

From structure topology to chemical composition. XI. Titanium silicates: crystal structures of innelite-1*T* and innelite-2*M* from the Inagli massif, Yakutia, Russia, and the crystal chemistry of innelite

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ABSTRACT

The crystal structures of two polytypes of innelite, ideally $\text{Ba}_4\text{Ti}_2\text{Na}_2\text{M}^{2+}\text{Ti}(\text{Si}_2\text{O}_7)_2[(\text{SO}_4)(\text{PO}_4)]\text{O}_2[\text{O}(\text{OH})]$ where $\text{M}^{2+} = \text{Mn}, \text{Fe}^{2+}, \text{Mg}, \text{Ca}$: innelite-1*T*, a 5.4234(9), b 7.131(1), c 14.785(3) Å, α 98.442(4), β 94.579(3), γ 90.009(4)°, V 563.7(3) Å³, space group $P\bar{1}$, $D_{\text{calc.}} = 4.028 \text{ g/cm}^3$, $Z = 1$; and innelite-2*M*, a 5.4206(8), b 7.125(1), c 29.314(4) Å, β 94.698(3)°, V 1128.3(2) Å³, space group $P2_1/c$, $D_{\text{calc.}} = 4.024 \text{ g/cm}^3$, $Z = 2$, from the Inagli massif, Yakutia, Russia, have been refined to R values of 8.99 and 7.60%, respectively. Electron-microprobe analysis gave the empirical formula for innelite as $(\text{Ba}_{3.94}\text{Sr}_{0.06})_{\Sigma 4.00}(\text{Na}_{2.16}\text{Mn}_{0.38}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.15}\text{Ca}_{0.10}\square_{0.04})_{\Sigma 3}(\text{Ti}_{2.97}\text{Nb}_{0.02}\text{Al}_{0.02})_{\Sigma 3.01}\text{Si}_{4.01}(\text{S}_{1.02}\text{P}_{0.81}\square_{0.17})_{\Sigma 2}\text{H}_{1.84}\text{O}_{25.79}\text{F}_{0.21}$ which is equivalent to $(\text{Ba}_{3.94}\text{Sr}_{0.06})_{\Sigma 4.00}(\text{Ti}_{1.97}\text{Nb}_{0.02}\text{Al}_{0.02})_{\Sigma 2.01}(\text{Na}_{2.16}\text{Mn}_{0.38}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.15}\text{Ca}_{0.10}\square_{0.04})_{\Sigma 3}\text{Ti}(\text{Si}_{4.01}\text{O}_{14})[(\text{SO}_4)_{1.02}(\text{PO}_4)_{0.81}(\text{OH})_{0.51}\text{H}_2\text{O}_{0.17}]\text{O}_2[(\text{OH}_{0.99}\text{F}_{0.21})_{\Sigma 1.20}\text{O}_{0.80}]$, calculated on the basis of 26 (O + F) anions, with H₂O calculated from structure refinement. The crystal structure of innelite is a combination of a TS (titanium silicate) block and an I (intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral) and exhibits linkage and stereochemistry typical for Ti-disilicate minerals of Group III (Ti = 3 a.p.f.u.): two H sheets connect to the O sheet such that two (Si₂O₇) groups link to the *trans* edges of a Ti octahedron of the O sheet. The I block contains *T* sites, statistically occupied by S and P, and Ba atoms. In the structures of innelite-1*T* and innelite-2*M*, TS blocks are related by an inversion centre and a c_y glide plane, respectively. HRTEM images show a coherent intergrowth of the two polytypes, together with an as-yet unidentified ~10 Å phase.

KEYWORDS: innelite-1*T*, innelite-2*M*, crystal structure refinement, polytypism, EMP analysis, HRTEM, chemical formula, Ti-disilicate minerals, Group III.

Introduction

INNELITE from the Inagli massif, Yakutia, Russia was described by Kravchenko *et al.* (1961). They

reported triclinic symmetry, chemical analysis and a simplified formula $(\text{Na,Ca,Mg,Fe}^{3+},\text{Fe}^{2+})_3(\text{Ba,K,Mn})_4(\text{Ti,Al})_3\text{Si}_4\text{O}_{24}(\text{OH,F})_{1.5}\text{S}_{1.15}$, with $D_{\text{meas.}} = 3.96 \text{ g/cm}^3$. Chernov *et al.* (1971) solved the crystal structure of innelite, a 14.76, b 7.14, c 5.38 Å, α 90, β 95, γ 99°, space group $P1$, $Z = 1$, using intensities from Weissenberg photographs on a *definite* single crystal; prior to finding the crystal they had looked at more than

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600 crystals that were twinned. They worked on innelite samples from the collections of S.M. Kravchenko and A.F. Efimov, specifically sample #81801 deposited at the Fersman Mineralogical Museum. Chernov *et al.* (1971) described the main features of the structure topology of innelite and suggested the ideal formula $\text{Na}_2\text{Ba}_3(\text{Ba}, \text{K}, \text{Mn})(\text{Ca}, \text{Na})\text{Ti}(\text{TiO}_2)_2[\text{Si}_2\text{O}_7]_2(\text{SO}_4)_2$. Pekov *et al.* (2006) described a new mineral phosphoinnelite, ideally $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{F})_3$, from the Kovdor massif, Kola Peninsula, Russia.

Sokolova (2006) established the relation between structure topology and chemical composition for Ti-disilicate minerals and divided them into four groups, each characterized by a different topology and stereochemistry of the titanium silicate (TS) block. Each group of structures has a different linkage of H (heteropolyhedral) and O (octahedral) sheets in the TS block and a different arrangement of Ti (= Ti + Nb) polyhedra. In Groups I, II III and IV, Ti equals 1, 2, 3 and 4 a.p.f.u. (atoms per formula unit), respectively. Each structure is a combination of TS and intermediate (I) blocks. Based on the structure work of Chernov *et al.* (1971), Sokolova (2006) reported a structural formula for innelite, $\text{Ba}_2\text{Ba}_2\text{Ti}_2\text{Na}_2\text{CaTi}(\text{Si}_2\text{O}_7)_2(\text{SO}_4)_2\text{O}_4$, which corresponds to the general formula $\text{A}_2^{\text{P}}\text{B}_2^{\text{P}[5]}\text{M}_2^{\text{H}}\text{M}_4^{\text{O}}(\text{Si}_2\text{O}_7)_2(\text{TO}_4)_2\text{X}_4^{\text{O}}$, where A_2^{P} and B_2^{P} = cations at the peripheral (P) sites of the TS block, M_2^{H} and M_4^{O} = cations in the H and O sheets, respectively; T = tetrahedrally coordinated cations in the I block, and X_4^{O} = anions of the O sheet which are not bonded to Si atoms. She considered innelite, ideally $\text{Na}_2\text{Ba}_4\text{CaTi}_3\text{O}_4(\text{Si}_2\text{O}_7)_2(\text{SO}_4)_2$, a Group-III mineral with Ti (= Ti + Nb) = 3 a.p.f.u., and suggested re-investigation of the crystal structure and chemical composition of innelite as there were some discrepancies between the chemical formulae reported in the literature, e.g. $\text{Na}_2\text{CaBa}_4\text{Ti}_3\text{O}_4(\text{Si}_2\text{O}_7)_2(\text{SO}_4)_2$ (Anthony *et al.*, 1995, p. 369) and $(\text{Ba}, \text{K}, \text{Mn})_4(\text{Na}, \text{Mg}, \text{Ca})_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2(\text{SO}_4)_2\text{O}_3(\text{OH}, \text{F})$ (Back and Mandarino, 2008). Excluding innelite, there are seven minerals with known structures in Group III: lamprophyllite, nabalamprophyllite, barytolamprophyllite, epistolite, vuonnemite, bornemanite and nechelyustovite (Table 1). In Group III, the TS block exhibits linkage 1 where the (Si_2O_7) groups of two H sheets link to the Ti octahedron of the O sheet. So far, polytypism has been reported for two minerals in Group III, lamprophyllite and nabalamprophyllite (Table 1). Observations by

TEM and X-ray powder (Rietveld) data on lamprophyllite and barytolamprophyllite samples from the Gardiner Complex, East Greenland (Johnsen, 1996), showed three polytypes: lamprophyllite-2M (space group $C2/m$), lamprophyllite-2O (space group $Pnmm$) and barytolamprophyllite-2M (space group $C2/m$). Structure work by Krivovichev *et al.* (2003) on lamprophyllite-2M and lamprophyllite-2O confirmed the findings of Johnsen (1996). Sokolova and Hawthorne (2008a) described the crystal structure of nabalamprophyllite-2O (space group $Pnmm$) and named nabalamprophyllite (space group $P2_1/m$) of Rastsvetaeva and Chukanov (1999) and Chukanov *et al.* (2004) as nabalamprophyllite-2M.

Following Sokolova (2006), other work on Ti-disilicate minerals includes the discovery of the new Group-II mineral cámaraité (Sokolova *et al.*, 2009b; Cámara *et al.*, 2009); determination of the crystal structures of bornemanite, nechelyustovite, jinshajiangite and nacarenioisite-(Ce) (Cámara and Sokolova, 2007, 2009; Sokolova *et al.*, 2009a; Sokolova and Hawthorne, 2008b) and revision of the chemical formula and crystal chemistry of delindeite, barytolamprophyllite, rinkite and murmanite (Sokolova and Cámara, 2007, 2008a,b; Cámara *et al.*, 2008).

Here, we report a re-investigation of the structure of innelite of Kravchenko *et al.* (1961) and Chernov *et al.* (1971) and the discovery of a new monoclinic polytype of innelite by means of X-ray single-crystal diffraction and transmission electron microscopy. Innelite, space group $P1$ (Kravchenko *et al.*, 1961; Chernov *et al.*, 1971) is a triclinic polytype, innelite-1T, and has been refined in space group $P\bar{1}$. A new monoclinic polytype of innelite, innelite-2M, is described with the space group $P2_1/c$; $c_{2M} = 2c_{1T}$. Intergrowth of innelite-1T and innelite-2M polytypes has been shown by transmission electron microscopy. Here, we will use the nomenclature of Guinier *et al.* (1984) for polytype structures following Johnsen (1996).

Sample description

The crystals of innelite used in this work are from the Inagli alkaline massif, Yakutia, Russia. Single crystals of innelite were selected from a sample of innelite (#81801) obtained from the Fersman Mineralogical Museum. Sample #81801 was deposited at the Fersman Mineralogical Museum by S.M. Kravchenko, and was previously used for the structure solution by Chernov *et al.* (1971).

TABLE 1. Structural formulae* and unit-cell parameters for Group-III minerals with the TS block.

