020_data/Jan2020_data.html)).