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#### Tazzoliite: a new mineral with a pyrochlore-related structure from the Euganei hills, Padova, Italy

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1	Revision 1
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3	Tazzoliite: a new mineral with a pyrochlore-related structure from
4	Euganei hills, Padova, Italy
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15	
16	Abstract
17	Tazzoliite, ideally Ba <sub>2</sub> CaSr <sub>0.5</sub> Na <sub>0.5</sub> Ti <sub>2</sub> Nb <sub>3</sub> SiO <sub>17</sub> [PO <sub>2</sub> (OH) <sub>2</sub> ] <sub>0.5</sub> , is a new mineral (IMA
18	2011-018) found at Monte delle Basse, Euganei Hills, Galzignano Terme, Padova,
19	Italy. It occurs as lamellar, light-orange crystals up to 0.3-0.4 mm in length and only a
20	few $\mu m$ in thickness, closely associated with a diopsidic pyroxene and titanite.
21	Tazzoliite crystals are transparent, have a white streak and pearly lustre. It is not
22	fluorescent and has a hardness of 6 (Mohs scale). The tenacity is brittle and crystals
23	have a perfect cleavage along $\{010\}$ . The calculated density is 4.517 g/cm <sup>3</sup> . Tazzoliite
24	is biaxial (-) with a 2V of about 50°; it does not show pleochroism and the average
25	refractive index is 2.04. No twinning was observed. Electron-microprobe analyses
26	gave the following chemical formula:

27  $(Ba_{1.93}Ca_{1.20}Sr_{0.52}Na_{0.25}Fe^{2+}_{0.10})_{\Sigma4}(Nb_{2.88}Ti_{2.05}Ta_{0.07}Zr_{0.01}V^{5+}_{0.01})_{\Sigma5.02}SiO_{17}$ 

 $28 \quad [(P_{0.13}Si_{0.12}S_{0.07})O_{0.66}(OH)_{0.66}][F_{0.09}(OH)_{0.23}]_{\Sigma 0.32}.$ 

Tazzoliite is orthorhombic, space group *Fmmm*, with unit-cell parameters: a =29 7.4116(3) Å, b = 20.0632(8) Å, c = 21.4402(8) Å, V = 3188.2(2) Å<sup>3</sup> and Z = 8. The 30 31 crystal structure, obtained by single-crystal X-ray diffraction data, was refined up to  $R_1(F^2) = 0.063$ . It consists of a framework of Nb(Ti)-octahedra and BaO<sub>7</sub> polyhedra 32 33 sharing apexes or edges, and Si-tetrahedra sharing apexes with Nb(Ti)-octahedra and 34  $BaO_7$  polyhedra. The structure, which is related to the pyrochlore structure, is 35 constituted by three Nb(Ti)-octahedra, two of them are Nb and Ti dominant, 36 respectively. Chains of A2O<sub>8</sub> polyhedra [A2 being occupied by Sr(Ca, Fe)] extend 37 along [100] and are surrounded by Nb-octahedra. Channels formed by six Nb(Ti)-38 octahedra and two tetrahedra, or four  $A1O_8(OH)$  polyhedra (A1 being occupied by Ba), 39 alternate along [100]. The channels are partially occupied by  $[PO_2(OH)_2]$  in two 40 possible mutually exclusive positions, alternating with fully occupied  $A3O_7$ 41 polyhedral pairs [A3 being occupied by Ca(Na)]. The eight strongest X-ray powder-42 diffraction lines  $[d \text{ in } \text{\AA} (I/I_0) (hkl)]$  are: 3.66 (60) (044), 3.16 (30) (153), 3.05 (100) 43 (204), 2.98 (25) (240), 2.84 (50) (004), 2.72 (20) (155), 1.85 (25) (400) and 1.82 (25) (268). Raman spectra of tazzoliite were collected in the range 150-3700 cm<sup>-1</sup> and 44 45 confirm the presence of (OH) groups. Tazzoliite is named after Vittorio Tazzoli in 46 recognition of his contribution to the fields of mineralogy and crystallography.

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48 Key-words: tazzoliite, new mineral, crystal structure, pyrochlore, Raman
49 spectroscopy, Euganei Hills.

#### 51 Introduction

52 The new mineral tazzoliite, here described, was found in the vicinity of Monte delle Basse at the Euganei Hills, south of Galzignano Terme, Padova, Italy (45° 18' 30" N 53 - 43° 49' 47" E) by mineral collector Mr. Bruno Fassina. The geology is characterised 54 55 by lower Oligocene rhyolites and trachytes (Figure 1). In the area of tazzoliite finding 56 also scarce syenitic and gabbroic rocks are present, which, based on an old hypothesis, 57 would represent the deep segregation products of rhyolitic and trachytic magmas (Dal 58 Piaz, 1935). Skarn and calcsilicate rocks can also be observed in contact with the 59 intrusives (Stark, 1936). These rocks are comprised of wollastonite, garnet (grossular), 60 gehlenite, sanidine, gyrolite, hibschite, kilchoanite, pectolite, rankinite and plagioclase, 61 and rarely sanidine xenoliths rich in vugs up to several millimeters across. Inside these 62 vugs tazzoliite was found as fan-shaped groups of platy crystals (Figure 2), light-63 orange in colour, up to 0.3-0.4 mm in length and only a few µm in thickness.