Mineral	Structural formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Space group	<i>Z</i>	α (°)	β (°)	γ (°)	Ref.
Group III, Ti = 3 a.p.f.u.										
Lamprophyllite-2M	(SrNa) Ti ₂ Na ₃ Ti (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.215	7.061	5.3719	C2/m	2	90	96.797	90	(1)
Lamprophyllite-2O	(SrNa) Ti ₂ Na ₃ Ti (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.128	7.0799	5.3824	<i>Pmmn</i>	2	90	90	90	(1)
Nabalamprophyllite-2M	BaNa Ti ₂ Na ₃ Ti (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.741	7.105	5.408	<i>P2/m</i>	2	90	96.67	90	(2)
Nabalamprophyllite-2O	(BaK) Ti ₂ Na ₃ Ti (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.564	7.1173	5.414	<i>Pmmn</i>	2	90	90	90	(3)
Barytolamprophyllite	(BaK) Ti ₂ Na ₃ Ti (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.8971	7.1165	5.4108	C2/m	2	90	96.676	90	(4)
Epistolite	(Na□) Nb ₂ Na ₃ Ti (Si ₂ O ₇) ₂ O ₂ (OH) ₂ (H ₂ O) ₄	5.460	7.170	12.041	<i>P</i> $\bar{1}$	1	103.63	96.01	89.98	(5)
Vuonnemite	Na ₆ Nb ₂ Nb ₂ Na ₃ Ti (Si ₂ O ₇) ₂ (PO ₄) ₂ O ₃ F	5.4984	7.161	14.450	<i>P</i> $\bar{1}$	1	92.60	95.30	90.60	(6)
Bormemanite	Na ₃ Ba NbTi Na ₃ Ti (Si ₂ O ₇) ₂ (PO ₄) O ₂ (OH)F	5.4587	7.1421	24.528	<i>P</i> $\bar{1}$	2	96.790	96.927	90.326	(7)
Nechelyustovite**	(Na _{0.5} □ _{0.5})(Ba ₂ □)Ti ₃ Nb (Na _{3.5} Mn _{1.5} □)Ti ₂ (Si ₂ O ₇) ₄ O ₄ (OH) ₃ F (H ₂ O) ₆	5.447	7.157	47.259	<i>P</i> $\bar{1}$	2	95.759	92.136	89.978	(8)
Innelite-17***	Ba ₄ Ti ₂ Na ₂ M ²⁺ Ti (Si ₂ O ₇) ₂ [(SO ₄)(PO ₄)]O ₂ [O(OH)]	5.4234	7.131	14.785	<i>P</i> $\bar{1}$	1	98.442	94.579	90.009	(9)
Innelite-2M****	Ba ₄ Ti ₂ Na ₂ M ²⁺ Ti (Si ₂ O ₇) ₂ [(SO ₄)(PO ₄)]O ₂ [O(OH)]	5.4206	7.125	29.314	<i>P2/c</i>	2	90.00	94.698	90.00	(9)
Group II, Ti = 2 a.p.f.u.										
Yoshimuraite***	Ba ₄ Ti ₂ Mn ₄ (Si ₂ O ₇) ₂ (PO ₄) ₂ O ₂ (OH) ₂	5.386	6.999	14.748	<i>P</i> $\bar{1}$	1	89.98	93.62	95.50	(10)

* For all minerals (except for bormemanite and innelite, this work), ideal structural formulae are from Sokolova (2006). The invariant core of the TS block, **M₂^H M₂^O (Si₂O₇)₂ X₄^O**, is shown in bold: M^H = cations of the H sheet; M^O = cations of the O sheet; X₄^O = anions of the O sheet; M²⁺ = Mn²⁺, Fe²⁺, Mg²⁺, Ca²⁺; ** doubled structural formula;

*** Ba₄ = A₂^P + B₂^P (see text).

References: † (1) Krivovichev *et al.* (2003); Rastsvetaeva and Dorfman (1995); Rastsvetaeva *et al.* (1990), Saf'yanov *et al.* (1983), Woodrow (1964);

(2) Rastsvetaeva and Chukanov (1999); (3) Sokolova and Hawthorne (2008a); (4) Sokolova and Cámara (2008b); Rastsvetaeva *et al.* (1995), Peng *et al.* (1984);

(5) Sokolova and Hawthorne (2004); (6) Ereit *et al.* (1998), Drozdov *et al.* (1974); (7) Cámara and Sokolova (2007); (8) Cámara and Sokolova (2009); (9) this work, Chernov *et al.* (1971); (10) McDonald *et al.* (2000), Takeuchi *et al.* (1997)

† The latest reference on the structure is the first entry in the numbered list of references.

Careful inspection of innelite crystals in polarized light under an optical microscope showed that none of them is a single crystal.

Chemical composition

Electron-microprobe analysis

As innelite is extremely unstable under the electron beam and the crystals used for collection of the structural data are thin plates ($0.019 \times 0.107 \times 0.125$ and $0.055 \times 0.08 \times 0.08$ mm), we used two larger crystals of innelite ($\sim 0.08 \times 0.20 \times 0.25$ mm) from sample #81801 for chemical analysis. These crystals were analysed using a Cameca SX-100 electron-microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μ m and count times on peak and background of 20 and 20 s, respectively. The following standards were used for $K\alpha$ or $L\alpha$ X-ray lines (analysing crystals are given in brackets): F(LTAP): F-bearing riebeckite; Na(TAP): albite; Si(TAP), Ca(LPET): diopside; Nb(PET): $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$; P(LPET): apatite; Ti(LLiF): titanite; Sr(LPET): SrTiO_3 ; Ta(LLiF): $\text{MnNb}_2\text{Ta}_2\text{O}_9$; Mn(LLiF): spessartine; Mg(TAP): forsterite; Fe(LLiF): fayalite; Zr(LPET): zircon; S(LPET), Ba(LiF, $L\beta$): baryte; Al(LTAP): andalusite; K(LPET): orthoclase. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The chemical composition of innelite is given in Table 2 and is the mean of 10 determinations.

Empirical formula

The empirical formula for innelite (Table 2) was calculated on the basis of 26 (O + F) anions: $(\text{Ba}_{3.94}\text{Sr}_{0.06})_{\Sigma 4.00}(\text{Na}_{2.16}\text{Mn}_{0.38}^{2+}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.15}\text{Ca}_{0.10}\square_{0.04})_{\Sigma 3}(\text{Ti}_{2.97}\text{Nb}_{0.02}\text{Al}_{0.02})_{\Sigma 3.01}\text{Si}_{4.01}(\text{S}_{1.02}\text{P}_{0.81}\square_{0.17})_{\Sigma 2}\text{H}_{1.84}\text{O}_{25.79}\text{F}_{0.21}$, ($\square$ represents a vacancy), $D_{\text{calc.}} = 4.028 \text{ g/cm}^3$, $Z = 1$ (innelite-1T) and 4.024 g/cm^3 , $Z = 2$ (innelite-2M). The content of H_2O was calculated from the structure refinement (see sections Anion considerations and Chemical formula). Our chemical data do not agree with the original chemical analysis for innelite given by Kravchenko *et al.* (1961) (Table 2) as they did not analyse for P. The omission of P resulted in unreasonable totals (a.p.f.u.) in the empirical formula because: (1) alkali cations in the O sheet are listed as 3.40, but must be ≤ 3.00 ; (2) (Ti + Nb) in the TS block are listed as 3.26, but must be 3.00 for

minerals of Group III, and (3) (Ba + Sr + K) in the I block are listed as 4.20, but must be ≤ 4.00 a.p.f.u. These discrepancies vanish when P_2O_5 is determined (Table 2). For site-population assignment, we use our analysis which was done on the sample of innelite deposited at the Fersman Mineralogical Museum by Kravchenko and Efimov.

High-resolution transmission electron microscopy

Experimental

To better understand the polytypism in innelite, we collected TEM data on additional crystals from sample #81801 with a Philips CM20 transmission electron microscope working at 200 kV with an EDAX EDS system for chemical analysis in STEM mode. The instrument has a CCD camera for acquisition of images. Samples were oriented and embedded in epoxy, thinned and doubly polished. The thin slices were glued to copper rings and thinned using a Gatan Dual ion miller until transparent to electrons.

Discussion

Figure 1 shows high-resolution images of sample #81801 down *a*. Most of the studied fragment corresponds to the innelite-2M polytype with a spacing of $\sim 29 \text{ \AA}$ (Fig. 1*a,b*). An intergrowth of two polytypes can be observed in Fig. 1*b* where thin domains of innelite-1T (labelled T, $\sim 14.7 \text{ \AA}$) occur in innelite-2M (labelled M, $\sim 29 \text{ \AA}$). The latter also shows the presence of twins (marked with a white arrow in Fig. 1*b*). Figure 1*a* shows an inclusion of a $\sim 10 \text{ \AA}$ phase in a matrix of innelite-2M. These inclusions are beam sensitive and have a composition very close to that of the host innelite (although we cannot exclude a contribution from fluorescence from the matrix). However, some significant differences can be seen: the chemical composition of area A in Fig. 1*a* (reported in Fig. 2*a*) has a higher P content and a lower S content than the host innelite (the EDS spectrum in Fig. 2*b* corresponds to zone B in Fig. 1*a*). Moreover, it also has no Mg detectable by EDS. Apart from these differences, the composition of the $\sim 10 \text{ \AA}$ phase is closely related to that of the host innelite. These inclusions are not very important volumetrically but are widely distributed within the sample. If areas containing these inclusions were analysed by EMP the resultant data would have a relatively higher P

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TABLE 2. Chemical composition (wt.%) and unit formula (a.p.f.u.) for innelite.

Oxide	This work	Kravchenko <i>et al.</i> (1961)	Formula unit	This work	Kravchenko <i>et al.</i> (1961)
SO ₃	6.03	7.19	S	1.02	1.24
Nb ₂ O ₅	0.18	n.a.	P	0.81	0
P ₂ O ₅	4.24	n.a.	Si	4.01	4.33
ZrO ₂	n.d.	n.a.			
TiO ₂	17.50	18.50	Ti	2.97	3.20
SiO ₂	17.76	18.78	Nb	0.02	0
Al ₂ O ₃	0.06	0.23	Al	0.02	0.06
Fe ₂ O ₃	0	0.66	$\Sigma 2M^{H+}M^O$	3.01	3.26
FeO	0.89	0.57			
MnO	1.98	1.04	Na	2.16	2.51
MgO	0.43	0.83	Mn ²⁺	0.38	0.20
BaO	44.59	44.16	Fe ²⁺	0.17	0.11
SrO	0.48	n.a.	Fe ³⁺	0	0.11
CaO	0.40	0.72	Mg	0.15	0.29
K ₂ O	0.00	0.72	Ca	0.10	0.18
Na ₂ O	4.95	5.63	$\Sigma 3M^O$	2.96	3.40
H ₂ O	1.22*	0.88			
F	0.30	0.40	Ba	3.94	3.99
O=F	−0.13	−0.17	K	0	0.21
Total	100.88	100.14	Sr	0.06	0
			$\Sigma 2A^P + 2B^P$	4.00	4.20
			Σ cations	15.81	16.43
			OH	0.99	1.27
			F	0.21	0.29
			$\Sigma 2X_A^O$ **	1.20**	1.56
			H ⁺ ***	0.85	0
			Total H ⁺	1.84	1.27

This work: EMPA; Kravchenko *et al.* (1961): wet chemistry;

n.a. = not analysed; n.d. = not detected;

* calculated from structure refinement;

** monovalent anions of the O sheet;

*** content of H⁺ from (OH)_{0.51} + (H₂O)_{0.17} in the **I** block (see text).

content. These high-P inclusions are coherent with innelite and well ordered linear defects limit their lateral extent (linear dislocations are shown in Fig. 1c by black arrows). No known Ti silicate has an ~10 Å spacing perpendicular to the plane of the TS block and these high-P inclusions could be either metastable segregations within the innelite matrix or a new mineral of Group III.

