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Biagioni et al.

Revision 1

The tetrahedrite group: nomenclature and classification

Cristian BIAGIONI[1*], Luke L. GEORGE[2], Nigel J. COOK[2], Emil MAKOVICKY[3], Yves MOËLO[4], Marco PASERO[1], Jiří SEJKORA[5], Chris J. STANLEY[6], Mark D. WELCH[6], and Ferdinando BOSI[7]

[1] Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy

[2] School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide S.A. 5005, Australia

[3] Department of Geoscience and Natural Resources Management, University of Copenaghen, Østervoldgade 10, DK1350 Copenaghen, Denmark

[4] Institut des Matériaux Jean Rouxel, UMR 6502, CNRS, Université de Nantes, 2 rue de la Houssinière, F-44322 Nantes Cedex 3, France

[5] Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193-00 Prague 9, Czech Republic

[6] Department of Earth Sciences, Natural History Museum, London SW7 5BD, United Kingdom

[7] Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Roma, Italy

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

Biagioni et al.

Abstract: The classification of the tetrahedrite group minerals in keeping with the current IMA-accepted nomenclature rules 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 $^{M(2)}A_6{}^{M(1)}(B_4C_2)_{\Sigma 6}{}^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$, where A = Cu^+, Ag^+, □ (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 □. 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 could 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.

Key-words: tetrahedrite group, sulfosalts, nomenclature, classification.

Biagioni et al.

1. 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 isotypic 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 lacking. 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.

2. Crystal-chemistry of the tetrahedrite group minerals

2.1. 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 derived from a sphalerite-type substructure. However, a more detailed description of the structural arrangement of tetrahedrite was given thirty years later by Wuensch (1964). Tetrahedrite is cubic, with space group symmetry $I\bar{4}3m$. Three independent cation sites and two anion sites occur (Fig. 1):

- $M(1)$ site, at the Wyckoff position 12d, with atomic coordinates (¼, ½, 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);

125   • $X(3)$ site, at the Wyckoff position $8c$, with atomic coordinates (x, x, x);

126   • S(1) site, at the Wyckoff position $24g$, with atomic coordinates (x, x, z);

127   • S(2) site, at the Wyckoff position $2a$, with atomic coordinates (0, 0, 0).

128   On this basis, the structural formula of minerals belonging to the tetrahedrite group can be

129 written as $M(2)_6 M(1)_6 X(3)_4 S(1)_{12} S(2)$ ($Z = 2$). The crystal structure of tetrahedrite (and those of its

130 isotypes) is an example of a sulfidic sodalite-like (SOD) framework, with cavities that can be

131 described as Laves truncated tetrahedra (e.g., Johnson et al. 1988). The stoichiometric relationship

132 with sodalite becomes obvious by rearranging the chemical formula to yield $|Cu_{12}Sb_8S_2|[Cu_{12}S_{24}]$.

133 Indeed, tetrahedrite is made up of a considerably collapsed sodalite-like framework of corner-

134 connected $M(1)S(1)_4$ tetrahedra with cages containing S(2)-centered $M(2)_6$-octahedra, encircled by

135 four $X(3)S(1)_3$ trigonal pyramids (e.g., Johnson et al. 1988; Depmeier 2005). The dual character of

136 the tetrahedrite structure, i.e., its sodalite-like and sphalerite-omission derivative, explains many of

137 its properties.

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139 **2.2. Chemical variability**

140   The crystal structure of tetrahedrite is rather flexible in a chemical sense, accommodating

141 several cations of medium to small ionic radius and variable formal charge (from +1 to +4). The

142 occurrence of vacancies or interstitial atoms have been confirmed through structural studies (e.g.,

143 Maske and Skinner 1971; Makovicky and Skinner 1979; Rozhdestvenskaya et al. 1993; Makovicky

144 et al. 2005; Welch et al. 2018). The chemical variability encompasses anions too, with the

145 substitution of S by Se, or with the occurrence of vacancies. For such a wide range of possible

146 substitutions, tetrahedrite has been referred to as a "sulfide amphibole" (Sack and Loucks 1985).

147   The general structural formula of the tetrahedrite group minerals can best be defined as

148 $^{M(2)}A_6{}^{M(1)}(B_4C_2)_{\Sigma 6}{}^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$, where the upper cases represent the following constituents:

149   A = Cu^+, Ag^+, □ (vacancy); $(Ag_6)^{4+}$ clusters are also possible, coupled with Z vacancies (see

150 § 3.4);

151   B = Cu^+, Ag^+;

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

153   D = Sb^{3+}, As^{3+}, Bi^{3+}, Te^{4+};

154   Y = S^{2-}, Se^{2-};

155   Z = S^{2-}, Se^{2-}, □.

156   The crystal-chemistry of the tetrahedrite group was first examined by Charlat and Lévy

157 (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 (Ag^+ + 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 (S^{2-} + Se^{2-}) *apfu*, yielding 26 negative charges. As the sum of 10 monovalent cations (Ag^+ + Cu^+ = A and B constituents) and 4 trivalent cations (Sb^{3+} + As^{3+} + Bi^{3+} = 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 natural samples (e.g., Makovicky et al. 2005); the apparent excess of negative charges could be compensated by the presence of Cu^{2+} (Pattrick et al. 1993).

Maske and Skinner (1971) identified Cu excess in synthetic tennantite, $Cu_{12+x}As_{4+y}S_{13}$, 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 $Cu_{12+x}Sb_4S_{13}$ (x varies continuously between less than 0.1 and 1.9) exsolves, below 120°C, to a composition close to $Cu_{12}Sb_4S_{13}$ (a = 10.32 Å) and to a Cu-excess composition, close to $Cu_{14-x}Sb_4S_{13}$ (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.

3. 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 ten species within the tetrahedrite group.

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3.1. Annivite

Annivite was considered the Bi-dominant analogue 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: $(Cu_{9.93}Fe_{1.22}Zn_{0.55})_{\Sigma 11.70} (As_{2.60}Sb_{1.28}Bi_{0.42})_{\Sigma 4.30}S_{13.15}$, 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 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; Gołębiowska 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.

3.2. Argentotennantite

Argentotennantite was first described by Spiridonov et al. (1986a) from the polymetallic Kvartsitoviye 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 $(Ag_{5.67}Cu_{0.33})_{\Sigma 6.00}$ $(Cu_{4.15}Zn_{1.52}Fe_{0.37}Pb_{0.01}Cd_{0.01})_{\Sigma 6.06}(As_{2.14}Sb_{1.89})_{\Sigma 4.03}S_{12.90}$, which leads to the end-member formula $Ag_6(Cu_4Zn_2)As_4S_{13}$. The crystal structure of argentotennantite is currently unsolved.

Števko 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.

3.3. 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-CNMMN. Moëlo et al. (2008) reported this species as a member of the tetrahedrite isotypic series, with chemical composition $Ag_{10}(Fe,Zn)_2Sb_4S_{13}$. They pointed out that a redefinition through a formal proposal to the CNMNC

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was highly desirable. Finally, using new compositional and structural data for a sample from the Keno Hill Ag-Pb-Zn deposit, Yukon (Canada), having Fe > Zn, Welch et al. (2018) redefined argentotetrahedrite as the Sb counterpart of argentotennantite, with the simplified formula $Ag_6Cu_4(Fe,Zn)_2Sb_4S_{13}$. Crystal structure analysis confirmed that all Ag is ordered at the $M(2)$ site.

Foit and Ulbricht (2001) reported a sample from the O'Keefe claims, Harney County, Oregon (USA) having 5.78 Ag *apfu* and Hg dominant over Zn and Fe which leads to the end-member composition $Ag_6(Cu_4Hg_2)Sb_4S_{13}$. 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 chemical formula $Cu_{6.88}Ag_{2.96}(Hg_{1.83}Zn_{0.17})_{\Sigma2.00}(Sb_{3.36}As_{0.71})_{\Sigma4.07}S_{13.09}$. 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.*, $^{M(2)}(Ag_{2.96}Cu_{2.88})_{\Sigma5.84}$. The classification of this sample, without structural data, is uncertain: it may be considered either as the Ag-rich variety of $Cu_6(Cu_4Hg_2)Sb_4S_{13}$ or as argentotetrahedrite with Hg as the dominant divalent cation, i.e., $Ag_6(Cu_4Hg_2)Sb_4S_{13}$.

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 $Ag_6(Cu_4Cd_2)Sb_4S_{13}$.

3.4. 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 Sb = 4 *apfu*, to $Ag_{5.74}Cu_{4.61}Fe_{2.12}Zn_{0.30}Sb_{4.00}S_{13.06}$.

The definition of freibergite is much debated, being often 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

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257 *a*-parameter, and only when Ag content exceeds *ca*. 23 wt% (~ 4 *apfu*) does the abnormal trend in

258 the behavior of the *a*-parameter, typical of freibergite, occur.

259 The crystal structure of freibergite was reported by Rozhdestvenskaya et al. (1993). At the

260 $M(2)$ site, Cu is mainly or completely substituted by Ag; at the same time, the S(2) site, having

261 octahedral coordination, is progressively emptied, allowing the formation of $(Ag_6)^{4+}$ octahedral

262 clusters. Thus, the ideal formula of freibergite is $Ag_6(Cu_4Fe_2)Sb_4S_{12}$, and as such it is a distinct

263 species from argentotetrahedrite. Moëlo et al. (2008) reported the idealized formula $(Ag_{4+2x}Cu_{2-2x})$

264 $[(Cu,Ag)_4(Fe,Zn)_2]_{\Sigma6}Sb_4S_{12}S_{1-x}$ (0 < x < 1). The boundary between freibergite and Ag-rich

265 tetrahedrite is unknown and further studies are required.

266 Welch et al. (2018) refined the structure of freibergite with (Fe,Zn) as divalent cations and

267 the octahedral cluster nearly fully occupied by Ag. The S(2) site refined to zero occupancy (i.e.,

268 vacant). Charge-balance was rationalized by invoking intermetallic bonding in the $^{M(2)}(Ag_6)$ group,

269 having a formal charge of +4, as has been shown for synthetic organometallic compounds (e.g.,

270 Kikukawa et al. 2013).

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272 **3.5. Giraudite**

273 Giraudite was described by Johan et al. (1982) from the Chaméane uranium deposit, Puy-de-

274 Dôme, Auvergne (France) as the As-analogue of hakite. It occurs as grains up to 400 μm in size.

275 Three sets of chemical data are given in the type description, corresponding to the empirical

276 formulae $(Cu_{5.32}Ag_{0.68})_{\Sigma6.00}(Cu^+_4Zn_{1.16}Cu^{2+}_{0.72}Hg_{0.08}Fe_{0.04})_{\Sigma6.00}(As_{2.20}Sb_{1.76})_{\Sigma3.96}Se_{11.04}S_{2.00}$,

277 $(Cu_{5.24}Ag_{0.76})_{\Sigma6.00}(Cu^+_4Zn_{1.12}Cu^{2+}_{0.84}Fe_{0.08}Hg_{0.04})_{\Sigma6.08}(As_{2.16}Sb_{1.88})_{\Sigma4.04}Se_{11.08}S_{1.80}$, and

278 $(Cu_{5.68}Ag_{0.32})_{\Sigma6.00}(Cu^+_4Zn_{1.00}Cu^{2+}_{0.92}Hg_{0.04})_{\Sigma6.00}(As_{2.60}Sb_{1.28})_{\Sigma3.88}Se_{10.52}S_{2.64}$. Formally, Cu^{2+} occurs in

279 giraudite. The end-member formula is $Cu_6(Cu_4Zn_2)As_4Se_{13}$. Its crystal structure has not been solved

280 yet.

281 Förster et al. (2002) described a complete substitution series between giraudite and hakite

282 from the Niederschlema-Alberoda uranium deposit, Erzgebirge (Germany). Indeed, they did not

283 describe giraudite but a mercurian giraudite, ideally $Cu_6(Cu_4Hg_2)As_4Se_{13}$; one spot analysis

284 corresponded to a cuprian giraudite, having formally Cu^{2+} as dominant divalent C constituent.

