Tennantite-(Cu), Cu$_{12}$As$_4$S$_{13}$, from Layo, Arequipa Department, Peru: a new addition to the tetrahedrite-group minerals

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Abstract

Tennantite-(Cu), Cu$_{12}$As$_4$S$_{13}$, was approved as a new mineral species from the Layo epithermal deposit, Castilla Province, Arequipa Department, Peru, where it occurs as black metallic anhedral grains, up to 0.1 mm across, replacing enargite and associated with chalcopyrite and vinciennite. In reflected light, tennantite-(Cu) is isotropic, grey with a bluish shade. Reflectance data for the four COM wavelengths in air are $\lambda$(nm): 470: 29.1; 546: 28.4; 589: 27.4; and 650: 25.0. Electron microprobe analysis for holotype material gave (in wt. % – average of 10 spot analyses): Cu 49.32(27), Fe 2.20(12), Zn 0.09(2), Sn 0.03(5), As 19.45(43), Sb 1.94(10), Te 0.02(5), S 27.75(43), total 100.80(20). On the basis of (As + Sb + Te) = 4 atoms per formula unit (apfu), the empirical formula of tennantite-(Cu) is (Cu$_{11.27}$Fe$_{0.57}$Zn$_{0.02}$)$_{2}$S$_{27.75}$(As$_{3.77}$Sb$_{0.23}$). Tennantite-(Cu) is cubic, F$\overline{3}$m, with unit-cell parameters $a = 10.1710(10)$ Å, $V = 1052.21(2)$ Å$^3$ and $Z = 2$. Its crystal structure was refined by single-crystal X-ray diffraction data to a final $R = 0.0178$ on the basis of 263 unique reflections with $F_o > 4o(F_o)$ and 24 refined parameters. Tennantite-(Cu) is isotypic with other tetrahedrite-group minerals. Previous findings of tennantite-(Cu) are reported and some nomenclature issues, related to the Fe and Cu oxidation states, are discussed. At the Layo epithermal deposit, tennantite-(Cu) is the result of the replacement of enargite under decreasing $f_S$ conditions.

Keywords: tennantite-(Cu), new mineral, sulfosalt, copper, arsenic, crystal structure, Layo, Peru

Introduction

Tetrahedrite-group minerals are characterised by the general structural formula $M^{(2)}A_6M^{(1)}(B_4C_2)X^{(3)}Y^{s(1)}Z^{s(2)}$, where the capital letters indicate several chemical constituents. Among the different species, the most common belongs to the tetrahedrite and tennantite series and are characterised by $A = Cu^+$, $B = Sb^{3+}$ or $As^{3+}$, and $Y = S^{2-}$. Different C constituents, usually represented by divalent transition elements, identify the species belonging to these series (Biagioni et al., 2020).

‘Tennantite’ was the first name of a mineral belonging to the tetrahedrite group to be introduced by the brothers Richard and William Phillips (R. Phillips, 1819; W. Phillips, 1819) and it honours the English chemist Smithson Tennant (1761–1815). The mineral studied, from Cornwall, England, was Fe-rich. Later, ‘zinccian tennantite’ was reported from some localities (e.g. Freiberg, Saxony, Germany – Plattner, 1846; Lengenbach, Binn Valley, Switzerland – Des Cloizeaux, 1855; Miedzianka, Świętokrzyskie Voivodeship, Poland – Morozewicz, 1926). Biagioni et al. (2020) renamed these species as tennantite-(Fe) and tennantite-(Zn).

Iron and Zn are the most common divalent elements occurring in tennantite-series minerals; moreover, since the publication of the nomenclature of tetrahedrite-group minerals (Biagioni et al., 2020), three other species belonging to the tennantite series have been approved by the International Mineralogical Association – Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC), i.e. tennantite-(Hg) (Biagioni et al., 2021), tennantite-(Ni) (Wang et al., 2021), and tennantite-(Cd) (Biagioni et al., 2022). Other potential end-member compositions are known in the literature. Among them, compositions corresponding to ideal Cu$_{12}$As$_4$S$_{13}$ have been reported, for instance, from Canada, France and Peru (Johan and Le Bel, 1980; Thouvenin, 1983; Cesbron et al., 1985; Marcoux et al., 1994).