Tazzoliite was approved by the IMA-Commission on New Minerals, Nomenclature and Classification (IMA 2011-018). The name is in honour of Professor Vittorio Tazzoli (b. 1938) in recognition of his contribution to the fields of mineralogy and crystallography, particularly in the area of pyroxenes. He has contributed to the structure solution of numerous minerals. Type material is deposited in the collections of the Museo di Mineralogia di Padova, Italy, registration number MMP M9426.

70

## 71 Association and physical properties

Tazzoliite is associated with a green diopsidic pyroxene and titanite. It is light-orange
in colour. It shows a white streak; the lustre is pearly and crystals are transparent. It is
not fluorescent and has a hardness of 6 on the Mohs scale (VHN load 15g, mean 788 kg

75 mm<sup>-2</sup>). The tenacity is brittle and crystals have a perfect cleavage along {010}. No
76 parting was observed and the fracture is uneven.

77 Optically, tazzoliite is biaxial (-), and based on the Gladstone-Dale method (Mandarino,

- 1976) the calculated average refractive index is 2.04. The 2V (meas.) is 50(5)° and no
- 79 pleochroism was observed. No twinning was detected.
- 80

## 81 Experimental methods

#### 82 Microprobe analysis

83 Microprobe analyses (7 WDS spots) were obtained on the same crystal fragment used 84 for the structural study using a CAMECA SX-50 electron microprobe. Operating 85 conditions were 20 kV and 20 nA, spot size 2 µm, for Si, Ti, V, Nb, Ta, Fe, Mn, Sn, 86 Zr, Ca, Ba, and 20 kV and 10 nA, spot size 10 µm for F, Na, P, S, Sr. The second scheme was adopted to avoid beam damage. The crystal was found to be 87 88 homogeneous within analytical uncertainty. H<sub>2</sub>O was calculated and checked on the 89 basis of the structure refinement. K, Cr and Cl were not detected. REE were sought 90 for but were below detection limit. Analytical data are given in Table 1. The empirical 91 formula is calculated by iterative process on the basis of (18 + 2x) (O,F) apfu with x =92 [P + S + (Si-1)] < 0.5 apfu, to take into account partial occupancy of anionic groups at 93 channels crystal description). We the (see structure obtain  $(Ba_{1,93}Ca_{1,20}Sr_{0.52}Na_{0.25}Fe^{2+}_{0.10})_{\Sigma4}(Nb_{2.88}Ti_{2.05}Ta_{0.07}Zr_{0.01})_{\Sigma4}$ 94

95 
$$V_{0.01}^{5+}$$
  $\Sigma_{5.02}$ SiO<sub>17</sub>[(P<sub>0.13</sub>Si<sub>0.12</sub>S<sub>0.07</sub>)O<sub>0.66</sub>(OH)<sub>0.66</sub>][F<sub>0.09</sub>(OH)<sub>0.23</sub>] <sub>$\Sigma_{0.32}$</sub> .

96

97 *X-ray diffraction* 

A single crystal of tazzoliite  $(0.100 \times 0.040 \times 0.015 \text{ mm}^3)$ , inclusion- and twinningfree with sharp optical extinction and sharp reflections, was selected for the X-ray

100 diffraction analysis. The sample was measured using a Bruker AXS single-crystal 101 diffractometer equipped with a CCD Smart APEX detector and MoKa graphite-102 monochromatized radiation. Images were collected with an  $\omega$  increment of 0.2°. Cell 103 parameters were refined using 5584 reflections with  $I/\sigma(I) > 10$ . A total of 12200 reflections were collected in the 20 range 3.8-60.0°, of which 1312 were unique ( $R_{int}$ 104 105 = 5.4%); absorption and Lp correction were applied. The structure was solved using Superflip software (Palatinus and Chapuis, 2007). Weighted full-matrix least-squares 106 refinement on  $F^2$  was performed using SHELX97 (Sheldrick, 2008). Crystal data are 107 108 reported in Table 2 whereas the calculated X-ray powder diffraction pattern (114.6 109 mm diameter Gandolfi camera -  $CuK\alpha$ ) is given in Table 3. Final atom positions and 110 displacement parameters are listed in Table 4 and bond lengths in Table 5.

111 Unit cell parameters refined from powder data are as follows: a = 7.4116(3) Å, b = 112 20.0632(8) Å, c = 21.4402(8) Å, and V = 3188.2(2) Å<sup>3</sup>.

