

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

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[Received 11 January 2012; Accepted 16 March 2012; Associate Editor: G. Diego Gatta]

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) from Monte delle Basse, Euganei Hills, Galzignano Terme, Padova, Italy. It occurs as lamellar pale orange crystals, which are typically a few μm thick and up to 0.4 mm long, closely associated with a diopsidic pyroxene and titanite. Tazzoliite is transparent. It has a white streak, a pearly lustre, is not fluorescent and has a hardness of 6 (Mohs' scale). The tenacity is brittle and the crystals have a perfect cleavage along $\{010\}$. The calculated density is 4.517 g cm^{-3} . Tazzoliite is biaxial (–) with $2V_{\text{meas}}$ of $\sim 50^\circ$, it is not pleochroic and the average refractive index is 2.04. No twinning was observed. Electron microprobe analyses gave the following chemical formula: $(\text{Ba}_{1.93}\text{Ca}_{1.20}\text{Sr}_{0.52}\text{Na}_{0.25}\text{Fe}_{0.10}^{2+})_{\Sigma 4}(\text{Nb}_{2.88}\text{Ti}_{2.05}\text{Ta}_{0.07}\text{Zr}_{0.01}\text{V}_{0.01}^{5+})_{\Sigma 5.02}\text{SiO}_{17}[(\text{P}_{0.13}\text{Si}_{0.12}\text{S}_{0.07})_{\Sigma 0.32}\text{O}_{0.66}(\text{OH})_{0.66}][\text{F}_{0.09}(\text{OH})_{0.23}]_{\Sigma 0.32}$.

Tazzoliite is orthorhombic, space group $Fmmm$, with unit cell parameters a 7.4116(3), b 20.0632(8), c 21.4402(8) Å, V 3188.2(2) Å³ and Z 8. The crystal structure, obtained from single crystal X ray diffraction data, was refined to $R_1(F^2)$ 0.063. It consists of a framework of Nb(Ti) octahedra and BaO_7 polyhedra sharing apexes or edges, and Si tetrahedra sharing apexes with Nb(Ti) octahedra and BaO_7 polyhedra. The structure, which is related to the pyrochlore structure, contains three Nb(Ti) octahedra: two are Nb dominant and one is Ti dominant. Chains of $A2\text{O}_8$ polyhedra [$A2$ being occupied by Sr(Ca,Fe)] extend along $[100]$ and are surrounded by Nb octahedra. Channels formed by six Nb(Ti) octahedra and two tetrahedra, or four $A1\text{O}_8(\text{OH})$ polyhedra ($A1$ being occupied by Ba), alternate along $[100]$. The channels are partially occupied by $[\text{PO}_2(\text{OH})_2]$ in two possible mutually exclusive positions, alternating with fully occupied $A3\text{O}_7$ polyhedral pairs [$A3$ being occupied by Ca(Na)]. The seven strongest X ray powder diffraction lines [d in Å (hkl)] are: 3.66 (60) (044), 3.16 (30) (153), 3.05 (100) (204), 2.98 (25) (240), 2.84 (50) (064), 1.85 (25) (400) and 1.82 (25) (268). Raman spectra of tazzoliite were collected in the range 150–3700 cm^{-1} and confirm the presence of OH groups. Tazzoliite is named in honour of Vittorio Tazzoli in recognition of his contributions to the fields of mineralogy and crystallography.

KEYWORDS: tazzoliite, new mineral, crystal structure, pyrochlore, Raman spectroscopy, Euganei Hills.

Introduction

THE new mineral tazzoliite was found at Monte delle Basse in the Euganei Hills, south of Galzignano Terme, Padova, Italy ($45^\circ 18' 30''\text{N}$ $43^\circ 49' 47''\text{E}$) by Bruno Fassina. The geology is

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DOI: 10.1180/minmag.2012.076.4.01

dominated by lower Oligocene rhyolites and trachytes (Fig. 1). In the area where tazzoliite was found, syenitic and gabbroic rocks are present, which based on an old hypothesis, represent the deep segregation products of rhyolitic and trachytic magmas (Dal Piaz, 1935). Skarn and calc silicate rocks also occur in contact with the intrusives (Stark, 1936). These rocks are made up of wollastonite, grossular, gehlenite, sanidine, gyrolite, hibschite, kilchoanite, pectolite, rankinite and plagioclase, with rare sanidine xenoliths which contain cavities up to several millimetres across. Tazzoliite occurs in these cavities as fan shaped groups of platy crystals (Fig. 2), which are pale orange, and up to 0.4 mm long and a few μm thick.

Tazzoliite was approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2011 018). The name honours Professor Vittorio Tazzoli (b. 1938) in recognition of his contribu-

tion 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 under registration number MMP M9426.

Association and physical properties

Tazzoliite is associated with a green diopsidic pyroxene and titanite. It is pale orange with a white streak; the lustre is pearly and the crystals are transparent. It is not fluorescent and has a hardness of 6 on the Mohs' scale (VHN load 15 g, mean 788 kg mm^{-2}). The tenacity is brittle and crystals have a perfect cleavage along $\{010\}$. No parting was observed and the fracture is uneven.

Optically, tazzoliite is biaxial (-), and using on the Gladstone–Dale relationship (Mandarino, 1976) the calculated average refractive index is 2.04. The $2V_{\text{meas}}$ is $50(5)^\circ$ and no pleochroism was observed. No twinning was detected.

Experimental methods

Microprobe analysis

Microprobe analyses (7 WDS spots) were obtained on the same crystal fragment used in the structural study on a CAMECA SX 50 electron microprobe. Operating conditions were 20 kV and 20 nA with a spot size of $2 \mu\text{m}$, for Si, Ti, V, Nb, Ta, Fe, Mn, Sn, Zr, Ca and Ba; and 20 kV and 10 nA with a spot size of $10 \mu\text{m}$ for F, Na, P, S and Sr. The second

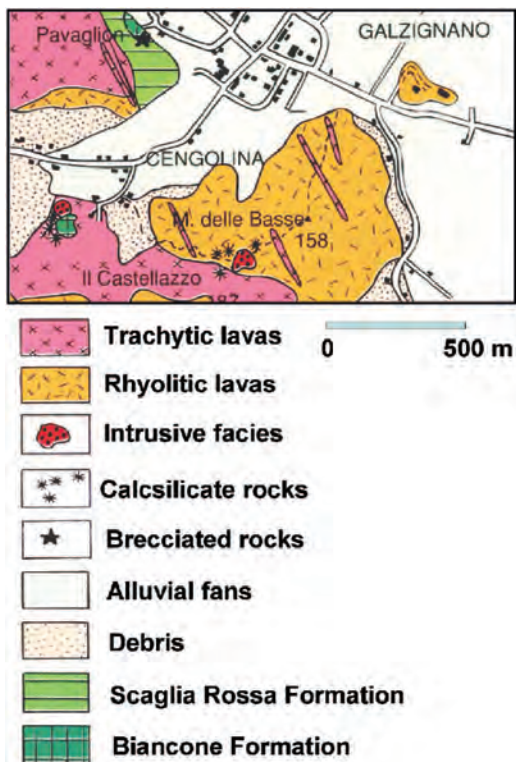


FIG. 1. Geological map of the area around Monte delle Basse where tazzoliite was found (modified from Astolfi and Colombara, 2003).