285 Moreover, Förster and Rhede (2004) reported an extensive substitution series between giraudite and

286 tennantite, involving the Se^{2-}-S^{2-} substitution. These authors gave chemical data corresponding to

287 Fe- and Cu^{2+}-terms, ideally $Cu_6(Cu_4Fe_2)As_4Se_{13}$ and $Cu_6(Cu_4Cu^{2+}_2)As_4Se_{13}$, respectively. Mercury-

288 and Cu-dominant giraudites were also recently described from the Příbram uranium and base-metal

289 district (Czech Republic) by Škácha et al. (2017).

3.6. Goldfieldite

Goldfieldite was first identified by Sharwood (1907) and later reported in the mineralogical literature by Ransome (1909) from the Mohawk mine, Goldfield, Nevada (USA). 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 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) synthetized phases along the tetrahedrite-goldfieldite and tennantite-goldfieldite joins in order 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.

3.7. Hakite

Hakite was first described by Johan and Kvaček (1971) from Předbořice, Central Bohemia region (Czech Republic), as anhedral grains up to 300 μm in size. The studied material showed variable Se:S atomic ratios, ranging between the empirical compositions

323    $Cu_6(Cu_{4.08}Hg_{1.83})_{\Sigma5.91}(Sb_{3.05}As_{1.03})_{\Sigma4.08}(Se_{10.35}S_{2.62})_{\Sigma12.97}$ and

324    $Cu_6(Cu_{4.22}Hg_{1.73})_{\Sigma5.95}(Sb_{3.83}As_{0.22})_{\Sigma4.05}Se_{11.90}$. These two compositions correspond to unit-cell

325   parameters a = 10.83(1) and 10.88(1) Å, respectively. Johan and Kvaček (1971) proposed the

326   existence of a substitution series between hakite and tetrahedrite. From the same locality, Brodin

327   (1981) reported the occurrence of Ag-bearing hakite; however, the recalculation of its chemical

328   formula shows that Cu is still the dominant cation at the $M(2)$ site.

329   Förster et al. (2002) described a complete substitution series between hakite and mercurian

330   giraudite from the Niederschlema-Alberoda uranium deposit, Erzgebirge (Germany). The sum (Se +

331   S) varies between 13.00 and 13.10 *apfu*.

332   Škácha et al. (2016) described hakite from Příbram, Central Bohemia (Czech Republic), and

333   stressed the occurrence of different compositions characterized by the dominance of Hg^{2+}, Zn^{2+}, or

334   Cd^{2+}. They indicated these different compositions as "Hg-hakite", "Zn-hakite", and "Cd-hakite",

335   ideally $Cu_6(Cu_4Hg_2)Sb_4Se_{13}$, $Cu_6(Cu_4Zn_2)Sb_4Se_{13}$, and $Cu_6(Cu_4Cd_2)Sb_4Se_{13}$, respectively. The

336   crystal structure of "Hg-hakite" was solved through electron diffraction tomography, confirming the

337   isotypic relations with tetrahedrite and the occurrence of Hg^{2+} at the $M(1)$ site. Later, Škácha et al.

338   (2017) described also Fe- and Cu-dominant hakite samples from the same occurrence on the base of

339   electron microprobe data.

340   Finally, Karup-Møller and Makovicky (1999) synthesized a sample having 1.8 Fe *apfu*,

341   leading to the end-member composition $Cu_6(Cu_4Fe_2)Sb_4Se_{13}$, as well as fully Zn substituted

342    $Cu_6(Cu_4Zn_2)Sb_4Se_{13}$. The $Cu_6Cu_6Sb_4Se_{13}$ composition resulted in the orthorhombic phase Cu_3SbSe_3

343   and not in tetrahedrite-like structure.

344

345   **3.8. Rozhdestvenskayaite**

346   Silver hyper-rich tetrahedrite varieties, with Ag > 8 *apfu* and increased *a*-parameter, were

347   first described by Russian authors. Zhdanov et al. (1992) described a Cu-free sample of Ag-rich

348   tetrahedrite from the deposit of Hachakchansk (up to 54.2 wt% Ag, corresponding to 10.74 Ag *apfu*

349   on the basis of 29 *apfu*; a = 10.92 Å). Later, Samusikov and Gamyanin (1994) presented an almost

350   Ag-pure sample (52 wt% Ag, with only 0.7 wt% Cu; a = 10.90 Å) from Yakutia (Russia) and

351   named it "tarynite" from the locality. Unfortunately, no official proposal was submitted to the then

352   IMA-CNMMN by these authors.

353   Finally, rozhdestvenskayaite, ideally $Ag_6(Ag_4Zn_2)Sb_4S_{13}$, was recently described as a new

354   tetrahedrite group mineral by Welch et al. (2018). The type locality is the Moctezuma mine

355   (Bambolla mine), Sonora (Mexico).

356   Foit and Ulbricht (2001) documented samples corresponding to rozhdestvenskayaite from
357   the O'Keefe claims, Oregon (USA), in which Hg is the dominant divalent cation, thus
358   corresponding to the end-member composition $Ag_6(Ag_4Hg_2)Sb_4S_{13}$. Zhdanov et al. (1992)
359   examined an Fe-rich Ag-pure end-member, $Ag_6(Ag_4Fe_2)Sb_4S_{13}$, with unit-cell parameter $a = 10.92$
360   Å.

361   Ixer and Stanley (1983) analyzed a tetrahedrite group grain of composition
362    $(Ag_{8.18}Cu_{1.91}Zn_{1.44}Fe_{0.49}Pb_{0.17}Cd_{0.16})_{\Sigma12.35}(As_{2.22}Sb_{1.93})_{\Sigma4.15}S_{12.5}$ which could have Ag dominant at
363   both $M(2)$ and $M(1)$ sites, and As > Sb at $X(3)$, but close to $^{S(2)}(S_{0.5}\square_{0.5})$ boundary. Consequently, it
364   could be either the As-analogue of rozhdestvenskayaite or the As-analogue of freibergite (if $^{S(2)}\square >$
365   0.5). The As-analogue of rozhdestvenskayaite was also possibly reported from the Manson Lode,
366   Ulu Sokor gold-base metal deposit, Kelantan (Malaysia) (Gan 1980).

367

368   **3.9. Tennantite**

369   Tennantite was first described by the two brothers W. Phillips (1819) and R. Phillips (1819)
370   from Cornwall (England, UK). Even if no accurate quantitative chemical data are available, the
371   latter author reported that Cu, Fe, As, and S are the elements occurring in the studied material.
372   Consequently, it could be that original tennantite was close to the ideal composition
373    $Cu_6(Cu_4Fe_2)As_4S_{13}$.

374   Makovicky et al. (2003) observed Fe^{2+}, Fe^{3+} and Fe^{n+} with intermediate valence ($+2 < n <$
375    $+3$) in synthetic Fe-bearing tennantite through Mössbauer spectroscopy. Tennantite with a low Fe
376   content contains Fe^{3+}, whereas Fe^{2+} appears at higher Fe contents, becoming the dominant valence
377   state at Fe content larger than 1 *apfu* (in Cu-excess samples) and 1.4 *apfu* in stoichiometric samples.
378   The occurrence of charge-transfer phenomena (manifested as "intermediate valence iron") was
379   reported (Makovicky et al. 2003). In every case, the sum of the aggregate charge of the C-cations is
380    $+4$; this sum is produced by $2Cu^{2+} \rightarrow Cu^+ + Fe^{3+} \rightarrow 2Fe^{2+}$ combinations, in a continuous process of
381   exchange, with a possible share of $Cu^{2+} + Fe^{2+}$.

382   After the structural model proposed by Pauling and Neuman (1934), the crystal structure of
383   tennantite was refined by Wuensch et al. (1966) using a crystal of the variety known as "binnite"
384   from the Lengenbach quarry, Binn Valley (Switzerland). Chemical data suggested a composition
385   corresponding to the end-member $Cu_6(Cu_4Zn_2)As_4S_{13}$. Zincian tennantite was reported under the
386   name *Kupferblende* by Plattner (1846) from the Prophet Jonas Mine, Zug near Freiberg, Saxony
387   (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 $(Cu_{5.97}Ag_{0.03})_{\Sigma6.00}(Cu_{5.63}Fe_{0.37})_{\Sigma6.00}(As_{3.28}Sb_{0.38})_{\Sigma3.66}S_{13}$ (basis: 12 Me atoms) (Thouvenin 1983; Marcoux et al. 1994). Despite a weak As- and Sb-deficit, this analysis clearly points to a Cu^{2+} dominant C-cation at the $M(1)$ site. A sample of tennantite with dominant 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 peculiar 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 $Cu_6(Cu_4Hg_2)As_4S_{13}$.

3.10. 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*, *grey 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 $Cu_6(Cu_4Fe_2)Sb_4S_{13}$ 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; Makovicky et al. 2003; Andreasen et al. 2008; Nasonova et al. 2016). Spectroscopic Mössbauer studies indicated that along the join $Cu_{12+x}(Sb,As)_4S_{13} - Cu_{10}Fe_2(Sb,As)_4S_{13}$, the replacement of Cu by Fe starts by incorporation of Fe^{3+}, which is the only type of Fe present in $Cu_6(Cu_{5.5}Fe_{0.5})(Sb,As)_4S_{13}$. Then, Fe^{2+} starts to be incorporated, together with the gradual reduction of Fe^{3+} to Fe^{2+}, up to the composition $Cu_6(Cu_4Fe_2)(Sb,As)_4S_{13}$ (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 Cu^{2+} as the dominating C-cation is known in

13

Biagioni et al.

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 $Cu_6(Cu_4Cu_2)Sb_4S_{13}$. The compositions $Cu_{12+x}Sb_4S_{13}$ (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 $Cu_{9.9}Hg_{1.4}Fe_{0.7}Zn_{0.4}Sb_{3.2}S_{13}$. 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 (USA), in agreement with the end-member composition $Cu_6(Cu_4Hg_2)Sb_4S_{13}$, 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 (USA). 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 Pattrick (1978) at Tyndrum (Scotland, UK). 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, $Cu_6(Cu_4Cd_2)Sb_4S_{13}$ is another potential natural end-member composition. Jia et al. (1988) actually gave the empirical formula $(Cu_{6.95}Ag_{3.03})_{\Sigma9.98}(Cd_{1.85}Zn_{0.15}Fe_{0.15})_{\Sigma2.15}$ $(Sb_{4.19}As_{0.25})_{\Sigma4.44}S_{13}$; taking into account the partitioning of Ag at the *M*(2) site, this formula could represent an intermediate composition between an hypothetical end-member $Ag_6(Cu_4Cd_2)Sb_4S_{13}$ and $Cu_6(Cu_4Cd_2)Sb_4S_{13}$.

Basu et al. (1984) described a 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 $Cu_6(Cu_4Mn_2)Sb_4S_{13}$. Makovicky and Karup-Møller (1994) synthesized tetrahedrite containing up to

14

454 1.91 Mn *apfu*. The crystal structure of a synthetic tetrahedrite with 1.4 Mn *apfu* was solved by
455 Chetty et al. (2015b).

456   Finally, Vavelidis and Melfos (1997) documented tetrahedrite from the Maronia area
457 (Greece), where Pb dominated over both Fe and Zn and assumed that Pb is hosted at the tetrahedral
458 $M(1)$ site, implying the occurrence of a potential end-member $Cu_6(Cu_4Pb_2)Sb_4S_{13}$. However,
459 Makovicky and Karup-Møller (1994) observed a maximum Pb content during their syntheses of
460 0.45 *apfu*; moreover, there is still much uncertainty on these results and the occurrence of very fine
461 exsolution of Pb-rich phases cannot be excluded. Finally, even if Pb enters the crystal structure of
462 tetrahedrite, its oxidation state is currently unknown. Indeed, Pb^{2+} is too large and displays a
463 different coordination environment, making its presence in tetrahedrite unlikely. Lead could occur
464 as Pb^{4+}, as could Ge and Sn. In this case, its crystal-chemical role has to be understood.

465   Although undocumented in nature, Makovicky and Karup-Møller (1994) synthesized
466 tetrahedrite compositions having both 2 Co and 2 Ni *apfu*. Barbier et al. (2015) gave the crystal
467 structure of a synthetic tetrahedrite with 1.6 Ni *apfu*. Natural analogues are unknown, however,
468 even if D'Achiardi (1881) reported a Ni-bearing tetrahedrite from the Frigido mine, Apuan Alps,
469 Tuscany (Italy), naming it "*frigidite*". More recent studies indicated that this sample was actually an
470 intergrowth of tetrahedrite [approximated formula $Cu_6(Cu_4Fe_{1.5}Zn_{0.5})Sb_4S_{13}$] and Ni-bearing
471 minerals (Carrozzini et al. 1991).