113

#### 114 Raman spectroscopy

115 Raman spectra were collected with a home-built micro-Raman system, based on a 116 single 320 mm focal length imaging spectrograph, a Triax-320 ISA instrument, equipped with a holographic 1800 g/mm grating and a liquid-nitrogen-cooled CCD 117 118 detector (Spectrum One ISA Instruments). The excitation source was a Spectra 119 Physics Ar laser (Stabilite 2017-06S) operating at 514.5 nm. A Kaiser Optical System 120 holographic notch filter (514.5 nm) was used to reduce the stray-light level. An 121 Olympus BX 40 optical microscope equipped with three objectives,  $20 \times /0.35$ , 122  $50 \times /0.75$ , and  $100 \times /0.90$ , was optically coupled to the spectrograph. This made it 123 possible to observe the sample with the microscope and then to select particular 124 micrometric regions for Raman analysis. With the 100× objective, the lateral resolution is estimated to be 0.5  $\mu$ m and the depth of focus 1–2  $\mu$ m. To avoid optical damage to the sample, the power of the exciting radiation was maintained between 10 and 50 mW. Raman spectra were recorded between 147 and 4000 cm<sup>-1</sup> with an instrumental resolution of about 2 cm<sup>-1</sup>.

129

# 130 **Results and discussion**

131 Crystal structure

Tazzoliite is orthorhombic, space group *Fmmm*, with the following unit-cell parameters: a = 7.4105(4) Å, b = 20.0675(11) Å, c = 21.4471(11) Å, V = 3189.4(3)Å<sup>3</sup> (Z = 8). The calculated density is 4.517 g/cm<sup>3</sup> using the empirical formula. Tazzoliite has no synthetic or natural analogue.

136 The structure of tazzoliite (Figure 3) consists of a framework of Nb(Ti)-octahedra and A1O<sub>8</sub>(OH) polyhedra sharing apexes or edges, and Si-tetrahedra sharing apexes with 137 138 Nb(Ti)-octahedra and A1O<sub>8</sub>(OH) polyhedra. Tazzoliite is constituted by three 139 different Nb(Ti)-octahedra, two of them are Nb dominant (site populations of 140 Nb<sub>0.86</sub>Ti<sub>0.14</sub> and Nb<sub>0.76</sub>Ti<sub>0.24</sub>, respectively) and one is Ti dominant (site population: 141 Ti<sub>0.80</sub>Nb<sub>0.20</sub>). Ti-dominant octahedra form pairs sharing an edge along [010], which 142 extend along [100] forming a double chain. Nb-dominant octahedra form a chain 143 along [100], decorated by 4 Nb-dominant octahedra sharing apexes.

144 Chains of A2O<sub>8</sub> polyhedra extend along [100] and are surrounded by Nb-octahedra.

145  $A2O_8$  polyhedra share edges with *Nb*1- and *Ti*3-octahedra.

We can consider also the presence of channels formed by six Nb-octahedra and two tetrahedra, or four  $A1O_8(OH)$  polyhedra, which alternate along [100]. The channels may be partially occupied by  $[PO_2(OH)_2]$  in two mutually excluding positions, alternating with fully occupied  $A3O_6(OH)$  polyhedral pairs. The  $[PO_2(OH)_2]$  anionic

group may show heterovalent substitution at the cation site (P site), which may be 150 151 occupied by P, S or Si. This is the most complicated part of the structure: the partial 152 occupation of the P sites rules the calculation of the end-member formulae. First of all, 153 due to the mutual exclusive position of the *P* sites, it is implicit that a composition of 154 tazzoliite with  $[PO_2(OH)_2]_{x>0.5}$  would never be possible. In addition, on the basis of 155 charge requirements, S cannot be dominant on the site. The observed P-O distances are rather short, due to the difficulty of solving the complicated environment in the 156 157 presence of  $[PO_2(OH)_2]$  groups. Each P atom at the P sites is coordinated with two O9 158 sites and with two O10 sites. (OH) groups are present at the O9 site when the P site is 159 occupied and at the O8 site when the P site is vacant. Moreover, the anion sites O8 160 and O10 are mutually exclusive. The same applies to H bonded to O9 [O8], only one 161 alternative position can be occupied. Therefore, in terms of formula normalization, if 162 the *P* site is vacant it means that there are 17 oxygen atoms per asymmetric unit plus 163 one (OH) group at the O8 site, *i.e.* 18 anions. Fluorine may be also present at the O8 164 site. Therefore, (OH) + F must be 1 apfu. An occupation of the P site of x requires 2x165 additional oxygen atoms present at the O10 sites. Thus, the total amount of anions is 18 + 2x, being x the occupation of the P site [*i.e.*, P + S + (Si - 1)]. As previously 166 167 stated, x cannot be > 0.5, and therefore the maximum quantity of anions is 19 apfu.