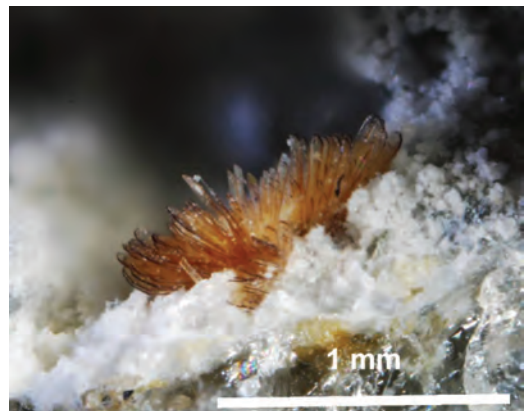


FIG. 2. A high magnification image of tazzoliite showing its colour and crystal form (photo by Bruno Fassina).

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scheme was used to minimize beam damage and volatilization. The crystal was found to be homogeneous to within analytical uncertainty. The H₂O content was calculated and checked on the basis of the structure refinement. The elements K, Cr and Cl were sought but not detected. Rare earth elements were also sought, but were below the detection limit of the instrument. Analytical data are given in Table 1. The empirical formula was calculated using an iterative process on the basis of (18 + 2x) (O,F) a.p.f.u. with x = [P + S + (Si - 1)] < 0.5 a.p.f.u., to take into account the partial occupancy of anionic groups in the channels (see crystal structure description). The empirical formula is (Ba_{1.93}Ca_{1.20}Sr_{0.52}Na_{0.25}Fe_{0.10}²⁺)_{Σ4}(Nb_{2.88}Ti_{2.05}Ta_{0.07}Zr_{0.01}V_{0.01}⁵⁺)_{Σ5.02}SiO₁₇[(P_{0.13}Si_{0.12}S_{0.07})_{Σ0.32}O_{0.66}(OH)_{0.66}][F_{0.09}(OH)_{0.23}]_{Σ0.32}.

X-ray diffraction

A single crystal of tazzoliite (0.100 × 0.040 × 0.015 mm), free from inclusions and not twinned, with sharp optical extinction and sharp reflections, was selected for the analysis by X ray diffraction. Measurements were made on a Bruker AXS

single crystal diffractometer equipped with a Smart APEX CCD detector, using graphite monochromated MoK α radiation. Images were collected at an ω increment of 0.2°. Cell parameters were refined using 5584 reflections with $I/\sigma(I) > 10$. A total of 12,200 reflections were collected in the 2 θ range 3.8–60.0°, of which 1312 were unique ($R_{\text{int}} = 5.4\%$); absorption and Lorentz polarization corrections 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 and 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. A crystallographic information file has been deposited with the Principal Editors of *Mineralogical Magazine* and is available at http://www.minersoc.org/pages/e_journals/dep_mat.html.

Unit cell parameters refined from powder data are as follows: $a = 7.4116(3)$, $b = 20.0632(8)$, $c = 21.4402(8)$ Å and $V = 3188.2(2)$ Å³.

TABLE 1. Composition of tazzoliite.

Constituent	Mean 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			

[†] Values are means of seven analyses.

* Water calculated from crystal structure stoichiometry.

TABLE 2. Crystal data for tazzoliite.

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 × 0.04 × 0.10
Radiation/filter	MoK α /graphite
2 θ range for data collection (°)	1.90 to 30.00
<i>R</i> _{int} (%)	5.40
Reflections collected	12,200
Index ranges	-10 ≤ <i>h</i> ≤ 10, -28 ≤ <i>k</i> ≤ 28, -30 ≤ <i>l</i> ≤ 30
Independent reflections	1312
<i>F</i> _o > 4 σ <i>F</i>	1300
Refinement method	Full matrix least squares on <i>F</i> ² , fixed weights proportional to 1/ σ <i>F</i> _o ²
No. of refined parameters	95
Final <i>R</i> _{obs} (%) [<i>F</i> _o > 4 σ <i>F</i>]	6.25
<i>R</i> ₁	6.33
<i>wR</i> ₂	15.81
Goodness of fit on <i>F</i> ²	1.246

Raman spectroscopy

Raman spectra were collected using a micro Raman spectrometer of our own design, based on a single 320 mm focal length imaging spectrograph (Triax 320 ISA Instruments), equipped with a 1800 lines mm⁻¹ holographic grating and a liquid nitrogen cooled CCD detector (Spectrum One ISA Instruments). The excitation source was a Spectra Physics Argon ion 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 20 × /0.35, 50 × /0.75, and 100 × /0.90 objectives was coupled to the spectrograph. This made it possible to observe the sample with the microscope and then to select particular areas for Raman analysis. With the 100 × objective, the lateral resolution is estimated to be 0.5 μ m and the depth of focus 1–2 μ m. To avoid 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 at 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), *b* = 20.0675(11), *c* = 21.4471(11) Å, *V* = 3189.4(3) Å³ and *Z* = 8. The calculated density is 4.517 g cm⁻³ using the empirical formula. Tazzoliite has no synthetic or natural analogues.

The structure of tazzoliite (Fig. 3) consists of a framework of Nb(Ti) octahedra and *AlO*₈(OH) polyhedra sharing apexes or edges, and Si tetrahedra sharing apexes with Nb(Ti) octahedra and *AlO*₈(OH) polyhedra. Tazzoliite contains three different Nb(Ti) octahedra: two are Nb dominant (with site populations of Nb_{0.86}Ti_{0.14} and Nb_{0.76}Ti_{0.24}, respectively) and one is Ti dominant (with a site population of Ti_{0.80}Nb_{0.20}). The Ti dominant octahedra form pairs sharing an edge along [010], and they extend along [100] forming a double chain. The Nb dominant octahedra form a chain along [100], which is decorated by four Nb dominant octahedra sharing apexes.

Chains of *A2O*₈ polyhedra extend along [100] and are surrounded by Nb octahedra. The *A2O*₈

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TABLE 3. X ray powder diffraction data for tazzoliite.

