

Revision 1

The tetrahedrite group: nomenclature and classification

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68 **Abstract:** The classification of the tetrahedrite group minerals in keeping with the current IMA-
69 accepted nomenclature rules is discussed. Tetrahedrite isotypes are cubic, with space group
70 symmetry $I\bar{4}3m$. The general structural formula of minerals belonging to this group can be written
71 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 (Ag₆)⁴⁺ clusters; B =
72 Cu⁺, and Ag⁺; C = Zn²⁺, Fe²⁺, Hg²⁺, Cd²⁺, Mn²⁺, Cu²⁺, Cu⁺, and Fe³⁺; D = Sb³⁺, As³⁺, Bi³⁺, and Te⁴⁺;
73 Y = S²⁻, and Se²⁻; and Z = S²⁻, Se²⁻, and □. The occurrence of both *Me*⁺ and *Me*²⁺ cations at the *M*(1)
74 site, in a 4:2 atomic ratio, is a case of valency-imposed double site-occupancy. Consequently,
75 different combinations of B and C constituents should be regarded as separate mineral species. The
76 tetrahedrite group is divided into five different series on the basis of the A, B, D, and Y
77 constituents, *i.e.*, the tetrahedrite, tennantite, freibergite, hakite, and giraudite series. The nature of
78 the dominant C constituent (the so-called “charge-compensating constituent”) is made explicit using
79 a hyphenated suffix between parentheses. Rozhdestvenskayaite, arsenofreibergite, and goldfieldite
80 could be the names of three other series. Eleven minerals belonging to the tetrahedrite group are
81 considered as valid species: argentotennantite-(Zn), argentotetrahedrite-(Fe),
82 kenoargentotetrahedrite-(Fe), giraudite-(Zn), goldfieldite, hakite-(Hg), rozhdestvenskayaite-(Zn),
83 tennantite-(Fe), tennantite-(Zn), tetrahedrite-(Fe), and tetrahedrite-(Zn). Furthermore, annivite is
84 formally discredited. Minerals corresponding to different end-member compositions could be
85 approved as new mineral species by the IMA-CNMNC following the submission of regular
86 proposals. The nomenclature and classification system of the tetrahedrite group, approved by the
87 IMA-CNMNC, allows the full description of the chemical variability of the tetrahedrite minerals
88 and it is able to convey important chemical information not only to mineralogists but also to ore
89 geologists and industry professionals.

90

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

92

93 **1. Introduction**

94 Minerals of the ‘tetrahedrite group’ are the most common sulfosalts in many types of
95 hydrothermal ore deposits and represent one of the most complex isotypic series among sulfides,
96 owing to the potential occurrence of multiple homo- and heterovalent substitutions (Moëlo et al.
97 2008).

98 This chemical variability results in several mineral species so far accepted and reported in
99 the official IMA-CNMNC List of Mineral Names. Notwithstanding this wide chemical variability,
100 the classification of the tetrahedrite group minerals was still based on the *Report of the Sulfosalt*
101 *sub-committee of IMA Commission on Ore Mineralogy* (IMA-COM) (Moëlo et al. 2008), and an
102 up-to-date classification, based upon the ongoing rules recommended by the IMA Commission on
103 New Minerals, Nomenclature and Classification (IMA-CNMNC), was lacking. Indeed, a
104 classification and nomenclature for members of the tetrahedrite group should account for and
105 describe the full chemical variability of these sulfosalts, thus providing information pertinent not
106 only to mineral systematics but also to ore mineralogy. The aim of this report, based on the voting
107 proposal IMA 18-K “*Nomenclature and classification of the tetrahedrite group*”, approved by the
108 IMA-CNMNC in April 2019, is to fill this gap, rationalizing and updating the classification of the
109 tetrahedrite group.

110

111 **2. Crystal-chemistry of the tetrahedrite group minerals**

112 **2.1. Crystal structure**

113 The crystal structure of tetrahedrite was first determined by Machatschki (1928a, 1928b), who
114 assumed the ideal composition Cu_3SbS_3 . Some years later, Pauling and Neuman (1934) concluded
115 that the formula $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ was in closer agreement with available chemical data. They proposed a
116 crystal structure derived from a sphalerite-type substructure. However, a more detailed description
117 of the structural arrangement of tetrahedrite was given thirty years later by Wuensch (1964).
118 Tetrahedrite is cubic, with space group symmetry $I\bar{4}3m$. Three independent cation sites and two
119 anion sites occur (Fig. 1):

- 120 • $M(1)$ site, at the Wyckoff position $12d$, with atomic coordinates $(\frac{1}{4}, \frac{1}{2}, 0)$;
- 121 • $M(2)$ site, at the Wyckoff position $12e$, with atomic coordinates $(x, 0, 0)$. There is clear
122 evidence that this triangular site is split into two flat pyramidal sub-sites located at
123 Wyckoff positions $24g$ and atomic coordinates (x, x, z) , each with half occupancy
124 (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 $M(2)_6M(1)_6X(3)_4S(1)_{12}S(2)$ ($Z = 2$). 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 $[\text{Cu}_{12}\text{Sb}_8\text{S}_2][\text{Cu}_{12}\text{S}_{24}]$.
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.

138

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 $M(2)_6M(1)_6(\text{B}_4\text{C}_2)_{\Sigma 6}X(3)_4\text{D}_4\text{S}(1)_{12}\text{Y}_{12}\text{S}(2)_2\text{Z}$, where the upper cases represent the following constituents:

149 $A = \text{Cu}^+, \text{Ag}^+, \square$ (vacancy); $(\text{Ag}_6)^{4+}$ clusters are also possible, coupled with Z vacancies (see
150 § 3.4);

151 $B = \text{Cu}^+, \text{Ag}^+$;

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

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

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

155 $Z = \text{S}^{2-}, \text{Se}^{2-}, \square$.

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

158 Mozgova and Tsepina (1983). Similarly, Johnson et al. (1986) examined the compositional data of
159 1271 natural samples and 295 synthetic compounds. In all these samples, no more than 2 atoms per
160 formula unit (*apfu*) of divalent metals (Me^{2+}) occur and the sum of the monovalent metals ($Ag^+ +$
161 Cu^+) is usually about 10 *apfu*, with six of them hosted at the $M(2)$ site and four at $M(1)$. The total
162 number of anions is usually 13 ($S^{2-} + Se^{2-}$) *apfu*, yielding 26 negative charges. As the sum of 10
163 monovalent cations ($Ag^+ + Cu^+ = A$ and B constituents) and 4 trivalent cations ($Sb^{3+} + As^{3+} + Bi^{3+}$
164 $= D$ constituent) gives +22 charges, the excess of -4 charges is balanced by the accommodation of 2
165 Me^{2+} -cations statistically distributed over the $M(1)$ sites (C constituent). The latter acts as a “charge
166 compensating cation” that fixes the (B:C) constituent atomic ratio to (4:2) in the general formula.

