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Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/111225> since

Published version:

DOI:10.1180/minmag.2012.076.4.01

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(Article begins on next page)

This is the author's final version of the contribution published as:

Cámara F; Nestola F; Bindi L; Guastoni A; Zorzi F; Peruzzo L; Pedron D.
Tazzoliite: a new mineral with a pyrochlore-related structure from the
Euganei hills, Padova, Italy. MINERALOGICAL MAGAZINE. 76 pp:
827-838.

DOI: 10.1180/minmag.2012.076.4.01

The publisher's version is available at:

<http://minmag.geoscienceworld.org/cgi/doi/10.1180/minmag.2012.076.4.01>

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<http://hdl.handle.net/2318/111225>

Revision 1

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

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Abstract

Tazzoliite, ideally $\text{Ba}_2\text{CaSr}_{0.5}\text{Na}_{0.5}\text{Ti}_2\text{Nb}_3\text{SiO}_{17}[\text{PO}_2(\text{OH})_2]_{0.5}$, is a new mineral (IMA 2011-018) found at Monte delle Basse, Euganei Hills, Galzignano Terme, Padova, Italy. It occurs as lamellar, light-orange crystals up to 0.3-0.4 mm in length and only a few μm in thickness, closely associated with a diopsidic pyroxene and titanite. Tazzoliite crystals are transparent, have a white streak and pearly lustre. It is not fluorescent and has a hardness of 6 (Mohs scale). The tenacity is brittle and crystals have a perfect cleavage along $\{010\}$. The calculated density is 4.517 g/cm^3 . Tazzoliite is biaxial (-) with a $2V$ of about 50° ; it does not show pleochroism and the average refractive index is 2.04. No twinning was observed. Electron-microprobe analyses gave the following chemical formula:

27 $(\text{Ba}_{1.93}\text{Ca}_{1.20}\text{Sr}_{0.52}\text{Na}_{0.25}\text{Fe}^{2+}_{0.10})_{\Sigma 4}(\text{Nb}_{2.88}\text{Ti}_{2.05}\text{Ta}_{0.07}\text{Zr}_{0.01}\text{V}^{5+}_{0.01})_{\Sigma 5.02}\text{SiO}_{17}$

28 $[(\text{P}_{0.13}\text{Si}_{0.12}\text{S}_{0.07})\text{O}_{0.66}(\text{OH})_{0.66}][\text{F}_{0.09}(\text{OH})_{0.23}]_{\Sigma 0.32}$.

29 Tazzoliite is orthorhombic, space group *Fmmm*, with unit-cell parameters: $a =$
30 $7.4116(3) \text{ \AA}$, $b = 20.0632(8) \text{ \AA}$, $c = 21.4402(8) \text{ \AA}$, $V = 3188.2(2) \text{ \AA}^3$ and $Z = 8$. The
31 crystal structure, obtained by single-crystal X-ray diffraction data, was refined up to
32 $R_1(F^2) = 0.063$. It consists of a framework of Nb(Ti)-octahedra and BaO_7 polyhedra
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 A_2O_8 polyhedra [A_2 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 $\text{A}_1\text{O}_8(\text{OH})$ polyhedra (A_1 being occupied by Ba),
39 alternate along [100]. The channels are partially occupied by $[\text{PO}_2(\text{OH})_2]$ in two
40 possible mutually exclusive positions, alternating with fully occupied A_3O_7
41 polyhedral pairs [A_3 being occupied by Ca(Na)]. The eight strongest X-ray powder-
42 diffraction lines [d 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)
44 (268). Raman spectra of tazzoliite were collected in the range $150\text{--}3700 \text{ cm}^{-1}$ and
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.

47

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

50

51 **Introduction**

52 The new mineral tazzerite, here described, was found in the vicinity of Monte delle
53 Basse at the Euganei Hills, south of Galzignano Terme, Padova, Italy (45° 18' 30" N
54 – 43° 49' 47" E) by mineral collector Mr. Bruno Fassina. The geology is characterised
55 by lower Oligocene rhyolites and trachytes (Figure 1). In the area of tazzerite 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 tazzerite 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.

64 Tazzerite was approved by the IMA-Commission on New Minerals, Nomenclature and
65 Classification (IMA 2011-018). The name is in honour of Professor Vittorio Tazzoli (b.
66 1938) in recognition of his contribution to the fields of mineralogy and
67 crystallography, particularly in the area of pyroxenes. He has contributed to the
68 structure solution of numerous minerals. Type material is deposited in the collections
69 of the Museo di Mineralogia di Padova, Italy, registration number MMP M9426.