The re-examination of a specimen from the Peruvian epithermal deposit of Layo (Marcoux et al., 1994) allowed the description of the new mineral species tennantite-(Cu). The new mineral and its name (symbol Tnt-Cu) have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC), under the voting number 2020-096. Part of holotype material of tennantite-(Cu) is deposited in the collections of the Department of Mineralogy and Petrology, National Museum in Prague, Cirkusová 1740, 193 00 Praha 9, Czech Republic under the catalogue number P1P 74/2020, in the collections of the Museo de Storia Naturale dell’Università di Pisa, Via Roma 79, 56126 Pisa, Italy.

At the Layo epithermal deposit, tennantite-(Cu) is the result of the replacement of enargite under decreasing $f_S$ conditions. Previous findings of tennantite-(Cu) are reported and some nomenclature issues, related to the Fe and Cu oxidation states, are discussed. The crystal structure was refined by single-crystal X-ray diffraction data to a final $R = 0.0178$ on the basis of 263 unique reflections with $F_o > 4o(F_o)$ and 24 refined parameters. Tennantite-(Cu) is isotypic with other tetrahedrite-group minerals.

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Occurrence and physical properties
Tennantite-(Cu), described initially as ‘Cu-excess tennantite’ by Marcoux et al. (1994), was found in the Layo epithermal deposit (15°11′16″S, 72°14′30″W), Castilla Province, Arequipa Department, Peru (Fig. 1). The Layo vein system is formed by anastomosing veins hosted in Miocene–Pliocene volcanic rocks belonging to the Tazaca Group. This rock sequence is formed by two distinct successions: the first one is a 300 m thick sequence of ignimbritic lava flows and pyroclastic tuffs, dacitic to rhyolitic in compositions (Pisaca Formation), whereas the second one, known as the Jullujia Formation, is composed by discordant andesitic lava flows and domes, as well as by pyroclastic rocks. In the Layo area, the volcanic rocks are affected by a pervasive propylitic alteration. Around ore vein systems, propylitised rocks occur as relics within hydrothermally altered silicic-argillic zones. Marcoux et al. (1994) gave further details about the geological background of the Layo epithermal deposit.

Tennantite-(Cu) was collected in the eastern zone of the ore field, in the so-called Vetas 7 and 8. In these veins, a breccia, formed by silicified and alunited angular rock clasts, is cemented by an ore assemblage composed of complex Cu–As–Fe–Sn sulfides, showing banded and cockade textures related to the rhythmic alternation of pyrite and Cu–As–Sn sulfides, i.e. enargite, tennantite-(Cu), chalcocyprite and viniennite (Marcoux et al., 1994). The mineralogy is dominated by early pyrite succeeded by a late complex Cu–As–Sn association where tennantite-(Cu) is the prominent sulfide (Fig. 2). Tennantite-(Cu) is associated with enargite, chalcocyprite and viniennite, that often form ameboid oriented patches up to 80 μm in size, sometimes developed from relics of enargite. Secondary minerals also formed, such as bornite, covellite and digenite, at the expense of chalcocyprite, and scarce luzonite at the expense of enargite.

Tennantite-(Cu) is black in colour, with a black streak and metallic lustre. Mohs hardness was not measured, owing to the small size of the grains studied and their admixture with other sulfides, density was not measured; on the basis of empirical formula and the single-crystal X-ray diffraction data, the calculated density is 4.656 g cm⁻³. Tennantite-(Cu) is brittle, with a conchoidal fracture and an indistinct cleavage. Due to the small size of the grains studied and their admixture with other sulfides, density was not measured; on the basis of empirical formula and the single-crystal X-ray diffraction data, the calculated density is 4.656 g cm⁻³.

In reflected light, tennantite-(Cu) is isotropic. It is grey, with a bluish shade (Fig. 2). Internal reflections were not observed. Reflectance values measured in air on the holotype sample using a spectrophotometer MSP400 Tidas at Leica microscope, with a 50× objective, are given in Table 1 and shown in Fig. 3, where the reflectance curve for tennantite-(Cu) is compared with published data for other tetrahedrite-group minerals.