167 “Unsubstituted” tetrahedrite-tennantite (i.e., without metals other than Cu and Ag) is known,
168 both as synthetic as well as natural samples (e.g., Makovicky et al. 2005); the apparent excess of
169 negative charges could be compensated by the presence of Cu^{2+} (Patrick et al. 1993).

170 Maske and Skinner (1971) identified Cu excess in synthetic tennantite, $Cu_{12+x}As_{4+y}S_{13}$, with
171 $0 < x < 1.72$. The x value increased up to 1.99, when As was partly replaced by Sb (Luce et al.
172 1977). According to Makovicky and Skinner (1979), synthetic tetrahedrite $Cu_{12+x}Sb_4S_{13}$ (x varies
173 continuously between less than 0.1 and 1.9) exsolves, below 120°C, to a composition close to
174 $Cu_{12}Sb_4S_{13}$ ($a = 10.32 \text{ \AA}$) and to a Cu-excess composition, close to $Cu_{14-x}Sb_4S_{13}$ (x approximately
175 equal to 0.2; $a = 10.45 \text{ \AA}$). The Cu-excess variety could be more common than previously thought,
176 but, as stressed by Lind and Makovicky (1982), during electron-microprobe analysis a “loss” of Cu
177 over 12 *apfu* was observed, both in synthetic as well as natural samples of tetrahedrite and
178 tennantite. The only current way to detect the Cu-excess is through X-ray diffraction. In Cu-excess
179 tennantite (Makovicky et al. 2005), the distribution of excess Cu involves and partly splits the $M(2)$
180 site, whereas in Cu-excess synthetic tetrahedrite (Makovicky and Skinner 1979) the diffusion paths
181 involve and indirectly interconnect the 2/3-occupied $M(1)$ sites.

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

185 186 **3. Nomenclature of the tetrahedrite group minerals: state-of-the-art**

187
188 Ten different mineral species belonging to the tetrahedrite group have been so far
189 recognized in the official IMA-CNMNC List of Mineral Names (Table 1). In the following, we will
190 briefly report the main features of these ten species within the tetrahedrite group.

191

192 **3.1. Annivite**

193 Annivite was considered the Bi-dominant analogue of tetrahedrite and tennantite, although it
194 was reported as “questionable” in the official IMA-CNMNC List of Mineral Names. Indeed, the
195 chemical analysis of holotype annivite from the Anniviers Valley (Switzerland – Fellenberg 1854)
196 leads to the following empirical formula: $(\text{Cu}_{9.93}\text{Fe}_{1.22}\text{Zn}_{0.55})_{\Sigma 11.70}(\text{As}_{2.60}\text{Sb}_{1.28}\text{Bi}_{0.42})_{\Sigma 4.30}\text{S}_{13.15}$, which
197 corresponds to tennantite. Moreover, Breskovska and Tarkian (1994), through the examination of
198 214 analyses of natural members of the tetrahedrite group, found a maximum Bi content of 1.69
199 *apfu*. If we retroactively assume that annivite is the mineral with Bi^{3+} as the dominant D cation,
200 natural compounds with that composition have undoubtedly been reported (e.g., Bortnikov et al.
201 1979; Kieft and Eriksson 1984; Spiridonov et al. 1986b; Gołębiewska et al. 2012; Velebil and
202 Sejkora 2018). However, these data are not supported by any X-ray diffraction study. Synthetic Bi-
203 bearing tetrahedrite and tennantite were synthesized by Klünder et al. (2003) who found up to 1 Bi
204 *apfu* at 450° and 520 °C.

205

206 **3.2. Argentotennantite**

207 Argentotennantite was first described by Spiridonov et al. (1986a) from the polymetallic
208 Kvarstoviyе Gorki deposit (Kazakhstan) as small grains up to 0.1 mm. Its unit-cell parameter is a
209 = 10.583(4) Å. At the type locality, argentotennantite is associated with other members of the
210 tetrahedrite group. The empirical formula of the holotype material is $(\text{Ag}_{5.67}\text{Cu}_{0.33})_{\Sigma 6.00}$
211 $(\text{Cu}_{4.15}\text{Zn}_{1.52}\text{Fe}_{0.37}\text{Pb}_{0.01}\text{Cd}_{0.01})_{\Sigma 6.06}(\text{As}_{2.14}\text{Sb}_{1.89})_{\Sigma 4.03}\text{S}_{12.90}$, which leads to the end-member formula
212 $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$. The crystal structure of argentotennantite is currently unsolved.

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

216

217 **3.3. Argentotetrahedrite**

218 Argentotetrahedrite was first described by Spiridonov et al. (1986b) as the Sb-rich derivative
219 of argentotennantite, on the basis of electron microprobe analysis only (no X-ray data). Later,
220 Zhdanov et al. (1992) reported chemistry and unit-cell parameter of a Cu-free Ag-end-member, but
221 no formal proposal was submitted to the then IMA-CNMMN. Moëlo et al. (2008) reported this
222 species as a member of the tetrahedrite isotopic series, with chemical composition
223 $\text{Ag}_{10}(\text{Fe},\text{Zn})_2\text{Sb}_4\text{S}_{13}$. They pointed out that a redefinition through a formal proposal to the CNMNC

7

224 was highly desirable. Finally, using new compositional and structural data for a sample from the
225 Keno Hill Ag-Pb-Zn deposit, Yukon (Canada), having $Fe > Zn$, Welch et al. (2018) redefined
226 argentotetrahedrite as the Sb counterpart of argentotennantite, with the simplified formula
227 $Ag_6Cu_4(Fe,Zn)_2Sb_4S_{13}$. Crystal structure analysis confirmed that all Ag is ordered at the $M(2)$ site.