Crystal structure: experimental

Data collection and structure refinement

Analysis of the X-ray diffraction intensities from two individual crystals of innelite showed that

they are different polytypes with triclinic and monoclinic symmetry. These are named innelite-1T and innelite-2M (Table 1). Single-crystal X-ray diffraction data for innelite-1T and innelite-2M were collected with Siemens P4 and Bruker AXS diffractometers with SMART APEX CCD detectors and Mo-K α -radiation. The intensities of the reflections were collected to 60° 2 θ using 30 s per 0.2° frame, and an empirical absorption correction (*SADABS*, Sheldrick, 2008) was applied. The Bruker *SHELXTL* Version 5.1 system of programs (Sheldrick, 2008) was used for solution and refinement of both structures. As there were hardly any observed reflections at high

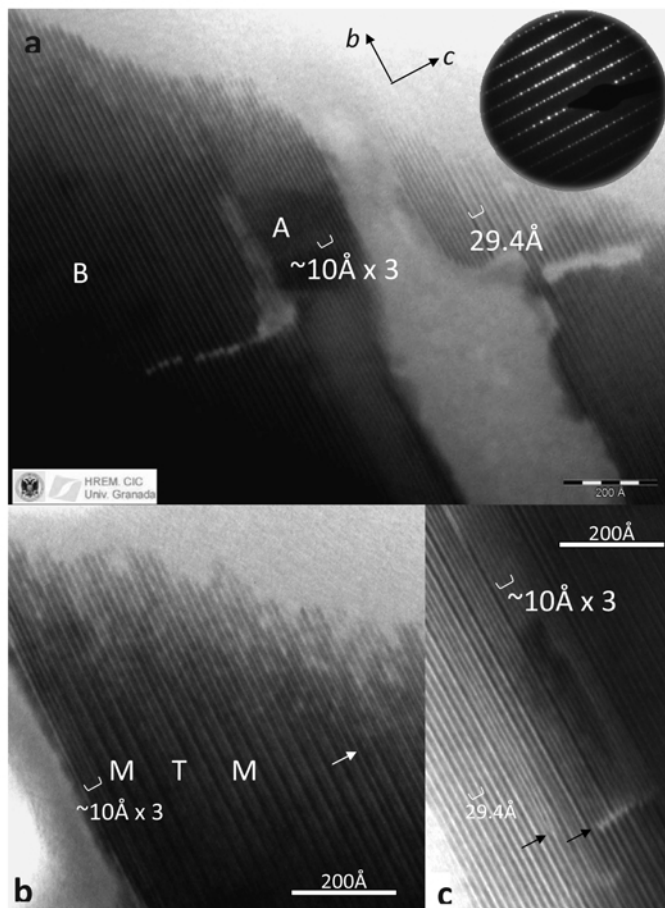


FIG. 1. High-resolution transmission-electron microscopy images of the studied innelite sample: (a) showing an inclusion of an ~ 10 Å phase coherent with innelite-2M (the upper right inset shows the diffraction pattern of innelite-2M); (b) showing the intergrowth of polytypes 1T and 2M related to the ubiquitous presence of the 10 Å phase and a twin boundary in the 2M polytype (with arrow); (c) detail of the lateral boundaries of the 10 Å phase inclusions terminated by linear dislocations (black arrows).

2θ , the refinement of the structures was based on the intensities of unique observed reflections ($F_o > 4\sigma F$) with $2\theta \leq 55^\circ$. The refinement was done on crystals of innelite where three phases could be present: (1) innelite-1T with a spacing of ~ 14.7 Å, (2) innelite-2M with a spacing of ~ 29.4 Å and (3) a phase with a spacing of ~ 10 Å. Hence the diffraction pattern comprised three components corresponding to phases (1) to (3), with strong partial overlap of all three components. The main question to be answered was how to extract information on the two polytypes of innelite in the presence of the third 10 Å phase? Refinement of

the crystal structure using the $(-1\ 0\ 0, 0\ -1\ 0, 1\ 0\ 1)$ matrix resulted in the volumes of ‘two’ components in the ratio 0.025(1):0.975(1) for innelite-1T and 0.734(2):0.266(2) for innelite-2M. We emphasize that this matrix is not a twin matrix, but it relates the two components via the twin option in the software. This operation partly accounts for the presence of diffraction data from the other polytype in the dataset for the host (dominant) structure. For innelite-2M, this operation possibly accounts for non-merohedral twinning as well (see Fig. 1b for an indication of twinning). The fact that this procedure is only an

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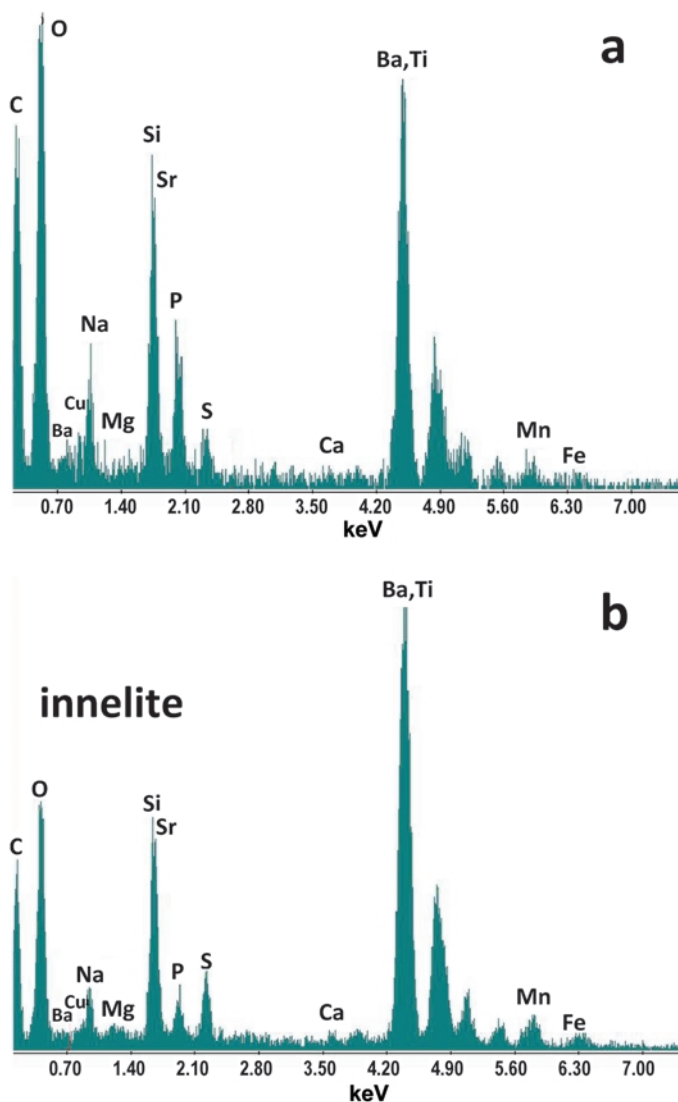


FIG. 2. Energy-dispersive spectra of areas marked A and B in Fig. 1a, corresponding to spectra (a) and (b), respectively. The main difference is the S/P ratio and the absence of Mg in the upper spectrum.

approximation is apparent from the presence of subsidiary peaks in difference-Fourier maps of the structures (see below). However, it does allow us to extract reasonable structures for the two innelite polytypes. The unit-cell parameters of innelite-1T are identical to those reported by Chernov *et al.* (1971), a 14.76, b 7.14, c 5.38 Å, α 90, β 95, γ 99°, space group $P1$ (the a and c axes are exchanged for better comparison with other Group-III minerals and yoshimuraite; Table 1). The occupancies of the Ti-dominant sites were

refined with the scattering factor of Ti; alkali-cation sites (Na and $M^{2+} = \text{Mn, Fe}^{2+}, \text{Mg, Ca}$) were refined with scattering factors of Na [innelite-1T: $M^O(2)$; innelite-2M: $M^O(2-4)$] and Ca [innelite-1T: $M^O(3)$]; Ba-dominant A^P and B^P sites, with the scattering curve of Ba; T sites, with the scattering factor of S. Neutral scattering factors were taken from the *International Tables for Crystallography* (Wilson, 1992). In the last stages of the refinement, eleven (innelite-1T) and eight (innelite-2M) subsidiary peaks were

included in the refinement. The presence of subsidiary peaks is a common feature in Ti silicates with the TS block; they are due to intimate intergrowths of these minerals and the presence of additional structure domains (see HRTEM results presented below). Refined site occupancies of subsidiary peaks were 2–17%. In Group III, subsidiary peaks were reported for lamprophyllite (Krivovichev *et al.*, 2003), epistolite (Sokolova and Hawthorne, 2004), borneminite (Cámara and Sokolova, 2007), nabalamprophyllite-2O (Sokolova and Hawthorne, 2008a) and nechelyustovite (Cámara and Sokolova, 2009). The details of X-ray data collection and structure refinement are given in Table 3. Lists of observed and calculated structure factors for innelite-1T and innelite-2M and anisotropic displacement parameters for groups of atoms in both structures have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Innelite-1T

The intensities of 6570 reflections with $-7 \leq h \leq 7$, $-9 \leq k \leq 9$, $-19 \leq l \leq 19$ were collected out to $2\theta = 55^\circ$. The refined unit-cell parameters were obtained from 6524 reflections ($I > 10\sigma I$) and are given in Table 3. Using the atom coordinates of Chernov *et al.* (1971), the structure of innelite-1T was refined in space group $P1$ and converged to $R_1 = 6.24\%$. However, the $P1$ structure model did not show any crystal-chemical reason for the absence of an inversion centre. Moreover, all cation sites were paired by a pseudo inversion centre, it was not possible to assemble coordination polyhedra in the **I** block, and several Si–O distances were too short or too long. Hence we refined the structure in space group $P\bar{1}$, with $R_1 = 8.99\%$, and a sensible structure model was obtained. Final atom parameters are given in Table 4, selected interatomic distances and angles in Table 6, refined site-scattering values and assigned populations for selected sites in Table 8, and bond-valence values in Table 10.