472   Minor gold (up to ∼ 1 wt%) is known in tetrahedrite and goldfieldite (Mozgova and Tsepin
473 1983). The same authors also described Sn-bearing tetrahedrite (up to ∼ 3 wt%). Tin contents up to
474 0.96 *apfu* was obtained in synthetic tetrahedrite by Hansen et al. (2003).

475

476 **4. Applying the IMA recommendations to the tetrahedrite group**

477

478 **4.1 Nomenclature rules**

479   The occurrence of Me^+ and Me^{2+} cations at the $M(1)$ site of the minerals of the tetrahedrite
480 group is a case of valency-imposed double-site occupancy (Hatert and Burke 2008). Consequently,
481 samples having different pairs of B and C constituents should be regarded as separate mineral
482 species. Since divalent metals are preferentially allocated at the $M(1)$ site, the nomenclature system
483 for the tetrahedrite isotypic series may be applied solely using chemical data, in accord with the
484 main requirement for a practical nomenclature system (Hatert and Burke 2008). In agreement with
485 Mills et al. (2009), the following nomenclature and classification is recommended.

486   1) A member of the tetrahedrite group is a sulfosalt having a considerably collapsed sodalite-

487   like framework compatible with the general structural formula $^{M(2)}A_6{}^{M(1)}(B_4C_2)^{X(3)}D_4{}^{S(1)}Y_{12}{}^{S(2)}Z$.

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

489   distinct root-name:

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

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

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

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

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

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

496   3) Each distinct mineral species within the tetrahedrite group must have a hyphenated suffix

497   between parentheses, indicating the dominant $^{M(1)}C$ constituent (the charge compensating

498   constituent), e.g., tetrahedrite-(Fe) for $Cu_6(Cu_4Fe_2)Sb_4S_{13}$.

499   4) Depending on the Cu^+/Ag^+ ratio, if two minerals have $^{M(1)}B$ = Cu and the same dominant

500   constituent at $^{X(3)}D$ and $^{S(1)}Y$, they will be assigned the same root-name. The adjectival prefix

501   "argento" will be added to the root-name if $^{M(2)}Ag > {}^{M(2)}Cu$ (no prefix when $^{M(2)}Cu > {}^{M(2)}Ag$).

502   Minerals with $^{M(1)}B$ = Ag deserve a different root-name.

503   5) The chemical composition of every member of the tetrahedrite group should be expressed

504   by an end-member formula as defined by Hawthorne (2002), i.e., an end-member composition must

505   be fixed, it must be compatible with the crystal structure, and it may have more than one type of

506   cation or anion at only one site if required by the electroneutrality principle. Note that an end-

507   member is an algebraic and chemical construct which is important to determine its thermodynamic

508   properties, regardless of whether the end-member exists as a stable mineral (Henry et al. 2011).

509   6) The established tetrahedrite group can be divided into series, on the basis of the

510   combination of $^{M(2)}A$, $^{M(1)}B$, $^{X(3)}D$, and $^{S(1)}Y$ constituents. Due to the ambiguities in the end-member

511   composition of tetrahedrite group minerals, in which poor attention has been paid to the dominant

512   charge compensating cation, and aiming at having minimum impact into the current nomenclature,

513   unsuffixed names – such as "tetrahedrite" or "tennantite" – from now on will become series names.

514   As the name freibergite has been applied to phases having composition $Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$ (Moëlo

515   et al. 2008), we suggest using this name as a series name to indicate different Ag-rich members of

516   the tetrahedrite group. The proposed series are as follow:

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

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

Biagioni et al.

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

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

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

522   Rozhdestvenskayaite could be the name of a series of tetrahedrite group minerals having B =

523   Ag. Goldfieldite (B = Cu, D = Te, Y = S) is an unassigned member, in agreement with Mills et al.

524   (2009). Argentotennantite-(Zn) is another unassigned member of the tetrahedrite group. Taking into

525   account the likely occurrence of the Fe-analogue of argentotennantite-(Zn), the "arsenofreibergite

526   series" could be proposed as the As-analogue of the freibergite series.

527   7) In the freibergite series, Ag at the $M(2)$ site can occur either as trigonally-coordinated

528   cation [argentotetrahedrite, $Ag_6(Cu_4Fe_2)Sb_4S_{13}$; Welch et al. (2018)] or as discrete $(Ag_6)^{4+}$ clusters,

529   characterized by Ag–Ag bonds coupled with vacancy at the S(2) site. The latter leads to the end-

530   member formula $(Ag_6)(Cu_4Fe_2)Sb_4S_{12\square\square}$ (Rozhdestvenskaya et al. 1993; Welch et al. 2018), for

531   which the prefix "keno" (from the Greek word κενός, meaning empty) is proposed on the root-name

532   argentotetrahedrite to indicate the strict relation between the S(2) vacant site and the peculiar

533    $(Ag_6)^{4+}$ cluster in the freibergite series.

534

4.2. Freibergite: status and relations with other Ag-rich members of the tetrahedrite group

536   The name freibergite has usually referred to a grandfathered mineral, having chemical

537   composition $Ag_6[Cu_4Fe_2]Sb_4S_{12}$ (official IMA-CNMNC List of Mineral Names – Updated January

538   2019). However, its definition is not straightforward and several authors confused freibergite with

539   Ag-rich tetrahedrite or the recently approved species argentotetrahedrite, e.g., Kalbskopf (1972),

540   Peterson and Miller (1986). Indeed, Moëlo et al. (2008) reported freibergite as $Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$.

541   A chronological review of the crystal-chemical studies performed on Ag-rich members of the

542   tetrahedrite group can help in clarifying the status of the different Ag-rich members of the

543   tetrahedrite group.

544   From the beginning of the 1970s to the end of the 1980s, the research focus was devoted to

545   the study of the relationships between chemistry and unit-cell parameter, as well as to the

546   understanding of the Ag speciation in the crystal structure of tetrahedrite. Petruk (1971) examined

547   some Ag-bearing tetrahedrites from some Canadian Ag-As ores, finding quite the same unit-cell

548   parameter (a ~ 10.49 Å) for Ag ~ 2.9 and 5.4 *apfu*. The lack of samples with intermediate Ag

549   content inhibits observation of the increase, followed by the decrease, of the unit-cell parameter.

550   Shimada and Hirowatari (1972), using natural samples, established the variation of the unit-cell

551   parameter with increasing Ag content. Kalbskopf (1972) first suggested the preferential occurrence

552   of Ag at the M(2) site. Two years later, Riley (1974) revealed the specific "freibergite trend" using

553   natural samples, i.e., a decrease of the unit-cell parameter with increasing Ag content. Charlat and

554   Lévy (1975) proposed a relation between Ag content and unit-cell parameter similar to that

555   observed by Shimada and Hirowatari (1972); the samples with the highest Ag content (3.41 *apfu*)

556   have a = 10.535 Å. Moreover, Sugaki et al. (1975) experimentally established the increase of the

557   unit-cell parameter with Ag content, up to 4.2 *apfu*. Pattrick and Hall (1983), following Hall (1972),

558   experimentally determined the increase of the unit-cell parameter with the Ag content, using

559   synthetic tetrahedrite. The largest a value (10.927 Å) was measured on a Cd-tetrahedrite having

560   7.02 Ag *apfu*. Finally, the structural results obtained by Kalbskopf (1972) were confirmed by

561   Johnson and Burnham (1985), Peterson and Miller (1986), and Charnock et al. (1988).

562   Starting from the mid-1980s, some nomenclature issues were discussed by several authors.

563   Spiridonov (1985) introduced the name "argentotetrahedrite" for phases having Ag > Cu and Sb >

564   As, on a theoretical basis. The Commission on Ore Microscopy of the IMA published the

565   *Quantitative Data File for Ore Minerals* (Criddle and Stanley 1986), reporting data for a sample of

566   "freibergite" from the Himmelsfürst mine, Saxony (Germany), with 4.5 Ag *apfu*, 12.03 S *apfu*, and

567   a = 10.50 Å. Argentotennantite was defined by Spiridonov et al. (1986) on the basis of Ag > Cu and

568   As > Sb. In the same study, two analyses of "argentotetrahedrite" were given (Ag range 5.05 – 6.74

569   *apfu*) as well as four analyses of "freibergite" (Ag range: 3.2 – 4.9 *apfu*; S ≈ 13 *apfu*).

570   Between the end of the 1980s and the mid-1990s, Russian authors were particularly active in

571   studying the crystal-chemistry of Ag-rich member of the tetrahedrite group. Samusikov et al. (1988)

572   confirmed the decrease of the unit-cell parameter with increasing Ag content (over 22 wt%,

573   corresponding to 4.5 Ag *apfu*). They noted correlatively the S deficiency, forming vacancy, and

574   proposed a regrouping of three-fold coordinated Ag atoms to explain the unit-cell contraction.

575   Balitskaya et al. (1989) presented similar results, in samples within the range 3.53 – 8.75 Ag *apfu*,

576   summarizing all the published results in a diagram a (Å) *vs*. Ag (apfu). Interestingly, one sample of

577   the "freibergite trend" had Ag contents close to 9 *apfu*, i.e., some three atoms over the $(Ag_6)^{4+}$

578   cluster. Figure 2, showing the relations between the Ag content and the unit-cell parameter of the

579   studied samples, is based on this work. The diagram has been completed taking into account all

580   papers published up to now, presenting both chemical data and unit-cell parameter, since the first

581   electron microprobe analysis of tetrahedrite (Springer, 1969). Note that the first electron microprobe

582   data of tennantite were given three years earlier by Wuensch et al. (1966).

583   Rozhdestvenskaya et al. (1989) presented the crystallographic results of four samples of the

584   tetrahedrite-"freibergite" series. In the Ag-richest sample (5.87 Ag *apfu*), "Ag–Ag distance equals

18

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 Gamyanin (1994) described Cu-free/poor samples of Ag-rich tetrahedrite, with Ag content overpassing the 8 *apfu* limit (see § 3.8). In the sample studied by Zhdanov et al. (1992), Fe is dominant over Zn (0.94 *vs.* 0.81 *apfu*, respectively; Hg = 0.2 *apfu*). In addition, Samusikov and Gamyanin (1994) proposed a nomenclature of the Ag-rich tetrahedrites, with a distinction between "tarynite" (Ag > 8 *apfu*) and "Cu-tarynite" (Ag < 8 *apfu*) on the increasing *a* trend, on the one hand, and, on the other hand, between hypothetical "freibergite" (Ag > 8 *apfu*) and "Cu-freibergite" (Ag < 8 *apfu*) on the decreasing *a* trend. The sample with 8.75 Ag *apfu* (and *a* = 10.34 Å) of Balitskaya et al. (1989) plots in the field of this so-called "freibergite", and may correspond potentially to a new mineral species: Ag > Cu, with Fe and Zn at the $M(1)$ site.

After more than twenty 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 occurrence of the $(Ag_6)^{4+}$ cluster replacing the S(2)-centered Ag_6 octahedron (Fig. 3), according to the substitution mechanism $6^{M(2)}Ag^+ + {}^{S(2)}S^{2-} = {}^{M(2)}(Ag_6)^{4+} + {}^{S(2)}\square$. 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, 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 $(Ag_6)^{4+}$ clusters. Specific structural information on the $M(2)$ and S(2) sites is therefore required to identify 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 $Ag_6(Cu_4Me_2)Sb_4S_{13-x}$, with end-member compositions corresponding to $x = 0$ [argentotetrahedrite-(Me), $Ag_6(Cu_4Me_2)Sb_4S_{13}$] and $x = 1$

618 [kenoargentotetrahedrite-(*Me*), $Ag_6(Cu_4Me_2)Sb_4S_{12}$]. The use of the historical name "freibergite" as

619 a series name is in keeping with the IMA-CNMNC guidelines for suffixes and prefixes (Hatert et al.

620 2013), suggesting that when historical names cannot be associated to unambiguously characterized

621 type materials [as stated above this name was used for phases with composition $Ag_6(Cu_4Fe_2)Sb_4S_{13-}$

622 $_x$; Moëlo et al. 2008], the name may need to be discredited as a species name but retained as a group

623 (in our case as a series) name.