228 Foit and Ulbricht (2001) reported a sample from the O'Keefe claims, Harney County,
229 Oregon (USA) having 5.78 Ag *apfu* and Hg dominant over Zn and Fe which leads to the end-
230 member composition $Ag_6(Cu_4Hg_2)Sb_4S_{13}$. Atanasov (1975) gave electron-microprobe and X-ray
231 powder diffraction data of a sample from the Chiprovtsi Pb-Ag deposit, Western Stara-Planina
232 mountains (Bulgaria); the average of three spot analyses gave the chemical formula
233 $Cu_{6.88}Ag_{2.96}(Hg_{1.83}Zn_{0.17})_{\Sigma 2.00}(Sb_{3.36}As_{0.71})_{\Sigma 4.07}S_{13.09}$. It is worth noting that if Cu is partitioned
234 between the $M(1)$ and $M(2)$ sites, the possible dominance of Ag at $M(2)$ results, *i.e.*,
235 $^{M(2)}(Ag_{2.96}Cu_{2.88})_{\Sigma 5.84}$. The classification of this sample, without structural data, is uncertain: it may
236 be considered either as the Ag-rich variety of $Cu_6(Cu_4Hg_2)Sb_4S_{13}$ or as argentotetrahedrite with Hg
237 as the dominant divalent cation, *i.e.*, $Ag_6(Cu_4Hg_2)Sb_4S_{13}$.

238 Finally, Repstock et al. (2016) reported 6.66 Ag *apfu* and 1.45 Cd *apfu* in a sample from the
239 Mavrokoryfi deposit (Greece), thus having end-member formula $Ag_6(Cu_4Cd_2)Sb_4S_{13}$.

240

241 **3.4. Freibergite**

242 Kenngott (1853) first used the name freibergite to indicate an Ag-rich tetrahedrite from
243 Freiberg, Saxony (Germany). The type locality is actually the Hab Acht Mine (later part of the
244 Beschert Glück Mine), Zug near Freiberg, Saxony, where it was first described by Weissenbach
245 (1831) with an analysis of Heinrich Rose. This analysis can be recalculated, on the basis of Sb = 4
246 *apfu*, to $Ag_{5.74}Cu_{4.61}Fe_{2.12}Zn_{0.30}Sb_{4.00}S_{13.06}$.

247 The definition of freibergite is much debated, being often confused with both Ag-rich
248 tetrahedrite and argentotetrahedrite. Indeed, Kalbskopf (1972) studied Ag-rich tetrahedrite (with *ca.*
249 13 wt% Ag) and not freibergite; however, this study first suggested the preferential occurrence of
250 Ag at the triangular coordinated $M(2)$ site. Similarly, freibergite from Keno Hill, Yukon (Canada),
251 examined by Peterson and Miller (1986), was actually argentotetrahedrite, as recently redefined by
252 Welch et al. (2018).

253 Since the pioneering study of Riley (1974), several authors (e.g., Samusikov et al. 1988;
254 Balitskaya et al. 1989) reported that an increase in the Ag content of freibergite is coupled with a
255 decrease in the *a*-parameter and an increase in the amount of vacancy at the S(2) site. However, the
256 Ag-for-Cu substitution in the tennantite-tetrahedrite pair actually results in a linear increase of the

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 (Ag₆)⁴⁺ octahedral
262 clusters. Thus, the ideal formula of freibergite is Ag₆(Cu₄Fe₂)Sb₄S₁₂, 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]_{Σ6}Sb₄S₁₂S_{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)}(Ag₆) group,
269 having a formal charge of +4, as has been shown for synthetic organometallic compounds (e.g.,
270 Kikukawa et al. 2013).

271

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})_{Σ6.00}(Cu⁺₄Zn_{1.16}Cu²⁺_{0.72}Hg_{0.08}Fe_{0.04})_{Σ6.00}(As_{2.20}Sb_{1.76})_{Σ3.96}Se_{11.04}S_{2.00},
277 (Cu_{5.24}Ag_{0.76})_{Σ6.00}(Cu⁺₄Zn_{1.12}Cu²⁺_{0.84}Fe_{0.08}Hg_{0.04})_{Σ6.08}(As_{2.16}Sb_{1.88})_{Σ4.04}Se_{11.08}S_{1.80}, and
278 (Cu_{5.68}Ag_{0.32})_{Σ6.00}(Cu⁺₄Zn_{1.00}Cu²⁺_{0.92}Hg_{0.04})_{Σ6.00}(As_{2.60}Sb_{1.28})_{Σ3.88}Se_{10.52}S_{2.64}. Formally, Cu²⁺ occurs in
279 giraudite. The end-member formula is Cu₆(Cu₄Zn₂)As₄Se₁₃. 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 Cu₆(Cu₄Hg₂)As₄Se₁₃; one spot analysis
284 corresponded to a cuprian giraudite, having formally Cu²⁺ as dominant divalent C constituent.
285 Moreover, Förster and Rhede (2004) reported an extensive substitution series between giraudite and
286 tennantite, involving the Se²⁻-S²⁻ substitution. These authors gave chemical data corresponding to
287 Fe- and Cu²⁺-terms, ideally Cu₆(Cu₄Fe₂)As₄Se₁₃ and Cu₆(Cu₄Cu²⁺₂)As₄Se₁₃, 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).

290

291 **3.6. Goldfieldite**

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

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

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

312 Kato and Sakurai (1970) and Spiridonov et al. (1984) suggested that the name goldfieldite
313 should be applied to members of the tetrahedrite solid solution with Te as the most abundant
314 semimetal; such an approach was also followed by Trudu and Knittel (1998). On the contrary,
315 Dmitrieva et al. (1987) suggested that the mineral can be named goldfieldite only when Te content
316 is greater than the sum of all other semimetals. The nomenclature of goldfieldite will be discussed
317 below.

318

319 **3.7. Hakite**

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

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323 $\text{Cu}_6(\text{Cu}_{4.08}\text{Hg}_{1.83})_{\Sigma 5.91}(\text{Sb}_{3.05}\text{As}_{1.03})_{\Sigma 4.08}(\text{Se}_{10.35}\text{S}_{2.62})_{\Sigma 12.97}$ and
324 $\text{Cu}_6(\text{Cu}_{4.22}\text{Hg}_{1.73})_{\Sigma 5.95}(\text{Sb}_{3.83}\text{As}_{0.22})_{\Sigma 4.05}\text{Se}_{11.90}$. These two compositions correspond to unit-cell
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 $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{Se}_{13}$, $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{Se}_{13}$, and $\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{Se}_{13}$, 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 $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{Se}_{13}$, as well as fully Zn substituted
342 $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{Se}_{13}$. The $\text{Cu}_6\text{Cu}_6\text{Sb}_4\text{Se}_{13}$ composition resulted in the orthorhombic phase 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 Gamyarin (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 $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, 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 $\text{Ag}_6(\text{Ag}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$. Zhdanov et al. (1992)
359 examined an Fe-rich Ag-pure end-member, $\text{Ag}_6(\text{Ag}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$, with unit-cell parameter $a = 10.92$
360 Å.