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (Å)*	<i>I</i> _{rel}	<i>d</i> _{calc} (Å)**	<i>I</i> _{rel}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (Å)*	<i>I</i> _{rel}	<i>d</i> _{calc} (Å)**	<i>I</i> _{rel}
0	0	2			10.724	2	2	10	4			1.676	4
0	2	0			10.034	36	4	4	4	1.652	10	1.653	6
0	2	2	7.3	15	7.327	15	3	9	1			1.650	3
0	0	4			5.362	3	1	11	5	1.636	5	1.637	4
0	4	0	5.0	15	5.017	13	0	8	10	1.629	5	1.630	4
2	0	0	3.71	10	3.705	11	2	6	10			1.623	3
0	4	4	3.66	60	3.663	47	2	0	12	1.610	5	1.610	4
1	1	5			3.650	8	0	12	4			1.596	2
2	0	2	3.49	20	3.502	10	0	6	12	1.575	5	1.576	5
1	5	1			3.482	17	4	4	6			1.563	3
2	2	2	3.31	10	3.307	8	4	6	4	1.552	10	1.551	13
1	3	5	3.25	5	3.246	5	3	9	5			1.544	2
1	5	3	3.16	30	3.165	29	4	0	8	1.523	10	1.524	8
2	0	4	3.05	100	3.048	100	3	3	11			1.492	3
2	4	0	2.979	25	2.981	25	2	12	4			1.466	2
2	2	4	2.918	10	2.917	11	3	11	1			1.464	2
0	4	6	2.910	15	2.911	12	3	11	3			1.438	2
2	4	2	2.872	10	2.872	10	1	11	9			1.422	2
0	6	4	2.835	50	2.838	47	2	12	6	1.401	5	1.402	4
1	1	7	2.801	10	2.804	8	1	1	15			1.401	2
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			1.856	3							
4	0	0	1.854	25	1.853	17							
3	3	7			1.848	3							
2	6	8	1.822	25	1.822	22							
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							

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

polyhedra share edges with Nb1 and Ti3 octahedra.

Tazzoliite contains channels formed by six Nb octahedra and two tetrahedra, or four AlO₈(OH) polyhedra, which alternate along [100]. The channels are partially occupied by [PO₂(OH)₂] in two mutually exclusive positions, alternating with fully occupied A3O₆(OH) polyhedral pairs. Heterovalent substitutions occur at the cation site (*P* site) in the [PO₂(OH)₂] anionic group, which may contain P, S or Si. This is the most complex part of the structure: the partial occupancy of the *P* sites is important in the calculation of possible endmember formulae. Due to the mutually exclusive position of the *P* sites, it is implicit that a composition of tazzoliite which contains [PO₂(OH)₂]_{*x*} with *x* > 0.5 is not possible. In addition, on the basis of charge requirements, S cannot be dominant at this site. The observed P–O distances are rather short, due to the difficulty of solving the complicated environment

TABLE 4. Atom coordinates and equivalent isotropic displacement parameters (\AA^2) for tazzoilite.

Atom	Wyckoff	Occupancy	x/a	y/b	z/c	U_{eq}^*
A1 (Ba)	16m	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	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.010(1)
A3 (Ca)	8h	0.76 Ca + 0.24 Na	$-\frac{1}{2}$	0.0963(3)	0	0.026(2)
Nb1	16m	0.86 Nb + 0.14 Ti	$-\frac{1}{2}$	0.17122(6)	0.13211(6)	0.009(1)
Nb2	8e	0.76 Nb + 0.24 Ti	$\frac{1}{4}$	$\frac{1}{4}$	0	0.010(1)
Ti3	16k	0.80 Ti + 0.20 Nb	$\frac{1}{4}$	0.07937(10)	$\frac{1}{4}$	0.012(1)
Si	8i	1.00	$\frac{1}{2}$	0	0.1470(2)	0.008(1)
O1	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)
O3	16m	1.00	0	0.2469(5)	0.1706(4)	0.007(2)
O4	16n	1.00	0.3188(13)	0	0.1927(4)	0.008(2)
O5	32p	1.00	0.3180(9)	0.1841(3)	0.0646(3)	0.011(1)
O6	16m	1.00	$-\frac{1}{2}$	0.0680(5)	0.1053(5)	0.013(2)
O7	16m	1.00	0	0.0723(5)	0.2180(5)	0.011(2)
O8	8g	0.43	-0.340(5)	0	0	0.018(10)
P	8g	0.28	0.066(4)	0	0	0.038(9)
O9	8i	0.82	0	0	0.065(2)	0.071(15)
H9	16n	0.43	0.11200	0	0.09000	0.0850
O10	16o	0.58	0.177(4)	0.0582(13)	0	0.036(8)

* The value of U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Selected geometric parameters for tazzoilite (\AA).

Nb1–O3	1.839(10)	A1–O7	2.663(11)
Nb1–O2 $\times 2$	1.978(7)	A1–O9	2.722(14)
Nb1–O5 $\times 2$	1.996(7)	A1–O5 $\times 2$	2.751(7)
Nb1–O6	2.15(1)	A1–O3	2.755(10)
<Nb1–O>	1.990	A1–O1	2.839(9)
Nb2–O5 $\times 4$	1.980(6)	A1–O2 $\times 2$	2.887(7)
Nb2–O1 $\times 2$	1.989(5)	A1–O10	2.972(18)
<Nb2–O>	1.983	<A1–O>	2.830
Ti3–O2 $\times 2$	1.870(6)	A2–O3 $\times 4$	2.517(6)
Ti3–O7 $\times 2$	1.981(4)	A2–O2 $\times 4$	2.556(6)
Ti3–O4 $\times 2$	2.075(6)	<A2–O>	2.537
<Ti3–O>	1.975	A3–O8	2.267(20)
Si–O6 ⁱⁱ $\times 2$	1.632(11)	A3–O6 $\times 2$	2.329(11)
Si–O4 $\times 2$	1.662(10)	A3–O10 ⁱ	2.513(29)
<Si–O>	1.647	A3 ⁱⁱ –O5 $\times 4$	2.616(8)
P–O10 $\times 2$	1.429(32)	<A3–O>*	2.484
P–O9 $\times 2$	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.

