

1 REVISION 3

2 Mcalpineite from the Gambatesa mine, Italy, and redefinition of the species

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12

### 13 **Abstract**

14 Mcalpineite has been found in the Gambatesa mine (eastern Liguria, Italy); it occurs in a  
15 quartz vein mainly as yellowish green earthy crusts consisting of poorly crystallized mcalpineite  
16 intergrown with an unidentified Cu-Te phase, as well as quite pure aggregates of well euhedral  
17 emerald green crystals (individually reaching up to 50 $\mu$ m), associated with black fragments of  
18 paratellurite (TeO<sub>2</sub>) and weissite (Cu<sub>2-x</sub>Te). The chemical formula of this rare mineral, found at the  
19 McAlpine mine (type-locality; California, U.S.A.) and at the Centennial Eureka mine (Utah,  
20 U.S.A., co-type locality), was originally given Cu<sub>3</sub>TeO<sub>6</sub>·H<sub>2</sub>O. X-ray powder diffraction and selected  
21 area electron diffraction data of mcalpineite are in good agreement with those of synthetic Cu<sub>3</sub>TeO<sub>6</sub>.  
22 In addition no evidence for structural OH group was detected by micro-Raman analysis carried out  
23 on samples from Gambatesa, Centennial Eureka and McAlpine (co-type sample) mines. Taking into  
24 account structural, topological and experimental evidence, the crystal structure and chemical  
25 composition of mcalpineite must be revised: the mineral crystallizes in the *Ia $\bar{3}$*  space group and the  
26 correct chemical formula is Cu<sub>3</sub>TeO<sub>6</sub>.

27

28 **Key-words:** mcalpineite, Gambatesa mine, crystal structure, TEM, XRPD

29 **1. Introduction**

30 Mcalpineite represents a very rare Cu-bearing tellurate mineral found at the type-locality,  
31 McAlpine mine, California, U.S.A.) and at the Centennial Eureka mine (Utah, U.S.A.; co-type  
32 locality) (Roberts et al. 1994). Mcalpineite was also recently found in a few other localities (Kampf  
33 et al. 2013a, and 2013b). Mcalpineite from the McAlpine mine occurs as emerald cryptocrystalline  
34 crusts on quartz whereas from the Eureka mine it occurs both as interstitial olive-green coatings and  
35 green-black cryptocrystalline nodules within drusy quartz (Roberts et al. 1994).

36 According to Roberts et al. (1994), this mineral crystallizes in the cubic system with a *P*-  
37 lattice (unknown S.G.) and its ideal formula may be referred to as  $\text{Cu}_3\text{TeO}_6 \cdot \text{H}_2\text{O}$ . X-ray analyses  
38 evidenced that the diffraction pattern of mcalpineite is consistent with that of synthetic  $\text{Cu}_3\text{TeO}_6$   
39 (*Ia*<sup>3</sup> S.G.), except for the presence of four medium to weak non-indexable diffraction lines. These  
40 authors suggested the presence of water on the basis of IR absorption spectra, showing O-H  
41 stretching and H-O-H bending bands centred at  $3320 \text{ cm}^{-1}$  and  $1600 \text{ cm}^{-1}$ , respectively. As a result,  
42 they concluded that the crystal structure hosts single  $\text{H}_2\text{O}$  group inside structural voids with a  
43 diameter of  $\sim 4 \text{ \AA}$ , causing a reduction of symmetry from an *I*- to a *P*-lattice.

44 Mcalpineite from the manganese Gambatesa mine (Val Graveglia, eastern Liguria, Italy) was  
45 found in association with paratellurite ( $\text{TeO}_2$ ) and weissite ( $\text{Cu}_{2-x}\text{Te}$ ; Bindi et al. 2013) in quartz  
46 veins crosscutting cherts (“Diaspri di Monte Alpe Formation”) overlaying Jurassic ophiolites.  
47 Tectono-metamorphic re-equilibration under prehnite-pumpellyite facies conditions affected  
48 ophiolites and their sedimentary covers producing complex veining processes (Cortesogno et al.  
49 1979; Lucchetti et al. 1990). Synmetamorphic fluids circulating within these vein systems, at  
50 decreasing metamorphic conditions, lead to the concentration of trace elements and the formation of  
51 a great variety of uncommon minerals, including many new species (Lucchetti et al. 1981; Basso *et*  
52 *al.*, 1991, 1992, 1993, 1994, 1997, 2000, 2003, 2005, 2008; Cabella et al. 1993, 1998 and  
53 references therein).