361 Ixer and Stanley (1983) analyzed a tetrahedrite group grain of composition
362 $(\text{Ag}_{8.18}\text{Cu}_{1.91}\text{Zn}_{1.44}\text{Fe}_{0.49}\text{Pb}_{0.17}\text{Cd}_{0.16})_{\Sigma 12.35}(\text{As}_{2.22}\text{Sb}_{1.93})_{\Sigma 4.15}\text{S}_{12.5}$ which could have Ag dominant at
363 both $M(2)$ and $M(1)$ sites, and $\text{As} > \text{Sb}$ at $X(3)$, but close to $^{\text{S}(2)}(\text{S}_{0.5}\square_{0.5})$ boundary. Consequently, it
364 could be either the As-analogue of rozhdestvenskayaite or the As-analogue of freibergite (if $^{\text{S}(2)}\square >$
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 $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$.

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 $2\text{Cu}^{2+} \rightarrow \text{Cu}^+ + \text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+}$ combinations, in a continuous process of
381 exchange, with a possible share of $\text{Cu}^{2+} + \text{Fe}^{2+}$.

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 $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$. 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).

388 As shown by several studies (e.g., George et al. 2017), the most common end-member
389 compositions of tennantite have either Fe or Zn as the dominant divalent cation. A Cu-rich
390 tennantite from the Huaron polymetallic ore deposit (Central Peru) gave the formula
391 $(\text{Cu}_{5.97}\text{Ag}_{0.03})_{\Sigma 6.00}(\text{Cu}_{5.63}\text{Fe}_{0.37})_{\Sigma 6.00}(\text{As}_{3.28}\text{Sb}_{0.38})_{\Sigma 3.66}\text{S}_{13}$ (basis: 12 *Me* atoms) (Thouvenin 1983;
392 Marcoux et al. 1994). Despite a weak As- and Sb-deficit, this analysis clearly points to a Cu^{2+}
393 dominant C-cation at the *M*(1) site. A sample of tennantite with dominant Mn^{2+} (up to 1.53 *apfu*)
394 was reported by Burkart-Baumann (1984) from the Quiruvilca deposit (Peru).

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

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

401

402 **3.10. Tetrahedrite**

403 Tetrahedrite is a grandfathered species. The name “tetrahedrite” was introduced by
404 Haidinger (1845) in agreement with the common tetrahedral form shown by its crystals. Previously,
405 tetrahedrite was known with different names, for instance *fahlerz*, *weissgiltigerz*, *grey ore*, or
406 *panabase*. Haidinger (1845) reported the occurrence of Fe and Zn in tetrahedrite. Indeed, these two
407 constituents are the most common divalent cations (e.g., George et al. 2017). For instance, Bechi
408 (1863) described the end-member $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$ from the Frigido mine, Apuan Alps, Tuscany
409 (Italy), indicating it with the discredited name *coppite*. The speciation of Fe in tetrahedrite has been
410 studied by several authors (e.g., Makovicky et al. 1990; Makovicky et al. 2003; Andreasen et al.
411 2008; Nasonova et al. 2016). Spectroscopic Mössbauer studies indicated that along the join
412 $\text{Cu}_{12+x}(\text{Sb,As})_4\text{S}_{13} - \text{Cu}_{10}\text{Fe}_2(\text{Sb,As})_4\text{S}_{13}$, the replacement of Cu by Fe starts by incorporation of
413 Fe^{3+} , which is the only type of Fe present in $\text{Cu}_6(\text{Cu}_{5.5}\text{Fe}_{0.5})(\text{Sb,As})_4\text{S}_{13}$. Then, Fe^{2+} starts to be
414 incorporated, together with the gradual reduction of Fe^{3+} to Fe^{2+} , up to the composition
415 $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)(\text{Sb,As})_4\text{S}_{13}$ (Makovicky et al. 1990, 2003).

416 The crystal structure of tetrahedrite was refined by Wuensch (1964) using a sample from
417 Horhausen, Westerwald (Germany); only old chemical data (dating back to the end of 19th and
418 beginning of 20th Century) were given, corresponding to phases having Cu or Zn as dominant C-
419 cation at *M*(1). Consequently, the actual chemical composition of the studied specimen is not
420 known. The occurrence of tetrahedrite samples having Cu^{2+} as the dominating C-cation is known in

421 literature. For instance, Repstock et al. (2016) documented Cu contents up to 11.78 *apfu* in
422 specimens from Northern Greece, corresponding to the ideal composition $\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{Sb}_4\text{S}_{13}$. The
423 compositions $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$ (minor x) are commonly obtained in synthetic runs.

424 In addition to Fe, Zn, and Cu as dominant divalent cations, many other elements have been
425 reported as C-constituents. Weidenbusch (1849) reported the analysis of a tetrahedrite group
426 mineral from Schwaz, Tyrol (Austria), having 15.9 wt% Hg and corresponding to the formula
427 $\text{Cu}_{9.9}\text{Hg}_{1.4}\text{Fe}_{0.7}\text{Zn}_{0.4}\text{Sb}_{3.2}\text{S}_{13}$. Later, Kenngott (1853) introduced the name “schwazite” to indicate
428 mercurian tetrahedrite. Actually, Arlt and Diamond (1998) proved that no samples with Hg as
429 dominant C constituent occur at Schwaz. Several other occurrences of mercurian tetrahedrite have
430 been reported: Foit and Ulbricht (2001) recorded up to 2.02 Hg *apfu* in samples from the epithermal
431 ore deposits of Harney County, Oregon (USA), in agreement with the end-member composition
432 $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$, that was obtained in synthetic samples by Karup-Møller and Makovicky
433 (2003). Karanović et al. (2003) reported the crystal structure of mercurian tetrahedrite from
434 Dragodol, Donja Trešnjica district (Serbia), confirming the results of Kalbskopf (1971) who
435 proposed the incorporation of Hg at the $M(1)$ site. Other structural investigations on mercurian
436 tetrahedrite were reported by Kaplunnik et al. (1980), who assumed a wrong structural model with
437 12 S *apfu*, and by Foit and Hughes (2004) for samples up to 1.23 Hg *apfu* from the Harney County,
438 Oregon (USA). Velebil (2014), on the basis of electron microprobe analysis and X-ray powder
439 diffraction, described Hg-dominant tetrahedrite (1.46 - 1.73 Hg *apfu*) from Jedová hora deposit
440 (Czech Republic) and from Rudňany (1.47 - 1.79 Hg *apfu*), Rožňava (1.65 Hg *apfu*) and Nižná
441 Slaná (1.07 - 1.39 Hg *apfu*), all in the Slovak Republic.