Chemical data
Quantitative chemical analyses were carried out using a Cameca SX 100 electron microprobe (National Museum of Prague, Czech Republic) and the following experimental conditions: wavelength dispersive spectroscopy mode, accelerating voltage = 25 kV and beam current = 20 nA, beam diameter = 1 μm. Standards (element, emission line) were: chalcopyrite (CuKα and SKo), pyrite (FeKα), ZnS (ZnKo), NiAs (AsLβ), Sn (SnLα), Sb2S3 (SbLα) and PbTe (TeMo). The contents of other sought elements with Z > 8 (Ag, Au, Bi, Cd, Co, Ga, Ge, Hg, In, Mn, Ni, Pb, Se and Tl) were below detection limits. Matrix correction by the PAP procedure (Pouchou and Pichoir, 1985) was applied to the data. Electron back-scattered images showed that tennantite-(Cu) is slightly zoned, with a domain richer in Sb, 30–40 μm in size, located on the margin of the grain. Results are given in Table 2.

X-ray crystallography
Single-crystal X-ray diffraction intensity data were collected on an anhedral grain of tennantite-(Cu), 60 μm × 40 μm × 30 μm in size, using a Bruker Apex II diffractometer (50 kV and 30 mA) equipped with a Photon II CCD detector and graphite-monochromatised MoKα radiation (Dipartimento di Scienze della Terra, Università di Pisa, Italy). The detector-to-crystal distance was set at 50 mm. Data were collected using g scan mode in 0.5° slices, with an exposure time of 30 s per frame, and they were corrected for Lorentz, polarisation, absorption and background effects using the software package Apex3 (Bruker AXS Inc., 2016). The refined unit-cell parameters are a = 10.1710(10) Å, V = 1052.2(2) Å³; and space group I4/m. The crystal structure of tennantite-(Cu) was refined using Shelx-2018 (Sheldrick, 2015) starting from the structural model of Johnson and Burnham (1985). The following neutral scattering curves, taken from the International Tables for Crystallography (Wilson, 1992) were used initially: Cu vs □ at M(2), Cu vs Fe at M(1), As vs Sb at X(3), S at S(1) and S(2) sites.

Several cycles of isotropic refinement converged to R₁ = 0.115, confirming the correctness of the structural model. The modelling of the racemic twin suggested that the structure had to be inverted.
Anisotropic refinement for cations only converged to $R_1 = 0.0280$. The relatively large $U_{eq}$ value of the $M(2)$ site suggested its split nature, in agreement with previous authors (Andreasen et al., 2008; Welch et al., 2018). After the addition of the split position, found in the difference-Fourier map, the $R_1$ value was lowered to 0.0210. The site occupancy factors (s.o.f.) at the two split positions $M(2a)$ and $M(2b)$ were constrained to be 1, as no Cu excess at the $M(2)$ site was detected. After several cycles of anisotropic refinement for all the atoms, the $R_1$ converged to 0.0178 for 263 unique reflections with $F_o > 4\sigma(F_o)$ and 24 refined parameters. Details of the data collection and crystal structure refinement are reported in Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 4, whereas Table 5 reports selected bond distances and Table 6 the weighted bond-valence sums (BVS) calculated according to the bond parameters of Brese and O’Keeffe (1991). The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Powder X-ray diffraction data were not collected, owing to the small size of the available grains and admixture with other phases (in particular, vinciennite). Table 7 reports the calculated X-ray powder diffraction pattern.

### Results and discussions

#### Chemical formula

As discussed in previous papers (e.g. Sejkora et al., 2021), there are different approaches to recalculate the chemical formulae of tetrahedrite-group minerals. The two better ones normalise the number of atoms on the basis of $\Sigma Me = 16$ atoms per formula unit (apfu) or on the basis of $(As + Sb + Te + Bi) = 4$ apfu. The former approach assumes that no vacancies occur at the $M(2)$, $M(1)$, and $X(3)$ sites, whereas the latter is based mainly on the results discussed by Johnson *et al.* (1986) who revealed that negligible variations in the ideal number of $X(3)$ atoms usually occur.