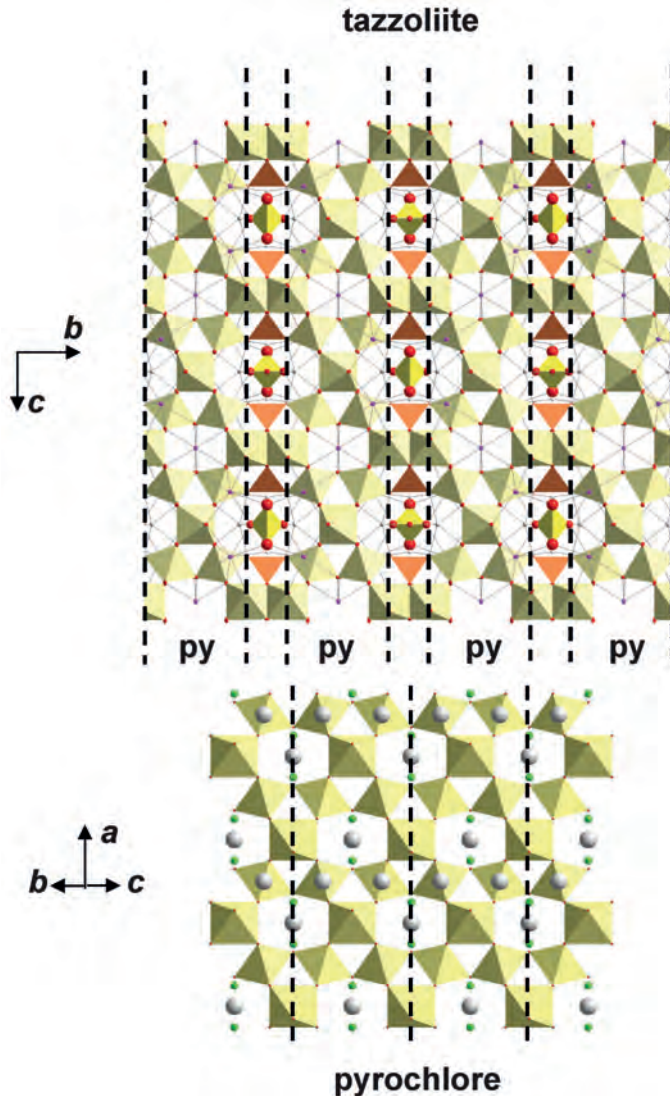


FIG. 3. The crystal structure of tazzoliite and its relationship with the pyrochlore structure. Light yellow polyhedra are Nb/Ti sites; orange tetrahedra are Si sites; yellow tetrahedra (P,Si,S) are partially occupied sites; violet spheres are A1 sites; grey spheres are Sr and Ca dominant sites (A2 and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

in the presence of $[\text{PO}_2(\text{OH})_2]$ groups. Each P atom at the *P* sites is coordinated by two O9 sites and two O10 sites, OH groups are present at the O9 site if the *P* site is occupied and at the O8 site if the *P* site is vacant. The anion sites O8 and O10 are mutually exclusive. The same applies to H bonded to O9 [O8], where only one alternative position can be occupied. Therefore, in terms of

formula normalization, if the *P* site is vacant 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 a.p.f.u. An occupation of the *P* site of x requires $2x$ additional oxygen atoms to be present at the O10 sites. Thus, the total number of anions is $18 + 2x$, where x is the occupancy of

the *P* site [i.e. $P + S + (Si - 1)$]. As previously stated, x cannot be >0.5 , and therefore the maximum quantity of anions is 19 p.f.u.

Raman spectroscopy

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

In the 200–400 cm^{-1} range the Raman bands are likely to be due to vibrations between large cations (e.g. Ba, Ca, Na, Sr) and oxygen atoms.

In the 400–600 cm^{-1} range the Raman bands can be assigned to symmetric Si–O–Si stretching vibrations and Si–O–Si bending.

In the 800–1200 cm^{-1} range the Raman bands are likely to be due to symmetric Si–O stretching motions of silicate units with one, two, three or four non bridging oxygen atoms. This region of the spectrum also provides information about the

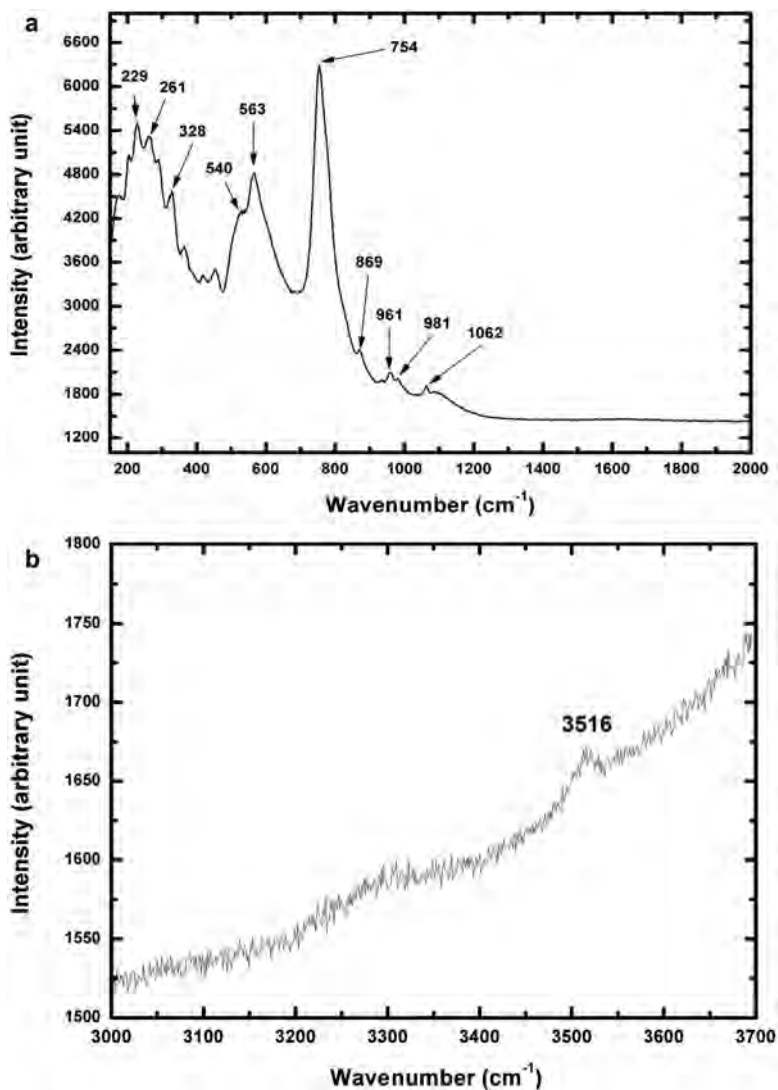


FIG. 4. Raman spectra of tazzoliite between 150 and 3700 cm^{-1} . (a) The range from ~ 150 to 2000 cm^{-1} and (b) the range from 3000 to 3700 cm^{-1} .