442 Many authors reported the occurrence of Cd contents up to 2 *apfu*, e.g., 1.92 *apfu* indicated
443 by Patrick (1978) at Tyndrum (Scotland, UK). Voudouris et al. (2011) reported 1.97 Cd *apfu* from
444 the Evia Island (Greece) and Jia et al. (1988) gave 1.85 Cd *apfu* in a sample from Xitieshan (China).
445 Consequently, $\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$ is another potential natural end-member composition. Jia et al.
446 (1988) actually gave the empirical formula $(\text{Cu}_{6.95}\text{Ag}_{3.03})_{\Sigma 9.98}(\text{Cd}_{1.85}\text{Zn}_{0.15}\text{Fe}_{0.15})_{\Sigma 2.15}$
447 $(\text{Sb}_{4.19}\text{As}_{0.25})_{\Sigma 4.44}\text{S}_{13}$; taking into account the partitioning of Ag at the $M(2)$ site, this formula could
448 represent an intermediate composition between an hypothetical end-member $\text{Ag}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$
449 and $\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$.

450 Basu et al. (1984) described a Mn-rich tetrahedrite (up to 1.71 Mn *apfu*) in the Rajpura-
451 Dariba polymetallic deposit (India). Dobbe (1992) analyzed tetrahedrite from Bergslagen (Sweden),
452 having Mn dominating over both Cd and Fe, leading to the end-member composition
453 $\text{Cu}_6(\text{Cu}_4\text{Mn}_2)\text{Sb}_4\text{S}_{13}$. Makovicky and Karup-Møller (1994) synthesized tetrahedrite containing up to

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 $\text{Cu}_6(\text{Cu}_4\text{Pb}_2)\text{Sb}_4\text{S}_{13}$. 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 $\text{Cu}_6(\text{Cu}_4\text{Fe}_{1.5}\text{Zn}_{0.5})\text{Sb}_4\text{S}_{13}$] and Ni-bearing
471 minerals (Carrozzini et al. 1991).

472 Minor gold (up to ~ 1 wt%) is known in tetrahedrite and goldfieldite (Mozgova and Tsepina
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 $M^{(2)}A_6M^{(1)}(B_4C_2)^{X(3)}D_4^{S(1)}Y_{12}^{S(2)}Z$.

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.

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, $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$; Welch et al. (2018)] or as discrete $(\text{Ag}_6)^{4+}$ clusters,
529 characterized by Ag–Ag bonds coupled with vacancy at the S(2) site. The latter leads to the end-
530 member formula $(\text{Ag}_6)(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{12}\square\square$ (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 $(\text{Ag}_6)^{4+}$ cluster in the freibergite series.

534

535 **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 $\text{Ag}_6[\text{Cu}_4\text{Fe}_2]\text{Sb}_4\text{S}_{12}$ (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 $\text{Ag}_6[\text{Cu}_4\text{Fe}_2]\text{Sb}_4\text{S}_{13-x}$.
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 ($a \sim 10.49 \text{ \AA}$) 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 $a = 10.535 \text{ \AA}$. Moreover, Sugaki et al. (1975) experimentally established the increase of the
557 unit-cell parameter with Ag content, up to 4.2 *apfu*. Patrick 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 \AA) 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 $a = 10.50 \text{ \AA}$. 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 \approx 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 (\AA) 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 $(\text{Ag}_6)^{4+}$
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

585 that in metallic Ag”, and the authors proposed the formation of “octahedral Ag-cluster [...] around
586 S2-site”. The details of the crystal structure of “freibergite”, with almost empty S(2) site, were then
587 published four years later (Rozhdestvenskaya et al. 1993). Around the same period, Zhdanov et al.
588 (1992) and Samusikov and Gamyranin (1994) described Cu-free/poor samples of Ag-rich
589 tetrahedrite, with Ag content overpassing the 8 *apfu* limit (see § 3.8). In the sample studied by
590 Zhdanov et al. (1992), Fe is dominant over Zn (0.94 vs. 0.81 *apfu*, respectively; Hg = 0.2 *apfu*). In
591 addition, Samusikov and Gamyranin (1994) proposed a nomenclature of the Ag-rich tetrahedrites,
592 with a distinction between “tarynite” (Ag > 8 *apfu*) and “Cu-tarynite” (Ag < 8 *apfu*) on the
593 increasing *a* trend, on the one hand, and, on the other hand, between hypothetical “freibergite” (Ag
594 > 8 *apfu*) and “Cu-freibergite” (Ag < 8 *apfu*) on the decreasing *a* trend. The sample with 8.75 Ag
595 *apfu* (and *a* = 10.34 Å) of Balitskaya et al. (1989) plots in the field of this so-called “freibergite”,
596 and may correspond potentially to a new mineral species: Ag > Cu, with Fe and Zn at the M(1) site.

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

601 Rozhdestvenskaya et al. (1993) and Welch et al. (2018) demonstrated that freibergite has
602 homeotypic relations with the other members of the tetrahedrite group, with the occurrence of the
603 (Ag₆)⁴⁺ cluster replacing the S(2)-centered Ag₆ octahedron (Fig. 3), according to the substitution
604 mechanism $6^{M(2)}\text{Ag}^+ + {}^{S(2)}\text{S}^{2-} = {}^{M(2)}(\text{Ag}_6)^{4+} + {}^{S(2)}\square$. These data are in agreement with EXAFS
605 analysis performed by Charnock et al. (1988) on a sample containing *ca.* 31 wt% Ag. They showed
606 the occurrence of a first shell of S atoms at 2.55 Å and a second shell, interpreted as due to Sb
607 atoms (but likely due to Ag atoms), at 2.75 Å. In addition, the number of S atoms coordinating Ag
608 is 1.8, to be compared to 2.8 in a sample poor in Ag, in agreement with the Ag-cluster model.

609 Consequently, freibergite and argentotetrahedrite are two different mineral species, forming
610 an anion-omission homeotypic series, with the latter being a sulfide and the former a sulfide-alloy
611 compound or a subsulfide (see Moëlo et al. 2008). However, the current S determination by routine
612 EPMA seems to be usually insufficient to reliably quantify the number of vacancies at the S(2) site
613 and thus the presence of (Ag₆)⁴⁺ clusters. Specific structural information on the M(2) and S(2) sites
614 is therefore required to identify these two mineral species.