The first approach gives the chemical formula $Cu_{11.36(10)}Fe_{0.58(3)}Zn_{0.02(1)}(As_{3.80(7)}Sb_{0.23(1)})_2(As_{12.67(24)}S_{13.51})$, whereas the other normalisation strategy corresponds to the formula $Cu_{11.27(31)}Fe_{0.57(3)}Zn_{0.02(1)}(As_{3.77(1)})_2(As_{12.57(47)}S_{13.51})$. These formulae are in agreement with previous results of Marcoux *et al.* (1994). Their average formula, recalculated on the basis of $\Sigma Me = 16$ apfu, taking into account the average formula given in their Table 3, is $Cu_{1.37}Fe_{0.66}Zn_{0.02}(As_{3.74}Sb_{0.21})_2S_{13.51}$. Copper, Fe and Zn contents agree with those found in this work, as well as the As/(As+Sb) atomic ratios.

The simplified formula of tennantite-(Cu) is $Cu_6Cu_4(Cu,Fe,Zn)_{3.5}(As,\text{Sb})_2S_{13}$. Corresponding to the end-member formula $Cu_6Cu_4Cu_{1.5}^2As_4S_{13}$. It corresponds to (in wt.%) Cu 51.56, As 20.26, S 28.18, total 100.00.

The Sb-enriched domain corresponds to the chemical formula (based on $\Sigma Me = 16$ apfu) $Cu_{11.35(3)}Fe_{0.65(1)}Zn_{0.03(1)}(As_{2.78(4)}Sb_{1.02(2)})_2(\text{Te}0.08(1))_2S_{12.85(8)}$. This domain is characterised by a distinctly higher Sb content [Sb/(As+Sb+Te) atomic ratio passing from 0.06 to 0.28] and detectable Te content.

#### Crystal structure description

Tennantite-(Cu) is isotypic with the other members of the tetrahedrite group. Its crystal structure (Fig. 4) can be described as a framework of corner-sharing $M(1)S(1)$ tetrahedra with cages hosting $X(3)S(1)_3$ trigonal pyramids around $S(2)M(2)_6$ octahedra (e.g. Johnson *et al.*, 1988). The tetrahedrally coordinated $M(1)$ site is a mixed (Cu,Fe) site, with only minor amounts of Zn. The refined site scattering is 171.48 electrons per formula unit (epfu), to be compared with the value calculated from the site population proposed on the
basis of electron microprobe data, $M^{(1)}(Cu_{5.40}Fe_{0.58}Zn_{0.02})$, i.e. 172.26 epfu. Average bond distance is 2.3075 Å. The BVS at the $M(1)$ site, 1.36 valence units (vu), agrees with a site with Cu+ mixed with higher valency cations.

The $M(2)$ site is split into two sub-positions, $M(2a)$ and $M(2b)$, separated by 0.60 Å, whereas the distance between two neighbouring $M(2b)$ positions is 1.20 Å. These distances are shorter than those observed in Cu-rich unsubstituted tennantite described by Makovicky et al. (2005), having $M(2a)$–$M(2b)$ and $M(2b)$–$M(2b)$ distances of 1.08 and 2.00 Å, respectively. The $M(2a)$ position has a triangular planar coordination, whereas $M(2b)$ has a flat trigonal pyramidal one. This feature agrees with previous studies (e.g. Andreasen et al., 2008; Welch et al., 2018).

Average bond distances are 2.230 and 2.307 Å for $M(2a)$ and $M(2b)$ positions, respectively. Such values can be compared with those reported in Cu-pure and unsplit $M(2)$ sites occurring in tetratetrite and tennantite studied by Wuensch (1964) and Wuensch et al. (1966), respectively, i.e. 2.259 and 2.240 Å, respectively, as well as with those reported by Makovicky et al. (2005), i.e. 2.217 Å for Cu2A and 2.467 Å for Cu2B. The Cu2B of Makovicky et al. (2005) is also close to the As site, 2.41 Å, whereas the $M(2b)$–X(3) distance is 2.835 Å in the sample from Layo. In this latter sample, copper was the only cation at the $M(2)$ site, in agreement with electron microprobe data. The larger size of the $M(2b)$ position is probably due to its average nature. During the refinement of tennantite-(Cu) from Layo, an unconstrained refinement of the s.o.f. at the $M(2a)$ and $M(2b)$ sites was performed, resulting in $M(2a) = Cu_{0.650(19)}$ and $M(2b) = Cu_{0.162(9)}$, not suggesting any Cu excess. For this reason, as described above, the sum of the s.o.f. at $M(2a)$ and $M(2b)$ was constrained to be 1. On the contrary, Makovicky et al. (2005) found a slight Cu excess, with a surplus of ca. 10%. The BVS at the $M(2)$ site [i.e. $M(2a) + 2 \times M(2b)$] (Table 6) is 1.04 valence units (vu), in agreement with the presence of monovalent cations.