70

71 **Association and physical properties**

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

75 mm⁻²). The tenacity is brittle and crystals have a perfect cleavage along {010}. No
 76 parting was observed and the fracture is uneven.
 77 Optically, tazzerite is biaxial (-), and based on the Gladstone-Dale method (Mandarino,
 78 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
 87 scheme was adopted to avoid beam damage. The crystal was found to be
 88 homogeneous within analytical uncertainty. H₂O 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 the channels (see crystal structure description). We obtain
 94 $(Ba_{1.93}Ca_{1.20}Sr_{0.52}Na_{0.25}Fe^{2+}_{0.10})_{\Sigma 4}(Nb_{2.88}Ti_{2.05}Ta_{0.07}Zr_{0.01}$
 95 $V^{5+}_{0.01})_{\Sigma 5.02}SiO_{17}[(P_{0.13}Si_{0.12}S_{0.07})O_{0.66}(OH)_{0.66}][F_{0.09}(OH)_{0.23}]_{\Sigma 0.32}.$

96

97 *X-ray diffraction*

98 A single crystal of tazzerite (0.100 × 0.040 × 0.015 mm³), inclusion- and twinning-
 99 free with sharp optical extinction and sharp reflections, was selected for the X-ray

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

Unit cell parameters refined from powder data are as follows: $a = 7.4116(3) \text{ \AA}$, $b = 20.0632(8) \text{ \AA}$, $c = 21.4402(8) \text{ \AA}$, and $V = 3188.2(2) \text{ \AA}^3$.

Raman spectroscopy

Raman spectra were collected with a home-built micro-Raman system, based on a 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 detector (Spectrum One ISA Instruments). The excitation source was a Spectra Physics Ar laser (Stabilite 2017-06S) operating at 514.5 nm. A Kaiser Optical System holographic notch filter (514.5 nm) was used to reduce the stray-light level. An Olympus BX 40 optical microscope equipped with three objectives, 20 $\times$ /0.35, 50 $\times$ /0.75, and 100 $\times$ /0.90, was optically coupled to the spectrograph. This made it possible to observe the sample with the microscope and then to select particular micrometric regions for Raman analysis. With the 100 $\times$ objective, the lateral

resolution is estimated to be 0.5 μm and the depth of focus 1–2 μm . 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^{-1} with an instrumental resolution of about 2 cm^{-1} .

Results and discussion

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, $V = 3189.4(3)$ Å³ ($Z = 8$). The calculated density is 4.517 g/cm^3 using the empirical formula. Tazzoliite has no synthetic or natural analogue.

The structure of tazzoliite (Figure 3) consists of a framework of Nb(Ti)-octahedra and $\text{AlO}_8(\text{OH})$ polyhedra sharing apexes or edges, and Si-tetrahedra sharing apexes with Nb(Ti)-octahedra and $\text{AlO}_8(\text{OH})$ polyhedra. Tazzoliite is constituted by three different Nb(Ti)-octahedra, two of them are Nb dominant (site populations of $\text{Nb}_{0.86}\text{Ti}_{0.14}$ and $\text{Nb}_{0.76}\text{Ti}_{0.24}$, respectively) and one is Ti dominant (site population: $\text{Ti}_{0.80}\text{Nb}_{0.20}$). Ti-dominant octahedra form pairs sharing an edge along [010], which extend along [100] forming a double chain. Nb-dominant octahedra form a chain along [100], decorated by 4 Nb-dominant octahedra sharing apexes.

Chains of AlO_8 polyhedra extend along [100] and are surrounded by Nb-octahedra. AlO_8 polyhedra share edges with Nb1- and Ti3-octahedra.