$\text{PO}_2(\text{OH})_2^-$ group. This group is very rare in minerals and few Raman spectra of substances containing it have been reported. In the spectra of synthetic compounds with the general formula $\text{M}[\text{PO}_2(\text{OH})_2] \cdot 2\text{H}_2\text{O}$, where M = Mg, Mn, Fe, Co, Zn, Ni, Cd (Koleva and Heffner, 2007), P–OH and P–O stretching produces two bands between 946 and 977 cm^{-1} , and 1046 and 1070 cm^{-1} , respectively. In synthetic compounds such as NaH_2PO_4 and Na_2HPO_4 , Dutta and Shieh (1985) report that the $\text{PO}_2(\text{OH})_2^-$ group produces strongly polarized bands at 880 cm^{-1} and 1060 cm^{-1} , which are due to the P–OH and P–O stretches, respectively. As the Raman spectrum of tazzoliite has one peak at 869 cm^{-1} , two peaks between 961 and 981 cm^{-1} , and a peak at 1062 cm^{-1} (Fig. 4) we are confident of the presence of $\text{PO}_2(\text{OH})_2^-$ groups.

In synthetic nenadkevichite $[(\text{Na},\text{K})_2(\text{Nb},\text{Ti})_2[\text{Si}_4\text{O}_{12}](\text{O},\text{OH})_2 \cdot 2\text{H}_2\text{O}]$, which has a structure related to tazzoliite (see below), the intense band at $\sim 750 \text{ cm}^{-1}$ has been assigned to the Ti–O stretching vibrations of TiO_6 units (Su *et al.*, 2000). The intense band in this region of the tazzoliite spectrum is also probably due to Ti–O and Nb–O stretching vibrations of TiO_6 and NbO_6 units. Further support for this comes from the infrared spectrum of komarovite $[(\text{Ca},\text{Mn})\text{Nb}_2[\text{Si}_2\text{O}_7](\text{O},\text{F})_3 \cdot 3.5\text{H}_2\text{O}]$ from Lovozero, Russia (most intense band at exactly 750 cm^{-1} ; Pekov *et al.*, 2004).

In the region of the Raman spectrum that is characteristic of OH stretching vibrations, tazzoliite has a very weak and broad peak at 3516 cm^{-1} , which corroborates the proposed crystal chemical formula. No evidence of H_2O bending at about 1600 cm^{-1} is present (even if present, the bending mode of H_2O 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

Tazzoliite has three large cation sites (*A1*, *A2*, *A3*), three octahedral sites (*Nb1*, *Nb2* and *Ti3*) and one tetrahedral site (*Si*). The *Si* site has an average bond distance $\langle \text{Si–O} \rangle = 1.647 \text{ \AA}$, corresponding to full occupancy by Si.

The Nb dominant octahedra (*Nb1* and *Nb2*) have mean bond lengths of 1.990 and 1.983 Å , respectively, which closely match the values of 1.9855 Å reported for kenopyrochlore [Bindi *et al.*, 2006; renamed from bariopyrochlore using

the new CNMNC–IMA approved nomenclature for the pyrochlore supergroup (Atencio *et al.*, 2010)] and 1.986 Å for hydroxyrochlore [Ercit *et al.*, 1994; renamed using the nomenclature for the pyrochlore supergroup, approved by the CNMNC–IMA (Atencio *et al.*, 2010)], with a *B* site population very close to that observed in tazzoliite. The Ti dominant octahedron has a mean bond length of 1.975 Å . This is consistent with the values obtained by considering the $\langle \text{Ti–O} \rangle$ bond length in pure $\text{Y}_2\text{Ti}_2\text{O}_7$ (1.953 Å ; Becker and Will, 1970), and the sum of the Nb and O ionic radii (2.040 Å ; Shannon, 1976). The molar fractions of Ti and Nb in tazzoliite (Ti = 0.80 and Nb = 0.20 a.p.f.u.) and the mean bond lengths noted above produce a weighted average of 1.970 Å . If we consider the chemical analyses, site assignment must account for 0.07 a.p.f.u. of Ta. The largest measured site scattering value is at the *Nb1* site. Therefore, we have assigned all the Ta to this site. The composition we obtain for the three octahedral sites is therefore $^{Nb1}(\text{Nb}_{1.64}\text{Ti}_{0.28}\text{Ta}_{0.07}\text{Zr}_{0.01})^{Nb2}(\text{Nb}_{0.78}\text{Ti}_{0.22})^{Ti3}(\text{Ti}_{1.55}\text{Nb}_{0.45})$, which corresponds to measured and calculated site scattering values of 76.78 vs. 78.91, 36.44 vs. 36.82 and 51.6 vs. 52.55 e.p.f.u., 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 and there is a long bond to the partially occupied O10 site. Site occupancy refinement shows that the *A1* site has 53.48 electrons per site (e.p.s.). As this is the largest cation site in the structure we assign all of the Ba to it. Chemical analyses show that there are 1.93 Ba atoms p.f.u., and there are 2 *A1* sites p.f.u. This corresponds to 0.965 Ba atoms per *A1* site; if the remaining atoms are assigned as Na, this produces a calculated site scattering of 54.43 e.p.s. The *A2* site is a highly regular polyhedron and has a measured site occupancy of 29 e.p.s. There is one *A2* site p.f.u. It is smaller and has a lower site scattering than the *A1* site and we therefore assign the smaller atoms (i.e. Ca, Fe^{2+} and Sr) to it. This results in $\text{Sr}_{0.55}\text{Ca}_{0.38}\text{Fe}_{0.09}^{2+}$, with a calculated site scattering of 30.08 e.p.s., which is slightly larger than the measured value, and a mean charge of 2. The *A3* site has sevenfold coordination. Its measured site scattering is 17.84 e.p.s. and it must therefore contain cations with low scattering factors. We assign 0.82 a.p.f.u. of Ca, and 0.18 Na a.p.f.u., producing a calculated site scattering of 18.38 e.p.s., which is slightly larger than the