The splitting of the $M(2)$ position is variable in the tetratetrite–tennantite sub-group. In Fe-bearing compounds synthesised at 450°C (Fe between ~0.3 and 2 epfu), Andreasen et al. (2008) only found a split (24g) site. A single-crystal synchrotron X-ray diffraction study of synthetic Cu12Sb4S13 and Cu12As4S13 was performed recently by Hathwar et al. (2019) from room temperature down to 70 K. Whereas in synthetic Cu12Sb4S13 there is only a single (12e) site (but with a high atomic displacement perpendicular to the triangle) the use of high resolution data allowed the resolution of the $M(2)$ site of synthetic Cu12As4S13 into six (24g) sub-positions.

The X(3) site shows an average bond distance of 2.266 Å. Taking into account the electron microprobe data, the site occupancy (As0.95Sb0.05) can be proposed. It corresponds to a mean atomic number of 33.90 electrons, to be compared with the refined mean atomic number of 34.03 electrons. Assuming idealised X–S distances of 2.26 and 2.45 Å for As3+ and Sb3+, respectively (calculated according to the bond parameters of Brese and O’Keeffe, 1991), an average X(3)–S(1) distance of 2.270 Å can be expected. The BVS is 3.06 vu.

The S(1) site is four-fold coordinated and is bonded to two $M(1)$, one $M(2)$ [i.e. $M(2a)$ or one of the two mutually-exclusive $M(2b)$] and one X(3). Its BVS is 2.04 vu. S(2) is octahedrally coordinated by atoms hosted at $M(2)$ sites, with a BVS of 2.16 vu. Both S sites were found fully occupied.

Coupling the results of the crystal structure refinement and the electron microprobe analysis, the structural formula of holotype tennantite-(Cu) can be written as $M^{(2)}Cu_{6.00}M^{(1)}(Cu_{5.40}Fe_{0.58}Zn_{0.02})X^{(3)}(As_{0.95}Sb_{0.05})_{4.13}$.

**Relation between unit-cell parameter and chemical composition**

Unit-cell parameter of tennantite-(Cu) from Layo (i.e. $a = 10.171$ Å) agrees with that of synthetic sample No. 2052 of Makovicky et al. (2003), having composition Cu11.23Fe0.57As5.98Sb13.00 and unit-cell parameter $a = 10.174(8)$ Å. The 'Cu-rich unsubstituted tennantite' of Makovicky et al. (2005) has $a = 10.1756(9)$ Å. Applying the relationships between chemistry and unit-cell parameter proposed by Johnson et al. (1987), to the sample from Layo one obtains a value of 10.22 Å, a better fit is obtained using the relations proposed by Charlat and Lévy (1975), i.e. 10.19 Å.
Several recent studies on synthetic Fe-free Cu$_{12}$As$_4$S$_{13}$ gave the following unit-cell parameter $a = 10.163(7)$ Å (Levinsky et al., 2019), with composition actually Cu$_{11.81}$As$_{4.19}$S$_{12.67}$, based on $\Sigma$Me = 16 apfu; $a = 10.157(2)$ Å at 293 K (Yaroslavzhev et al., 2021); and $a = 10.154(6)$ Å at 300 K (Hathwar et al., 2019).