54 In this work, samples from Gambatesa mine have been investigated by means of X-ray  
55 powder diffraction (XRPD), electron microprobe (SEM-EDS), micro-Raman and transmission

56 electron microscope (TEM) analyses in order to clarify the crystallochemical features of this rare  
57 mineral. Mcalpineite from the Centennial Eureka (co-type locality) and the Gambatesa mine have  
58 been studied and compared;  $\text{Cu}_3\text{TeO}_6$  has been synthesized at high temperature a stoichiometric  
59 powder mixture of binary oxides; this sample was used as a reference for the structural studies.  
60 Moreover, to better understand the role of water inside the structure co-type sample from Mcalpine  
61 mine (type-locality) from the Geological Survey of Canada (catalogue number NMC 67163) has  
62 been investigated.

63

## 64 **2. Materials and experimental procedures**

65 Mcalpineite from Gambatesa mine (GM) has been found in a single occurrence in a quartz  
66 vein mainly intergrowth in a yellowish green earthy crust as well as aggregates of emerald green  
67 crystals (up to  $50\mu\text{m}$ ), coating quartz crystals and black fragments of paratellurite and weissite (Fig.  
68 1).

69 In order to have a reference for our studies, we synthesized  $\text{Cu}_3\text{TeO}_6$  by reacting a  
70 stoichiometric powder mixtures of binary oxides at high temperature.

71 The samples GM and synthetic  $\text{Cu}_3\text{TeO}_6$  have been investigated by means of several  
72 analytical techniques.

73 X-ray powder diffraction analysis (XRPD) was carried out using a Philips PW1830  
74 diffractometer (Bragg-Brentano geometry; Ni-filtered  $\text{CuK}\alpha$  radiation; range  $10\text{--}90^\circ 2\theta$ ; step  
75  $0.025^\circ 2\theta$ , sampling time 10 s). The XRPD data collected on the synthetic  $\text{Cu}_3\text{TeO}_6$  were used for  
76 the structural refinement according to the Rietveld method (Young 1993) by the FullProf program;  
77 for this purpose, the crystallographic data reported by Falck et al. (1978) for synthetic  $\text{Cu}_3\text{TeO}_6$   
78 were used to define the starting structural model and the structure was refined in the  $Ia\bar{3}$  space  
79 group (S.G. 206). In the final cycle of the refinement the following parameters were refined: the  
80 scale factor; the zero point of detector; the background (parameters of the 5<sup>th</sup> order polynomial

81 function); the unit cell parameters; the atomic site coordinates not constrained by symmetry; the  
82 atomic displacement parameters; the profile shape and half-width parameters.

83 The XRPD data collected on the GM sample were fitted according to the Le Bail method (Le  
84 Bail et al. 1988); in this case the background was fixed using a linear interpolation between a set of  
85 fixed points; in addition a file describing the instrumental resolution function was used, obtained by  
86 refining a LaB<sub>6</sub> standard. The fitting was carried out refining the zero point of detector, the unit cell  
87 parameter and the Lorentzian isotropic size parameter.

88 SEM-EDS analysis was performed using a Philips SEM 515 electron microscope, equipped  
89 with an EDS spectrometer (accelerating voltage: 15 kV, beam current: 2.15 nA, beam spot size: 10–  
90 25 μm). Calibration was performed with a synthetic Cu<sub>3</sub>TeO<sub>6</sub>.