624   Taking into account the recently defined species argentotetrahedrite and rozhdestvenskayaite,

625 the following boundaries between Ag-members of the tetrahedrite group could be defined (Fig. 2):

626   i) $3 < Ag < 8$ *apfu*, $0.5 < {}^{S(2)}S < 1.0$ = argentotetrahedrite;

627   ii) $3 < Ag < 8$ *apfu*, $0.0 < {}^{S(2)}S < 0.5$ = kenoargentotetrahedrite;

628   iii) $8 < Ag < 10$ *apfu*, $0.5 < {}^{S(2)}S < 1.0$ = rozhdestvenskayaite.

629   Kenoargentotetrahedrite is the S-deficient homeotype of argentotetrahedrite, with localized

630 Ag–Ag bonds. These two phases belong to the freibergite series; a clear determination between

631 them seems to be possible only through single-crystal X-ray diffraction studies. On the basis of

632 published data in the 1980s, sample No. BM88668 from the Natural History Museum, London, may

633 be taken as a neotype for the redefinition of kenoargentotetrahedrite [now "kenoargentotetrahedrite-

634 (Fe)"]:

635   i) Card No 118 of the QDF/COM of the IMA (second issue, 1986) gives the locality

636 Himmelsfürst, Freiberg district, Saxony (Germany), the reflectance data, the unit cell parameter (*a*

637 $= 10.50$ Å – J. G. Francis), and the chemical composition (unpublished data from Criddle, Clark and

638 Stanley, 1985). The formula, based on $\Sigma Me = 12$ *apfu*, is:

639 $(Ag_{5.51}Cu_{4.52})_{\Sigma10.03}(Fe_{1.68}Zn_{0.29})_{\Sigma1.97}(Sb_{4.09}As_{0.01})_{\Sigma4.10}S_{12.03}$;

640   ii) on this same sample, the EXAFS spectroscopic study by Charnock et al. (1988) was

641 performed, validating the occurrence of $(Ag_6)^{4+}$ clusters.

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

643 material.

644

645 **4.3. Goldfieldite: end-member formula and relations with tellurian tetrahedrites**

646   The actual definition of goldfieldite has been debated. According to some authors (e.g., Kato

647 and Sakurai 1970; Spiridonov et al. 1984; Trudu and Knittel 1998), the name goldfieldite should be

648 applied to members of the tetrahedrite group having Te as the dominant D constituent, i.e., Te > Sb

649 and Te > As and Te > Bi. Another approach was followed by Dmitrieva et al. (1987), who

650 suggested that a tetrahedrite group mineral can be named goldfieldite only when Te is more

20

651 abundant than the sum of all the other semimetals, i.e., Te > (Sb+As+Bi). This latter approach

652 agrees with the dominant-valency rule, extension of the dominant-constituent rule that considers a

653 group of atoms with the same valency as a single constituent (Hatert and Burke 2008).

654   Makovicky and Karup-Møller (2017) discussed the substitution mechanisms involved in the

655 Fe-bearing tetrahedrite/tennantite - goldfieldite substitutional series. As pointed out by previous

656 authors (e.g., Kase 1986), the accommodation of Te^{4+} in the tetrahedrite-type structure is coupled

657 with an increase in content of Cu^+ (and minor Ag^+) from 10 to 12 *apfu*, according to the substitution

658 $(Sb,As)^{3+} + Me^{2+} = Te^{4+} + Cu^+$, where *Me* = (Fe, Zn…). This substitution is valid up to 2 Te *apfu*.

659 For higher Te contents, the charge balance is achieved through the formation of vacancies at $M(2)$,

660 according to the substitution mechanism $(Sb,As)^{3+} + Cu^+ = Te^{4+} + \square$. In synthetic Fe-bearing

661 phases, however, this latter mechanism can be considered an oversimplification because the

662 incomplete elimination of Fe for compositions with more than 2 Te *apfu* is compensated by the

663 early onset of Cu vacancies at $M(2)$ (Makovicky and Karup-Møller 2017).

664   In the tennantite/tetrahedrite-goldfieldite field, the following end-member compositions can

665 be proposed:

666   i) tennantite-(*Me*), $Cu_6(Cu_4Me_2)As_4S_{13}$ and tetrahedrite-(*Me*), $Cu_6(Cu_4Me_2)Sb_4S_{13}$, where *Me*

667 is a divalent constituent;

668   ii) $Cu_6Cu_6(As_2Te_2)S_{13}$ and $Cu_6Cu_6(Sb_2Te_2)S_{13}$;

669   iii) goldfieldite, $(Cu_4\square_2)Cu_6Te_4S_{13}$.

670   In accord with Hawthorne (2002), the intermediate compositions $Cu_6Cu_6(As_2Te_2)S_{13}$ and

671 $Cu_6Cu_6(Sb_2Te_2)S_{13}$ are end-member formulae as they cannot be obtained as a linear combination of

672 tetrahedrite/tennantite and goldfieldite end-member formulae. The names "arsenogoldfieldite" and

673 "stibiogoldfieldite" could be applied to these two potential new mineral species. Even if Makovicky

674 and Karup-Møller (2017) predict a miscibility gap on the tetrahedrite-goldfieldite join, the

675 $Cu_6Cu_6(Sb_2Te_2)S_{13}$ can be considered as a potential phase.

676   Although the data reported by Ransome (1909) indicate that goldfieldite might correspond to

677 a phase having an Sb:Te atomic ratio close to 1, that is, close to the end-member composition

678 $Cu_6Cu_6(Sb_2Te_2)S_{13}$, Trudu and Knittel (1998) recommended this name to "*those compositions of the*

679 *tetrahedrite$_{ss}$ that contain more than 3 apfu of Te*". Following this recommendation, Moëlo et al.

680 (2008) reported the formula $Cu_{10}Te_4S_{13}$ for goldfieldite.

681   In order to avoid further confusion, the name goldfieldite is maintained for the species

682 consistent with the end-member composition $(Cu_4\square_2)Cu_6Te_4S_{13}$ and new names have to be assigned

683 to the end-member compositions $Cu_6Cu_6(Sb_2Te_2)S_{13}$ and $Cu_6Cu_6(As_2Te_2)S_{13}$.

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

685   i) tetrahedrite/tennantite, with $0 < Te$ (*apfu*) < 1;

686   ii) new names, with $1 < Te$ (*apfu*) < 3. Two different names should be applied, taking into

687   account the dominant trivalent constituent;

688   iii) goldfieldite, with $3 < Te$ (*apfu*) < 4.

689   Natural occurrences of goldfieldite up to 3.77 Te *apfu* and phases corresponding to the end-

690   member formulae $Cu_6Cu_6(As_2Te_2)S_{13}$ and $Cu_6Cu_6(Sb_2Te_2)S_{13}$ are known in the literature

691   (Spiridonov and Okrugin 1985; Kase 1986; Knittel 1989; Shimizu and Stanley 1991; Voudouris

692   2006; Spiridonov et al. 2014; Repstock et al. 2016).

693

694   **4.4. Discreditation of annivite**

695   Annivite is discredited for the following reasons: 1) annivite is an ill-defined species, listed as

696   a questionable species in the current official IMA-CNMNC List of Mineral Names, 2) the holotype

697   annivite is certainly not a Bi^{3+}-dominant end-member, and 3) X-ray diffraction studies confirming

698   that a species with appropriate composition actually belongs to the tetrahedrite group have not been

699   carried out yet. Re-validation of the mineral and name on the basis of samples with Bi > Sb and Bi

700   > As should be done by submitting a formal proposal to the IMA-CNMNC.

701

702   **4.5. Valid mineral species in the tetrahedrite group and type materials**

703   Thirty-two potential natural end-member compositions are given in the literature (Table 2).

704   Among these, only eleven mineral species can be considered as valid species. The remaining

705   species need to follow the usual procedure for the approval as valid mineral species by the IMA-

706   CNMNC.

707   In the following, valid tetrahedrite group species, their type locality, and essential references

708   are reported.

709

710   *4.5.1 Argentotennantite-(Zn)*

711   Argentotennantite-(Zn), $Ag_6(Cu_4Zn_2)As_4S_{13}$, is renamed after "argentotennantite". Type

712   locality is the Kvartsitoviye Gorki deposit, Aksu, Stepnyak, Enbekshilder, Akmola (Kazahstan).

713   Type material is preserved in the Fersman mineralogical museum, Moscow (Russia). Reference:

714   Spiridonov et al. (1986a).

715

716   *4.5.2 Argentotetrahedrite-(Fe)*

717   Argentotetrahedrite-(Fe), $Ag_6(Cu_4Fe_2)Sb_4S_{13}$, is renamed after "argentotetrahedrite". Type

718   locality is Keno Hill, Mayo mining district, Yukon (Canada). Type material is preserved in the

719   Miller Museum collection, University of Western Ontario (Canada), under catalogue number

720   M8224. References: Peterson and Miller (1986); Welch et al. (2018).

721

722   *4.5.3 Kenoargentotetrahedrite-(Fe)*

723   Kenoargentotetrahedrite-(Fe), $Ag_6(Cu_4Fe_2)Sb_4S_{12}\square$, is renamed after "freibergite". Type

724   localities are the Hab Acht Mine (later part of the Beschert Glück Mine), Zug near Freiberg, Saxony

725   (Germany) and Himmelsfürst, Freiberg, Saxony (Germany). Neotype materials can be considered

726   the specimen number 2289Sa kept in the Senckenberg Museum Collection, Frankfurt (Germany),

727   and studied by Welch et al. (2018), and the specimen number BM88668 of the Natural History

728   Museum (London, U.K.), studied by the *Commission on Ore Microscopy of the IMA* (Criddle and

729   Stanley 1986). References: Criddle and Stanley (1986); Welch et al. (2018).

730

731   *4.5.4 Giraudite-(Zn)*

732   Giraudite-(Zn), $Cu_6(Cu_4Zn_2)As_4Se_{13}$, is renamed after "giraudite". Type locality is the

733   Chaméane uranium deposit, Chaméane, Puy-de-Dôme, Auvergne-Rhône-Alpes (France). Type

734   material is deposited in the mineralogical collections of Ecoles de Mines of Paris (France).

735   Reference: Johan et al. (1982).

736

737   *4.5.5 Goldfieldite*

738   Goldfieldite is defined as $(Cu_4\square_2)Cu_6Te_4S_{13}$. Its type locality was given as Mohawk mine,

739   Goldfield, Goldfield district, Esmeralda County, Nevada (USA). However, no information about

740   type material is available and its actual composition is doubtful. We strongly suggest proposing a

741   formal redefinition of goldfieldite, indicating a new type locality and neotype material. References:

742   Lévy (1967); Trudu and Knittel (1998).

743

744   *4.5.6 Hakite-(Hg)*

745   Hakite-(Hg), $Cu_6(Cu_4Hg_2)Sb_4Se_{13}$, is renamed after "hakite". Type locality is Předbořice,

746   Central Bohemia region (Czech Republic). Type material is kept in the collection of the

747   mineralogical laboratory of the Charles University in Prague (Czech Republic), and in the

748   mineralogical collection of the Écoles de Mines of Paris (France). Reference: Johan and Kvaček

749   (1971).

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Biagioni et al.

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4.5.7 Rozhdestvenskayaite-(Zn)

Rozhdestvenskayaite-(Zn), $Ag_6(Ag_4Zn_2)Sb_4S_{13}$, 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 catalogue number BM2016,120. Reference: Welch et al. (2018).

4.5.8 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 $Cu_6(Cu_4Fe_2)Sb_4S_{13}$, $Cu_6(Cu_4Zn_2)Sb_4S_{13}$, $Cu_6(Cu_4Fe_2)As_4S_{13}$, and $Cu_6(Cu_4Zn_2)As_4S_{13}$, respectively. Their type localities and type materials are the following.