We can consider also the presence of channels formed by six Nb-octahedra and two tetrahedra, or four $\text{AlO}_8(\text{OH})$ polyhedra, which alternate along [100]. The channels may be partially occupied by $[\text{PO}_2(\text{OH})_2]$ in two mutually excluding positions, alternating with fully occupied $\text{AlO}_6(\text{OH})$ polyhedral pairs. The $[\text{PO}_2(\text{OH})_2]$ anionic

group may show heterovalent substitution at the cation site (*P* site), which may be occupied by P, S or Si. This is the most complicated part of the structure: the partial occupation of the *P* sites rules the calculation of the end-member formulae. First of all, due to the mutual exclusive position of the *P* sites, it is implicit that a composition of tazzoliite with $[\text{PO}_2(\text{OH})_2]_x$ $x > 0.5$ would never be possible. In addition, on the basis of 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 presence of $[\text{PO}_2(\text{OH})_2]$ groups. Each P atom at the *P* sites is coordinated with two O9 sites and with two O10 sites. (OH) groups are present at the O9 site when the *P* site is occupied and at the O8 site when the *P* site is vacant. Moreover, the anion sites O8 and O10 are mutually exclusive. The same applies to H bonded to O9 [O8], only one alternative position can be occupied. Therefore, in terms of formula normalization, if the *P* site is vacant it means that there are 17 oxygen atoms per asymmetric unit plus one (OH) group at the O8 site, *i.e.* 18 anions. Fluorine may be also present at the O8 site. Therefore, (OH) + F must be 1 apfu. An occupation of the *P* site of x requires $2x$ 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.*, $\text{P} + \text{S} + (\text{Si} - 1)$]. As previously stated, x cannot be > 0.5 , and therefore the maximum quantity of anions is 19 apfu.

Raman spectroscopy

The Raman spectrum of tazzoliite (Figure 4) can be divided in three main regions: (1) 200–400 cm^{-1} ; (2) 400–600 cm^{-1} ; (3) 800–1200 cm^{-1} . The most intense peak at about 750 cm^{-1} needs to be discussed separately.

200–400 cm^{-1} range: this part of the spectrum is most likely due to vibrations between large cations (*e.g.*, Ba, Ca, Na, Sr) and oxygen atoms.

175 400–600 cm^{-1} : the Raman peaks in this region can be assigned to the Si-O-Si
 176 symmetric stretching vibrations and bending motions of Si-O-Si.
 177 800–1200 cm^{-1} : finally, the high-frequency region Raman bands could be assigned to
 178 symmetric Si-O stretching motions of silicate units with one, two, three, or four non-
 179 bridging oxygen atoms. This region of the tazoliite spectrum can also provide
 180 information about the $\text{PO}_2(\text{OH})_2^{-1}$ group. Such group is very rare in minerals and not
 181 many Raman spectroscopy data are present in literature providing its vibrational
 182 modes. However, we found data on synthetic compounds like $\text{M}[\text{PO}_2(\text{OH})_2] \cdot 2\text{H}_2\text{O}$
 183 with $\text{M} = \text{Mg, Mn, Fe, Co, Zn, Ni, Cd}$ (Koleva and Heffenberger, 2007) for which the
 184 P-OH and P-O show two bands between 946 and 977 cm^{-1} and 1046 and 1070 cm^{-1} ,
 185 respectively. Moreover, for synthetic compounds like NaH_2PO_4 and Na_2HPO_4 , Dutta
 186 and Shieh (1985) report that the $\text{PO}_2(\text{OH})_2^{-1}$ group shows two strong polarized bands
 187 at 880 cm^{-1} and 1060 cm^{-1} due to the P-OH and P-O stretches, respectively.
 188 Considering that the Raman spectrum of tazoliite shows one peak at 869 cm^{-1} , two
 189 peaks between 961 and 981 cm^{-1} and a fourth peak at 1062 cm^{-1} (Figure 4) we are
 190 strongly confident about the presence of the $\text{PO}_2(\text{OH})_2^{-1}$ group.
 191 Relative to the most intense peak found at about 750 cm^{-1} , it has been reported in
 192 literature (Su *et al.*, 2000) that for synthetic nenadkevichite
 193 $[(\text{Na,K})_2(\text{Nb,Ti})_2[\text{Si}_4\text{O}_{12}](\text{O,OH})_2 \cdot 2\text{H}_2\text{O}]$, with a structure related to tazoliite (see
 194 below), such a band has been assigned to Ti-O stretching vibrations of TiO_6 units.
 195 Similarly, for tazoliite we could assign this band to Ti-O and Nb-O stretching
 196 vibrations of TiO_6 and NbO_6 units. Further evidence for this comes from the IR
 197 spectrum of komarovite $[(\text{Ca,Mn})\text{Nb}_2[\text{Si}_2\text{O}_7](\text{O,F})_3 \cdot 3.5\text{H}_2\text{O}]$ from Lovozero (most
 198 intense band at exactly 750 cm^{-1} ; Pekov *et al.*, 2004). Concerning the OH group
 199 region, tazoliite shows a very weak and broad peak at 3516 cm^{-1} , consistent with OH

stretching and confirming the crystal chemical formula proposed for tazoliite. No evidence of H₂O bending at about 1600 cm⁻¹ is present (even if present, the bending mode of H₂O at 1600 cm⁻¹ would be too weak to be visible with respect to the already weak peak for OH stretching at 3516 cm⁻¹).