### Comparison between tennantite-(Cu) and previous findings of Cu-rich tennantite

Natural members of the tennantite series are usually characterised by the formula Cu$_x$(Cu$_y$Me$_2$)$_2$As$_4$S$_{13}$, where Me is commonly Fe and Zn. However, synthetic Cu$_{12}$As$_4$S$_{13}$ has been synthesised, in some cases showing a Cu excess with respect to the ideal 12 apfu. For instance, Maske and Skinner (1971) studied the system Cu–As–S and found a compositional field Cu$_{12+x}$As$_4$S$_{13}$, with $0 < x < 1.72$ and $0 < y < 0.08$. Unit-cell variation from 10.168 to 10.222 Å was reported for compositions $\sim$Cu$_{12}$As$_4$S$_{13}$ and $\sim$Cu$_{13}$As$_4$S$_{13}$, respectively. Lind and Makovicky (1982) highlighted an analytical problem during electron microprobe analysis of synthetic tennantite-group phases; indeed, those compositions having Cu > 12 apfu gave the same analytical results as those having 12 Cu apfu. This effect was noted for both Sb- and As-members of this sulfosalts group.

In literature, the term ‘Cu-excess’ was first used by Marcoux et al. (1994) to indicate a Cu content higher than 10 apfu. According to the work of Lind and Makovicky (1982) and Makovicky et al. (2005), this term ought to be reserved to compounds with Cu over 12 apfu. Some of these Cu-rich tennantite-series minerals (Cu > 10 apfu) correspond to what is now classified as tennantite-(Cu), whereas others are simply Cu-rich varieties of tennantite-(Fe). For instance, sample M14 of Charlat and Lévy (1974), from Trevisane, Cornwall, England, having a chemical formula Cu$_{10.70}$Fe$_{1.27}$Zn$_{0.03}$As$_{3.97}$S$_{13.90}$ may be labelled as tennantite-(Fe), as its formula can be recast as Cu$_{11}$[Cu$_{4.27}$Cu$_{0.70}$Zn$_{0.03}$]As$_{3.97}$S$_{13.90}$. On the contrary, samples from Huaron, Peru (Thouvenin, 1983), Chizeuil, France (Cesbron et al., 1985) and Lormex, Canada (Johan and Le Bel, 1980) correspond to tennantite-(Cu); at the French locality, a potential tetrarhodite-(Cu) was also reported.

Other findings of tennantite-(Cu) were reported by Kouzmanov et al. (2004) from the Radka deposit, Bulgaria. The samples studied by these authors show Cu contents ranging from 10.88 to 11.26 apfu, Fe between 0.79 and 1.14 apfu, and Zn below the detection limit. The observed As/(As+Sb+Bi) atomic ratio is in the range 0.90–0.98. Ideally, samples from this locality correspond to the formula Cu$_{11}$Fe$_x$(As$_{1.8}$Sb$_{0.2}$)S$_{13}$.
Nomenclature issues in Cu-rich tennantite

Type of tennantite-(Cu) has a chemical composition close to Cu$_{11.4}$Fe$_{0.6}$(As$_{3.76}$Sb$_{0.24}$)S$_{13.42}$, with a formula Cu$_{11}$Fe$_{3+}$As$_4$S$_{13}$ (3.2). This chemical formula can be idealised to the end-member formula Cu$_{10}$Cu$_{2+}$As$_4$S$_{13}$, forming that formally divalent Cu$^{2+}$ is the most abundant C constituent. However, in agreement with the results of Mössbauer studies performed by Makovicky et al. (2003) on synthetic Fe-bearing tennantite, the most probable composition of the sample studied by Layo could be Cu$_{10}$Cu$_{2+}$As$_4$S$_{13}$ (4.1). Indeed, sample 2052 of Makovicky et al. (2003), with chemical formula Cu$_{11.32}$Fe$_{0.57}$As$_{3.9}$S$_{13}$ (similar to that of the natural Peruvian specimen), showed Fe$^{3+}$ as the dominant iron species. If so, applying the site-total-charge approach (Bosi et al., 2019), the end-member formula Cu$_{10}$Cu$_{2+}$As$_4$S$_{13}$ is achieved. This result is in agreement with the hypothesis of Marcoux et al. (1994) about the presence of Fe$^{3+}$ in the specimen from Layo, due to the high $f_{\text{Cu}}$.