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

b) Tennantite-(Zn) has been known since the mid-XIX 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).

c) Tetrahedrite-(Fe): the first ferroan tetrahedrite is likely "*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 Universiy 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, Bari (Italy) and the specimen #7936 belonging to the mineral collections of the Museo di Storia Naturale, Pisa University, Pisa (Italy).

d) Tetrahedrite-(Zn): Charlat and Lévy (1974, 1975, 1976) characterized samples of tetrahedrite (samples No. M11 and M12) from Horhausen, Westernwald, Rhineland (Germany). These samples have chemical formulae $Cu_{10.08}Zn_{1.74}Fe_{0.18}Sb_{3.97}As_{0.09}S_{13.4}$ (M11) and

24

783     $Cu_{10.06}Ag_{0.06}Zn_{1.62}Fe_{0.27}Sb_{3.90}As_{0.06}S_{12.7}$ (M2), unit-cell parameter $a = 10.383(2)$ Å for both samples,

784   and reflectance spectra in the range 440 – 800 nm are given in Charlat and Lévy (1976). It is worth

785   noting that the structure refinement of tetrahedrite reported by Wuensch (1964) was obtained using

786   a sample from this German locality. We re-examined sample M11 of Charlat and Lévy (1974. 1975,

787   1976), refining its crystal structure to $R_1 = 0.0144$ for 364 unique reflections with $F_o > 4\sigma(F_o)$. Unit-

788   cell parameter is $a = 10.3798(8)$ Å. The corresponding CIF is available as Supplementary Material.

789   This sample was deposited in the mineralogical collection of the Museo di Storia Naturale, Pisa

790   University (Italy) (catalogue number #19910) and of the Musée de Minéralogie, Mines Paris-Tech

791   (France) (catalogue number #83693) as neotype material of tetrahedrite-(Zn). Co-neotype material

792   can be considered the specimen of tetrahedrite-(Zn) from the Namex deposit, Huffman Township,

793   western Abitibi Greenstone Belt, Ontario (Canada), characterized by McDonald et al. (in

794   preparation) and kept in the Canadian Museum of Nature, Gatineau (Canada) under catalogue

795   number CMNMC 87261.

796

797   **5. Implications**

798   The present nomenclature of the tetrahedrite group minerals is based on the end-member

799   formula, a concept extremely useful for unambiguously identifying and classifying complex mineral

800   compositions (e.g., Hawthorne 2002). Moreover, it highlights the frequent occurrence of the

801   "valency-imposed double site-occupancy" (Hatert and Burke 2008) in the sulfosalt realm.

802   Consequently, it is fully consistent with the current nomenclature rules.

803   Often the dominant divalent cation in tetrahedrite group minerals has been identified by the

804   use of a prefix, e.g., Fe-tennantite and Zn-tennantite (Kemkin and Kemkina 2013), or using

805   descriptors like "Zn-rich", "Fe-bearing", or "Ag-enriched", preceding the mineral name (e.g., Arlt

806   and Diamond 1998; Foit and Ulbricht 2001; Förster and Rhede 2004; Gallego Hernández and

807   Akasaka 2010; Gołębiowska et al. 2012; Plotinskaya et al. 2015; Škácha et al. 2016, 2017). Even

808   when such terminology is well defined, inconsistent usages by different authors have inadvertently

809   led to unnecessary complication in comparing different members of the tetrahedrite group. The

810   reason for which so many authors add compositional information to the tetrahedrite nomenclature is

811   because such chemical information is very useful in the context of a wide range of mineralogical

812   studies. Such a trend is likely to continue, especially as characterization of mineral species in terms

813   of ore textures and electron microprobe data is increasingly complemented by quantitative trace

814   element data that can provide additional constraints of value. Indeed, the wide compositional

815   variations in the tetrahedrite isotypes reflect spatial and temporal changes in physico-chemical

25

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; Gołębiowska 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.

Acknowledgments

References

Andreasen, J.W., Makovicky, E., Lebech, B., and Karup Møller, S. (2008) The role of iron in tetrahedrite and tennantite determined by Rietveld refinement of neutron powder diffraction data. Physics and Chemistry of Minerals, 35, 447–454.

Arlt, T., and Diamond, L.W. (1998) Composition of tetrahedrite-tennantite and 'schwazite' in the Schwaz silver mines, North Tyrol, Austria. Mineralogical Magazine, 62, 801–820.

Atanasov, V.A. (1975) Argentian mercurian tetrahedrite, a new variety, from the Chiprovtsi ore deposit, Western Stara-Planina mountains, Bulgaria. Mineralogical Magazine, 40, 233–237.

Balitskaya, O.V., Mozgova, N.N., Borodaev, Yu.S., Efimova, A.V., and Tsepin, A.I. (1989) Evolution of the unit cell parameter of fahlores with their silver content. Izvestiya Akademii Nauk SSSR, Seriya Geologicheskaya, 9, 112–120 (in Russian).

Barbier, T., Lemoine, P., Gascoin, S., Lebedev, O.I., Kaltzoglou, A., Vaquiero, P., Powell, A.V., Smith, R.I., and Guilmeau, E. (2015) Structural stability of the synthetic thermoelectric ternary and nickel-substituted tetrahedrite phases. Journal of Alloys and Compounds, 634, 253–262.

Basu, K., Bortnikov, N.S., Mookherjee, A., Mozgova, N.N., Sivtsov, A.V., Tsepin, A.I., and Vrublevskaja, Z.V. (1984) Rare minerals from Rajpura-Dariba, Rajasthan, India. V: The first recorded occurrence of a manganoan fahlore. Neues Jahrbuch für Mineralogie, Abhandlungen, 149, 105–112.

Bechi, E. (1863) Lavori eseguiti nel laboratorio di Chimica del R. Istituto Tecnico di Firenze. Continuazione degli Atti della R. Accademia economico-agraria dei Georgofili di Firenze, 10, 201–206.

Bortnikov, N.S., Kudryavtsev, A.S., and Troneva, N.V. (1979) Bi-rich tetrahedrite from the Tary-Ekan deposit (East Karamazar, Central asia). Mineralogiceskij Zhurnal, 198, 61–64 (in Russian).

Breskovska, V., and Tarkian, M. (1994) Compositional variations in Bi-bearing fahlores. Neues Jahrbuch für Mineralogie, Monatshefte, 1994, 230–240.

Brodin, B.V. (1981) Silver-bearing hakite. International Geology Review, 23, 71–73.

Burkart-Baumann, I. (1984) Unusual tennantite from Quiruvilca, Peru. In G. Moh: Sulfosalts: observations and mineral descriptions, experiments and applications. Neues Jahrbuch für Mineralogie, Abhandlungen, 150, 25–64.

Carrozzini, B., Garavelli, C.L., and Vurro, F. (1991) Tetrahedrite (supposed «Frigidite») and associated Ni minerals from Frigido mine (Apuane Alps). Periodico di Mineralogia, 60, 5–14.

27

Biagioni et al.

Catchpole, H., Kouzmanov, K., and Fontboté, L. (2012) Copper-excess stannoidite and tennantite-tetrahedrite as proxies for hydrothermal fluid evolution in a zoned Cordilleran base metal district, Morococha, central Peru. The Canadian Mineralogist, 50, 719–743.

Charlat, M., and Lévy, C. (1974) Substitutions multiples dans la série tennantite-tétraédrite. Bulletin de la Société française de Minéralogie et de Cristallographie, 97, 241–250.

Charlat, M., and Lévy, C. (1975) Influence des principales substitutions sur le paramètre cristallin dans la série tennantite-tétraédrite. Bulletin de la Société française de Minéralogie et de Cristallographie, 98, 152–158.

Charlat, M., and Lévy, C. (1976) Influence des principales substitutions sur les propriétés optiques dans la série tennantite-tétraédrite. Bulletin de la Société française de Minéralogie et de Cristallographie, 99, 29–37.

Charnock, J.M., Garner, C.D., Pattrick, R.A.D., and Vaughan, D.J. (1988) Investigation into the nature of copper and silver sites in argentian tetrahedrites using EXAFS spectroscopy. Physics and Chemistry of Minerals, 15, 296–299.

Chetty, R., Bali, A., and Mallik, R.C. (2015a) Tetrahedrites as thermoelectric materials: an overview. Journal of Materials Chemistry C, 3, 12364–12378.

Chetty, R., Prem Kumar, D.S., Rogl, G., Rogl, P., Bauer, E., Michor, H., Suwas, S., Puchegger, S., Giester, G., and Mallik, R.C. (2015b) Thermoelectric properties of a Mn substituted synthetic tetrahedrite. Physical Chemistry Chemical Physics, 17, 1716–1727.

Criddle, A.J., Stanley, C.J., eds. (1986) The Quantitative Data File for Ore Minerals of the Commission on Ore Microscopy of the International Mineralogical Association (2nd edition). British Museum (Natural History), 420 pp.

D'Achiardi, A. (1881) Su di alcuni minerali della miniera del Frigido presso Massa nelle Alpi Apuane. Atti della Società Toscana di Scienze Naturali, Processi Verbali, 2, 171–178.

Depmeier, W. (2005) The sodalite family – A simple but versatile framework structure. Reviews in Mineralogy and Geochemistry, 57, 203–240.

Des Cloizeaux, M. (1855) Notices Minéralogiques. Sur les formes cristallines de la Dufrénoysite. Annales des Mines, 5, 389–398.

Dmitrieva, M.T., Yefremov, V.A., and Kovalenker, V.A. (1987) Crystal structure of As-goldfieldite. Doklady Akademii Nauk SSSR, Earth Science Section, 297, 141–144.

Dobbe, R.T.M. (1992) Manganoan-cadmian tetrahedrite from the Tunaberg Cu-Co deposit, Bergslagen, central Sweden. Mineralogical Magazine, 56, 113–115.

Fellenberg, L.R. (1854) Über ein eigenthümliches Fahlerz aus dem Einfischthale im Kanton Wallis. Mittheilungen der Naturfoschenden Gesellschaft in Bern, 317-318, 57–59.

Foit, F.F., and Ulbricht, M.E. (2001) Compositional variation in mercurian tetrahedrite-tennantite from the epithermal deposits of the Steens and Pueblo Mountains, Harney Country, Oregon. The Canadian Mineralogist, 39, 819–830.

Foit, F.F., and Hughes, J.M. (2004) Structural variations in mercurian tetrahedrite. American Mineralogist, 89, 159–163.

Förster, H.-J., and Rhede, D. (2004) Mineralogy of the Niederschlema–Alberoda U – Se – polymetallic deposit, Erzgebirge, Germany. III. First indication of complete miscibility between tennantite and giraudite. The Canadian Mineralogist, 42, 1719–1732.

Förster, H.-J., Rhede, D., and Tischendorf, G. (2002) Continuous solid-solution between mercurian giraudite and hakite. The Canadian Mineralogist, 40, 1161–1170.

Gallego Hernández, A.N., and Akasaka, M. (2010) Ag-rich Tetrahedrite in the El Zancudo Deposit, Colombia: Occurrence, Chemical Compositions and Genetic Temperatures. Resource Geology, 60, 218–233.

Gan, L.C. (1980) Manson Lode, a stratabound base metal-silver deposit in North Kelantan, Malaysia. Unpublished thesis, Montan-Universität Leoben, Austria, 171 p.

George, L.L., Cook, N.J., and Ciobanu, C.L. (2017) Minor and trace elements in natural tetrahedrite-tennantite: effects on element partitioning among base metal sulphides. Minerals, 7, 17.

Glocker, E.F. (1847) Generum et Specierum Mineralium Secundum Ordines Naturales digestorum Synopsis. Halle, Eduard Anton, 347 p.

Gołębiowska, B., Pieczka, A., and Parafiniuk, J. (2012) Substitution of Bi for Sb and As in minerals of the tetrahedrite series from Rędziny, Lower Silesia, southwestern Poland. The Canadian Mineralogist, 50, 267–279.

Haidinger, W. (1845) Zweite Klasse: Geogenide. XIV. Ordnung, Glanze, I. Dystomglanz, Tetraedrit. In: Handbuch der Bestimmenden Mineralogie, Bei Braumüller and Seidel, Wien, 563–570.

Hall, A. (1972) Substitution of Cu by Zn, Fe and Ag in synthetic tetrahedrite, $Cu_{12}Sb_4S_{13}$. Bulletin de la Société française de Minéralogie et de Cristallographie, 95, 583–594.

Hansen, M.K., Makovicky, E., and Karup-Møller, S. (2003) Exploratory studies on substitutions in tetrahedrite-tennantite solid solution. Part IV. Substitution of germanium and tin. Neues Jahrbuch für Mineralogie, Abhandlungen, 179, 43–71.

29

Biagioni et al.

934 Hatert, F., and Burke, E.A.J. (2008) The IMA–CNMNC dominant-constituent rule revisited and
935   extended. The Canadian Mineralogist, 46, 717–728.