615 Taking into account the widespread use of the term freibergite, it should be used to indicate
616 the members of the anion-omission homeotypic series Ag₆(Cu₄Me₂)Sb₄S_{13-x}, with end-member
617 compositions corresponding to *x* = 0 [argentotetrahedrite-(*Me*), Ag₆(Cu₄Me₂)Sb₄S₁₃] and *x* = 1

618 [kenoargentotetrahedrite-(*Me*), $\text{Ag}_6(\text{Cu}_4\text{Me}_2)\text{Sb}_4\text{S}_{12}$]. The use of the historical name “freibergite” as
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 $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13-x}$;
622 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) $3 < \text{Ag} < 8 \text{ apfu}$, $0.5 < \text{S}^{(2)} < 1.0$ = argentotetrahedrite;
627 ii) $3 < \text{Ag} < 8 \text{ apfu}$, $0.0 < \text{S}^{(2)} < 0.5$ = kenoargentotetrahedrite;
628 iii) $8 < \text{Ag} < 10 \text{ apfu}$, $0.5 < \text{S}^{(2)} < 1.0$ = 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 $\Sigma \text{Me} = 12 \text{ apfu}$, is:
639 $(\text{Ag}_{5.51}\text{Cu}_{4.52})_{\Sigma 10.03}(\text{Fe}_{1.68}\text{Zn}_{0.29})_{\Sigma 1.97}(\text{Sb}_{4.09}\text{As}_{0.01})_{\Sigma 4.10}\text{S}_{12.03}$;

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

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

644 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., $\text{Te} > \text{Sb}$
649 and $\text{Te} > \text{As}$ and $\text{Te} > \text{Bi}$. 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

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 “stibiofieldite” 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 $0 < \text{Te (apfu)} < 1$;
686 ii) new names, with $1 < \text{Te (apfu)} < 3$. Two different names should be applied, taking into
687 account the dominant trivalent constituent;
688 iii) goldfieldite, with $3 < \text{Te (apfu)} < 4$.

689 Natural occurrences of goldfieldite up to 3.77 Te *apfu* and phases corresponding to the end-
690 member formulae $\text{Cu}_6\text{Cu}_6(\text{As}_2\text{Te}_2)\text{S}_{13}$ and $\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$ are known in the literature
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 $\text{Bi} > \text{Sb}$ and Bi
700 $> \text{As}$ 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), $\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, is renamed after “argentotennantite”. Type
712 locality is the Kvarstoviyе Gorki deposit, Aksu, Stepnyak, Enbekshilder, Akmola (Kazakhstan).
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), $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$, 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), $\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{12}\square$, 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), $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{Se}_{13}$, 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 $(\text{Cu}_4\square_2)\text{Cu}_6\text{Te}_4\text{S}_{13}$. 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), $\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{Se}_{13}$, 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).

750

751 *4.5.7 Rozhdestvenskayaite-(Zn)*

752 Rozhdestvenskayaite-(Zn), $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, is renamed after “rozhdestvenskayaite”. Type
753 locality is the Moctezuma mine, Moctezuma, Sonora (Mexico). Type material is kept in the Natural
754 History Museum (London, U.K.), under catalogue number BM2016,120. Reference: Welch et al.
755 (2018).

756

757 *4.5.8 Redefinition of tennantite and tetrahedrite*

758 Since the two grandfathered minerals tennantite and tetrahedrite have been historically known
759 with both Zn- or Fe-dominance as the C-constituents, these two species are split into the pairs
760 tetrahedrite-(Fe) and tetrahedrite-(Zn), and tennantite-(Fe) and tennantite-(Zn). Their end-member
761 compositions are $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$, $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, $\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$, and
762 $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, respectively. Their type localities and type materials are the following.

763 a) Tennantite-(Fe) corresponds to the species described by W. Phillips (1819) and R. Phillips
764 (1819) from Cornwall (England, UK). No type material is known.

765 b) Tennantite-(Zn) has been known since the mid-XIX Century, e.g., Plattner (1846)
766 described zincian tennantite under the name *Kupferblende* from Freiberg, Saxony (Germany). Nine
767 years later, Des Cloizeaux (1855) described zincian tennantite from Lengenbach, Binn Valley
768 (Switzerland), under the name “*binnite*”. Since a sample of “*binnite*” was used by Wuensch et al.
769 (1966) for the refinement of the crystal structure of tennantite-(Zn) [the Zn/(Zn+Fe) atomic ratio is
770 0.63], the type locality of tennantite-(Zn) can be considered to be Lengenbach, Binn Valley
771 (Switzerland). Type material is the specimen L2120 from the collection of the Mineralogical
772 Institute of the University of Bern (Switzerland).

773 c) Tetrahedrite-(Fe): the first ferroan tetrahedrite is likely “*coppite*” (Bechi, 1863). It
774 corresponds to tetrahedrite-(Fe). Carrozzini et al. (1991) reexamined tetrahedrite from the Frigido
775 mine, Apuan Alps, Tuscany (Italy) using samples from the University of Pisa and from the Pelloux
776 collection. Type material can be considered the specimen 9964 of the Pelloux collection kept in the
777 mineralogical collections of the Geomineralogical Department of the Bari University, Bari (Italy)
778 and the specimen #7936 belonging to the mineral collections of the Museo di Storia Naturale, Pisa
779 University, Pisa (Italy).

780 d) Tetrahedrite-(Zn): Charlat and Lévy (1974, 1975, 1976) characterized samples of
781 tetrahedrite (samples No. M11 and M12) from Horhausen, Westernwald, Rhineland (Germany).
782 These samples have chemical formulae $\text{Cu}_{10.08}\text{Zn}_{1.74}\text{Fe}_{0.18}\text{Sb}_{3.97}\text{As}_{0.09}\text{S}_{13.4}$ (M11) and

24

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783 $\text{Cu}_{10.06}\text{Ag}_{0.06}\text{Zn}_{1.62}\text{Fe}_{0.27}\text{Sb}_{3.90}\text{As}_{0.06}\text{S}_{12.7}$ (M2), unit-cell parameter $a = 10.383(2)$ Å for both samples,
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; Gołębiewska 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

816 conditions during processes of ore formation (e.g., Sack and Loucks 1985; Sack and Ebel 1993;
817 Förster and Rhede 2004; Staude et al. 2010; Catchpole et al. 2012; Gołębiowska et al. 2012;
818 Plotinskaya et al. 2015; Repstock et al. 2016). Last but not least, tetrahedrite group minerals attract
819 interest from the perspective of minerals processing and geometallurgy, as potential, often
820 significant, hosts for both unwanted elements (particularly As, but also Cd and Hg) as well as
821 potential by-products such as Ag and even Sb, Au or Te.