91 Micro-Raman investigations have been taken using a Renishaw Ramascope equipped with  
92 He-Ne laser (633 nm) in the Raman shift range 100–4000 cm<sup>-1</sup> and connected to a Leica optical  
93 microscope equipped with an Olympus SLM plan 20 × long focal objective. This experimental set-  
94 up allowed to analyse only the desired mineral phase, excluding the contribution of the matrix  
95 composed of quartz.

96 Transmission electron microscope (TEM) analyses were carried out with a Jeol JEM-2010  
97 TEM equipped with an EDS spectrometer system (accelerating voltage: 200 kV). The samples for  
98 TEM examination were prepared by milling selected amounts of mineral that were subsequently  
99 dispersed in pentanol and then deposited onto a Cu support grid coated with a mesh carbon film.

100 Mcalpineite from Centennial Eureka Mine (CEM) occurs as interstitial olive-green coatings  
101 directly associated with hydrated copper tellurates and minor goethite. Due to small size of the  
102 CEM samples, only a few crystals have been prepared for micro-Raman, SEM and TEM analysis.  
103 In addition, a probe mount of mc Alpineite from Mc Alpine mine has been prepared for only non-  
104 destructive micro Raman analyses.

105

106 INSERT FIGURE 01

107

### 108 **3. Results**

#### 109 *3.1 SEM investigations*

110 SEM-EDS studies on GM samples indicated that Cu-Te-bearing phases are present in  
111 different modes of occurrence, sometimes coexisting in the same samples: a) as cryptocrystalline  
112 porous aggregates coating quartz crystals (Fig. 2a, c, and e) which correspond to the yellowish  
113 green crusts, b) as cryptocrystalline vermicular aggregates together with relics of paratellurite (Fig.  
114 2b and d) which correspond to a blackish, altered grain, and c) as small emerald green crystal  
115 fragments at the rim of altered paratellurite grains (Fig. 2f).

116 SEM-EDS investigations on the coatings show an irregular porous aggregate with some more  
117 compact elongated grains embedded in a porous granular matrix (Fig. 2c and e). Analytical results  
118 indicate the presence a Cu-Te mineral phase. Analyses on polished sections show a variable total  
119 weight percent in oxides ranging from 82.80 to 97.08, possibly related to the porosity. In fact, the  
120 Cu:Te ratio is nearly constant, around 3:1, pointing to the presence of a unique mineral phase.

121 The analysis of blackish fragments support the presence of Cu-Te minerals mixed together  
122 with Te oxide (Fig. 2b and d). Spot analyses suggest mcalpineite forms at the expense of Te oxide  
123 as a secondary product possibly due to the interaction with Cu-rich circulating fluids. EDS analyses  
124 on emerald green fragments (Fig. 2f) show a Cu:Te ratio nearly equal to 3:1, like in a and b types of  
125 occurrence and in good agreement with the stoichiometry of mcalpineite.

126 For comparison, Centennial Eureka mine (CEM) sample of mcalpineite has been analyzed;  
127 EDS spot analyses show Cu:Te ratio equal to those of GM samples (3:1) with a total weight percent  
128 in oxides ranging from 84.76 to 87.16.

129 INSERT FIGURE 02

130

#### 131 *3.2 XRPD analysis*

132 The structural data obtained for synthetic  $\text{Cu}_3\text{TeO}_6$  after Rietveld refinement (Table 1) are in  
133 very good agreement with those reported by Falck et al. (1978) (Table 2); slight differences range  
134 between the experimental error.

135 XRPD analysis was performed on yellowish green earthy crusts hand-picked from quartz  
136 coatings mixed with emerald green aggregates of GM samples; patterns of both occurrences are  
137 similar, indicating the presence of mcalpineite as the main phase.