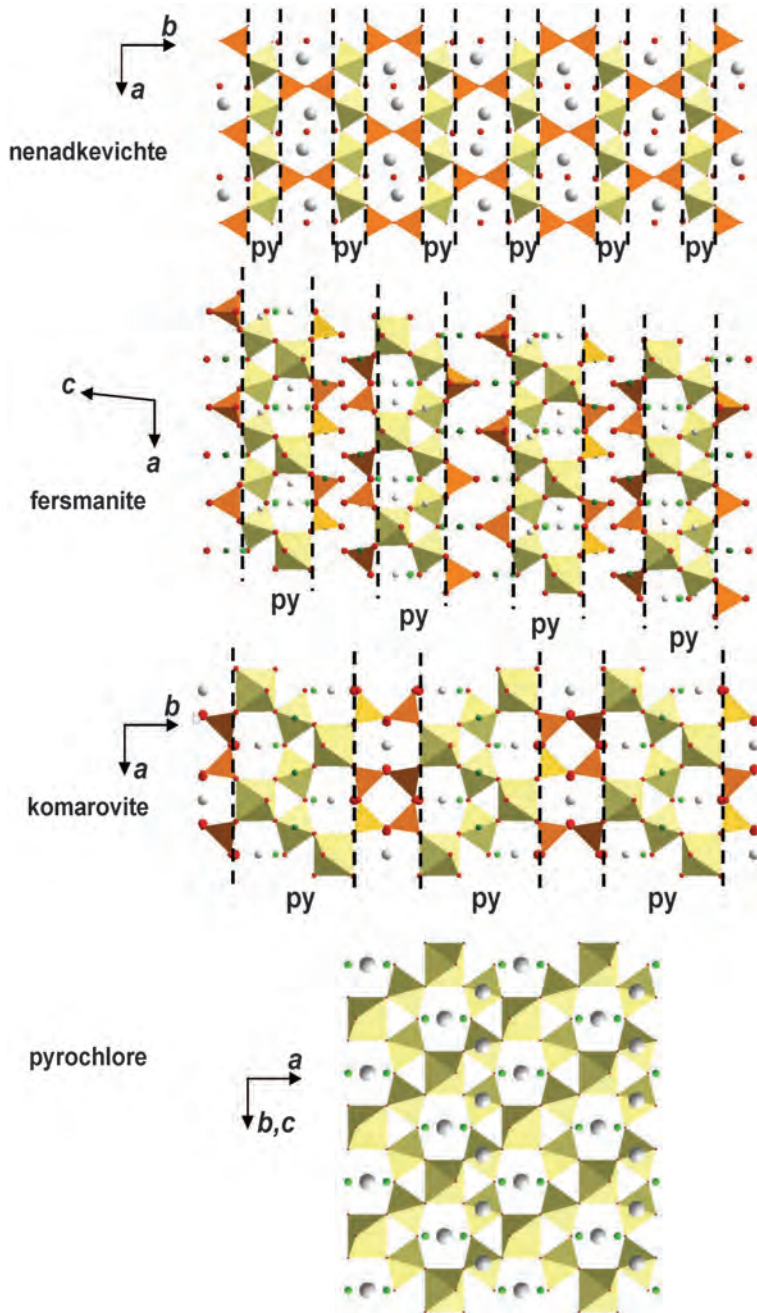


FIG. 5. Relationships among known pyrochlore like structures.

measured value. The overall composition of the cation sites is $A^1(Ba_{1.93}Na_{0.06})A^2(Sr_{0.53}Ca_{0.38}Fe_{0.09}^{2+})A^3(Ca_{0.82}Na_{0.18})$

$Nb^1(Nb_{1.64}Ti_{0.28}Ta_{0.07}Zr_{0.01})^{Nb2}(Nb_{0.78}Ti_{0.22})Ti^3(Ti_{1.55}Nb_{0.45})Si$. Ideally, we have $Ba_2SrCaNb_3Ti_2Si$ with a charge of +35.

Anion sites

There are 7 anion sites fully occupied by oxygen atoms in the structure of tazzoliite, which accounts for 17 a.p.f.u. Three anion sites are related to the $[\text{PO}_2(\text{OH})_2]$ anionic group: O8, O9 and O10. The *P* site is coordinated by two OH groups at the O9 anion site and two oxygen atoms at the O10 site and it has a maximum occupancy of 50% as the two 8g positions are mutually exclusive. This also implies that only half of the 16o positions of the O10 sites can be occupied. The excess site occupancy of 0.58 at O10 (Table 4) can be ascribed to the difficulty in the refinement of a structure with this level of positional disorder. During the refinement the site occupancies at the O9 and O10 sites and the isotropic displacement parameters were not constrained. The dihydrogen phosphate groups must therefore alternate in two positions along [100], otherwise they would share an edge with a very short P–P distance. If the *P* site is vacant, the O8 site is occupied by OH groups or F and the O9 and O10 sites are vacant. In this situation, the *A*1 polyhedron has sevenfold coordination, and the *A*3 polyhedron maintains its coordination number and has a smaller volume, as the *A*3–O8 bond is shorter than *A*3–O10, in agreement with a full occupancy by Ca.

Therefore, the anion composition is $\text{O}_{17} + [\text{PO}_2(\text{OH})_2]_{0.5}$, with a total charge of -34.5 , or $\text{O}_{17} + \text{OH}$, with a total charge of -35 . The latter matches the charge of the ideal cationic composition. The former requires a reduction in charge of $+0.5$, which is accomplished by substituting a divalent cation by 0.5 a.p.f.u. of a monovalent cation, such as Na.

The arguments outlined above show that the ideal composition of this structural type ranges from $\text{Ba}_2\text{SrCaNb}_3\text{Ti}_2\text{SiO}_{17}(\text{OH})$ 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 leads to two endmember compositions. The mineral we have studied has $[\text{P} + \text{S} + (\text{Si} - 1)] > 0.25$ and thus we define tazzoliite as $\text{Ba}_2\text{CaSr}_{0.5}\text{Na}_{0.5}\text{Nb}_3\text{Ti}_2\text{SiO}_{17}[\text{PO}_2(\text{OH})_2]_{0.5}$, which requires P_2O_5 3.24, Nb_2O_5 36.47, SiO_2 5.50, TiO_2 14.62, BaO 28.06, CaO 5.13, SrO 4.74, Na_2O 1.42, H_2O 0.82; total 100.00 wt.%. A mineral with the composition $\text{Ba}_2\text{SrCaNb}_3\text{Ti}_2\text{SiO}_{17}(\text{OH})$ would correspond to a new species.

Relationship to other structures

Tazzoliite is related to the pyrochlore structure (Atencio *et al.*, 2010) with the addition of a slab

containing $\text{SiTiO}_3[\text{PO}_2(\text{OH})_2]_{0.5}$ every 0.5 *b* translation parallel to [110] of pyrochlore (Fig. 3). Other pyrochlore related structures have been described by Ferraris *et al.* (2008) although they have alternate one [K rich nenadkevichite $(\text{Na},\text{K})(\text{Nb},\text{Ti})_2[\text{Si}_4\text{O}_{12}](\text{O},\text{OH})_2 \cdot 1.6\text{H}_2\text{O}$, Rastsvetayeva *et al.*, 1994], two [fersmanite $(\text{Ca}_{5.49}\text{Na}_{2.37}\text{Sr}_{0.08}\text{Fe}_{0.06})(\text{Nb}_{1.61}\text{Ti}_{2.39})(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$, Sokolova *et al.*, 2002], or three [Na rich komarovite $\text{Na}_{5.5}\text{Ca}_{0.8}\text{La}_{0.2}\text{Ti}_{0.5}\text{Nb}_{5.5}\text{Si}_4\text{O}_{26}\text{F}_2 \cdot \text{H}_2\text{O}$, Balič Žunič *et al.*, 2002] octahedra thick (100) pyrochlore slabs with SiO_4 groups with different degrees of polymerization (four membered rings being the most common unit) (Fig. 5). Tazzoliite thus represents a novel type of pyrochlore related structure, which includes anionic groups other than SiO_4 . One of the anionic groups coordinates with OH groups. The dominant cation at the centre of the *MO*₄ anionic group is phosphorous. The presence of dihydrogen phosphate groups has been observed in girvasite, $(\text{NaCa}_2\text{Mg}_3(\text{PO}_4)_2[\text{PO}_2(\text{OH})_2](\text{CO}_3)(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Sokolova *et al.*, 1990).