168

#### 169 Raman spectroscopy

170 The Raman spectrum of tazzoliite (Figure 4) can be divided in three main regions: (1)

171 200–400 cm<sup>-1</sup>; (2) 400–600 cm<sup>-1</sup>; (3) 800–1200 cm<sup>-1</sup>. The most intense peak at about

172  $750 \text{ cm}^{-1}$  needs to be discussed separately.

173 200–400 cm<sup>-1</sup> range: this part of the spectrum is most likely due to vibrations between

174 large cations (*e.g.*, Ba, Ca, Na, Sr) and oxygen atoms.

400–600 cm<sup>-1</sup>: the Raman peaks in this region can be assigned to the Si-O-Si
symmetric stretching vibrations and bending motions of Si-O-Si.

800–1200 cm<sup>-1</sup>: finally, the high-frequency region Raman bands could be assigned to 177 symmetric Si-O stretching motions of silicate units with one, two, three, or four non-178 179 bridging oxygen atoms. This region of the tazzoliite spectrum can also provide information about the  $PO_2(OH)_2^{-1}$  group. Such group is very rare in minerals and not 180 181 many Raman spectroscopy data are present in literature providing its vibrational 182 modes. However, we found data on synthetic compounds like  $M[PO_2(OH)_2)]\cdot 2H_2O$ 183 with M = Mg, Mn, Fe, Co, Zn, Ni, Cd (Koleva and Heffenberger, 2007) for which the P-OH and P-O show two bands between 946 and 977 cm<sup>-1</sup> and 1046 and 1070 cm<sup>-1</sup>, 184 185 respectively. Moreover, for synthetic compounds like NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>, Dutta and Shieh (1985) report that the  $PO_2(OH)_2^{-1}$  group shows two strong polarized bands 186 at 880 cm<sup>-1</sup> and 1060 cm<sup>-1</sup> due to the P-OH and P-O stretches, respectively. 187 Considering that the Raman spectrum of tazzoliite shows one peak at 869 cm<sup>-1</sup>, two 188 peaks between 961 and 981 cm<sup>-1</sup> and a fourth peak at 1062 cm<sup>-1</sup> (Figure 4) we are 189 strongly confident about the presence of the  $PO_2(OH)_2^{-1}$  group. 190

Relative to the most intense peak found at about 750 cm<sup>-1</sup>, it has been reported in 191 192 literature (Su 2000) for synthetic nenadkevichite et al., that  $[(Na,K)_2(Nb,Ti)_2[Si_4O_{12}](O,OH)_2 \cdot 2H_2O]$ , with a structure related to tazzoliite (see 193 194 below), such a band has been assigned to Ti-O stretching vibrations of TiO<sub>6</sub> units. 195 Similarly, for tazzoliite we could assign this band to Ti-O and Nb-O stretching vibrations of TiO<sub>6</sub> and NbO<sub>6</sub> units. Further evidence for this comes from the IR 196 197 spectrum of komarovite [(Ca,Mn)Nb<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>](O,F)<sub>3</sub> · 3.5H<sub>2</sub>O] from Lovozero (most intense band at exactly 750 cm<sup>-1</sup>; Pekov et al., 2004). Concerning the OH group 198 region, tazzoliite shows a very weak and broad peak at 3516 cm<sup>-1</sup>, consistent with OH 199

stretching and confirming the crystal chemical formula proposed for tazzoliite. No evidence of H<sub>2</sub>O bending at about 1600 cm<sup>-1</sup> is present (even if present, the bending mode of H<sub>2</sub>O at 1600 cm<sup>-1</sup> would be too weak to be visible with respect to the already weak peak for OH stretching at 3516 cm<sup>-1</sup>).

204

205 Site assignement

206 *Cation sites* 

Tazzoliite has 3 large cation sites (A1, A2, A3), 3 octahedral sites (Nb1, Nb2 and Ti3) and one tetrahedral site (Si). Regarding the Si site, it shows an average bond distance  $\langle Si-O \rangle = 1.647$  Å, corresponding to a full occupation by Si.

210 Concerning the octahedral sites, the Nb-dominant octahedra (Nb1 and Nb2) show mean bond distances of 1.990 and 1.983 Å, respectively, that closely match the values 211 212 found for kenopyrochlore [1.9855 Å – Bindi et al., 2006; renamed from 213 bariopyrochlore after the approval of the new scheme of nomenclature for the 214 pyrochlore supergroup, approved by the CNMNC-IMA (Atencio et al., 2010)] and 215 the value of 1.986 Å observed in hydropyrochlore [Ercit *et al.*, 1994; renamed after 216 new scheme of nomenclature for the pyrochlore supergroup, approved by the 217 CNMNC-IMA (Atencio et al., 2010)], having a B-site population very close to that 218 observed in tazzoliite. On the other hand, the Ti-dominant octahedron shows a mean bond distance of 1.975 Å, which is consistent with the value obtained by considering 219 220 the  $\langle \text{Ti-O} \rangle$  bond of the pure Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (1.953 Å – Becker and Will, 1970), and the sum of the Nb-O ionic radii (2.040 Å, respectively – Shannon, 1976). Indeed, taking into 221 account the molar fractions of Ti and Nb in tazzoliite (*i.e.*, Ti = 0.80 and Nb = 0.20222 223 *a.p.f.u.*) and the mean bond distances for the pure components, we obtain a value of 224 1.970 Å. If we consider the chemical analyses, site assignment must account for 0.07