Site assignment

Cation sites

Tazoliite 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 $\langle \text{Si-O} \rangle = 1.647 \text{ \AA}$, corresponding to a full occupation by Si.

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 found for kenopyrochlore [1.9855 Å – Bindi *et al.*, 2006; renamed from bariopyrochlore after the approval of the new scheme of nomenclature for the pyrochlore supergroup, approved by the CNMNC–IMA (Atencio *et al.*, 2010)] and the value of 1.986 Å observed in hydropyrochlore [Ercit *et al.*, 1994; renamed after new scheme of nomenclature for the pyrochlore supergroup, approved by the CNMNC–IMA (Atencio *et al.*, 2010)], having a B-site population very close to that observed in tazoliite. 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 the $\langle \text{Ti-O} \rangle$ bond of the pure Y₂Ti₂O₇ (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 account the molar fractions of Ti and Nb in tazoliite (*i.e.*, Ti = 0.80 and Nb = 0.20 *a.p.f.u.*) and the mean bond distances for the pure components, we obtain a value of 1.970 Å. If we consider the chemical analyses, site assignment must account for 0.07

apfu of Ta. The highest site scattering observed is at the *Nb1* site. Therefore, we have assigned all the Ta at this site. The composition we obtain for the three octahedral 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 correspond to the observed and calculated site scattering values of 76.78 vs. 78.91, 36.44 vs. 36.82, 51.6 vs. 52.55 e- pfu, respectively.

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

$^{A1}(Ba_{1.93}Na_{0.06})^{A2}(Sr_{0.53}Ca_{0.38}Fe^{2+}_{0.09})^{A3}(Ca_{0.82}Na_{0.18})^{Nb1}(Nb_{1.64}Ti_{0.28}Ta_{0.07}Zr_{0.01})^{Nb2}(Nb_{0.78}Ti_{0.22})^{Ti3}(Ti_{1.55}Nb_{0.45})Si$. Ideally, we have $Ba_2SrCaNb_3Ti_2Si$ with a charge of +35.

250 *Anion sites.*

251 There are 7 anion sites fully occupied by oxygen atoms in the structure of tazoliite,
252 which account for 17 apfu. There are 3 anion sites which are related to the
253 $[\text{PO}_2(\text{OH})_2]$ 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.
266 Therefore, the anion composition is $\text{O}_{17} + [\text{PO}_2(\text{OH})_2]_{0.5}$ with a charge of -34.5 or O_{17}
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 monovalent cation, for
270 example Na.

271 Therefore the ideal composition of this structural type will range from
272 $\text{Ba}_2\text{SrCaNb}_3\text{Ti}_2\text{SiO}_{17}(\text{OH})$ to $\text{Ba}_2\text{SrCa}_{0.5}\text{Na}_{0.5}\text{Nb}_3\text{Ti}_2\text{SiO}_{17}[\text{PO}_2(\text{OH})_2]_{0.5}$. This would
273 lead to two ideal compositions. The mineral composition we have studied has
274 $[\text{P}+\text{S}+(\text{Si}-1)] > 0.25$ and thus we define tazoliite as $\text{Ba}_2\text{CaSr}_{0.5}\text{Na}_{0.5}\text{Nb}_3\text{Ti}_2\text{SiO}_{17}$

[PO₂(OH)₂]_{0.5}, which requires P₂O₅ 3.24, Nb₂O₅ 36.47, SiO₂ 5.50, TiO₂ 14.62, BaO 28.06, CaO 5.13, SrO 4.74, Na₂O 1.42, H₂O 0.82, Total 100.00 wt%, and a mineral with Ba₂SrCaNb₃Ti₂Si O₁₇(OH) would correspond to a new species.