Acknowledgements

We are delighted to contribute this manuscript to an issue of *Mineralogical Magazine* dedicated to Mark Welch, a well known European mineralogical crystallographer. Most of us have collaborated with him. His longstanding studies of hydrous silicates are especially noteworthy and are very valuable to the wider scientific community.

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

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_reflns_number_gt	1300
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_computing_molecular_graphics    ?
_computing_publication_material ?
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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit P are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sqrt{\langle F^2 \rangle}$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

```
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```

```
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_refine_ls_weighting_details
'calc w=1/[\s^2^(Fo^2^)+(0.0607P)^2^+564.6627P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   difmap
_refine_ls_hydrogen_treatment    refU
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns         1312
_refine_ls_number_parameters      95
_refine_ls_number_restraints      0
_refine_ls_R_factor_all          0.0633
_refine_ls_R_factor_gt           0.0625
_refine_ls_wR_factor_ref         0.1581
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_refine_ls_goodness_of_fit_ref    1.246
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Alb Ca 0.0000 0.12852(5) 0.10553(4) 0.0128(3) Uani 0.07(2) 2 d PP . .
Nb1 Nb -0.5000 0.17122(6) 0.13211(6) 0.0094(4) Uani 0.86(3) 2 d PP . .
Ti1 Ti -0.5000 0.17122(6) 0.13211(6) 0.0094(4) Uani 0.14(3) 2 d PP . .
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Nb2 Nb 0.2500 0.2500 0.0000 0.0099(6) Uani 0.76(3) 4 d PP . .
Ti2 Ti 0.2500 0.2500 0.0000 0.0099(6) Uani 0.24(3) 4 d PP . .
Ti3 Ti 0.2500 0.07937(10) 0.2500 0.0115(7) Uani 0.80(2) 2 d PP . .
Nb3 Nb 0.2500 0.07937(10) 0.2500 0.0115(7) Uani 0.20(2) 2 d PP . .
A2a Ca 0.2500 0.2500 0.2500 0.0104(8) Uani 0.750(14) 4 d PP . .
A2b Ba 0.2500 0.2500 0.2500 0.0104(8) Uani 0.250(14) 4 d PP . .
A3a Ca -0.5000 0.0963(3) 0.0000 0.026(2) Uani 0.76(7) 4 d PP . .
A3b Na -0.5000 0.0963(3) 0.0000 0.026(2) Uani 0.24(7) 4 d PP . .
Si Si 0.5000 0.0000 0.1470(2) 0.0076(11) Uani 1 4 d P . .
O1 O 0.0000 0.2139(7) 0.0000 0.008(2) Uani 1 4 d P . .
O2 O 0.3040(9) 0.1426(3) 0.1887(3) 0.0104(14) Uani 1 1 d . . .
O3 O 0.0000 0.2469(5) 0.1706(4) 0.0068(17) Uiso 1 2 d P . .
O4 O 0.3188(13) 0.0000 0.1927(4) 0.0083(17) Uani 1 2 d P . .
O5 O 0.3180(9) 0.1841(3) 0.0646(3) 0.0110(14) Uani 1 1 d . . .
O6 O -0.5000 0.0680(5) 0.1053(5) 0.013(2) Uani 1 2 d P . .
O7 O 0.0000 0.0723(5) 0.2180(5) 0.0108(19) Uani 1 2 d P . .
O8 O -0.340(5) 0.0000 0.0000 0.018(10) Uiso 0.43(6) 4 d PP . .
P P 0.066(4) 0.0000 0.0000 0.038(9) Uiso 0.26(3) 4 d PP . .
O9 O 0.0000 0.0000 0.065(2) 0.071(15) Uiso 0.82(9) 4 d PP . .
H9 H 0.1120 0.0000 0.0900 0.085 Uiso 0.43(6) 2 d PP . .
O10 O 0.177(4) 0.0582(13) 0.0000 0.036(8) Uiso 0.58(5) 2 d PP . .

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Alb 0.0128(4) 0.0157(5) 0.0100(4) 0.0020(3) 0.000 0.000
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Ti1 0.0096(7) 0.0079(6) 0.0108(7) 0.0008(4) 0.000 0.000
Nb2 0.0094(9) 0.0116(10) 0.0088(9) 0.000 0.000 0.0013(7)
Ti2 0.0094(9) 0.0116(10) 0.0088(9) 0.000 0.000 0.0013(7)
Ti3 0.0164(11) 0.0063(9) 0.0118(10) 0.000 0.0051(7) 0.000
Nb3 0.0164(11) 0.0063(9) 0.0118(10) 0.000 0.0051(7) 0.000
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A2b 0.0092(11) 0.0081(11) 0.0140(12) 0.000 0.000 0.000
A3a 0.060(5) 0.009(3) 0.010(3) 0.000 0.000 0.000
A3b 0.060(5) 0.009(3) 0.010(3) 0.000 0.000 0.000
Si 0.006(2) 0.010(2) 0.007(2) 0.000 0.000 0.000
O1 0.004(5) 0.011(6) 0.008(6) 0.000 0.000 0.000
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O4 0.008(4) 0.012(4) 0.005(4) 0.000 -0.002(3) 0.000
O5 0.012(3) 0.009(3) 0.012(3) 0.001(2) -0.004(3) -0.002(2)
O6 0.016(5) 0.009(4) 0.014(5) 0.011(4) 0.000 0.000
O7 0.010(4) 0.010(4) 0.012(4) 0.006(3) 0.000 0.000

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All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

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Ala O3 2.756(9) . ?
Ala O1 2.838(8) . ?
Ala O2 2.887(7) . ?
Ala O2 2.887(7) 19 ?
Ala O10 2.971(17) 19 ?
Ala O10 2.971(17) . ?
Nb1 O3 1.839(9) 14_455 ?
Nb1 O2 1.978(7) 19 ?
Nb1 O2 1.978(7) 1_455 ?
Nb1 O5 1.995(7) 1_455 ?
Nb1 O5 1.995(7) 19 ?
Nb1 O6 2.150(11) . ?
Nb1 A3a 3.208(3) . ?
Nb2 O5 1.980(7) 18 ?
Nb2 O5 1.980(7) 14 ?
Nb2 O5 1.980(7) 29 ?
Nb2 O5 1.980(7) . ?
Nb2 O1 1.989(5) . ?
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Ti3 O2 1.870(7) . ?
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Ti3 O7 1.980(4) . ?
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Ti3 O4 2.075(6) . ?
Ti3 O4 2.075(6) 25 ?
Ti3 Nb3 3.186(4) 25 ?
Ti3 Ti3 3.186(4) 25 ?
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A2a O3 2.517(6) 26 ?
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A3a O8 2.27(2) 17_455 ?
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Si O6 1.632(10) 1_655 ?
Si O4 1.662(10) 2_655 ?
Si O4 1.662(10) . ?
O1 Ti2 1.989(5) 15_455 ?
O1 Nb2 1.989(5) 15_455 ?
O1 Alb 2.838(8) 18 ?