TABLE 3. Miscellaneous refinement data for innelite-1T and innelite-2M.

	Innelite-1T	Innelite-2M
a (Å)	5.4234(9)	5.4206(8)
b (Å)	7.131(1)	7.125(1)
c (Å)	14.785(3)	29.314(4)
α (°)	98.442(4)	
β (°)	94.579(3)	94.698(3)
γ (°)	90.009(4)	
V (Å ³)	563.7(3)	1128.3(2)
Space group	$P\bar{1}$	$P2_1/c$
Z	1	2
Absorption coefficient (mm ⁻¹)	8.78	8.78
$F(000)$	625.3	1250.6
D_{calc} (g/cm ³)	4.028	4.024
Crystal size (mm)	$0.055 \times 0.08 \times 0.08$	$0.019 \times 0.107 \times 0.120$
Radiation/filter	Mo-K α /graphite	Mo-K α /graphite
2 θ -range for structure refinement (°)	55.00	50.0
$R(\text{int})$ (%)	1.29	3.47
Reflections collected	6570	9585
Independent reflections	2576	2017
$F_o > 4\sigma F$	2564	1934
Refinement method	Full-matrix least squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$	
No. of refined parameters	191	199
Final $R_{(\text{obs})}$ (%) [$F_o > 4\sigma F$]	8.99	7.60
R_1	9.03	7.81
wR_2	21.62	20.91
Goodness of fit on F^2	1.285	1.120

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TABLE 4. Atom coordinates and isotropic displacement parameters ($\text{\AA}^2$) for innelite-1T.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Si(1)	0.8163(7)	0.2314(6)	0.8097(3)	0.0010(7)
Si(2)	0.8173(8)	0.6576(6)	0.8108(3)	0.0028(7)
M ^H	0.6857(5)	0.0589(4)	0.2005(2)	0.0045(5)*
M ^O (1)	0	½	0	0.0232(12)*
M ^O (2)	0	0	0	0.015(2)*
M ^O (3)	0.4988(11)	0.7402(9)	0.9993(4)	0.0247(17)*
T	0.7551(10)	0.2981(8)	0.5231(4)	0.0175(16)*
A ^P	0.2887(2)	0.41429(19)	0.68274(10)	0.0209(3)*
B ^P	0.77374(19)	0.87957(14)	0.60954(7)	0.0096(2)*
O(1)	0.838(2)	0.2712(15)	0.9205(7)	0.004(2)
O(2)	0.562(2)	0.1207(16)	0.7673(8)	0.007(2)
O(3)	0.054(2)	0.1180(16)	0.7658(8)	0.006(2)
O(4)	0.806(2)	0.4313(16)	0.7683(8)	0.005(2)
O(5)	0.560(2)	0.7414(15)	0.7690(7)	0.004(2)
O(6)	0.055(2)	0.7393(16)	0.7674(8)	0.005(2)
O(7)	0.839(2)	0.6804(17)	0.9210(8)	0.010(2)
O(8)	0.662(2)	0.022(2)	0.0852(9)	0.016(3)*
O(9)	0.286(3)	0.479(2)	0.9240(10)	0.026(3)*
O(10)	0.986(3)	0.197(2)	0.5539(9)	0.024(3)*
O(11)	0.537(3)	0.193(2)	0.5529(10)	0.023(3)*
O(12)	0.729(3)	0.265(3)	0.4140(16)	0.044(5)*
O(13)	0.770(4)	0.497(3)	0.5683(16)	0.039(4)
Subsidiary peaks**				
1	0.762(5)	0.024(4)	0.5263(18)	0.02
2	0.782(6)	0.243(5)	0.569(2)	0.02
3	0.711(2)	0.0168(19)	0.3274(10)	0.02
4	0.320(6)	0.554(4)	0.800(2)	0.02
5	0.298(13)	0.321(12)	0.659(5)	0.02
6	0.7741(15)	0.4953(11)	0.6106(6)	0.02
7	0.754(5)	0.406(4)	0.5207(17)	0.02
8	0.732(9)	0.970(6)	0.419(3)	0.02
M ^H (A)	0.717(8)	0.204(6)	0.273(3)	0.02
M ^H (B)	0.708(5)	1.000(4)	0.303(2)	0.02
Si(2A)	0.821(9)	0.842(7)	0.818(3)	0.02

* U_{eq} ** site occupancies for 1–8 vary from 0.02 to 0.17 (scattering factor of Ba); for M^H(A,B), 0.08 and 0.15 (scattering factor of Ti); Si(2A), 0.12 (scattering factor of Si).*Innelite-2M*

The intensities of 9585 reflections with $-6 \leq h \leq 6$, $-7 \leq k \leq 8$, $-34 \leq l \leq 31$ were collected out to $2\theta = 50.0^\circ$. The refined unit-cell parameters were obtained from 4447 reflections ($I > 10\sigma I$) and are given in Table 3. The *c* cell parameter of innelite-2M is twice the *c* cell parameter of innelite-1T, and this is the first discovery of a new polytype of innelite. The crystal structure of innelite-2M was solved and refined in space group *P2* to $R_1 = 7.22\%$. In the difference-Fourier map,

we found eight peaks which we identified as O atoms, four of them tetrahedrally coordinating the central cation with T–O ~1.46 Å and another four tetrahedrally coordinating the central cation with T–O ~1.53 Å. When these eight anions were added to the refinement in space group *P2*, the two TO₄ tetrahedra refined to approximately the same mean T–O bond-lengths, converging to an R_1 index of 7.06%. We also refined the structure in *P2* with DFIX constraints that preserved the initial T–O distances, which converged to an R_1 index of

7.22%. Lastly, we refined the structure in space group $P2/c$, in which there is only one T site, and the refinement converged to an R_1 index of 7.60%. It is not clear which refinement is to be preferred. On the one hand, the difference-Fourier map indicates that S and P are ordered over the two T sites, forcing the space group to be $P2$, whereas on the other hand, the least-squares refinement indicates that S and P are disordered over the two T sites, suggesting that the space group is $P2/c$. As we do not have convincing evidence of S-P order (space group $P2$), we adopt the simpler model and present the $P2/c$ structure for the inelilite-2*M* polytype. Final atom parameters are

given in Table 5, selected interatomic distances and angles in Table 7, refined site-scattering values and assigned populations for selected sites in Table 9 and bond-valence values in Table 11.

Site-population assignment

We divide the cation sites into three groups: M^H and Si sites of the H sheet, M^O sites of the O sheet, and T , A^P and B^P sites of the I block (see general formula above). Consider first the Ti + Nb dominant sites. We know that the Ti (+ Nb) dominant sites are always fully occupied. Table 2 shows that the $2M^H$ and $1M^O$ sites are occupied by

TABLE 5. Atom coordinates and isotropic displacement parameters ($\text{\AA}^2$) for inelilite-2*M*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
Si(1)	0.3164(11)	0.9364(7)	0.15620(16)	0.0053(10)
Si(2)	0.3146(11)	0.3677(8)	0.15437(17)	0.0098(10)
M^H	0.8128(7)	0.6470(5)	0.14953(11)	0.0089(7)
M^O (1)	$\frac{1}{2}$	0.1543(8)	$\frac{1}{4}$	0.0259(15)
M^O (2)	$\frac{1}{2}$	0.6565(17)	$\frac{1}{4}$	0.017(3)
M^O (3)	0	0.9096(17)	$\frac{1}{4}$	0.026(4)
M^O (4)	0	0.3945(10)	$\frac{1}{4}$	0.014(2)
T	0.2557(12)	0.2075(8)	0.01132(18)	0.0165(16)
A^P	0.7870(3)	0.13514(19)	0.09047(5)	0.0229(3)
B^P	0.2720(3)	0.65559(17)	0.05453(4)	0.0137(3)
O(1)	0.067(3)	0.838(2)	0.1355(4)	0.013(3)
O(2)	0.563(3)	0.8379(19)	0.1349(4)	0.009(3)
O(3)	0.343(3)	0.948(2)	0.2118(5)	0.012(3)
O(4)	0.304(3)	0.1514(19)	0.1338(4)	0.011(3)
O(5)	0.539(2)	0.4627(19)	0.1320(4)	0.012(3)
O(6)	0.047(3)	0.458(2)	0.1326(5)	0.012(3)
O(7)	0.334(3)	0.3664(19)	0.2095(4)	0.011(3)
O(8)	0.845(3)	0.636(2)	0.2076(5)	0.021(3)
O(9)	0.789(4)	0.168(3)	0.2136(6)	0.038(5)
O(10)	0.271(5)	0.025(2)	0.0342(8)	0.049(6)
O(11)	0.041(4)	0.315(2)	0.0264(5)	0.023(4)
O(12)	0.486(3)	0.314(2)	0.0260(5)	0.020(4)
O(13)	0.763(4)	0.794(3)	0.0402(6)	0.031(4)
Subsidiary peaks**				
1	0.851(14)	0.564(12)	0.087(3)	0.02
2	0.738(17)	0.666(13)	0.039(3)	0.02
3	0.407(16)	0.185(12)	0.093(3)	0.02
4	0.235(10)	0.120(9)	0.077(2)	0.02
5	0.822(11)	0.632(10)	0.072(3)	0.02
6	0.689(15)	0.627(12)	0.054(3)	0.02
7	0.258(11)	0.126(8)	0.099(2)	0.02
8	0.852(15)	0.667(12)	0.055(3)	0.02

* U_{eq}

** site occupancies for 1–8 are ~0.02 (scattering factor of Ba).

CRYSTAL STRUCTURES OF INNELITE-1T AND INNELITE-2M

TABLE 6. Selected interatomic distances (Å) and angles (°) for innelite-1T.