936 Hatert, F., Mills, S.J., Pasero, M., and Williams, P.A. (2013) CNMNC guidelines for the use of
937   suffixes and prefixes in mineral nomenclature, and for the preservation of historical names.
938   European Journal of Mineralogy, 25, 113–115.

939 Hawthorne, F.C. (2002) The use of end-member charge-arrangements in defining new mineral
940   species and heterovalent substitutions in complex minerals. The Canadian Mineralogist, 40,
941   699–710.

942 Henry, D.J., Novák, M., Hawthorne, F.C., Ertl, A., Dutrow, B.L., Uher, P., and Pezzotta, F. (2011)
943   Nomenclature of the tourmaline-supergroup minerals. American Mineralogist, 96, 895–913.

944 Jia, D., Fu, Z., Zhang, H., and Zhao, C. (1988) The first discovery of Cd-freibergite in China. Acta
945   Mineralogica Sinica, 8, 136–137 (in Chinese, with English abstract).

946 Ixer, R.A., and Stanley, C.J. (1983) Silver mineralization at Sark's Hope mine, Sark, Channel
947   Islands. Mineralogical Magazine, 47, 539–545.

948 Johan, Z., and Kvaček, M. (1971) La hakite, un noveau minéral du groupe de la tétraédrite. Bulletin
949   de la Société française de Minéralogie et de Cristallographie, 94, 45–48.

950 Johan, Z., Picot, P., and Ruhlmann, F. (1982) Evolution paragénétique de la minéralisation
951   uranifère de Chaméane (Puy-de-Dôme), France: chaméanite, geffroyite et giraudite, trois
952   séléniures nouveaux de Cu, Fe, Ag, et As. Tschermaks Mineralogische und Petrographische
953   Mitteilungen, 29, 151–167.

954 Johnson, M.L., and Burnham, C.W. (1985) Crystal structure refinement of an arsenic-bearing
955   argentian tetrahedrite. American Mineralogist, 70, 165–170.

956 Johnson, N.E., Craig, J.R., and Rimstidt, J.D. (1986) Compositional trends in tetrahedrite. Canadian
957   Mineralogist, 24, 385–397.

958 Johnson, N.E., Craig, J.R., and Rimstidt, J.D. (1988) Crystal chemistry of tetrahedrite. American
959   Mineralogist, 73, 389–397.

960 Kalbskopf, R. (1971) Die Koordination des Quecksilbers in Schwazit. Tschermaks Mineralogische
961   und Petrographische Mitteilungen, 16, 173–175.

962 Kalbskopf, R. (1972) Strukturverfeinerung des Freibergits. Tschermaks Mineralogische und
963   Petrographische Mitteilungen, 18, 147–155.

964 Kalbskopf, R. (1974) Synthese und Kristallstruktur von $Cu_{12-x}Te_4S_{13}$, dem Tellur-Endglied der
965   Fahlerze. Tschermaks Mineralogische und Petrographische Mitteilungen, 21, 1–10.

Biagioni et al.

Kaplunnik, L.N., Pobedimskaya, E.A., and Belov, N.V. (1980) The crystal structure of schwazite $(Cu_{4.4}Hg_{1.6})Cu_6Sb_4S_{12}$. Doklady Akademii Nauk SSSR, 253, 105–107.

Karanović, L., Cvetković, L., Poleti, D., Balić-Žunić, T. and Makovicky, E. (2003) Structural and optical properties of schwazite from Dragodol (Serbia). Neues Jahrbuch für Mineralogie, Monatshefte, 2003, 503–520.

Karup-Møller, S., and Makovicky, E. (1999) Exploratory studies of element substitutions in synthetic tetrahedrite. Part II. Selenium and tellurium as anions in Zn-Fe tetrahedrites. Neues Jahrbuch für Mineralogie, Monatshefte, 1999, 385–399.

Karup-Møller, S., and Makovicky, E. (2003) Exploratory studies of element substitutions in synthetic tetrahedrite. Part V. Mercurian tetrahedrite. Neues Jahrbuch für Mineralogie, Abhandlungen, 179, 73-83.

Kase, K. (1986) Tellurian tennantite from the Besshi-type deposits in the Sambagawa metamorphic belt, Japan. Canadian Mineralogist, 24, 399–404.

Kato, A., and Sakurai, K. (1970) Re-definition of goldfieldite, $Cu_{12}(Te,As,Sb)_4S_{13}$. Journal of the Mineralogical Society of Japan, 10, 122 (in Japanese).

Kemkin, I.V., and Kemkina, R.A. (2013) Microheterogeneity of the Koupol Deposit Fahlores as a Reflection of Changing of Physicochemical Parameters of the Ore-Forming Solution. Journal of Earth Science, 24, 179–187.

Kenngott, A. (1853) Das Mohs'sche Mineralsystem, dem gegenwärtigen Standpuncte der Wissenschaft gemäss bearbeitet. Verlag und Druck von Carl Gerold & Sohn (Wien), 164 p.

Kieft, K., and Eriksson, G. (1984) Regional zoning and metamorphic evolution of the Vindfall Pb-Zn ore, east central Sweden. Geologiska Föreningens i Stockholm Förhandlingar, 106, 305–317.

Kikukawa, Y, Kuroda, Y., Suzuki, K., Hibino, M., Yamaguchi, K., and Mizuno, N. (2013) A discrete octahedrally shaped $[Ag_6]^{4+}$ cluster encapsulated within silicotungstate ligands. Chemical Communications, 49, 376–378.

Klünder, M.H., Karup-Møller, S., and Makovicky, E. (2003) Exploratory studies on substitutions in the tetrahedrite-tennantite solid solution series Part III. The solubility of bismuth in tetrahedrite-tennantite containing iron and zinc. Neues Jahrbuch für Mineralogie, Monatshefte, 2003, 153–175.

Knittel, U. (1989) Composition and association of arsenian goldfieldite from the Marian gold deposit, northern Luzon, Philippines. Mineralogy and Petrology, 40, 145–154.

998   Lévy, C. (1967) Contribution à la minéralogie des sulfures de cuivre du type Cu_3XS_4. Mémoires du
999   Bureau de Recherches Géologiques et Minières, 54, 1–178.

1000   Lind, I.L., and Makovicky, E. (1982) Phase relations in the system $Cu – Sb – S$ at 200°C, 10^8 Pa by
1001   hydrothermal synthesis. Microprobe analyses of tetrahedrite – a warning. Neues Jahrbuch für
1002   Mineralogie, Abhandlungen, 145, 134–156.

1003   Luce, F.D., Tuttle, C.L., and Skinner, B.J. (1977) Studies of sulfosalts of copper. V. Phases and
1004   phase relations in the system Cu-Sb-As-S between 350° and 500°C. Economic Geology, 72,
1005   271–289.

1006   Machatschki, F. (1928a) Formel und Kristallstruktur des tetraedrites. Norsk Geologische Tidsskrift,
1007   10, 23–32.

1008   Machatschki, F. (1928b) Präzisionsmessungen der Gitterkonstanten verschiedener Fahlerze. Formel
1009   und struktur derselben. Zeitschrift für Kristallographie, 68, 204–222.

1010   Makovicky, E., and Karup-Møller, S. (1994) Exploratory studies on substitution of minor elements
1011   in synthetic tetrahedrite. Part I. Substitution by Fe, Zn, Co, Ni, Mn, Cr, V and Pb. Unit-cell
1012   parameter changes on substitution and the structural role of "Cu^{2+}". Neues Jahrbuch für
1013   Mineralogie, Abhandlungen, 167, 89–123.

1014   Makovicky, E., and Karup-Møller, S. (2017) Exploratory studies of substitutions in the
1015   tetrahedrite/tennantite-goldfieldite solid solution. The Canadian Mineralogist, 55, 233–244.

1016   Makovicky, E., and Skinner, B.J. (1979) Studies of the sulfosalts of copper. VII. Crystal structures
1017   of the exsolution products $Cu_{12.3}Sb_4S_{13}$ and $Cu_{13.8}Sb_4S_{13}$ of unsubstituted synthetic
1018   tetrahedrite. The Canadian Mineralogist, 17, 619–634.

1019   Makovicky, E., Forcher, K., Lottermoser, W., and Amthauer, G. (1990) The role of Fe^{2+} and Fe^{3+} in
1020   synthetic Fe-substituted tetrahedrite. Mineralogy and Petrology, 43, 73–81.

1021   Makovicky, E., Tippelt, G., Forcher, K., Lottermoser, W., Karup-Møller, S., and Amthauer, G.
1022   (2003) Mössbauer study of Fe-bearing synthetic tennantite. The Canadian Mineralogist, 41,
1023   1125–1134.

1024   Makovicky, E., Karanović, L., Poleti, D., Balić-Žunić, T., and Paar, W.H. (2005) Crystal structure
1025   of copper-rich unsubstituted tennantite, $Cu_{12.5}As_4S_{13}$. The Canadian Mineralogist, 43, 679–
1026   688.

1027   Marcoux, E., Moëlo, Y., and Milési, J.-P. (1994) Vinciennite and Cu-excess tennantite from the
1028   Layo (Cu, Sn, As, Au) epithermal deposit (Southern Peru). Mineralogy and Petrology, 51,
1029   21–36.

Biagioni et al.

1030   Maske, S., and Skinner, B.J. (1971) Studies of the sulphosalts of copper. I. Phases and phase
1031   relations in the system Cu–As–S. Economic Geology, 66, 901–918.

1032   Mills, S.J., Hatert, F., Nickel, E.H., and Ferraris, G. (2009) The standardisation of mineral group
1033   hierarchies: application to recent nomenclature proposals. European Journal of Mineralogy,
1034   21, 1073–1080.

1035   Moëlo, Y., Makovicky, E., Mozgova, N.N., Jambor, J.L., Cook, N., Pring., A., Paar, W.H., Nickel,
1036   E.H., Graeser, S., Karup-Møller, S., Balić-Žunić, T., Mumme, W.G., Vurro, F., Topa, D.,
1037   Bindi, L., Bente, K., and Shimizu, M. (2008) Sulfosalt systematics: a review. Report of the
1038   sulfosalt sub-committee of the IMA Commission on Ore Mineralogy. European Journal of
1039   Mineralogy, 20, 7–46.

1040   Mozgova, N.N., and Tsepin, A.I. (1983) Grey ores. USSR Academy of Sciences, Nauka ed.,
1041   Moscow, 280 p. (in Russian).

1042   Mozgova, N.N., Tsepin, A.I., Ozerova, N.N., Bortnikov, N.S., and Tronieva, N.V. (1979)
1043   Mercuriferous grey copper ores. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva,
1044   108, 437–452 (in Russian).

1045   Nasonova, D.I., Presniakov, I.A., Sobolev, A.V., Verchenko, V.Yu., Tsirlin, A.A., Wei, Z.,
1046   Dikarev, E., and Shevelkov, A.V. (2016) Role of iron in synthetitc tetrahedrites revisited.
1047   Journal of Solid State Chemistry, 235, 28–35.

1048   Pattrick, R.A.D. (1978) Microprobe analysis of cadmium-rich tetrahedrites from Tyndrum,
1049   Perthshire, Scotland. Mineralogical Magazine, 42, 286–288.

1050   Pattrick, R.A.D., and Hall, A.J. (1983) Silver substitution into synthetic zinc, cadmium, and iron
1051   tetrahedrites. Mineralogical Magazine, 47, 441–451.

1052   Pattrick, R.A.D., van der Laan, G., Vaughan, D.J., and Henderson, C.M.B. (1993) Oxidation state
1053   and electronic configuration determination of copper in tetrahedrite group minerals by L-edge
1054   X-ray absorption spectroscopy. Physics and Chemistry of Minerals, 20, 395–401.

1055   Pauling, L., and Neuman, E.W. (1934) The crystal structure of binnite $(Cu,Fe)_{12}As_4S_{13}$ and the
1056   chemical composition and structure of minerals of the tetrahedrite group. Zeitschrift für
1057   Kristallographie, 88, 54–62.

1058   Peterson, R.C., and Miller, I. (1986) Crystal structure and cation distribution in freibergite and
1059   tetrahedrite. Mineralogical Magazine, 50, 717–721.

1060   Petruk, W. and staff (1971) Characteristics of the sulphides. The Canadian Mineralogist, 11, 196–
1061   231.

Biagioni et al.