138 Due to the paucity of material, the statistics are not high and the quality of the diffraction  
139 pattern is poor, preventing the possibility to carry out a structural refinement by the Rietveld  
140 method. In any case, all the diffraction lines may be indexed according to the crystal structure  
141 reported for synthetic  $\text{Cu}_3\text{TeO}_6$  (JCPDS 22-251), except for a medium peak at  $\sim 20.93^\circ 2\theta$ ,  
142 corresponding to an interplanar spacing of  $\sim 4.26 \text{ \AA}$ . This diffraction line was also observed by  
143 Roberts et al. (1994) together with three other peaks (2.76, 2.08, and  $1.77 \text{ \AA}$ ) that, according to these  
144 authors, could not be indexed in the  $Ia\bar{3}$  space group. Due to the presence of these unindexed peaks,  
145 they concluded that the body-centered cubic lattice of  $\text{Cu}_3\text{TeO}_6$  reduced to a primitive cubic lattice  
146 on account of  $\text{H}_2\text{O}$  groups located in structural voids. Note that in the Table 2 reported by Roberts  
147 et al. (1994) the line corresponding to the  $2.758 \text{ \AA}$  interplanar spacing is erroneously marked as  
148 non-indexable in the  $Ia\bar{3}$  space group, whereas it corresponds to the highest intensity peak of  
149 synthetic  $\text{Cu}_3\text{TeO}_6$  (222 line). In the pattern of the GM sample the lines at 2.08, and  $1.77 \text{ \AA}$  cannot  
150 be detected and hence they are not produced by mcalpineite. As obtained by the Le Bail fit ( $R_{\text{Bragg}} =$   
151  $0.72$ ;  $R_{\text{F}} = 1.14$ ), the unit cell is slightly expanded ( $a = 9.546(2) \text{ \AA}$ ) compared to the synthetic  
152 analogue ( $a = 9.5393(1) \text{ \AA}$ ). The profile of all diffraction lines is very broadened, (FWHM of the  
153 highest intensity 222 line  $\sim 0.5 \text{ \AA}$ ; Fig. 3) and the size of the coherent diffracting domains is  $\sim 13$   
154 nm on average, as obtained from the refinement of the Lorentzian isotropic size parameter in the Le  
155 Bail fit.

156

157 INSERT TABLE 01 AND FIGURE 03

158 *3.3 Micro-Raman analysis*

159 The micro-Raman spectra of the yellowish green earthy crusts and emerald green aggregates  
160 (GM sample) show no evidence for a structural OH group (inset of Figure 4): no signal is observed  
161 in the Raman shift range 3000-4000  $\text{cm}^{-1}$ , where bands should be located structural OH groups, if  
162 present. Only two strong bands may be observed at  $\sim 690 \text{ cm}^{-1}$  and  $\sim 740 \text{ cm}^{-1}$ , together with other  
163 faint contributions at lower Raman shift. A very faint band due to the admixed quartz may be  
164 observed at  $467 \text{ cm}^{-1}$  (for pure quartz this is the most intense Raman band). A weak and very  
165 broadened band is present in the Raman shift range  $\sim 2000\text{--}4000 \text{ cm}^{-1}$ ; similar bands are observed in  
166 IR and Raman spectra of acceptor-doped perovskites containing a large amount of lattice hydroxyl  
167 groups, incorporated into materials such as  $\text{BaCeO}_3$ ,  $\text{BaZrO}_3$ , and  $\text{BaSnO}_3$  (Kreuer 1999; Buscaglia  
168 et al. 2003); note that the crystal structures of these compounds do not change on account of the  
169 inclusion of these lattice groups. It is hence likely that during the hydrothermal process leading to  
170 the formation of malpeneite some hydroxyl groups or  $\text{H}_2\text{O}$  molecule can be trapped inside its  
171 lattice.

172 The comparison of GM and CEM samples spectra (Fig. 4) prove completely similarity in both  
173 chemical composition and structure. In particular, both spectra exhibit two strong bands located at  
174  $690$  and  $740 \text{ cm}^{-1}$ ; conversely, the synthetic sample is characterized by only one strong band around  
175  $730 \text{ cm}^{-1}$ . According to Choi et al. (2008), this band is created by an  $A_g$  Raman-active mode and, in  
176 general, the high frequency modes in the  $600\text{--}750 \text{ cm}^{-1}$  region corresponding to the stretching modes  
177 of the Te-O bonds. As a consequence, the band detected in the GM and CEM samples spectra at  
178  $740 \text{ cm}^{-1}$  is due to an  $A_g$  mode as in the synthetic sample, whereas the band at  $690 \text{ cm}^{-1}$  is a  
179 stretching mode of the Te-O bonds of the admixed phase (see below TEM analysis).