822 Consequently, this new nomenclature system, allowing the full description of the chemical
823 variability of the tetrahedrite group minerals, would be able to convey important chemical
824 information not only to geoscientists (crystallographers, mineralogists, petrologists, ore geologists,
825 and so on) but also to industry professionals as well.

826

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835

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- 1172

1173 **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

1178 **Figure captions**

1179 **Fig. 1** – The cation and anion sites occurring in tetrahedrite group minerals (a) and the three-
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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 Gamyranin (1994); [15, 16] Welch et al. (2018).

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

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

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

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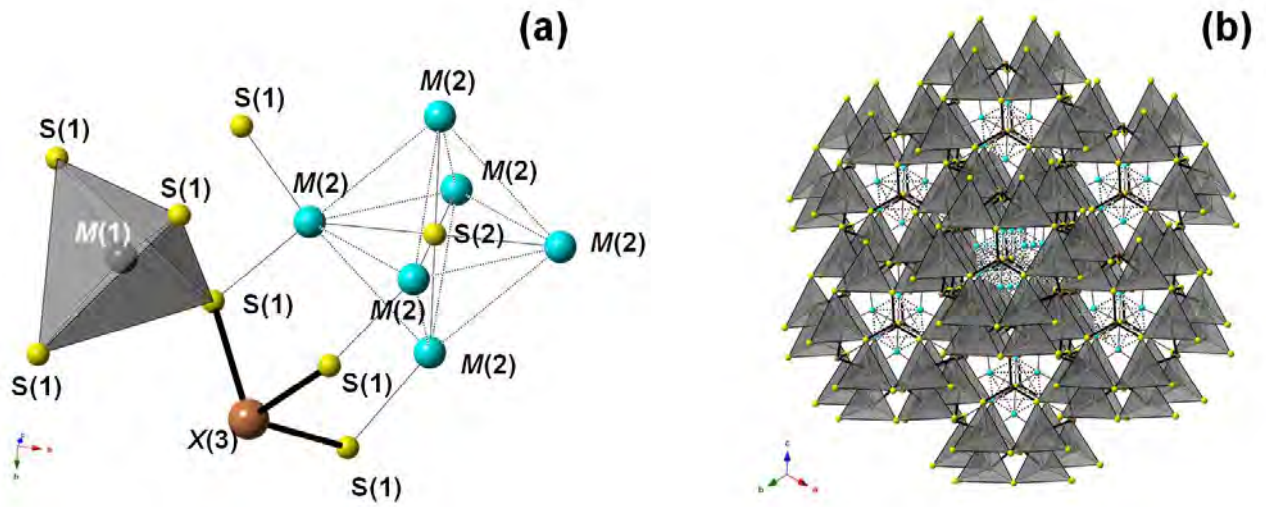
1200 **Table 2** – Nomenclature and classification of the tetrahedrite group minerals.

Tetrahedrite group			
<u>Tetrahedrite series</u>		<u>Tennantite series</u>	
Tetrahedrite-(Fe)	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Fe)	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$
Tetrahedrite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$	Tennantite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$
<i>Tetrahedrite-(Cd)</i>	$\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$	<i>Tennantite-(Cu)</i>	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{As}_4\text{S}_{13}$
<i>Tetrahedrite-(Cu)</i>	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{Sb}_4\text{S}_{13}$	<i>Tennantite-(Hg)</i>	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{As}_4\text{S}_{13}$
<i>Tetrahedrite-(Hg)</i>	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$	<i>Tennantite-(Mn)</i>	$\text{Cu}_6(\text{Cu}_4\text{Mn}_2)\text{As}_4\text{S}_{13}$
<i>Tetrahedrite-(Mn)</i>	$\text{Cu}_6(\text{Cu}_4\text{Mn}_2)\text{Sb}_4\text{S}_{13}$		
<u>Freibergite series</u>		<u>Arsenofreibergite series</u>	
Argentotetrahedrite-(Fe)	$\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$	Argentotennantite-(Zn)	$\text{Ag}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$
Kenoargentotetrahedrite-(Fe)	$\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{S}_{12}\square$	<i>Argentotennantite-(Fe)</i>	$\text{Ag}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{S}_{13}$
<i>Argentotetrahedrite-(Cd)</i>	$\text{Ag}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{S}_{13}$		
<i>Argentotetrahedrite-(Hg)</i>	$\text{Ag}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$		
<u>Hakite series</u>		<u>Giraudite series</u>	
Hakite-(Hg)	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{Sb}_4\text{Se}_{13}$	Giraudite-(Zn)	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{As}_4\text{Se}_{13}$
<i>Hakite-(Cd)</i>	$\text{Cu}_6(\text{Cu}_4\text{Cd}_2)\text{Sb}_4\text{Se}_{13}$	<i>Giraudite-(Cu)</i>	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{As}_4\text{Se}_{13}$
<i>Hakite-(Cu)</i>	$\text{Cu}_6(\text{Cu}_4\text{Cu}_2)\text{Sb}_4\text{Se}_{13}$	<i>Giraudite-(Fe)</i>	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{As}_4\text{Se}_{13}$
<i>Hakite-(Fe)</i>	$\text{Cu}_6(\text{Cu}_4\text{Fe}_2)\text{Sb}_4\text{Se}_{13}$	<i>Giraudite-(Hg)</i>	$\text{Cu}_6(\text{Cu}_4\text{Hg}_2)\text{As}_4\text{Se}_{13}$
<i>Hakite-(Zn)</i>	$\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{Se}_{13}$		
<u>Rozhdestvenskayaite series</u>		<u>Goldfieldite series</u>	
Rozhdestvenskayaite-(Zn)	$\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$	Goldfieldite	$(\text{Cu}_4\square_2)\text{Cu}_6\text{Te}_4\text{S}_{13}$
<i>Rozhdestvenskayaite-(Fe)</i>	$\text{Ag}_6(\text{Ag}_4\text{Fe}_2)\text{Sb}_4\text{S}_{13}$	<i>“Stibiogoldfieldite”</i>	$\text{Cu}_6\text{Cu}_6(\text{Sb}_2\text{Te}_2)\text{S}_{13}$
<i>Rozhdestvenskayaite-(Hg)</i>	$\text{Ag}_6(\text{Ag}_4\text{Hg}_2)\text{Sb}_4\text{S}_{13}$	<i>“Arsenogoldfieldite”</i>	$\text{Cu}_6\text{Cu}_6(\text{As}_2\text{Te}_2)\text{S}_{13}$