Phillips, R. (1819) Analysis of the copper ore, described in the preceding paper. The Quarterly Journal of Science, Literature and the Arts, 7, 100–102.

Phillips, W. (1819) Description of an ore of copper from Cornwall. The Quarterly Journal of Science, Literature and the Arts, 7, 95–100.

Plattner, C.F. (1846) Chemische Analyse der Kuperfblende. Annalen der Physik und Chemie, 143, 422–423.

Plotinskaya, O.Yu., Grabezhev, A.I., and Seltmann, R. (2015) Fahlores compositional zoning in a porphyry-epithermal system: Biksizak occurrence, South Urals, Russia as an example. Geology of Ore Deposits, 57, 42–63.

Pohl, D., Ließmann, W., and Okrugin, V.M. (1996) Rietveld analysis of selenium-bearing goldfieldites. Neues Jahrbuch für Mineralogie, Monatshefte, 1996, 1–8.

Ransome, F.L. (1909) Geology and ore deposits of Goldfield, Nevada. U.S. Geological Survey, Professional Papers, 66.

Repstock, A., Voudouris, P., Zeug, M., Melfos, V., Zhai, M., Li, H., Kartal, T., and Matuszczak, J. (2016): Chemical composition and varieties of fahlore-group minerals from Oligocene mineralization in the Rhodope area, southern Bulgaria and northern Greece. Mineralogy and Petrology, 110, 103–123.

Riley, J.F. (1974) The tetrahedrite–freibergite series, with reference to the Mount Isa Pb–Zn–Ag orebody. Mineralium Deposita, 9, 117–124.

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, 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).

Sack, R.O., and Ebel, D.S. (1993) As-Sb exchange energies in tetrahedrite-tennantite fahlores and bournonite-seligmannite solid solutions. Mineralogical Magazine, 57, 635–642.

Sack, R.O., and Loucks, R.R. (1985) Thermodynamic properties of tetrahedrite-tennantite: Constraints on the interdependence of the Ag = Cu, Fe = Zn, and As = Sb exchange reactions. American Mineralogist, 70, 1270–1289.

Samusikov, V.P., and Gamyanin, G.N. (1994) Nomenclature of mineral species of Cu-Ag isomorphous tetrahedrite. 16th IMA General Meeting, Pisa, Italy, 4-9 September 1994, Abstract volume, 363–364.

Biagioni et al.

1095   Samusikov, V.P., Zayakina, N.V., and Leskova, N.V. (1988) Relation between unit cell of fahlores
1096   and Ag-concentration. Doklady Akademii Nauk USSR, 299, 468–471 (in Russian).

1097   Sharwood, W.J. (1907) Gold tellurides. Mining and Scientific Press, 94, 731–732.

1098   Shimada, N., and Hirowatari, F. (1972) Argentian tetrahedrites from the Taishu-Shigekuma mine,
1099   Tsushima Island, Japan. Mineralogical Journal, 1, 77–87.

1100   Shimizu, M., and Stanley, C.J. (1991) Coupled substitutions in goldfieldite-tetrahedrite minerals
1101   from the Iriki mine, Japan. Mineralogical Magazine, 55, 515–519.

1102   Škácha, P., Sejkora, J., Palatinus, L., Makovicky, E., Plášil, J., Macek, I., and Goliáš, V. (2016)
1103   Hakite from Příbram, Czech Republic: compositional variability, crystal structure and the role
1104   in Se mineralization. Mineralogical Magazine, 80, 1115–1128.

1105   Škácha, P., Sejkora J., and Plášil, J. (2017) Selenide mineralization in the Příbram Uranium and
1106   Base-Metal District (Czech Republic). Minerals, 7, 91.

1107   Spiridonov, E.M. (1985) Mineral species and varieties of tetrahedrite-tennantite ores and practical
1108   nomenclature of this group minerals. Some observations on the formation conditions of the
1109   tetrahedrite-tennantite ores. Novye Dannye o Mineralakh, 32, 128–146 (in Russian).

1110   Spiridonov, E.M., and Okrugin, V.M. (1985) Selenious goldfieldite – a new variety of fahlores.
1111   Doklady Akademii Nauk SSSR, 280, 476–478 (in Russian).

1112   Spiridonov, E.M., Chvileva, T.N., Sokolova, N.F., Okrugin, V.M., and Badalov, A.S. (1984) Effect
1113   of tellurium on optical properties of fahlore (tetrahedrite-tennantite) minerals. Doklady
1114   Akademii Nauk USSR, Earth Science Section, 280, 474–478.

1115   Spiridonov, E.M., Sokolova, N.G., Gapeev, A.K., Dashevskaya, D.M., Evstigneeva, T.L., Chvileva,
1116   T.N., Demidov, V.G., Balashov, E.P., and Shulga, V.I. (1986a) A new mineral –
1117   argentotennantite. Doklady Akademii Nauk SSSR, 290, 206–210 (in Russian).

1118   Spiridonov, E.M., Chvileva, T.N., Borodaev, Yu.S., Vinogradova, R.A., and Kononov, O.V.
1119   (1986b) The influence of bismuth on optical properties of gray copper. Doklady Akademii
1120   Nauk SSSR, 290, 1475–1478 (in Russian).

1121   Spiridonov, E.M., Ivanova, Yu.N., and Yapaskurt, V.O. (2014) Selenium-bearing goldfieldite and
1122   fischesserite $AuAg_3Se_2$ – petzite $AuAg_3Te_2$ solid solutions in ores of the Ozernovskoe
1123   Volcanogenic Deposit (Kamchatka). Doklady Earth Science, 458, 1139–1142.

1124   Springer, G. (1969) Electron probe analyses of tetrahedrite. Neues Jahrbuch für Mineralogie,
1125   Monatshefte, 1969, 24–32.

1126   Staude, S., Mordhorst, T., Neumann, R., Prebeck, W., and Markl, G. (2010) Compositional
1127   variation of the tennantite-tetrahedrite solid-solution series in the Schwarzwald ore district

35

Biagioni et al.

(SW Germany): The role of mineralization processes and fluid source. Mineralogical Magazine, 74, 309–339.

Števko, M., Sejkora, J., Dolníček, Z., and Škácha, P. (2018) Selenium-rich Ag-Au mineralization at the Kremnica Ag-Au epithermal deposit, Slovak Republic. Minerals, 8, 572.

Sugaki, A., Shima, H., and Kitakaze, A. (1975) Experimental study of argentian tetrahedrite (Prof. T. Takéuchi Memorial vol.). Scientific Reports of the Tohoku University, 2nd ser. Spec., 7, 63–72 (in Japanese).

Thompson, R.M. (1946) Golfieldite = tellurian tetrahedrite. University of Toronto Studies, Geological Series, 50, 77–78.

Thouvenin, J.-M. (1983) Les minéralisations polymétalliques à Pb-Zn-Cu-Ag de Huaron (Pérou Central). Minéralographie des minerais et pétrographie des altérations des épontes. Unpublished thesis, École Nationale Supérieure des Mines de Paris, 223 p.

Trudu, A.G., and Knittel, U. (1998) Crystallography, mineral chemistry and chemical nomenclature of goldfieldite, the tellurian member of the tetrahedrite solid-solution series. Canadian Mineralogist, 36, 1115–1137.

Vavelidis, M., and Melfos, V. (1997) Two plumbian tetrahedrite-tennantite occurrences from Maronia area (Thrace) and Milos island (Aegean sea), Greece. European Journal of Mineralogy, 9, 653–658.

Velebil, D. (2014) A contribution to knowledge of chemistry of mercurian tetrahedrites: localities Jedová hora (Czech Republic), Rudňany, Rožňava, Nižná Slaná, Slovinky (Slovakia) and Maškara (Bosnia and Herzegovina). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, 22, 1, 131-143. (in Czech).

Velebil, D., and Sejkora, J. (2018) Bi-rich tennantites from Jáchymov (Czech Republic). Bulletin Mineralogie Petrologie, 26, 213–222 (in Czech).

Voudouris, P.C. (2006) Mineralogy of telluride-bearing epithermal ores in the Kassiteres-Sappes area, western Thrace, Greece. Mineralogy and Petrology, 87, 31–52.

Voudouris, P.C., Spry, P.G., Sakellaris, G.A., and Mavrogonatos, C. (2011) A cervelleite-like mineral and other Ag-Cu-Te-S minerals [Ag_2CuTeS and $(Ag,Cu)_2TeS$] in gold-bearing veins in metamorphic rocks of the Cycladic Blueschist Unit, Kallianou, Evia Island, Greece. Mineralogy and Petrology, 101, 169–183.

Weidenbusch, H. (1849) Analyse des quecksilberhaltigen Fahlerzes von Schwatz in Tyrol. Annalen der Physik und Chemie, 152, 86–88.

36

Biagioni et al.

1160   Weissenbach, C.G.A. von (1831) Ueber die Gehalte der beym sächsischen Bergbau vorkommenden
1161   Silbererze. Kalender für den Sächsischen Berg- und Hüttenmann auf das Jahr 1831, 223–248.

1162   Welch, M.D., Stanley, C.J., Spratt, J., and Mills, S.J. (2018) Rozhdestvenskayaite $Ag_{10}Zn_2Sb_4S_{13}$
1163   and argentotetrahedrite $Ag_6Cu_4(Fe^{2+}, Zn)_2Sb_4S_{13}$: two Ag-dominant members of the
1164   tetrahedrite group. European Journal of Mineralogy, 30, 1163–1172.

1165   Wuensch, B.J. (1964) The crystal structure of tetrahedrite, $Cu_{12}Sb_4S_{13}$. Zeitschrift für
1166   Kristallographie, 119, 437–453.

1167   Wuensch, B.J., Takéuchi, Y., and Nowacki, W. (1966) Refinement of the crystal structure of
1168   binnite, $Cu_{12}As_4S_{13}$. Zeitschrift für Kristallographie, 123, 1–20.

1169   Zhdanov, Yu.Ya., Amuzinskiy, V.A., and Andrianov, N.G. (1992) A natural variety of high-silver
1170   fahlerz with a large unit-cell parameter. Doklady Akademii Nauk SSR, Earth Science Section,
1171   327A, 134–138.

1172

Table captions

1174   **Table 1** – Mineral species belonging to the tetrahedrite group, following the Official IMA CNMNC

1175   List of Mineral Names (January 2019).

1176   **Table 2** – Nomenclature and classification of the tetrahedrite group minerals.

1177

Figure captions

1179   **Fig. 1** – The cation and anion sites occurring in tetrahedrite group minerals (a) and the three-

1180   dimensional sodalite-like framework (b). Incorporation of $X(3)S(1)_3$ pyramids is connected with the

1181   collapse of the sodalite motif.

1182   **Fig. 2** – Relations between the unit-cell parameter a (Å) and the Ag content (*apfu*). Dashed vertical

1183   lines indicate the boundaries between the tetrahedrite and freibergite series and between the

1184   freibergite and the rozhdestvenskayaite series. References: [1] Petruk (1971); [2, 3] Shimada and

1185   Hirowatari (1972); [4] Kalbskopf (1972); [5] Riley (1974); [6] Charlat and Lévy (1975); [7] Sugaki

1186   et al. (1975); [8] Pattrick and Hall (1983); [9] Criddle and Stanley (1986); [10] Peterson and Miller

1187   (1986); [11] Balitskaya et al. (1989); [12] Rozhdestvenskaya et al. (1989); [13] Zhdanov et al.

1188   (1992); [14] Samusikov and Gamyanin (1994); [15, 16] Welch et al. (2018).

1189   **Fig. 3** – Details of the coordination of the $M(2)$ site in argentotetrahedrite (a) and "freibergite" (b).

1190   In the former, Ag–Ag distances are 3.24 Å and S(2) is occupied, whereas in the latter the Ag–Ag

1191   distances are 2.84 Å, in agreement with Ag–Ag bonds in native silver, and S(2) site is vacant.

1192   Crystallographic data after Welch et al. (2018). Symbols: circles indicate $M(2)$ (grey), $X(3)$

1193   (orange), S(1) and S(2) (yellow) sites.

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Biagioni et al.

1195 **Table 1** – Mineral species belonging to the tetrahedrite group, following the Official IMA CNMNC
1196 List of Mineral Names (January 2019).