225 apfu of Ta. The highest site scattering observed is at the *Nb*1 site. Therefore, we have 226 assigned all the Ta at this site. The composition we obtain for the three octahedral 227 sites is therefore  $^{Nb1}(Nb_{1.64}Ti_{0.28}Ta_{0.07}Zr_{0.01})$   $^{Nb2}(Nb_{0.78}Ti_{0.22})$   $^{Ti3}(Ti_{1.55}Nb_{0.45})$ , which 228 correspond to the observed and calculated site scattering values of 76.78 vs. 78.91, 229 36.44 vs. 36.82, 51.6 vs. 52.55 e- pfu, respectively.

230 The large cation sites have different coordination environments and site populations. 231 The A1 site is coordinated by 7 oxygen atoms and one (OH) group, plus a long bond 232 to the partially occupied O10 site. Site occupancy refinement shows that A1 site has 233 53.48 electrons per site (eps). As this is the largest cation site in the structure we 234 assign all the Ba to this site. Chemical analyses report 1.93 apfu and there are 2 A1 235 sites pfu. This corresponds to 0.965 atoms of Ba per A1 site and the remaining can be 236 assigned as Na, which makes a calculated site scattering of 54.43 eps. The A2 site is a 237 highly regular polyhedron and has refined site occupancy of 29 eps. There is one A2 238 site pfu. This site is the smaller site and the lower observed site scattering with respect to A1 site lead us to assign mostly smaller species, i.e. Ca,  $Fe^{2+}$  and Sr to this site. 239 This makes  $Sr_{0.53}Ca_{0.38}Fe^{2+}_{0.09}$ , which corresponds to a calculated site scattering of 240 241 30.08 eps and a mean charge of 2. This is just slightly higher than the observed value. 242 Regarding the A3 site, it shows 7-fold coordination. Its observed site scattering is 243 17.84 eps requiring thus the lower scattering species at this site. We have left 0.82 244 apfu of Ca, and 0.18 Na apfu, which makes a calculated site-occupancy of 18.38 eps, 245 just slightly higher than the observed value. In overall, the composition of cation sites 246 is 12 2 42

247 
$$^{A1}(Ba_{1.93}Na_{0.06})^{A2}(Sr_{0.53}Ca_{0.38}Fe^{2+}_{0.09})^{A3}(Ca_{0.82}Na_{0.18})^{Nb1}(Nb_{1.64}Ti_{0.28}Ta_{0.07}Zr_{0.01})^{Nb2}(Nb_{0.28}Ta_{0.28}Ta_{0.07}Zr_{0.01})^{Nb2}(Nb_{0.28}Ta_{0.07}Zr_{0.07}Zr_{0.01}$$

250 Anion sites.

251 There are 7 anion sites fully occupied by oxygen atoms in the structure of tazzoliite, 252 which account for 17 apfu. There are 3 anion sites which are related to the 253  $[PO_2(OH)_2]$  anionic group environment, O8, O9 and O10. The P site is coordinated by 254 2 (OH) groups at the O9 anion site and two oxygen atoms at the O10 site, and can be 255 occupied at maximum at 50% as the two 8g positions are mutually exclusive. This 256 also implies that only half of the 16o positions of the O10 sites can be occupied. The 257 observed excess site occupancy of 0.58 at O10 (Table 4) should be ascribed to the 258 difficulty to refine the positional disorder. During the refinement we have not 259 constrained the site occupancies at the O9 and O10 sites, nor the isotropic 260 displacement parameters. The dihydrogen phosphate group will therefore alternate in 261 two positions along [100], otherwise would share one edge, with a very short P-P 262 distance. When the P site is vacant, the O8 site is occupied by (OH) groups or F and 263 both the O9 and O10 sites are vacant. Thus, the A1 polyhedron turns seven-fold 264 coordinated, while the A3 polyhedron maintains its coordination number but turns 265 smaller, as A3-O8 is shorter than A3-O10, in agreement with a full occupation by Ca. Therefore, the anion composition is  $O_{17} + [PO_2(OH)_2]_{0.5}$  with a charge of -34.5 or  $O_{17}$ 266 267 + (OH) with a charge of -35. The latter matches the charge of the ideal cationic 268 composition. The former needs a reduction of charge of +0.5, which is accomplished 269 by substitution of a divalent cation by up to 0.5 apfu of a monavalent cation, for

example Na.