O1 Al_a 2.838(8) 18 ?
O2 Ti₁ 1.978(7) 1_655 ?
O2 Nb₁ 1.978(7) 1_655 ?
O3 Ti₁ 1.839(9) 14_455 ?
O3 Nb₁ 1.839(9) 14_455 ?
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O3 A_{2a} 2.517(6) 21 ?
O4 Nb₃ 2.075(6) 25 ?
O4 Ti₃ 2.075(6) 25 ?
O5 Ti₁ 1.995(7) 1_655 ?
O5 Nb₁ 1.995(7) 1_655 ?
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O5 A_{3a} 2.616(8) 1_655 ?
O6 Si 1.632(10) 1_455 ?
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O8 O₁₀ 1.68(4) 17 ?
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O8 A_{3a} 2.27(2) 17_455 ?
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P O₁₀ 1.43(3) 3 ?
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P O₁₀ 2.14(4) 17 ?
P O₁₀ 2.14(4) 19 ?
P Al_b 3.466(5) 17 ?
P Al_a 3.466(5) 17 ?
O₉ P 1.48(4) 17 ?
O₉ Al_a 2.722(14) 2 ?
O₉ Al_b 2.722(14) 2 ?
O₁₀ O₈ 1.68(4) 17 ?
O₁₀ P 2.14(4) 17 ?
O₁₀ A_{3b} 2.51(3) 1_655 ?
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O2 Ala O2 102.6(3) . 19 ?
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O3 Nb1 O5 102.1(3) 14_455 1_455 ?
O2 Nb1 O5 168.2(3) 19 1_455 ?
O2 Nb1 O5 89.2(3) 1_455 1_455 ?
O3 Nb1 O5 102.1(3) 14_455 19 ?

O2 Nb1 O5 89.2(3) 19 19 ?
O2 Nb1 O5 168.2(3) 1_455 19 ?
O5 Nb1 O5 85.0(4) 1_455 19 ?
O3 Nb1 O6 168.8(4) 14_455 . ?
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O3 Nb1 A2b 43.46(18) 14_455 21 ?
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O5 Nb1 A2b 96.2(2) 19 21 ?
O6 Nb1 A2b 128.80(19) . 21 ?
A3a Nb1 A2b 147.916(15) . 21 ?
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O2 Nb1 A2a 45.70(19) 19 21 ?
O2 Nb1 A2a 94.4(2) 1_455 21 ?
O5 Nb1 A2a 145.17(19) 1_455 21 ?
O5 Nb1 A2a 96.2(2) 19 21 ?
O6 Nb1 A2a 128.80(19) . 21 ?
A3a Nb1 A2a 147.916(15) . 21 ?
A2b Nb1 A2a 0.0 21 21 ?
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O2 Nb1 A2a 94.4(2) 19 1_455 ?
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O5 Nb1 A2a 96.2(2) 1_455 1_455 ?
O5 Nb1 A2a 145.17(19) 19 1_455 ?
O6 Nb1 A2a 128.80(19) . 1_455 ?
A3a Nb1 A2a 147.916(15) . 1_455 ?
A2b Nb1 A2a 63.70(2) 21 1_455 ?
A2a Nb1 A2a 63.70(2) 21 1_455 ?
O3 Nb1 A2b 43.46(18) 14_455 1_455 ?
O2 Nb1 A2b 94.4(2) 19 1_455 ?
O2 Nb1 A2b 45.70(19) 1_455 1_455 ?
O5 Nb1 A2b 96.2(2) 1_455 1_455 ?
O5 Nb1 A2b 145.17(19) 19 1_455 ?
O6 Nb1 A2b 128.80(19) . 1_455 ?
A3a Nb1 A2b 147.916(15) . 1_455 ?
A2b Nb1 A2b 63.70(2) 21 1_455 ?
A2a Nb1 A2b 63.70(2) 21 1_455 ?
A2a Nb1 A2b 0.0 1_455 1_455 ?
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O5 Nb2 O1 90.4(3) . 29 ?
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O1 Nb2 A3b 80.4(4) . 29_455 ?
O1 Nb2 A3b 99.6(4) 29 29_455 ?
O5 Nb2 A3b 45.3(2) 18 1_655 ?
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O5 Nb2 A3a 45.3(2) 14 29_455 ?
O5 Nb2 A3a 45.3(2) 29 29_455 ?
O5 Nb2 A3a 134.7(2) . 29_455 ?
O1 Nb2 A3a 80.4(4) . 29_455 ?
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A3b Nb2 A3a 0.0 29_455 29_455 ?
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O1 Nb2 A1a 133.3(2) . 14 ?
O1 Nb2 A1a 46.7(2) 29 14 ?
A3b Nb2 A1a 72.64(3) 29_455 14 ?
A3b Nb2 A1a 107.36(3) 1_655 14 ?
A3a Nb2 A1a 72.64(3) 29_455 14 ?
A3a Nb2 A1a 107.36(3) 1_655 14 ?
O5 Nb2 A1b 44.0(2) 18 18 ?
O5 Nb2 A1b 136.0(2) 14 18 ?
O5 Nb2 A1b 83.55(19) 29 18 ?
O5 Nb2 A1b 96.45(19) . 18 ?
O1 Nb2 A1b 46.7(2) . 18 ?
O1 Nb2 A1b 133.3(2) 29 18 ?
A3b Nb2 A1b 107.36(3) 29_455 18 ?
A3b Nb2 A1b 72.64(3) 1_655 18 ?
A3a Nb2 A1b 107.36(3) 29_455 18 ?
A3a Nb2 A1b 72.64(3) 1_655 18 ?
A1a Nb2 A1b 180.00(3) 14 18 ?
O2 Ti3 O2 94.6(4) . 12 ?
O2 Ti3 O7 90.3(3) . . ?
O2 Ti3 O7 95.3(4) 12 . ?
O2 Ti3 O7 95.3(4) . 26 ?
O2 Ti3 O7 90.3(3) 12 26 ?
O7 Ti3 O7 171.8(6) . 26 ?
O2 Ti3 O4 93.0(3) . . ?
O2 Ti3 O4 171.6(3) 12 . ?

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