Si(1)–O(1)	1.62(1)	Si(2)–O(7)	1.61(1)	T–O(13)	1.48(2)
Si(1)–O(2)	1.62(1)	Si(2)–O(5)	1.63(1)	T–O(10)	1.52(2)
Si(1)–O(4)	1.63(1)	Si(2)–O(6)a	1.63(1)	T–O(11)	1.53(2)
Si(1)–O(3)a	1.65(1)	Si(2)–O(4)	1.64(1)	T–O(12)	1.59(2)
<Si(1)–O>	1.63	<Si(2)–O>	1.63	<T–O>	1.53
Si(1)–O(4)–Si(2)	136.1(7)				
M ^H –O(8)	1.68(1)	M ^O (1)–O(9)d	1.98(2) × 2	M ^O (2)–O(8)e	2.30(1) × 2
M ^H –O(3)b	1.98(1)	M ^O (1)–O(7)	2.02(1) × 2	M ^O (2)–O(7)	2.53(1) × 2
M ^H –O(5)c	1.98(1)	M ^O (1)–O(1)c	2.02(1) × 2	M ^O (2)–O(1)b	2.53(1) × 2
M ^H –O(2)b	1.99(1)	<M ^O (1)–O>	2.01	<M ^O (2)–O>	2.45
M ^H –O(6)c	1.99(1)				
<M ^H –O>	1.92	A ^P –O(10)e	2.72(2)	B ^P –O(13)	2.71(2)
		A ^P –O(11)	2.74(2)	B ^P –O(11)h	2.78(2)
M ^O (3)–O(7)	2.26(1)	A ^P –O(6)	2.82(1)	B ^P –O(10)h	2.79(2)
M ^O (3)–O(1)f	2.27(1)	A ^P –O(5)	2.84(1)	B ^P –O(11)c	2.80(1)
M ^O (3)–O(9)	2.28(2)	A ^P –O(12)c	2.87(2)	B ^P –O(10)i	2.82(1)
M ^O (3)–O(9)f	2.33(2)	A ^P –O(2)	2.93(1)	B ^P –O(12)c	2.89(2)
M ^O (3)–O(8)g	2.35(2)	A ^P –O(3)	2.93(1)	B ^P –O(12)i	2.91(2)
M ^O (3)–O(8)c	2.37(1)	A ^P –O(4)	2.98(1)	B ^P –O(3)j	2.97(1)
<M ^O (3)–O>	2.31	A ^P –O(4)e	2.99(1)	B ^P –O(6)B	2.98(1)
		<A ^P –O>	2.87	B ^P –O(2)h	2.98(1)
				B ^P –O(5)	3.00(1)
				<B ^P –O>	2.88

a: $x+1, y, z$; b: $-x+1, -y, -z+1$; c: $-x+1, -y+1, -z+1$; d: $x, y, z-1$; e: $x-1, y, z$; f: $-x+1, -y+1, -z+2$; g: $x, y+1, z+1$; h: $x, y+1, z$; i: $-x+2, -y+1, -z+1$; j: $x+1, y+1, z$.

2.97 Ti + 0.02 Nb + 0.02 Al a.p.f.u. [66.4 e.p.f.u. (electrons per formula unit)]. The aggregate refined scattering at these sites in both structures (66 e.p.f.u., Tables 8 and 9) is in close accord with this composition. We assign 1.97 Ti + 0.02 Nb and 0.01 Al to the M^H site in innelite-1T (Table 8) and innelite-2M (Table 9); 1.00 Ti to the $M^O(1)$ site in innelite-1T and innelite-2M. Although Table 2 shows that the $2M^H$ and $1M^O$ sites are 99% occupied by Ti (see above), calculated bond-valence values at the Ti-dominant site in the O sheet are significantly low: 3.48 (innelite-1T) and 3.44 v.u. (valence units) (innelite-2M) when compared to an aggregate charge of 4^+ for each site (Tables 10 and 11). We have encountered the same problem in other Group-III minerals: bornemanite (3.71 v.u. vs 3.92^+) (Cámara and Sokolova, 2007), barytolamprophyllite (3.50 v.u. vs 3.96^+) (Sokolova and Cámara, 2008a) and nechelyustovite (3.52 v.u. vs 4.00^+) (Cámara and Sokolova, 2009). We do not fully understand why Ti in the O sheet shows low incident bond-valence sums and we are currently working on

this issue. Consider next the alkali-cation sites in the O sheet (3 a.p.f.u.): $M^O(2,3)$ (innelite-1T) and $M^O(2-4)$ (innelite-2M). Table 2 gives 2.16 Na + 0.38 Mn + 0.17 Fe^{2+} + 0.15 Mg + 0.10 Ca + 0.04 $\square$ = 2.96 atoms p.f.u. with a total scattering of 41.5 e.p.f.u. The total scattering at the alkali sites varies from 42.0 (innelite-1T) to 40.5 e.p.f.u. (innelite-2M). The $M^O(2)$ site in innelite-1T and innelite-2M have similar mean bond-lengths, 2.45 and 2.44 Å (Tables 8 and 9), site-occupancy refinement using the scattering curve of Na converged to integer values of 1.0 and 1.0, and we assign Na to these sites (Tables 8 and 9). That leaves us with 1.16 Na + 0.38 Mn + 0.17 Fe^{2+} + 0.15 Mg + 0.10 Ca + 0.04 $\square$ = 1.96 atoms p.f.u. (with a total scattering of 30.5 e.p.f.u.) to assign to the $M^O(3)$ site in innelite-1T (Table 8) and to the $M(3,4)$ sites in innelite-2M (Table 9). In innelite-2M, the $M^O(3)$ site has a refined site-scattering of 12.0 e.p.f.u., significantly less than 17.5 e.p.f.u. for the $M^O(4)$ site, and the $M^O(4)$ site has significantly shorter mean bond-lengths, 2.23 Å, than the $M^O(3)$ site (2.35 Å). Therefore

TABLE 7. Selected interatomic distances (Å) and angles (°) for innelite-2*M*.

Si(1)—O(1)	1.60(2)	Si(2)—O(5)	1.579(9)	T—O(10)	1.46(2)
Si(1)—O(3)	1.63(1)	Si(2)—O(7)	1.61(1)	T—O(11)	1.49(2)
Si(1)—O(4)a	1.67(1)	Si(2)—O(4)	1.65(1)	T—O(12)	1.50(2)
Si(1)—O(2)	1.67(2)	Si(2)—O(6)	1.66(2)	T—O(13)b	1.51(2)
<Si(1)—O>	1.64	<Si(2)—O>	1.62	<T—O>	1.49
Si(1)—O(4)—Si(2)c	135.6(8)				
M ^H —O(8)	1.70(1)	M ^O (1)—O(9)	1.97(2) × 2	M ^O (2)—O(8)	2.33(2) × 2
M ^H —O(2)	1.94(2)	M ^O (1)—O(3)c	1.99(1) × 2	M ^O (2)—O(3)	2.48(2) × 2
M ^H —O(6)d	1.94(2)	M ^O (1)—O(7)	2.08(1) × 2	M ^O (2)—O(7)	2.51(2) × 2
M ^H —O(1)d	2.01(2)	<M ^O (1)—O>	2.01	<M ^O (2)—O>	2.44
M ^H —O(5)	2.02(1)				
<M ^H —O>	1.92	A ^P —O(12)	2.71(2)	B ^P —O(10)a	2.70(2)
		A ^P —O(11)d	2.74(2)	B ^P —O(12)b	2.80(1)
M ^O (3)—O(3)	2.26(2) × 2	A ^P —O(2)c	2.81(1)	B ^P —O(11)h	2.81(2)
M ^O (3)—O(9)e	2.37(2) × 2	A ^P —O(13)c	2.84(2)	B ^P —O(11)	2.82(2)
M ^O (3)—O(8)f	2.43(1) × 2	A ^P —O(1)g	2.86(2)	B ^P —O(12)	2.85(2)
<M ^O (3)—O>	2.35	A ^P —O(6)d	2.92(1)	B ^P —O(13)	2.90(2)
		A ^P —O(4)d	2.98(2)	B ^P —O(13)i	2.93(2)
M ^O (4)—O(9)f	2.20(2) × 2	A ^P —O(5)	3.00(1)	B ^P —O(5)	2.93(1)
M ^O (4)—O(8)f	2.24(2) × 2	A ^P —O(4)	3.00(2)	B ^P —O(1)	3.00(1)
M ^O (4)—O(7)	2.25(1) × 2	<A ^P —O>	2.94	B ^P —O(2)	3.02(1)
<M ^O (4)—O>	2.23			B ^P —O(6)	3.03(1)
				<B ^P —O>	2.89

a: *x*, *y*+1, *z*; b: $-x+1$, $-y+1$, $-z$; c: *x*, *y*-1, *z*; d: *x*+1, *y*, *z*; e: *x*-1, *y*+1, *z*; f: $-x+1$, *y*, $-z+\frac{1}{2}$; g: *x*+1, *y*-1, *z*; h: $-x$, $-y+1$, $-z$; i: *x*-1, *y*, *z*.

we assign more Na and the larger Ca cation to the *M*^O(3) site, the smaller Mg and Fe²⁺ cations to the *M*^O(4) site, and we distribute Mn and minor vacancy over the *M*^O(3,4) sites (Table 9).

Consider last the cation sites in the **I** block. We assign 1.02 S + 0.81 P + 0.17 □ p.f.u. (Table 2) to the *T* site in innelite-1*T* and innelite-2*M* (Tables 8 and 9). We assign Ba with minor Sr to the peripheral *A*^P and *B*^P sites.

Structure description

Site nomenclature

The cation sites are divided into 3 groups: the *M*^O sites of the O sheet, the *M*^H and *Si* sites of the H sheet, and the peripheral *A*^P and *B*^P sites and the *T* sites in the **I** block. In accord with Sokolova (2006), we label the anions X_M^O and X_A^O (anions of the O sheet); X_M^O = common vertices of *M*^O and *M*^H polyhedra; X_A^O = common vertices of *M*^O and *A*^P polyhedra. In the crystal structure of innelite, the X_A^O anion is bonded only to three *M*^O cations (and not to an *A*^P cation: *A*^P—X_A^O ≥ 3.5 Å).

Cation sites in innelite-1*T*

There are four cation sites in the O sheet: the *M*^O(1) site is occupied solely by Ti and is coordinated by four O atoms and two X_A^O [= O(9)] anions (see section Anion considerations below) with a <*M*^O(1)—O> distance of 2.00 Å (Tables 4, 6 and 8; Fig. 3a). The *M*^O(2) site is solely occupied by Na and is coordinated by six O atoms, with a <*M*^O(2)—O> distance of 2.45 Å (Table 8). The *M*^O(3) site is occupied mainly by Na and *M*²⁺ (= Mn > Fe > Mg > Ca) and is coordinated by four O atoms and two X_A^O anions, with <*M*^O(3)—O> distance of 2.31 Å (Table 8). For the O sheet, the sum of the 4 *M*^O cations is [(Na_{2.16}M_{0.80}²⁺□_{0.04})Ti]_{Σ4}, ideally [(Na₂M²⁺)Ti]_{Σ4} a.p.f.u.