Relation to other structures

Tazzoliite is related to the pyrochlore structure (Atencio et al., 2010) with the addition of a slab of SiTiO₃[PO₂(OH)₂]_{0.5} every 0.5 *b* translation parallel to [110] of pyrochlore (Figure 3). Other pyrochlore-related structures have been described by Ferraris *et al.* (2008) although they have alternate one [K-rich nenadkevichite (Na,K)(Nb,Ti)₂[Si₄O₁₂](O,OH)₂·1.6H₂O, Rastsvetayeva *et al.*, 1994], two [fersmanite (Ca_{5.49}Na_{2.37}Sr_{0.08}Fe_{0.06})(Nb_{1.61}Ti_{2.39})(Si₂O₇)₂O₈F₃, Sokolova *et al.*, 2002], or three [Na-rich komarovite Na_{5.5}Ca_{0.8}La_{0.2}Ti_{0.5}Nb_{5.5}Si₄O₂₆F₂·H₂O, Balič Žunič *et al.*, 2002] octahedra-thick (100)-pyrochlore slabs with (SiO₄) groups with different degrees of polymerization (four-membered rings being the most frequent unit) (Figure 5). Tazzoliite thus represents a novel type of pyrochlore-related structure, which includes further anionic groups other than (SiO₄). One of the anionic groups coordinates with (OH) groups. The dominant cation at the centre of the (MO₄) anionic group is phosphorous. The presence of dihydrogen phosphate groups has been observed in girvasite, (NaCa₂Mg₃(PO₄)₂[PO₂(OH)₂](CO₃)(OH)₂·4H₂O (Sokolova *et al.*, 1990).

Acknowledgments

We are really delighted to contribute to this issue dedicated to Mark Welch, a well-known European mineralogical crystallographer. Most of us collaborated with him during the last years and Mark gave, as usual, a very remarkable contribution. His

longstanding studies on hydrous silicates are especially noteworthy, and they undoubtedly represent a solid basis for all the scientific community.

We would like to thank Bruno Fassina for providing us tazzerite. We also thank Mr. Fassina for the photo of tazzerite shown in Figure 1. L. Tauro and E. Masiero are thanked for sample preparation and R. Carampin for the microprobe analysis. The work was supported by “Progetto d’Ateneo 2006 from University of Padova” to F. Nestola. We thank Associate Editor Diego Gatta, Stuart Mills and one anonymous referee for constructive comments, which helped to improve the manuscript.

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Table and figure captions

Table 1. Microprobe analyses for tazzerliite based on 7 analysis points.

Table 2. Crystal data for tazzerliite.

Table 3. X-ray powder diffraction patterns for tazzerliite.

Table 4. Atom coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for tazzerliite. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected geometric parameters ($\text{\AA}$).

Figure 1. Geological map of the Monte delle Basse zone where Tazzerliite was found (modified from Astolfi and Colombara, 2003).

Figure 2. Appearance of tazzerliite under a conventional stereoscopic microscope (photo by Bruno Fassina).

Figure 3. Crystal structure of tazzerliite and its relationships with pyrochlore structure. Light yellow polyhedra are Nb/Ti sites; orange tetrahedra are Si sites; yellow tetrahedra (P,Si,S) are partially occupied sites; violet spheres indicate A1 sites; grey spheres are Sr and Ca dominant sites (A2 and A3); red spheres are O atoms; small white spheres are H atoms; green spheres are F atoms.

Figure 4. Raman spectrum of tazzerliite collected between 150 and 3700 cm^{-1} . In figure 3a and 3b the ranges between 150 and 2000 cm^{-1} and 3000 and 3700 cm^{-1} are shown, respectively.

Figure 5. Relationships among known pyrochlore-like structures.

Table 1

Constituent	wt%	Range	SD	Probe Standard (analysing crystals)
SO ₃	0.51	0.36-0.66	0.10	BaSO ₄ (PET)
Nb ₂ O ₅	34.51	33.53-35.38	0.63	Pure metal for Nb (PET)
Ta ₂ O ₅	0.89	0.66-1.16	0.16	Pure metal for Ta (LiF)
V ₂ O ₃	0.05	0.00-0.11	0.04	Vanadinite (LiF)
P ₂ O ₅	0.85	0.85-0.85		Apatite (TAP)
SiO ₂	6.10	5.74-6.31	0.19	Diopside (Si TAP; Ca PET)
TiO ₂	14.77	14.42-15.09	0.27	MnTiO ₃ (PET)
SnO ₂	0.04	0.00-0.09	0.03	SnO ₂ (PET)
ZrO ₂	0.11	0.07-0.21-	0.10	Synthetic zircon (PET)
FeO	0.63	0.55-0.66	0.04	Fe ₂ O ₃ (LiF)
MnO	0.01	0.00-0.03	0.17	MnTiO ₃ (LiF)
CaO	6.07	5.67-6.60	0.02	Diopside (PET)
BaO	26.75	26.31-27.28	0.39	BaSO ₄ (LiF)
SrO	4.92	4.18-5.72	0.48	Celestine (PET)
Na ₂ O	0.70	0.64-0.77	0.05	Amelia (TAP)
H ₂ O*	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.