Therefore the ideal composition of this structural type will range from Ba<sub>2</sub>SrCaNb<sub>3</sub>Ti<sub>2</sub>Si O<sub>17</sub>(OH) to Ba<sub>2</sub>SrCa<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>3</sub>Ti<sub>2</sub>SiO<sub>17</sub>[PO<sub>2</sub>(OH)<sub>2</sub>]<sub>0.5</sub>. This would lead to two ideal compositions. The mineral composition we have studied has [P+S+(Si-1)] > 0.25 and thus we define tazzoliite as Ba<sub>2</sub>CaSr<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>3</sub>Ti<sub>2</sub>SiO<sub>17</sub> 275 [PO<sub>2</sub>(OH)<sub>2</sub>]<sub>0.5</sub>, which requires P<sub>2</sub>O<sub>5</sub> 3.24, Nb<sub>2</sub>O<sub>5</sub> 36.47, SiO<sub>2</sub> 5.50, TiO<sub>2</sub> 14.62, BaO

276 28.06, CaO 5.13, SrO 4.74, Na<sub>2</sub>O 1.42, H<sub>2</sub>O 0.82, Total 100.00 wt%, and a mineral

277 with Ba<sub>2</sub>SrCaNb<sub>3</sub>Ti<sub>2</sub>Si O<sub>17</sub>(OH) would correspond to a new species.

278

#### 279 Relation to other structures

280 Tazzoliite is related to the pyrochlore structure (Atencio et al., 2010) with the addition 281 of a slab of  $SiTiO_3[PO_2(OH)_2]_{0.5}$  every 0.5 b translation parallel to [110] of pyrochlore 282 (Figure 3). Other pyrochlore-related structures have been described by Ferraris et al. 283 (2008)although they have alternate one [K-rich nenadkevichite 284  $(Na,K)(Nb,Ti)_{2}[Si_{4}O_{12}](O,OH)_{2}\cdot 1.6H_{2}O$ , Rastsvetayeva *et al.*, 1994], two [fersmanite 285 (Ca<sub>5.49</sub>Na<sub>2.37</sub>Sr<sub>0.08</sub>Fe<sub>0.06</sub>)(Nb<sub>1.61</sub>Ti<sub>2.39</sub>)(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>O<sub>8</sub>F<sub>3</sub>, Sokolova *et al.*, 2002], or three 286 [Na-rich komarovite Na<sub>5.5</sub>Ca<sub>0.8</sub>La<sub>0.2</sub>Ti<sub>0.5</sub>Nb<sub>5.5</sub>Si<sub>4</sub>O<sub>26</sub>F<sub>2</sub>·H<sub>2</sub>O, Balič Žunič *et al.*, 2002] 287 octahedra-thick (100)-pyrochlore slabs with (SiO<sub>4</sub>) groups with different degrees of 288 polymerization (four-membered rings being the most frequent unit) (Figure 5). 289 Tazzoliite thus represents a novel type of pyrochlore-related structure, which includes 290 further anionic groups other than (SiO<sub>4</sub>). One of the anionic groups coordinates with 291 (OH) groups. The dominant cation at the centre of the  $(MO_4)$  anionic group is 292 phosphorous. The presence of dihydrogen phosphate groups has been observed in 293 girvasite, (NaCa<sub>2</sub>Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>[PO<sub>2</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)(OH)<sub>2</sub>·4H<sub>2</sub>O (Sokolova et al., 1990).

294

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365	
366	Table and figure captions
367	
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388	Light yellow polyhedra are Nb/Ti sites; orange tetrahedra are Si sites; yellow
389	tetrahedra (P,Si,S) are partially occupied sites; violet spheres indicate A1 sites; grey
390	spheres are Sr and Ca dominant sites (A2 and A3); red spheres are O atoms; small
391	white spheres are H atoms; green spheres are F atoms.
392	
393	Figure 4. Raman spectrum of tazzoliite collected between 150 and 3700 cm <sup>-1</sup> . In
394	figure 3a and 3b the ranges between 150 and 2000 cm <sup>-1</sup> and 3000 and 3700 cm <sup>-1</sup> are
395	shown, respectively.
396	
397	Figure 5. Relationships among known pyrochlore-like structures.
398	