In the H sheet, there are two tetrahedrally coordinated *Si* sites, occupied by Si, with a <Si—O> distance of 1.63 Å (Table 6; Fig. 3a). The [5]-coordinated *M*^H site is occupied mainly by Ti (Table 8) and is coordinated by O atoms, with a <*M*^H—O> distance of 1.92 Å; the very short *M*^H—O(8) distance of 1.68 Å (Table 6) is in

TABLE 8. Refined site-scattering (e.p.f.u.) and assigned site-populations (a.p.f.u.) for innelite-17.

Site	Refined site-scattering	Site population	Calculated site-scattering	$\langle X-\varphi \rangle_{\text{calc}}^*$ (Å)	$\langle X-\varphi \rangle_{\text{obs}}$ (Å)
$^{[5]}M^{H**}$	44.0	1.97 Ti + 0.02 Nb + 0.01 Al	44.3	1.89	1.92
$M^O(1)$	22.0	1.00 Ti	22	1.97	2.00
$M^O(2)$	11.0	1.00 Na	11	2.40	2.45
$M^O(3)$	31.0(7)	1.16 Na + 0.38 Mn + 0.17 Fe ²⁺ + 0.15 Mg + 0.10 Ca + 0.04 □	30.5	2.32	2.31
$^{[4]}T$	27.6(7)	1.02 S + 0.81 P + 0.17 □	28.5	1.52	1.53
$^{[9]}A^P$	112.0	1.97 Ba + 0.03 Sr	111.5	2.85	2.87
$^{[11]}B^P$	112.0	1.97 Ba + 0.03 Sr	111.5	2.94	2.88

* calculated by summing constituent ionic radii; values from Shannon (1976), φ = O, OH;

** coordination numbers are given for non-[6]-coordinated sites.

TABLE 9. Refined site-scattering (e.p.f.u.) and assigned site-populations (a.p.f.u.) for innelite-2M.

Site	Refined site-scattering	Site population	Calculated site-scattering	$\langle X-\varphi \rangle_{\text{calc}}^*$ (Å)	$\langle X-\varphi \rangle_{\text{obs}}$ (Å)
$^{[5]}M^{H**}$	44.0	1.97 Ti + 0.02 Nb + 0.01 Al	44.3	1.89	1.92
$M^O(1)$	22.0	1.00 Ti	22	1.97	2.01
$M^O(2)$	11.0	1.00 Na	11	2.40	2.44
$M^O(3)$	12.0(5)	0.81 Na + 0.10 Ca + 0.07 Mn + 0.02 □	12.7	2.37	2.35
$M^O(4)$	17.5(5)	0.35 Na + 0.31 Mn + 0.17 Fe ²⁺ + 0.15 Mg + 0.02 □	17.8	2.24	2.23
$^{[4]}T$	30.9(6)	1.02 S + 0.81 P + 0.17 □	28.5	1.52	1.49
$^{[9]}A^P$	112.0	1.97 Ba + 0.03 Sr	111.5	2.85	2.94
$^{[11]}B^P$	112.0	1.97 Ba + 0.03 Sr	111.5	2.94	2.89

* calculated by summing constituent ionic radii; values from Shannon (1976), φ = O, OH;

** coordination numbers are given for non-[6]-coordinated sites.

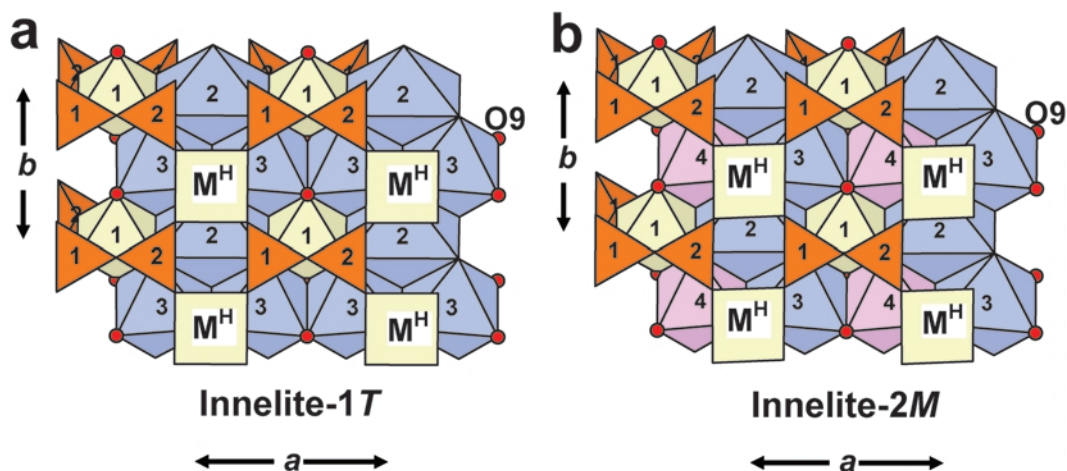


FIG. 3. The TS block in the crystal structure of innelite viewed down [001]: (a) innelite-1*T* and (b) innelite-2*M*; (SiO₄) tetrahedra are orange, Ti⁴⁺-dominant polyhedra are yellow, Na-dominant and (NaM²⁺) octahedra are navy blue, M²⁺-dominant octahedra are pink, X_A^O anions [O(9)] are shown as small red spheres. Labels 1 and 2 (on orange) correspond to Si(1,2) tetrahedra, respectively. Labels 1–4 correspond to M^O(1–4) octahedra in the O sheet, respectively: M^O(2) octahedra in innelite-1*T* and innelite-2*M* are occupied by Na; M^O(3) octahedra in innelite-1*T* are occupied by Na and M²⁺ in the ratio 1:1, i.e. (NaM²⁺); M^O(3) octahedra in innelite-2*M* are occupied by Na and M²⁺, where Na > M²⁺ and M^O(4) octahedra in innelite-2*M* are occupied by Na and M²⁺, where Na < M²⁺.

accord with the structure topology of Group-III minerals (Sokolova, 2006). For the two H sheets, the sum of the cations is ideally Ti₂Si₄ a.p.f.u.

In the **I** block, there are two distinct peripheral *A*^P and *B*^P sites (Fig. 4a). The [9]-coordinated *A*^P and [11]-coordinated *B*^P sites are occupied mainly by Ba (Table 8). The *A*^P and *B*^P sites are coordinated by O atoms of the H sheet and O atoms (or OH and H₂O groups) of the **I** block (see below), with <*A*^P–O> and <*B*^P–O> distances of 2.87 and 2.88 Å, respectively. We write the ideal composition of these two sites as Ba₄ a.p.f.u. There is one *T* site occupied by S_{1.02}P_{0.81}□_{0.17} p.f.u. and coordinated by four O atoms, with <T–O> = 1.53 Å (Table 5; Fig. 4a). To summarize, the three sites in the **I** block ideally give: (1) *A*^P site, Ba₂ a.p.f.u.; (2) *B*^P site, Ba₂ a.p.f.u.; (3) *T* site, (SP) a.p.f.u. = Ba₄(SP) a.p.f.u.

We write the cation part of the ideal formula as the sum of (1) the **I** block + (2) two H sheets + (3) one O sheet: (1) Ba₄(SP) + (2) Ti₂Si₄ + (3) [(Na₂M²⁺)Ti] = Ba₄(Na₂M²⁺)Ti₃Si₄(SP) with a total charge of 51⁺.

Cation sites in innelite-2*M*

There are four cation sites in the O sheet: the M^O(1) site is occupied solely by Ti and is

coordinated by four O atoms and two X_A^O [= O(9)] anions with a <M^O(1)–O> distance of 2.01 Å (Tables 7 and 9; Fig. 3b). The M^O(2) site is occupied solely by Na and is coordinated by O atoms, with a <M^O(2)–O> distance of 2.44 Å (Table 9). The M^O(3) and M^O(4) sites are occupied by Na and M_{0.17}²⁺ (= Ca > Mn) and Mn and M_{0.63}²⁺ (= Mn > Fe > Mg) and Na_{0.35}, respectively, and are coordinated by four O atoms and two X_A^O anions, with <M^O(3)–O> = 2.35 and <M^O(4)–O> = 2.23 Å (Table 9). For the O sheet, the total of the 4M^O cations is [(Na_{2.16}M_{0.80}²⁺□_{0.04})Ti]_{Σ4}, ideally (Na₂M₁²⁺)Ti₁ a.p.f.u.

In the H sheet, there are two tetrahedrally coordinated Si sites occupied by Si with a <Si–O> distance of 1.63 Å (Table 7 and 9; Fig. 3b). The [5]-coordinated M^H(1) site is occupied mainly by Ti (Table 9) and is coordinated by O atoms, with a <M^H–O> distance of 1.92 Å; the short M^H–O(8) distance of 1.70 Å (Table 7) is in accord with the structure topology of Group-III minerals (Sokolova, 2006). For the 2H sheet, the total of M^H and Si cations is (Ti_{1.97}Nb_{0.02}Al_{0.01})Σ_{2.00}Si₄, ideally Ti₂Si₄ a.p.f.u.

In the **I** block, there are two *P* sites, a [9]-coordinated *A*^P site and an [11]-coordinated *B*^P site, occupied mainly by Ba (Table 9; Fig. 4b). The *A*^P and *B*^P sites are coordinated by O atoms