180 As regards the IR absorption bands of  $\text{H}_2\text{O}$  reported by Roberts et al. (1994), it is well known  
181 that strong bands may be originated by physically adsorbed water or fluid inclusions during IR  
182 analysis, whereas Raman analysis is much less sensitive to this kind of contribution. A closer  
183 inspection of the IR absorption spectrum reported in Roberts et al. (1994) shows four bands at

184 ~1085, ~1160, ~795, and ~775  $\text{cm}^{-1}$  that can be assigned to a quartz contribution (Scholl, 1981).  
185 Quartz is known to include fluid inclusions and also the profile of the broadened O-H stretching  
186 band centred at 3320  $\text{cm}^{-1}$  indicates that it is not created by non-structurally bonded water. In order  
187 to verify if our sample from Gambatesa Mine and mcalpineite from McAlpine Mine are identical, a  
188 sample (co-type sample - NMC 67163) has been studied. The sample is in a micromount holding  
189 two grains of mcalpineite (Fig. 4); the micro-Raman analyses shows that no structural water is  
190 present in either grains.

191

192 INSERT FIGURE 04

193 *3.4 TEM analysis*

194 TEM investigations on yellowish earthy crust and emerald green aggregates from GM mine  
195 indicate that the samples exhibit a low stability under the electron beam and tend to decompose.  
196 TEM observation of the yellowish earthy crust reveals rounded aggregates of mcalpineite (Figure  
197 5); these aggregates are intimately intergrown at a submicrometric scale with bundled elongated  
198 aggregates of acicular crystals constituted of an unidentified phase. EDS analysis reveals that Cu,  
199 Te, and O are the only detectable atomic species both in the bundled and in the rounded aggregates  
200 and that the Cu/Te ratio is similar in both phases. Fig. 6 shows a comparison between electron  
201 diffraction (ED) patterns collected on a yellowish crust from the GM and on the CEM sample,  
202 revealing a higher degree of crystallinity in the former sample; both patterns can be indexed as  
203 synthetic  $\text{Cu}_3\text{TeO}_6$ . A closer investigation at low angle on the former ED pattern (Fig. 7, on the left)  
204 shows a diffraction spot circle originating from diffraction planes with an interplanar spacing equal  
205 to 4.25 Å and indexed as 210 by Roberts et al. (1994) in according to a primitive cubic lattice; in  
206 addition, the 220 reflection ( $d = 3.37$  Å) is extremely faint, as also revealed by XRPD diffraction  
207 (reflection at  $\sim 26.4^\circ 2\theta$ ). This diffraction effect is due an intergrowth phase as demonstrated by  
208 selected area electron diffraction (SAED) analysis (Fig. 7, on the right) carried out on the edge of a  
209 bundled acicular crystal, exhibiting poor quality patterns with spots at 4.25 Å interplanar spacing. In



210 this SAED pattern spots originated by planes with interplanar spacing of 2.73 Å and 2.02 Å are also  
211 present, that cannot be distinguished in the XRPD pattern since they are superimposed on the 222  
212 and 332 diffraction lines of mc Alpineite. Figure 8 compares two SAED patterns collected along the  
213 [100] zone axis, the former from the GM sample, the latter from synthetic  $\text{Cu}_3\text{TeO}_6$ ; their complete  
214 coincidence is evident confirming that mc Alpineite is the mineral analogue of synthetic  $\text{Cu}_3\text{TeO}_6$ .  
215 Figure 9 shows two high-resolution TEM (HRTEM) images collected on different regions of the  
216 GM sample; in particular, in the yellowish earthy crust (Fig. 9a) the degree of crystallinity is quite  
217 poor, whereas in the emerald green aggregates (Fig. 9b) the lattice appears unaffected by structural  
218 defects.