# 399 400 401 **Table 1**402 403

Constituent	wt%	Range	SD	Probe Standard (analysing crystals)
SO <sub>3</sub>	0.51	0.36-0.66	0.10	BaSO <sub>4</sub> (PET)
$Nb_2O_5$	34.51	33.53-35.38	0.63	Pure metal for Nb (PET)
Ta <sub>2</sub> O <sub>5</sub>	0.89	0.66-1.16	0.16	Pure metal for Ta (LiF)
$V_2O_3$	0.05	0.00-0.11	0.04	Vanadinite (LiF)
$P_2O_5$	0.85	0.85-0.85		Apatite (TAP)
SiO <sub>2</sub>	6.10	5.74-6.31	0.19	Diopside (Si TAP; Ca PET)
$TiO_2$	14.77	14.42-15.09	0.27	MnTiO <sub>3</sub> (PET)
SnO <sub>2</sub>	0.04	0.00-0.09	0.03	SnO <sub>2</sub> (PET)
$ZrO_2$	0.11	0.07-0.21-	0.10	Synthetic zircon (PET)
FeO	0.63	0.55-0.66	0.04	Fe <sub>2</sub> O <sub>3</sub> (LiF)
MnO	0.01	0.00-0.03	0.17	MnTiO <sub>3</sub> (LiF)
CaO	6.07	5.67-6.60	0.02	Diopside (PET)
BaO	26.75	26.31-27.28	0.39	BaSO <sub>4</sub> (LiF)
SrO	4.92	4.18-5.72	0.48	Celestine (PET)
Na <sub>2</sub> O	0.70	0.64-0.77	0.05	Amelia (TAP)
$H_2O*$	0.74	0.64-0.73	0.05	
F	0.15	0.00-0.37	0.16	Fluorite (TAP)
O = F	-0.06			
Total	97.74			

\*From crystal structure stoichiometry.

4	1	6
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# **Table 2**

4	1	8
-	т	Ο

Space group	Fmmm
a (Å)	7.4105(4)
b	20.0675(11)
С	21.4471(11)
$V(\text{\AA}^3)$	3189.4(3)
Ζ	4
Absorption coefficient (mm <sup>-1</sup> )	8.864
<i>F</i> (000)	3941
$D_{\text{calc.}}(\text{g/cm}^3)$	4.489
Crystal size (mm)	0.015 x 0.04 x 0.10
Radiation/filter	Mo <i>K</i> α/graphite
2θ-range for data collection (°)	1.90 to 30.00°.
<i>R</i> (int) (%)	5.40
Reflections collected	12200
	$-10 \le h \le 10$
Index ranges	$-28 \le k \le 28,$
	$-30 \le l \le 30$
Independent reflections	1312
$F_{\rm o} > 4\sigma F$	1300
Refinement method	Full-matrix least squares on $F^2$ , fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	95
Final $R_{(obs)}$ (%)[ $F_o > 4\sigma F$ ]	6.25
$R_1$	6.33
$wR_2$	15.81
Goodness of fit on $F^2$	1.246

421	
422	Table 3

hkl	$d_{obs}({ m \AA})*$	I <sub>rel</sub>	$d_{calc}({ m \AA})^{**}$	I <sub>rel</sub>
0 0 2			10.724	2
0 2 0			10.034	36
0 2 2	7.3	15	7.327	15
0 0 4			5.362	3
0 4 0	5.0	15	5.017	13
$2 \ 0 \ 0$	3.71	10	3.705	11
0 4 4	3.66	60	3.663	47
1 1 5			3.650	8
$2 \ 0 \ 2$	3.49	20	3.502	10
1 5 1			3.482	17
2 2 2	3.31	10	3.307	8
1 3 5	3.25	5	3.246	5
1 5 3	3.16	30	3.165	29
2 0 4	3.05	100	3.048	100
2 4 0	2.979	25	2.981	25
2 2 4	2.918	10	2.917	11
0 4 6	2.910	15	2.911	12
2 4 2	2.872	10	2.872	10
0 6 4	2.835	50	2.838	47
1 1 7	2.801	10	2.804	8
1 5 5	2.723	20	2.725	18
0 0 8	2.678	20	2.681	19
1 7 1	2.652	5	2.653	5
1 3 7	2.606	5	2.607	3
2 4 4			2.605	5
0 8 0	2.510	5	2.508	3
2 6 0	2.483	15	2.483	12
2 4 6			2.289	3
1 7 5	2.270	15	2.269	14
1 1 9			2.254	3
2 0 8			2.172	3
1 3 9			2.148	3
1 9 1	2.126	10	2.125	8
0 6 8			2.092	3
1 9 3			2.046	4
3 5 3	2.015	10	2.018	8
2 4 8	1.995	20	1.993	17
0 4 10			1.972	2
2 8 4			1.937	4
3 1 7	1.913	15	1.914	6
1 9 5			1.911	9
3 5 5	1.889	5	1.889	6
3 7 1			1.864	3
2 0 10	1.854	25	1.856	3
4 0 0			1.853	17
3 3 7			1.848	3

2 6 8	1.822	25	1.822	22423
1 3 11	1.813	5	1.815	6
2 8 6	1.795	5	1.796	6
179			1.779	2
1 11 1	1.765	10	1.765	8
2 4 10	1.741	10	1.741	8
1 11 3			1.719	2
2 10 4			1.676	4
4 4 4	1.652	10	1.653	6
3 9 1			1.650	3
1 11 5	1.636	5	1.637	4
0 8 10	1.629	5	1.630	4
2 6 10			1.623	3
2 0 12	1.610	5	1.610	4
0 12 4			1.596	2
0 6 12	1.575	5	1.576	5
4 4 6			1.563	3
4 6 4	1.552	10	1.551	13
3 9 5			1.544	2
4 0 8	1.523	10	1.524	8
3 3 11			1.492	3
2 12 4			1.466	2
3 11 1			1.464	2
3 11 3			1.438	2
1 11 9			1.422	2
2 12 6	1.401	5	1.402	4
1 1 15			1.401	2