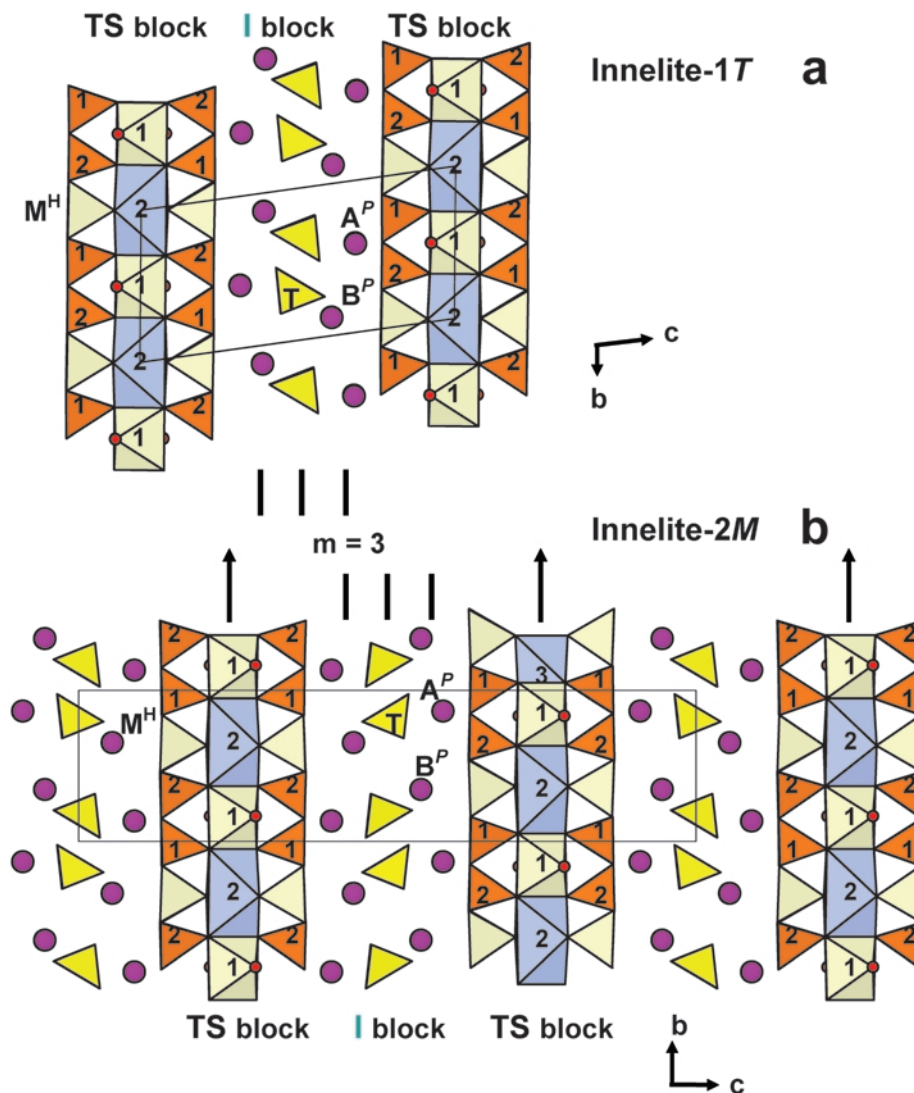


FIG. 4. The crystal structures of (a) innelite-1T and (b) innelite-2M projected onto (100). Legend as in Fig. 3; Ba atoms at the A^P and B^P sites are shown as raspberry-coloured spheres. T tetrahedra are yellow. The three vertical lines show the positions of the cation layers ($m = 3$) in the I block. Positions of the 2_y axis in innelite-2M are shown by black arrows.

of the H sheet and O atoms (or OH and H₂O groups) of the I block (see below), with mean $\langle A^P, B^P - O \rangle$ distances of 2.92 Å. The ideal composition of these two sites is Ba₄ a.p.f.u. There is one T site occupied by $S_{1.02}P_{0.81}\square_{0.17}$ p.f.u. and coordinated by four O atoms, with $\langle T - O \rangle = 1.49$ Å (Table 7; Fig. 4b). The three sites of the I block ideally give: (1) A^P site, Ba₂

a.p.f.u.; (2) B^P site, Ba₂ a.p.f.u.; (3) T site, (SP) a.p.f.u. = Ba₄(SP) a.p.f.u.

We write the cation part of the innelite-2M structure as the sum of (1) the I-block sites + (2) two H sheets + (3) one O sheet: (1) Ba₄(SP) + (2) Ti_2Si_4 + (3) $[(Na_2M^{2+})Ti] = Ba_4(Na_2M^{2+})Ti_3Si_4(SP)$ with a total charge of 51⁺.

Anion considerations

We calculated the empirical formula for innelite on the basis of 26 (O + F) anions. There are 13 anion sites in the crystal structures of innelite-1*T* and innelite-2*M*. Bond-valence values for anions are listed in Tables 10 (innelite-1*T*) and 11 (innelite-2*M*). In innelite-1*T* and innelite-2*M*, each anion site gives two anions p.f.u. Seven anion sites, O(1–7), are occupied by O atoms which form the tetrahedral coordination of the Si atoms (Tables 4 and 6). There is one site, O(8) (= X_M^O), which is a common anion for the M^H polyhedron and three octahedra of the O sheet (Tables 6 and 10). These anions receive bond valences of 1.93–2.15 v.u. (valence units) (Tables 10 and 11) and hence are O atoms (Tables 4 and 5), which give O_{16} a.p.f.u.

Short-range order at the X_A^O site

In innelite-1*T*, there is one [3]-coordinated site, O(9) (= X_A^O), that provides a common anion for the $M^O(1)$ (= Ti) and two $M^O(3)$ octahedra of the O sheet (Fig. 3*a*); note that the fourth cation, A^P ,

occurs at a distance of 3.53 Å and hence does not contribute. The O(9) anion receives bond valence of 1.11 v.u. and, from a long-range perspective, would be assigned as a monovalent anion. However, let us take into consideration the short-range order (SRO) of cations at the adjacent $M^O(3)$ site, which is occupied by $Na_{0.58}M_{0.40}^{2+}\square_{0.02}$ (= $Na_{1.16}M_{0.80}^{2+}\square_{0.04}$ a.p.f.u.). Where the $M^O(3)$ site is occupied by M^{2+} , the adjacent O(9) site receives bond-valence from Ti at the $M^O(1)$ site and two M^{2+} at the $M^O(3)$ site (Fig. 3*a*), and the O(9) site is locally occupied by O^{2-} . Where the $M^O(3)$ site is occupied by Na, the O(9) site receives bond valence from Ti at the $M^O(1)$ site and two Na at the $M^O(3)$ site (Fig. 3*a*), and the O(9) site is occupied by the monovalent anions, $(OH)^-$ and F^- . The $M^O(3)$ site composition is $Na_{0.58}M_{0.40}^{2+}\square_{0.02}$ (= $Na_{1.16}M_{0.80}^{2+}\square_{0.04}$ a.p.f.u.), and therefore the composition of the O(9) site is $(OH+F)_{0.60}O_{0.40}$ [= $(OH+F)_{1.20}O_{0.80}$ p.f.u.]. Chemical analysis gives $F_{0.21}$ p.f.u. (Table 2), and we write the composition of the O(9) site as $(OH)_{0.99}F_{0.21}O_{0.80}$ p.f.u., ideally $[(OH)O]$ p.f.u. The corresponding bond valence

TABLE 10. Bond-valence* (v.u.) table for innelite-1*T*.

Atom	Si(1)	Si(2)	M^H	$M^O(1)$	$M^O(2)$	$M^O(3)$	T	A^P	B^P	Σ
O(1)	1.05			$0.56 \times 2 \downarrow$	$0.16 \times 2 \downarrow$	0.26				2.03
O(2)	1.03		0.60					0.17	0.16	1.96
O(3)	0.97		0.62					0.17	0.17	1.93
O(4)	0.97	0.97						0.17		2.27
								0.16		
O(5)		1.00	0.62					0.23	0.15	2.00
O(6)		1.00	0.60					0.26	0.16	2.02
O(7)		1.05		$0.56 \times 2 \downarrow$	$0.17 \times 2 \downarrow$	0.27				2.05
O(8)			1.46		$0.25 \times 2 \downarrow$	0.22				2.15
						0.22				
$^{[3]}O(9)^{**}$				$0.62 \times 2 \downarrow$		0.26				1.11
						0.23				
O(10)							1.20	0.28	0.26	1.98
									0.24	
O(11)							1.16	0.28	0.26	1.95
									0.25	
O(12)							0.98	0.23	0.20	1.60
									0.19	
$^{[2]}O(13)$							1.34		0.31	1.65
Total	4.02	4.02	3.90	3.48	1.16	1.46	4.68	1.95	2.35	
Aggregate charge	4.00	4.00	4.00	4.00	1.0	1.38	5.09	2.00	2.00	

* bond-valence parameters from Brown (1981)

** coordination numbers are given for non-[4]-coordinated O atoms.

CRYSTAL STRUCTURES OF INNELITE-1T AND INNELITE-2M

TABLE 11. Bond-valence* (v.u.) table for innelite-2M.

Atom	Si(1)	Si(2)	M ^H	M ^O (1)	M ^O (2)	M ^O (3)	M ^O (4)	T	A ^P	B ^P	Σ
O(1)	1.08		0.57						0.22	0.15	2.02
O(2)	0.99		0.69						0.24	0.15	2.07
O(3)	1.00			0.60 × 2 ↓	0.18 × 2 ↓	0.28 × 2 ↓					2.06
O(4)	0.99	0.95							0.16		2.25
									0.15		
O(5)		1.15	0.56						0.15	0.18	2.04
O(6)		0.92	0.69						0.19	0.14	1.94
O(7)		1.05		0.48 × 2 ↓	0.17 × 2 ↓		0.27 × 2 ↓				1.97
O(8)			1.37		0.23 × 2 ↓	0.20 × 2 ↓	0.28 × 2 ↓				2.08
[³]O(9)**				0.64 × 2 ↓		0.22 × 2 ↓	0.30 × 2 ↓				1.16
[²]O(10)								1.44		0.32	1.76
O(11)								1.32	0.29	0.24	2.09
										0.24	
O(12)								1.28	0.31	0.25	2.06
										0.22	
O(13)								1.24	0.23	0.20	1.85
									0.18		
Total	3.88	4.07	3.88	3.44	1.16	1.40	1.70	5.28	1.94	2.27	
Aggregate charge	4.00	4.00	4.01	4.00	1.00	1.15	1.61	5.09	2.00	2.00	

* bond-valence parameters from Brown (1981);

** coordination numbers are given for non-[4]-coordinated O atoms.

incident at the O(9) site should be ~1.4 v.u., and the lower value of 1.11 v.u. (Table 10) is probably due to the fact that dominance of Na at the M^O(3) site is responsible for longer distances.

In innelite-2M, there is one [3]-coordinated site, O(9) (= X_A^O), that provides a common anion for the M^O(1) (= Ti) and two M^O(3,4) octahedra of the O sheet (Fig. 3b). The bond-valence sum incident at the O(9) anion is 1.16 v.u. (Table 11). The O(9) anion is coordinated by the M^O(1) (= Ti a.p.f.u.), M^O(3) (= Na_{0.81}M_{0.17}²⁺ a.p.f.u.) and M^O(4) (= M_{0.63}Na_{0.35}²⁺ a.p.f.u.) cations. The composition of the M^O(3,4) sites is Na_{1.16}M_{0.80}²⁺□_{0.04} (= Na_{1.16}M_{0.80}²⁺□_{0.04} a.p.f.u.), and the amount of M²⁺ cations that contribute bond valence to the O(9) anion is 0.80 a.p.f.u. Where the M^O(3,4) sites are occupied by M²⁺, the adjacent O(9) site receives bond-valence from Ti at the M^O(1) site and two M²⁺ at the M^O(3,4) sites (Fig. 3a), and the O(9) site is locally occupied by O²⁻. Where the M^O(3,4) sites are occupied by Na (or minor vacancy), the O(9) site is occupied by the monovalent anions, (OH)⁻ and F⁻. By analogy with the O(9) site in innelite-1T, we write the

composition of the O(9) site in innelite-2M as (OH)_{0.99}F_{0.21}O_{0.80} p.f.u., ideally [(OH)O] p.f.u.