Species	Chemical formula	IMA Status	IMA Number	Type locality
Annivite	$Cu_6[Cu_4(Fe,Zn)_2](Bi,Sb,As)_4S_{13}$	Q	2008 s.p.	Anniviers Valley, Switzerland
Argentotennantite	$Ag_6[Cu_4(Fe,Zn)_2]As_4S_{13}$	A	1985-026	Kvartsitovje Gorki deposit, Kazakhstan
Argentotetrahedrite	$Ag_6Cu_4(Fe,Zn)_2Sb_4S_{13}$	A	2016-093	Keno Hill, Yukon, Canada
Freibergite	$Ag_6[Cu_4Fe_2]Sb_4S_{12}$	G	1853	Freiberg, Saxony, Germany
Giraudite	$Cu_6[Cu_4(Fe,Zn)_2]As_4Se_{13}$	A	1980-089	Chaméane U deposit, France
Goldfieldite	$Cu_{10}Te_4S_{13}$	Rd	1998 s.p.	Mohawk mine, Goldfield, Nevada, USA
Hakite	$Cu_6[Cu_4Hg_2]Sb_4Se_{13}$	A	1970-019	Předbořice, Bohemia, Czech Republic
Rozhdestvenskayaite	$Ag_{10}Zn_2Sb_4S_{13}$	A	2016-094	Moctezuma mine, Sonora, Mexico
Tennantite	$Cu_6[Cu_4(Fe,Zn)_2]As_4S_{13}$	G	1819	Cornwall, United Kingdom
Tetrahedrite	$Cu_6[Cu_4(Fe,Zn)_2]Sb_4S_{13}$	A	1962 s.p.	unknown

1197   Note: A = approved; G = grandfathered; Q = questionable; Rd = redefined; s.p. = special procedure.
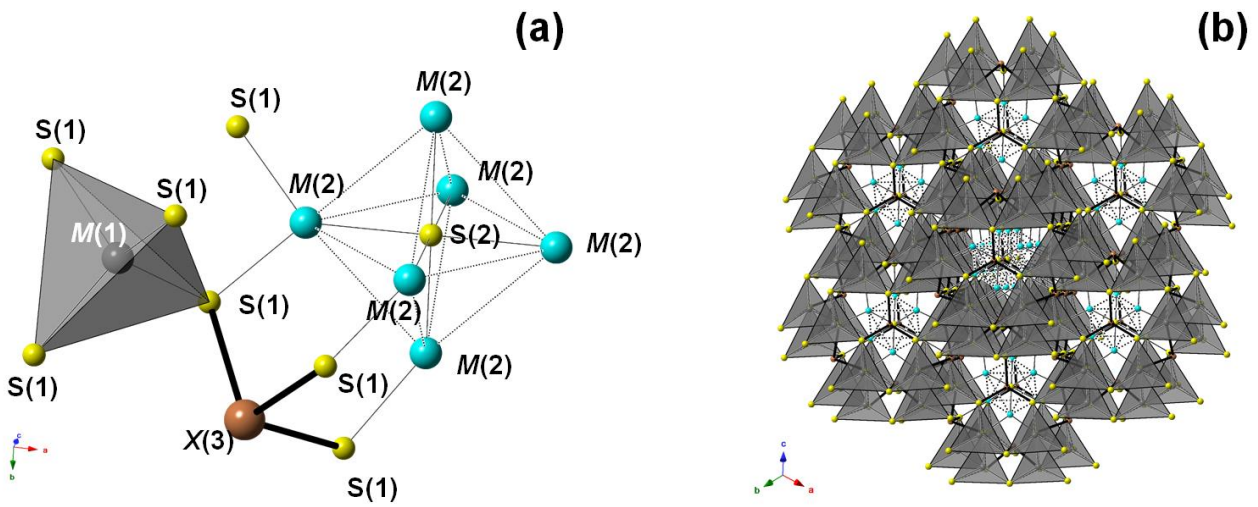
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Biagioni et al.

1200 **Table 2** – Nomenclature and classification of the tetrahedrite group minerals.

Tetrahedrite group			
Tetrahedrite series		**Tennantite series**	
Tetrahedrite-(Fe)	$Cu_6(Cu_4Fe_2)Sb_4S_{13}$	Tennantite-(Fe)	$Cu_6(Cu_4Fe_2)As_4S_{13}$
Tetrahedrite-(Zn)	$Cu_6(Cu_4Zn_2)Sb_4S_{13}$	Tennantite-(Zn)	$Cu_6(Cu_4Zn_2)As_4S_{13}$
Tetrahedrite-(Cd)	$Cu_6(Cu_4Cd_2)Sb_4S_{13}$	*Tennantite-(Cu)*	$Cu_6(Cu_4Cu_2)As_4S_{13}$
Tetrahedrite-(Cu)	$Cu_6(Cu_4Cu_2)Sb_4S_{13}$	*Tennantite-(Hg)*	$Cu_6(Cu_4Hg_2)As_4S_{13}$
Tetrahedrite-(Hg)	$Cu_6(Cu_4Hg_2)Sb_4S_{13}$	*Tennantite-(Mn)*	$Cu_6(Cu_4Mn_2)As_4S_{13}$
Tetrahedrite-(Mn)	$Cu_6(Cu_4Mn_2)Sb_4S_{13}$		
Freibergite series		***Arsenofreibergite series***	
Argentotetrahedrite-(Fe)	$Ag_6(Cu_4Fe_2)Sb_4S_{13}$	Argentotennantite-(Zn)	$Ag_6(Cu_4Zn_2)As_4S_{13}$
Kenoargentotetrahedrite-(Fe)	$Ag_6(Cu_4Fe_2)Sb_4S_{12\square}$	*Argentotennantite-(Fe)*	$Ag_6(Cu_4Fe_2)As_4S_{13}$
Argentotetrahedrite-(Cd)	$Ag_6(Cu_4Cd_2)Sb_4S_{13}$		
Argentotetrahedrite-(Hg)	$Ag_6(Cu_4Hg_2)Sb_4S_{13}$		
Hakite series		**Giraudite series**	
Hakite-(Hg)	$Cu_6(Cu_4Hg_2)Sb_4Se_{13}$	Giraudite-(Zn)	$Cu_6(Cu_4Zn_2)As_4Se_{13}$
Hakite-(Cd)	$Cu_6(Cu_4Cd_2)Sb_4Se_{13}$	*Giraudite-(Cu)*	$Cu_6(Cu_4Cu_2)As_4Se_{13}$
Hakite-(Cu)	$Cu_6(Cu_4Cu_2)Sb_4Se_{13}$	*Giraudite-(Fe)*	$Cu_6(Cu_4Fe_2)As_4Se_{13}$
Hakite-(Fe)	$Cu_6(Cu_4Fe_2)Sb_4Se_{13}$	*Giraudite-(Hg)*	$Cu_6(Cu_4Hg_2)As_4Se_{13}$
Hakite-(Zn)	$Cu_6(Cu_4Zn_2)Sb_4Se_{13}$		
Rozhdestvenskayaite series		***Goldfieldite series***	
Rozhdestvenskayaite-(Zn)	$Ag_6(Ag_4Zn_2)Sb_4S_{13}$	Goldfieldite	$(Cu_4\square_2)Cu_6Te_4S_{13}$
Rozhdestvenskayaite-(Fe)	$Ag_6(Ag_4Fe_2)Sb_4S_{13}$	*"Stibiogoldfieldite"*	$Cu_6Cu_6(Sb_2Te_2)S_{13}$
Rozhdestvenskayaite-(Hg)	$Ag_6(Ag_4Hg_2)Sb_4S_{13}$	*"Arsenogoldfieldite"*	$Cu_6Cu_6(As_2Te_2)S_{13}$

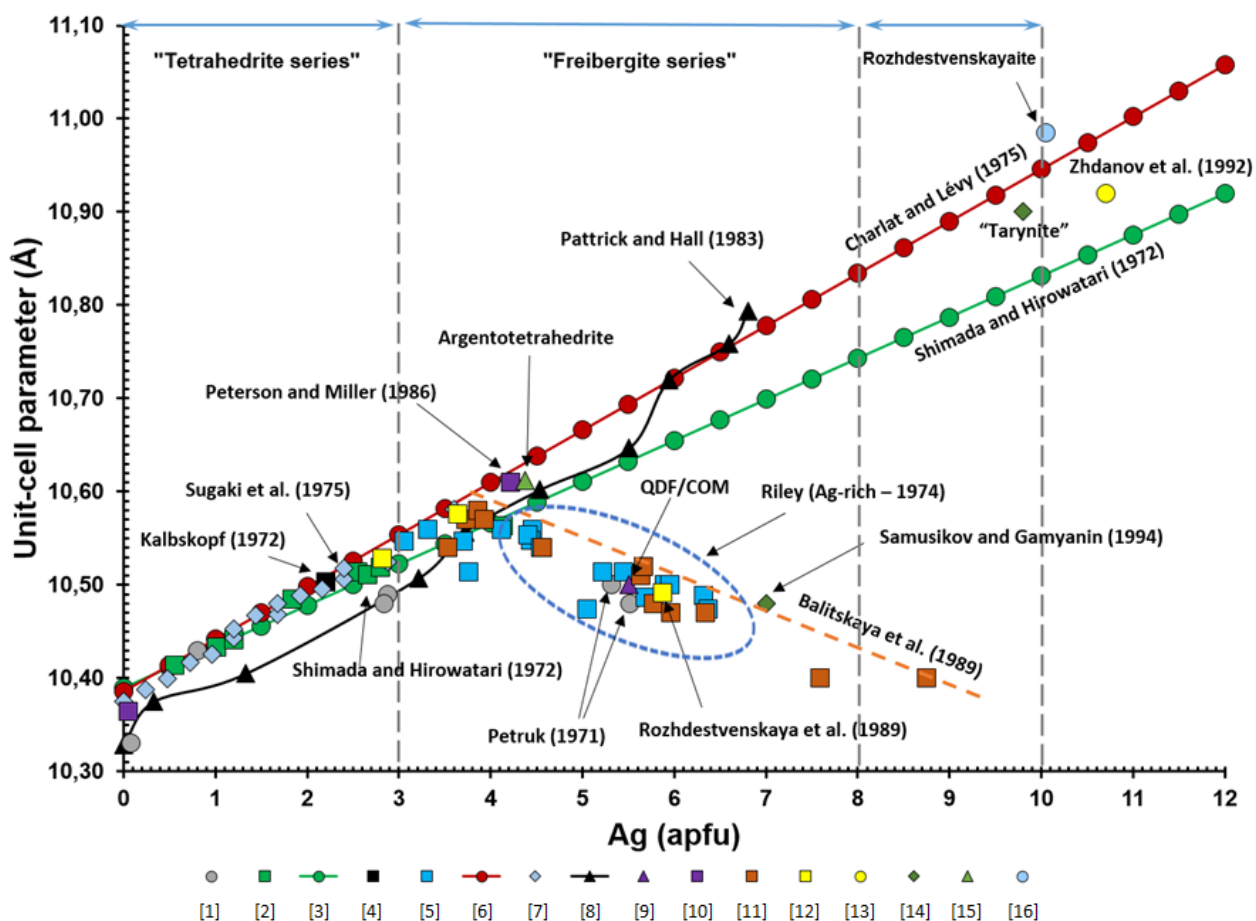1201 Note: italicized names require official approval by the IMA-CNMNC.

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1203   **Fig. 1** – The cation and anion sites occurring in tetrahedrite group minerals (a) and the three-
1204   dimensional sodalite-like framework (b). Incorporation of $X(3)S(1)_3$ pyramids is connected with the
1205   collapse of the sodalite motif.

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Biagioni et al.

Fig. 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] Pattrick 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 Gamyanin (1994); [15, 16] Welch et al. (2018).

42

Biagioni et al.

1218 **Fig. 3** – Details of the coordination of the *M*(2) site in argentotetrahedrite (a) and "freibergite" (b).

1219 In the former, Ag–Ag distances are 3.24 Å and S(2) is occupied, whereas in the latter the Ag–Ag

1220 distances are 2.84 Å, in agreement with Ag–Ag bonds in native silver, and S(2) site is vacant.

1221 Crystallographic data after Welch et al. (2018). Symbols: circles indicate *M*(2) (grey), *X*(3)

1222 (orange), S(1) and S(2) (yellow) sites.

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Biagioni et al.