416

417 **Table 2**

418

Space group	<i>Fmmm</i>
<i>a</i> (Å)	7.4105(4)
<i>b</i>	20.0675(11)
<i>c</i>	21.4471(11)
<i>V</i> (Å ³)	3189.4(3)
<i>Z</i>	4
Absorption coefficient (mm ⁻¹)	8.864
<i>F</i> (000)	3941
<i>D</i> _{calc.} (g/cm ³)	4.489
Crystal size (mm)	0.015 x 0.04 x 0.10
Radiation/filter	MoKα/graphite
2θ-range for data collection (°)	1.90 to 30.00°.
<i>R</i> (int) (%)	5.40
Reflections collected	12200
	$-10 \leq h \leq 10$
Index ranges	$-28 \leq k \leq 28,$ $-30 \leq l \leq 30$
Independent reflections	1312
$F_o > 4\sigma F$	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

419

420

421

422 **Table 3**

<i>hkl</i>	<i>d_{obs}</i> (Å)*	<i>I_{rel}</i>	<i>d_{calc}</i> (Å)**	<i>I_{rel}</i>
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
1	7	9			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 α 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).

424 **Table 4**
425

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)	8 <i>f</i>	0.75 Ca + 0.25 Ba	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.010(1)
A3 (Ca)	8 <i>h</i>	0.76 Ca + 0.24 Na	$-\frac{1}{2}$	0.0963(3)	0	0.026(2)
Nb1	16 <i>m</i>	0.86 Nb + 0.14 Ti	$-\frac{1}{2}$	0.17122(6)	0.13211(6)	0.009(1)
Nb2	8 <i>e</i>	0.76 Nb + 0.24 Ti	$\frac{1}{4}$	$\frac{1}{4}$	0	0.010(1)
Ti3	16 <i>k</i>	0.80 Ti + 0.20 Nb	$\frac{1}{4}$	0.07937(10)	$\frac{1}{4}$	0.012(1)
Si	8 <i>i</i>	1.00	$\frac{1}{2}$	0	0.1470(2)	0.008(1)
O1	8 <i>h</i>	1.00	0	0.2139(7)	0	0.008(2)
O2	32 <i>p</i>	1.00	0.3040(9)	0.1426(3)	0.1887(3)	0.010(1)
O3	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)
O5	32 <i>p</i>	1.00	0.3180(9)	0.1841(3)	0.0646(3)	0.011(1)
O6	16 <i>m</i>	1.00	$-\frac{1}{2}$	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)
O8	8 <i>g</i>	0.43	-0.340(5)	0	0	0.018(10)
P	8 <i>g</i>	0.28	0.066(4)	0	0	0.038(9)
O9	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	16 <i>o</i>	0.58	0.177(4)	0.0582(13)	0	0.036(8)

434 **Table 5**

Nb1—O3	1.839(10)	A1—O7	2.663(11)
Nb1—O2 x2	1.978(7)	A1—O9	2.722(14)
Nb1—O5 x2	1.996(7)	A1—O5 x2	2.751(7)
Nb1—O6	2.15(1)	A1—O3	2.755(10)
<Nb1—O>	1.990	A1—O1	2.839(9)
Nb2—O5 x4	1.980(6)	A1—O2 x2	2.887(7)
Nb2—O1 x2	1.989(5)	A1—O10	2.972(18)
<Nb2—O>	1.983	<A1—O>	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>	2.537
<Ti3—O>	1.975	A3—O8	2.267(20)
Si—O6 ⁱⁱ x2	1.632(11)	A3—O6 x2	2.329(11)
Si—O4 x2	1.662(10)	A3—O10 ⁱ	2.513(29)
<Si—O>	1.647	A3 ⁱⁱ —O5 x4	2.616(8)
P—O10 x2	1.429(32)	<A3—O>*	2.484
P—O9 x2	1.477(42)	<A3—O>**	2.519
<P—O>	1.453	O9—H9	0.988(23)
		O8—O10	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.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5