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

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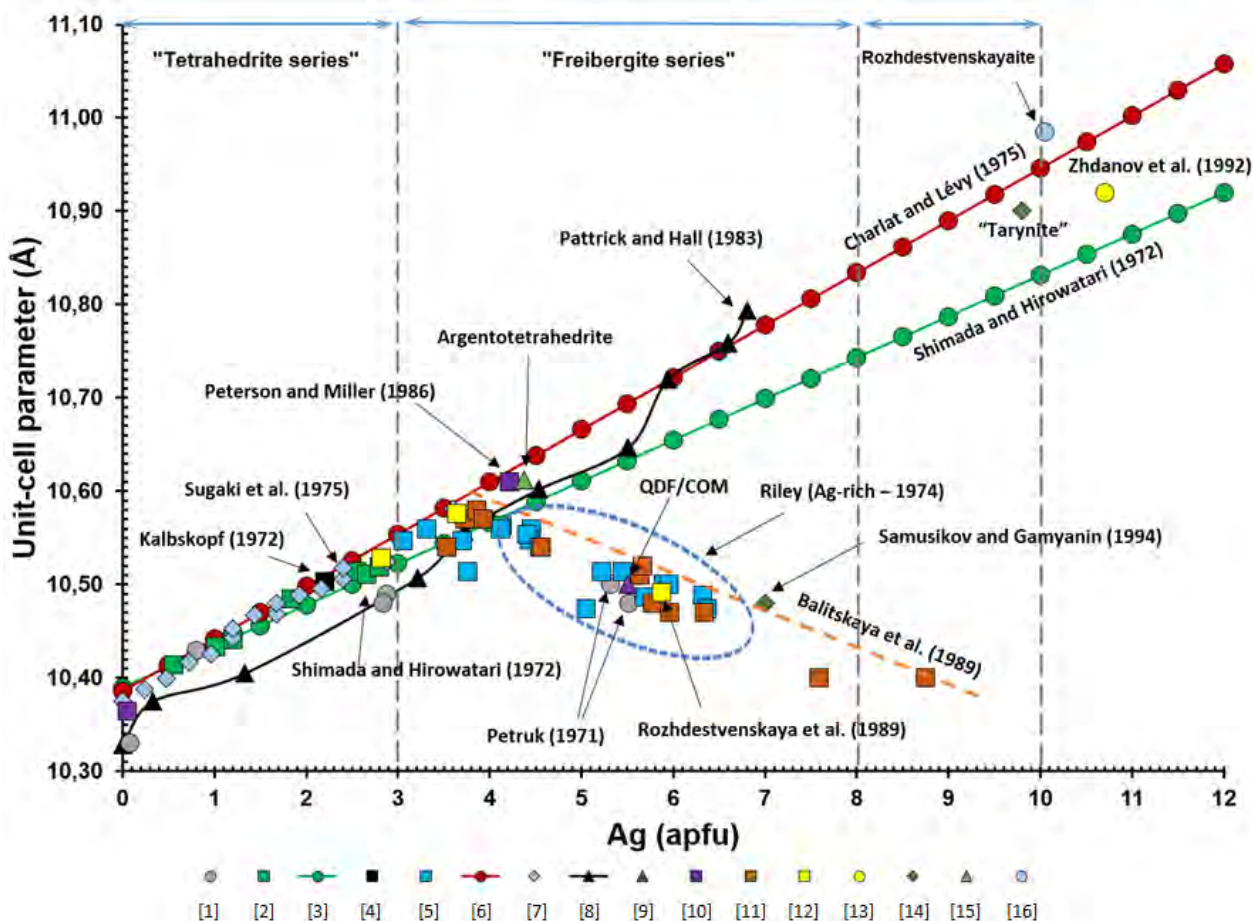
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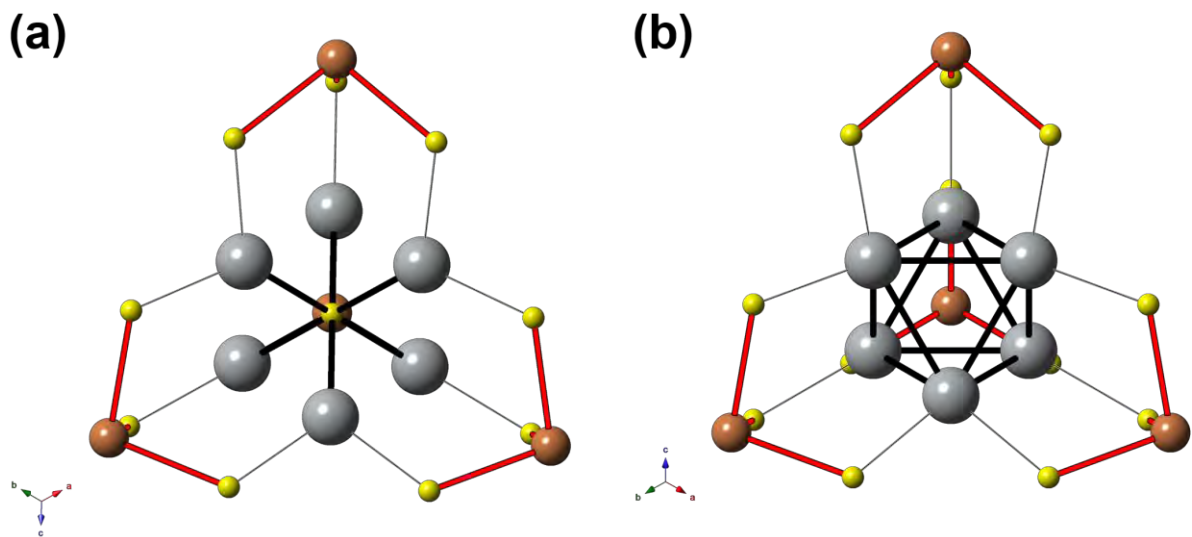
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 1212 et al. (1975); [8] Patrick and Hall (1983); [9] Criddle and Stanley (1986); [10] Peterson and Miller
 1213 (1986); [11] Balitskaya et al. (1989); [12] Rozhdestvenskaya et al. (1989); [13] Zhdanov et al.
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