It is worth noting that a virtually Fe-free or Fe-poor tennantite-(Cu) is reported by Repstock et al. (2015). Analyses 4 and 10 of these authors (Table 3) correspond (on the basis of $\Sigma ME = 16$ apfu) to Cu$_{10.95}$As$_{0.01}$Zn$_{0.05}$Fe$_{0.01}$As$_{5.00}$Sb$_{1.05}$Te$_{0.06}$, whereas analyses 7 and 8 have compositions Cu$_{11.18}$Zn$_{0.05}$Fe$_{0.06}$, Cu$_{11.14}$Zn$_{0.05}$Fe$_{0.00}$, Cu$_{11.18}$Zn$_{0.05}$Fe$_{0.06}$, and Cu$_{11.14}$Zn$_{0.05}$Fe$_{0.00}$, respectively. The two former analyses have a possible site population at M(1) corresponding to $\text{Cu}_{4.00}^+(\text{Cu}_{1.00}^0\text{Zn}_{0.88}\text{Fe}_{0.12})$, and the latter to $\text{Cu}_{4.00}^+(\text{Cu}_{1.00}^0\text{Zn}_{0.88}\text{Fe}_{0.12})$, with the C constituent represented by formally divalent Cu (Zn is the second most abundant C constituent). The remaining two analyses show Cu$^{2+}$ as the dominant C constituent, even considering Fe as Fe$^{3+}$: $\text{M}^{0.5+}\text{Cu}_{4.00}^0\text{Cu}_{10.00}^0\text{Cu}_{18.00}^0\text{Cu}_{18.00}^0\text{Zn}_{0.00}^0\text{Zn}_{0.00}^0\text{Fe}_{0.00}^0$, and $\text{M}^{0.5+}\text{Cu}_{4.00}^0\text{Cu}_{10.00}^0\text{Cu}_{18.00}^0\text{Cu}_{18.00}^0\text{Zn}_{0.00}^0\text{Zn}_{0.00}^0\text{Fe}_{0.00}^0$. The end-member formula Cu$_{10}$Cu$_{2+}$As$_4$S$_{13}$ can be applied to all these samples.

Thus, the solid solution from the Fe pole to the Cu pole would correspond ideally to the following sequence (ionic model): (i) Cu$_{10}$Fe$^{2+}$, (ii) Cu$_{10}$Fe$^{2+}$Fe$^{3+}$, (iii) Cu$_{11}$Fe$^{3+}$, (iv) Cu$_{11}$Fe$^{3+}$Cu$^{2+}$Fe$^{3+}$, (v) Cu$_{11}$Fe$^{3+}$Cu$^{2+}$Fe$^{3+}$, (vi) Cu$_{11}$Fe$^{3+}$Cu$^{2+}$Fe$^{3+}$Fe$^{3+}$. Compositions (1) to (3) correspond to the substitution rule $2\text{Fe}^{2+} \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+}$, and compositions (3) to (5) to $\text{Cu}^{2+} + \text{Fe}^{3+} \rightarrow 2\text{Cu}^{2+}$. This sequence, controlled by an increase of $f_{\text{Cu}}$, indicates that iron oxidation precludes the appearance of formally divalent copper. According to nomenclature rules, one ought to distinguish three species: (i) tennantite-(Fe$^{2+}$), from formula (1) up to formula (2), (ii) tennantite-(Fe$^{3+}$), from formula (2) up to formula (4), and (iii) tennantite-(Cu$^{2+}$), from formula (4) up to formula (5).