219 INSERT FIGURE 05-06-07-8-9

220

#### 221 **4. Discussion and conclusions**

222 Bond valence sum (BVS) calculations (Brese & O'Keeffe, 1991), using the structural data of  
223 synthetic  $\text{Cu}_3\text{TeO}_6$  obtained after Rietveld refinement, are in agreement with the expected values, as  
224 reported in Table 2, where the calculated bond distances are also reported together with the global  
225 instability index (GII) (bond valence parameters for  $\text{Te}^{6+}\text{-O}$  from Mills & Christy, 2013). According  
226 to Hawthorne (1992), in inorganic compounds  $\text{H}_2\text{O}$  may be present: 1) as a component of the  
227 structural unit, hence controlling many of the physical and chemical properties, as in newberyite; 2)  
228 bonded to interstitial cationic species, as in stringhamite; 3) not bonded to any interstitial cationic  
229 species, but participating in a hydrogen-bonding network, as in mandarinoite; 4) occluded inside the  
230 structure, as in beryl. In cases 2 and 3,  $\text{H}_2\text{O}$  occurs as a bonded component of the structure and as a  
231 consequence contributes to its stability of the structure, while it does not in case 4. The small  
232 discrepancy between the expected and the calculated valences could indicate that the structure of  
233  $\text{Cu}_3\text{TeO}_6$  cannot host  $\text{H}_2\text{O}$  without experiencing a strong re-organization of the lattice: in fact, in  
234 most cases  $\text{H}_2\text{O}$  acts as a bond-valence transformer when it is bonded to the structure. In the case  
235 that  $\text{H}_2\text{O}$  should act as a bond-valence transformer in the  $\text{Cu}_3\text{TeO}_6$  structure, a strong mismatch

236 between the Lewis basicity of the anionic species and acidity of the cationic species should result,  
237 leading to the destabilization of the structure. In fact, according to the valence-matching principle  
238 (Brown 1992), the most stable structures form when the Lewis acid strength of the cation closely  
239 matches the Lewis base strength of the anion. The  $\text{Cu}_3\text{TeO}_6$  compound contains the  $[\text{Te}^{6+}\text{O}_6]^{6-}$   
240 oxyanion: in particular,  $\text{Te}^{6+}$  is located at the centre of this structural unit, forming a regular  
241 octahedron (Fig. 10). Each O at the corner of this octahedron is bonded to one Te and three Cu  
242 cations; it receives 1.0 v.u. from the central  $\text{Te}^{6+}$  cationic species and the additional 1.0 v.u. will be  
243 supplied by the remaining 3 Cu cations. As a result, the Lewis basicity of the  $[\text{Te}^{6+}\text{O}_6]^{6-}$  oxyanion is  
244 equal to 0.33 v.u., the ratio between the valence to be supplied and the number of Cu-O bonds  
245 sharing this valence; the so-obtained value of the Lewis basicity matches up reasonably well the  
246 Lewis acid strength reported by Brown (1992) for  $\text{Cu}^{2+}$  (0.39 v.u.). The limited discrepancy  
247 observed between the Lewis basicity and acidity is probably related to the Jahn-Teller distortion due  
248 to the presence of the  $\text{Cu}^{2+}$  cationic species (Hawthorne 1992). It is then essential to determine  
249 where  $\text{H}_2\text{O}$  could be hosted in the  $\text{Cu}_3\text{TeO}_6$  structure in order to ascertain if this group could  
250 effectively act as a bond-valence transformer. By means of the program CAVITY (Basso & Della  
251 Giusta 1977) and using the ionic radii reported by Shannon (1976), a search for empty spherical  
252 voids which can be inscribed in the crystal structure of  $\text{Cu}_3\text{TeO}_6$  were carried out; as a result the  
253 centres of these cavities were found located only in the  $8a$  site ( $Ia\bar{3}$  space group). Twelve atoms  
254 surround the centre of the cavity: 6 O at  $\sim 2.315 \text{ \AA}$  and 6 Cu at  $2.40 \sim \text{Å}$ , a distance similar to one  
255 type of the Cu-O bond lengths reported in Table 2. It is very important that the centre of the cavity  
256 is surrounded by an equal number of cationic and anionic species: according to Schindler et al.  
257 (2000), in this particular topological arrangement  $\text{H}_2\text{O}$  does not act as a bond-valence transformer  
258 and therefore does not influence the stability of the structure. This conclusion seems to indicate that  
259  $\text{H}_2\text{O}$  could be effectively hosted inside the  $\text{Cu}_3\text{TeO}_6$  lattice voids, but does not explain why the  
260 crystal structure should change from a body-centred to a primitive lattice. A simulation of the  
261 XRPD pattern of the structure of  $\text{Cu}_3\text{TeO}_6$  with O in the  $8a$  site of the  $Ia\bar{3}$  space group is illustrated