\*: Observed powder pattern for obtained with a fully indexed 114.6 mm Gandolfi camera (Ni-filtered CuK $\alpha$  radiation).\*\*: Calculated pattern and indexing on the basis of a = 7.4105(4) Å, b = 20.0675(11) Å, c = 21.4471(11) Å, and with the atom coordinates and occupancies reported in Table 4. Intensities were calculated using XPOW software (Downs *et al.*, 1993).

Atom	Wyck.	Occ.	x/a	y/b	z/c	Ueq
A1 (Ba)	16 <i>m</i>	0.93 Ba + 0.07 Ca	0	0.12852(5)	0.10553(4)	0.013(1)
A2 (Ca)	8f	0.75 Ca + 0.25 Ba	1/4	1/4	1⁄4	0.010(1)
A3 (Ca)	8h	0.76 Ca + 0.24 Na	- 1/2	0.0963(3)	0	0.026(2)
Nb1	16 <i>m</i>	0.86 Nb + 0.14 Ti	- 1/2	0.17122(6)	0.13211(6)	0.009(1)
Nb2	8 <i>e</i>	0.76 Nb + 0.24 Ti	1/4	1/4	0	0.010(1)
Ti3	16k	0.80 Ti + 0.20 Nb	1/4	0.07937(10)	1⁄4	0.012(1)
Si	8 <i>i</i>	1.00	1/2	0	0.1470(2)	0.008(1)
01	8h	1.00	0	0.2139(7)	0	0.008(2)
O2	32p	1.00	0.3040(9)	0.1426(3)	0.1887(3)	0.010(1)
03	16 <i>m</i>	1.00	0	0.2469(5)	0.1706(4)	0.007(2)
O4	16 <i>n</i>	1.00	0.3188(13)	0	0.1927(4)	0.008(2)
05	32p	1.00	0.3180(9)	0.1841(3)	0.0646(3)	0.011(1)
06	16 <i>m</i>	1.00	- 1/2	0.0680(5)	0.1053(5)	0.013(2)
O7	16 <i>m</i>	1.00	0	0.0723(5)	0.2180(5)	0.011(2)
08	8g	0.43	-0.340(5)	0	0	0.018(10)
Р	8g	0.28	0.066(4)	0	0	0.038(9)
09	8 <i>i</i>	0.82	0	0	0.065(2)	0.071(15)
H9	16 <i>n</i>	0.43	0.11200	0	0.09000	0.0850
O10	160	0.58	0.177(4)	0.0582(13)	0	0.036(8)

Table 5

Nb103	1.839(10)	A1—07	2.663(11)
Nb1—O2 x2	1.978(7)	A1—09	2.722(14)
Nb1—O5 x2	1.996(7)	A1—O5 x2	2.751(7)
Nb1—O6	2.15(1)	A1—03	2.755(10)
<nb1o></nb1o>	1.990	A1—01	2.839(9)
Nb2—O5 x4	1.980(6)	A1—O2 x2	2.887(7)
Nb2—O1 x2	1.989(5)	A1-010	2.972(18)
<nb2—o></nb2—o>	1.983	<a1—0></a1—0>	2.830
Ti3—O2 x2	1.870(6)	A2—O3 x4	2.517(6)
Ti3—O7 x2	1.981(4)	A2—O2 x4	2.556(6)
Ti3—O4 x2	2.075(6)	<a2—o></a2—o>	2.537
<ti3—o></ti3—o>	1.975	A3—O8	2.267(20)
Si—O6 <sup>ii</sup> x2	1.632(11)	A3—O6 x2	2.329(11)
Si—O4 x2	1.662(10)	A3—O10 <sup>i</sup>	2.513(29)
<si< td=""><td>1.647</td><td>A3<sup>ii</sup>—O5 x4</td><td>2.616(8)</td></si<>	1.647	A3 <sup>ii</sup> —O5 x4	2.616(8)
P—O10 x2	1.429(32)	<a3—0>*</a3—0>	2.484
P—O9 x2	1.477(42)	<a3—0>**</a3—0>	2.519
<po></po>	1.453	O9—H9	0.988(23)
		<b>O8</b> — <b>O</b> 10	1 68(4)

Symmetry codes are (i): -1+x, y, z; (ii): 1+x, y, z; (iii): -x, -y, z; (iv): -2+x, y, z; (v): 1-x, -y, z. \*Average including O8 and excluding O10; \*\* average including O10 and excluding O8.



# 462 FIGURE 2







**FIGURE 4** 