On this basis, composition of tennantite-(Cu) from the Layo epithermal deposit falls in the field of tennantite-(Fe$^{3+}$). Nevertheless, studies of natural and synthetic samples of tetrathedrite-(Cu) and tennantite-(Cu) using various physical methods revealed a very complex crystal chemistry, not completely understood up to now. After initial examinations in the 1970s, the first detailed 57Fe-Mössbauer studies were performed on Fe-bearing tetrathedrite in the 1990s (Charnock et al., 1989; Makovicky et al., 1990 and references herein) and completed by Nasonova et al. (2016) and Sobolev et al. (2017). Iron-bearing synthetic tennantite was studied by Makovicky et al. (2003). Though the first studies confirm major Fe$^{3+}$ towards the Fe pole, and major Fe$^{3+}$ towards the Cu pole, examination of tennantite indicates the presence of Fe$^{3+}$ down to 0.5 Fe apfu, as well as mixed valence Fe. Mixed valence iron seems to represent a substantial fraction of total iron at room T, owing to charge-transfer phenomena between Cu and Fe.
a content of 0.5 Fe apfu, Makovicky et al. (2003) estimated a formal valence ranging between +2.68 and +2.69 (+2.68 for sample 2052). The oxidation state of Cu was determined by Patrick et al. (1993) and Gainov et al. (2008) on natural tetrahedrite and tennantite, and by Di Benedetto et al. (2005) on synthetic Cu$_{12}$Sb$_4$S$_{13}$. These three studies revealed the presence of divalent Cu in all Cu-rich samples. Nevertheless, though Di Benedetto et al. (2005) proposed two Cu$^{2+}$ apfu, located on the Cu1 site, Patrick et al. (1993), confirmed by Gainov et al. (2008), indicates that Cu$^{2+}$ located on the Cu2 triangular site, is sometimes present for compositions excluding it according to the ionic model. Moreover, in normal conditions, pure Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_{12}$Sb$_4$S$_{13}$ are metallic (Lu and Morelli, 2013), which would correspond to partial replacement of Cu$^{2+}$ by Cu$^+$ and one ligand hole (i.e. mobile S electron).

It thus appears that in Cu-rich tetrahedrite/tennantite one may have coexistence of Fe$^{3+}$, Fe$^{2+}$, Cu$^{2+}$ and Cu$^+$ (with ligand hole). The distinction between these three species envisaged above on the basis of a simple ionic model is not pertinent, and it is more convenient, for nomenclature purposes, to consider only two species, tennantite-(Fe) and tennantite-(Cu). The sample from Layo can thus be classified as tennantite-(Cu), as Cu is more abundant than Fe as the C constituent.

A special case is represented by In-bearing tennantite-series minerals reported by Voudouris et al. (2022) from Pefka, Greece. These samples show up to 0.893 In apfu, with 11.049 Cu apfu, thus corresponding to the end-member Cu$_{6}$(Cu$_{5}$In$_{3}$$^{3+}$)As$_{4}$S$_{13}$. As no ambiguity in the oxidation state of In can be assumed, this phase should be regarded as different from tennantite-(Cu), and it may represent the new species ‘tennantite-(In)’.

**Genesis of tennantite-(Cu)**

The ore assemblages where tennantite-(Cu) occurs are usually composed of enargite, Cu$_3$As$_5$S$_4$, vinciennite, Cu$_5$Cu$_2$$^{2+}$Fe$_2$$^{2+}$Fe$_2$$^{3+}$SnAs$_5$S$_{16}$, mawsonite, Cu$_4$Fe$_2$$^{3+}$Sn$_8$, and chalcopyrite, Cu$^+$$^{3+}$S$_2$ (e.g. Chizeuil, France – Cesbron et al., 1985; Layo, Peru – Marcoux et al., 1994; Radka, Bulgaria – Kouzmanov et al., 2004); these assemblages are typical of high-sulfidation conditions. Tennantite-(Cu) usually replaces enargite, probably as a consequence of decreasing $f$$_S$ in the crystallisation environment, usually during the early stages of the evolution of epithermal systems. On the contrary, Makovicky et al. (2005) proposed that ‘Cu-excess tennantite-(Cu)’ from Catamarca, Argentina, was related to (Fe/Zn)-poor late-stage hydrothermal solutions. However, the samples show inclusions of luzonite, the low T-dimorph of enargite (Maske and Skinner, 1971), and watananbeite, ideally Cu$_4$(As,Sb)$_5$$^{2+}$S$_8$; thus, a genesis similar to those proposed for other occurrences cannot be discarded.

**Conclusion**

The description of tennantite-(Cu) adds further complexity to the tetrahedrite group, confirming on one side the structural plasticity of these chalcogenides, hosting several metals typical of hydrothermal settings, and on the other side their role in recording the crystallisation conditions of ore assemblages.

In addition to improving the knowledge of ore mineralogy, the description of this new phase gives further information about the crystal chemistry of tetrahedrite-group minerals, with possible technological implications, as revealed by several recent studies focusing on the thermoelectric properties of these compounds (e.g. Chetty et al., 2015; Levinsky et al., 2019).

**Supplementary material.** To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2022.26

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