262 in Figure 11, where also the XRPD pattern of  $\text{Cu}_3\text{TeO}_6$  is reported; the difference between these  
263 patterns is plotted in the bottom of the figure. It is evident that the location of O in the structural  
264 cavities leads only to a rearrangement of the intensities of the peaks, but no new diffraction line is  
265 generated.

266 Another consideration suggesting the absence of structural  $\text{H}_2\text{O}$  is the geometry of the  
267 structural voids; in fact, the distance between the centre of the void and the 6 neighbouring O atoms  
268 is  $\sim 2.32 \text{ \AA}$ , as afore mentioned. This distance corresponds to the maximum O-O distance of the  
269 hypothetical O-H $\cdots$ O bond within the  $\text{Cu}_3\text{TeO}_6$  structure, but results noticeably shorter than the  
270 minimum bond length for the two hydrogen bonds donated by a water molecule (Ferraris & Ivaldi,  
271 1988) and also than the minimum possible O-O distance ( $2.36\text{--}2.44 \text{ \AA}$ ) (Brown, 1976). Notably no  
272 compound hosting OH groups is known where the O-H $\cdots$ O bond distance is shorter than  $2.35 \text{ \AA}$ ; as  
273 a consequence, the presence of structural water can be excluded from both analytical findings and  
274 topological considerations. For these reasons and for experimental evidences we consider that  
275 mcalpineite crystallizes in the  $Ia\bar{3}$  space group and its ideal formula must be referred to as  
276  $\text{Cu}_3\text{TeO}_6$ .

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278 INSERT FIGURE 10 AND 11

279

## 280 **Acknowledgements**

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285

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365

366 FIGURE CAPTIONS

367 **Figure 1.** Microphotograph taken using a binocular microscope (40x magnification) of (1)  
368 yellowish green earthy crust; (2) blackish fragments of paratellurite and weissite; (3) emerald green  
369 aggregates.

370 **Figure 2.** BSE and SE images of a) yellowish-green aggregates coating quartz crystals; b)  
371 aggregates of paraterullite and mcalpineite; c) compact elongated grains of mcalpineite embedded  
372 in a porous granular matrix; d) and e) enlargement of figure 2b and 2c respectively; f) BSE image of  
373 an emerald green fragment of mcalpineite. Abbreviations: Qz: quartz; Prt: paratellurite; Mc:  
374 mcalpineite.

375 **Figure 3.** XRPD data of the yellowish green earthy crusts fitted according to the Le Bail method.  
376 The XRPD pattern of synthetic  $\text{Cu}_3\text{TeO}_6$  is superposed for comparison.

377 **Figure 4.** Comparison between the micro-Raman spectra collected on the samples from Gambatesa  
378 mine (GM) and mcalpineite from Geological Survey of Canada, catalogue number NMC 67163,  
379 (NMC) up to  $4000\text{cm}^{-1}$  showing that no band for structural water is present. The inset shows also  
380 the spectra of Centennial Eureka mine (CEM), and  $\text{Cu}_3\text{TeO}_6$  synthetic analogue (synt). In the  
381 Raman spectra of NMC sample a broad band at  $1500\text{cm}^{-1}$  is originated by metallographic carbon.

382 **Figure 5.** Low magnification TEM image collected on a yellowish earthy crusts of GM sample  
383 showing the intergrowth between mcalpineite (rounded aggregates) and bundled elongated crystals  
384 of the unidentified phase.

385 **Figure 6.** SAED patterns collected on GM (on the left) and CEM (on the right) samples indexed  
386 according to the  $Ia\bar{3}$  space group.

387 **Figure 7.** On the left: ED pattern at low angles collected on the rounded aggregates of mcalpineite  
388 intergrown with bundled acicular crystals of an unidentified phase, showing the presence of the 4.25  
389 Å interplanar spacing; on the right: unindexed SAED pattern from an admixed acicular crystal of

390 the unidentified phase, intergrown with mc Alpineite, showing 4.25 Å, 2.73 Å, and 2.02 Å  
391 interplanar spacings.

392 **Figure 8.** Comparison between SAED patterns collected along [100] zone axis on the GM sample  
393 and synthetic  $\text{Cu}_3\text{TeO}_6$ .

394 **Figure 9.** a) HRTEM image collected on the yellowish earthy crust showing lattice fringes  
395 corresponding to 200 and 211 interplanar spacings; the inset shows its FT image. b): HRTEM  
396 image collected on the emerald green aggregates exhibiting a well crystallized lattice with 4.77 Å  
397 lattice fringes (200 interplanar spacing).

398 **Figure 10.** Crystal structure of mc Alpineite. Light-gray: Cu octahedron; dark gray: Te octahedron.

399 **Figure 11.** Comparison between the XRPD patterns of  $\text{Cu}_3\text{TeO}_6$  and  $\text{Cu}_3\text{TeO}_6$  with  $\text{H}_2\text{O}$  in the 8a  
400 site and on the bottom their difference is plotted.



401 TABLE CAPTIONS

402 **Table 1.** Structural data and *R* factors obtained after Rietveld refinement of synthetic Cu<sub>3</sub>TeO<sub>6</sub>.

403

<i>a</i> [Å]		9.5393(1)	
<i>V</i> [Å <sup>3</sup> ]		868.05(2)	
<b>Te<sup>+6</sup></b>	8 <i>b</i>	<i>x</i>	1/4
		<i>y</i>	1/4
		<i>z</i>	1/4
<b>Cu<sup>+2</sup></b>	24 <i>d</i>	<i>x</i>	0.9684(1)
		<i>y</i>	0
		<i>z</i>	1/4
<b>O</b>	48 <i>e</i>	<i>x</i>	0.3666(4)
		<i>y</i>	0.1750(3)
		<i>z</i>	0.3953(4)
<i>R</i> <sub>wp</sub>		3.84	
<i>R</i> <sub>p</sub>		2.85	
<i>R</i> <sub>Bragg</sub>		4.51	
<i>R</i> <sub>F</sub>		4.16	

404

405 **Table 2:** Bond distances and their multiplicity, BVS and GII calculations obtained after Rietveld

406 refinement of the our synthetic powder of Cu<sub>3</sub>TeO<sub>6</sub> (PS: powder sample) compared with the

407 structural data reported by Falck et al. (1978) on a single crystal (SC) of synthetic Cu<sub>3</sub>TeO<sub>6</sub>.

		SC	PS
<b>Bond distance [Å]</b>	Te – O × 6	1.921(2)	1.916(4)
	Cu – O × 2	2.031(2)	2.037(4)

	Cu – O × 2	2.369(3)	2.377(3)
	Cu – O × 2	1.949(2)	1.955(4)
	<hr/>		
	Te <sup>+6</sup>	6.00	6.05
<b>BVS [v.u.]</b>	<hr/>		
	Cu <sup>+2</sup>	2.05	2.05
	<hr/>		
	O <sup>-2</sup>	2.02	2.02
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<b>GII [v.u.]</b>		0.03	0.04
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