Short-range order of anions in the I block

In innelite-1T, there are four anions, O(10–13), that coordinate the T site which is occupied by 1.02 S + 0.81 P + 0.17 □ (Table 8). These anions receive bond valences of 1.60–1.98 v.u. (Table 10), and hence are O atoms (Table 3). Figure 5a shows the linkage of Ba atoms (at the A^P and B^P sites) and TO₄ tetrahedra via O(10–13). Where the T site is 91.5% occupied by S and P [(S,P)_{1.83}□_{0.17}], each of the O(10–13) anions is bonded to the T atom and three Ba atoms [O(10–12): A^P and 2B^P] or one Ba atom [O(13): B^P] (Table 10). The O(10–13) atoms give 0.915 × 4 = 3.66 O per TO₄ group or 1.83 × 4 O = 7.32 O a.p.f.u. What happens when the T site is 8.5% vacant [(S,P)_{1.83}□_{0.17}]? In this case, the O(10–13) anions receive bond-valence solely from Ba atoms, 0.78, 0.79, 0.62 and 0.31 v.u., respectively. Allowing for further minor contribution from hydrogen bonding suggests OH groups at the O(10–12) sites and an H₂O group at the

O(13) site (Fig. 5*b*). Hence, in the **I** block of the innelite-1*T* structure, Ba atoms connect via OH and H₂O groups where the *T* site is vacant. The total content of OH and H₂O groups is (0.17 × 3) OH and 0.17 H₂O p.f.u. We can write the anion

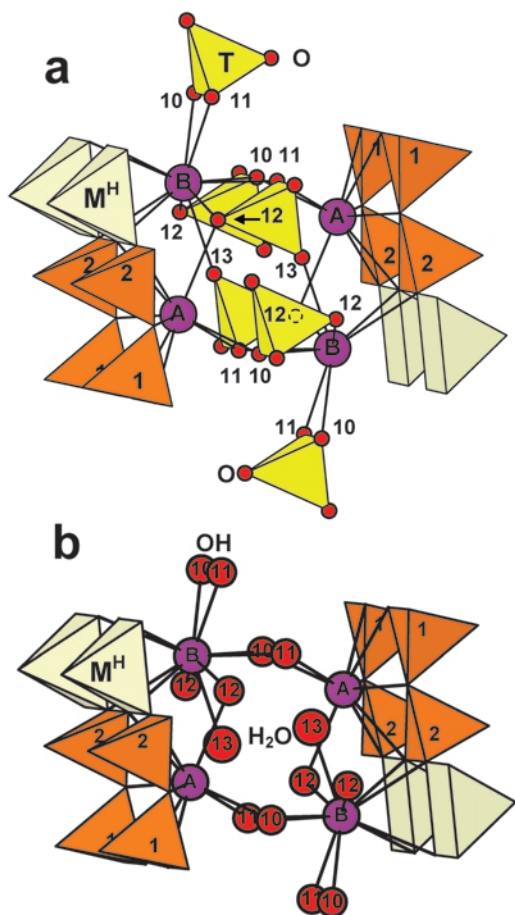


FIG. 5. Details of short-range order of anions in the **I** block for innelite-1*T*: (a) linkage of Ba atoms (at the $[9]A^P$ and $[11]B^P$ sites) and *T* tetrahedra where *T* tetrahedra are fully occupied by S and P; (b) linkage of Ba atoms at the A^P and B^P sites via (OH) [O(10,11,12)] and H₂O [O(13)] groups where *T* sites are vacant. Ba atoms at the A^P and B^P sites are shown as raspberry-coloured spheres and labelled A and B, respectively. Anions in the **I** block are shown as (a) small red spheres where they are O atoms which coordinate *T* sites occupied by S and P and (b) medium red (OH) and large red (H₂O) spheres where *T* sites are vacant. OH and H₂O groups shown in (b) correspond to labelled O atoms in (a).

content of the O(10–13) sites as 7.32 O (*T* site occupied) + (0.51 OH + 0.17 H₂O) (*T* site vacant) = $O_{7.32}(\text{OH})_{0.51}(\text{H}_2\text{O})_{0.17}$ p.f.u.

Note that in innelite-2*M*, where the *T* site is vacant in the **I** block, one anion, O(10), and three anions, O(11–13), receive bond-valence of 0.32 and 0.61–0.78 v.u. from Ba atoms. Hence we can assign H₂O and OH groups to the O(10) and O(11–13) sites, respectively. By analogy with innelite-1*T*, we assign $O_{7.32}(\text{OH})_{0.51}(\text{H}_2\text{O})_{0.17}$ p.f.u. to the anions in the **I** block of the innelite-2*M* structure. The ideal anion composition of the **I** block is O₈ a.p.f.u.

To conclude, we write the ideal anion part of the innelite structure as the sum of the anion sites: O₁₆ (14 O atoms of Si₄ tetrahedra and 2 O atoms at the X_M^O sites) + [(OH)O] (2 X_A^O) + O₈ (**I** block) = O₂₅(OH) p.f.u. with a total charge of 51[−]. This is in accord with the ideal cation part of the structure, Ba₄(Na₂M²⁺)Ti₃Si₄(SP), with a total charge of 51⁺.

Structure topology

The principal features of the structure topology of the innelite-1*T* and innelite-2*M* structures are in accord with the crystal structure for innelite reported by Chernov *et al.* (1971). The TS block consists of HOH sheets where H is a heteropolyhedral sheet including (Si₂O₇) groups, and O is a trioctahedral close-packed sheet. In the innelite-1*T* and innelite-2*M* structures, there is one TS block (Figs 3 and 4). The H and O sheets link *via* common vertices of M^H, Si and M^O polyhedra to form the TS block which is parallel to (001) (Fig. 4). In innelite-1*T* and innelite-2*M*, two H sheets of one TS block are related by an inversion centre and a *c_y* glide plane, respectively (Fig. 4). In innelite, the TS block exhibits linkage 1 and stereochemistry typical for Group III (Sokolova, 2006): two H sheets connect to the O sheet such that two (Si₂O₇) groups link to *trans* edges of the Ti octahedron of the O sheet. In innelite, the TS blocks alternate with intermediate (**I**) blocks. An **I** block is always intercalated between two TS blocks and cations of the **I** block form close-packed layers parallel to the TS block, where *m* denotes the number of those layers (Sokolova, 2006). In innelite, there is one type of **I** block where *m* = 3. In two *m* layers, Ba atoms at the A^P (1) and B^P (2) sites are arranged in a close-packed fashion where each atom is surrounded by six others at approximately equal distances of 5 Å.

Chemical formula

We write the ideal formula for innelite as the sum of the cation and anion sites: $\text{Ba}_4(\text{Na}_2\text{M}^{2+})\text{Ti}_3\text{Si}_4(\text{SP})$ (a total charge of 51^+) and $\text{O}_{25}(\text{OH})$ (a total charge of 51^-). We consider (Si_2O_7) , (PO_4) and (SO_4) groups as complex oxyanions and write ideal structural formulae of the form $\text{A}_2^P\text{B}_2^{P[5]}\text{M}_2^H\text{M}_4^O(\text{Si}_2\text{O}_7)_2(\text{TO}_4)_2\text{X}_4^O$ as defined by Sokolova (2006). The ideal structural formula for innelite is: $\text{Ba}_4\text{Ti}_2\text{Na}_2\text{M}^{2+}\text{Ti}(\text{Si}_2\text{O}_7)_2[(\text{SO}_4)(\text{PO}_4)]\text{O}_2[\text{O}(\text{OH})]$; with space group $P\bar{1}$, $Z = 1$, and space group $P2/c$, $Z = 2$, for innelite-1T and innelite-2M, respectively. The core part of the TS block, $\text{M}_2^H\text{M}_4^O(\text{Si}_2\text{O}_7)_2\text{X}_4^O$, is shown in bold: M^H = cations of the H sheet = Ti_2 ; M^O = cations of the O sheet = $\text{Na}_2\text{M}^{2+}\text{Ti}$; X_4^O = anions in the O sheet = $\text{O}_2[\text{O}(\text{OH})]$; $2\text{A}^P + 2\text{B}^P = \text{Ba}_4$; $(\text{TO}_4)_2 = [(\text{SO}_4)(\text{PO}_4)]$ (Table 1).

Above, we reported the empirical formula for innelite (Table 2) calculated on the basis of 26 (O + F) anions: $(\text{Ba}_{3.94}\text{Sr}_{0.06})_{\Sigma 4.00}(\text{Na}_{2.16}\text{Mn}_{0.38}^{2+}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.15}\text{Ca}_{0.10}\square_{0.04})_{\Sigma 3}(\text{Ti}_{2.97}\text{Nb}_{0.02}\text{Al}_{0.02})_{\Sigma 3.01}\text{Si}_{4.01}(\text{S}_{1.02}\text{P}_{0.81}\square_{0.17})_{\Sigma 2}\text{H}_{1.84}\text{O}_{25.79}\text{F}_{0.21}$, $Z = 1$ (innelite-1T) and $Z = 2$ (innelite-2M). We can now rewrite this formula taking into account our structure information as follows: $(\text{Ba}_{3.94}\text{Sr}_{0.06})_{\Sigma 4.00}(\text{Ti}_{1.97}\text{Nb}_{0.02}\text{Al}_{0.02})_{\Sigma 2.01}(\text{Na}_{2.16}\text{Mn}_{0.38}^{2+}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.15}\text{Ca}_{0.10}\square_{0.04})_{\Sigma 3}\text{Ti}(\text{Si}_{4.01}\text{O}_{14})[(\text{SO}_4)_{1.02}(\text{PO}_4)_{0.81}(\text{OH})_{0.51}\text{H}_2\text{O}_{0.17}]\text{O}_2[(\text{OH}_{0.99}\text{F}_{0.21})_{\Sigma 1.20}\text{O}_{0.80}]$. The validity of the ideal formula is supported by the close agreement between the charges for specific groups of cations in the ideal and empirical formulae: 8^+ for Ba_4 vs $(\text{Ba}_{3.94}\text{Sr}_{0.06})$; 8^+ for Ti_2 vs 8.04^+ for $(\text{Ti}_{1.97}\text{Nb}_{0.02}\text{Al}_{0.02})$; 4^+ for $(\text{Na}_2\text{M}^{2+})$ vs 3.76^+ for $(\text{Na}_{2.16}\text{Mn}_{0.38}^{2+}\text{Fe}_{0.17}^{2+}\text{Mg}_{0.15}\text{Ca}_{0.10}\square_{0.04})$; 5^- for $[(\text{SO}_4)(\text{PO}_4)]$ vs 4.98^- for $[(\text{SO}_4)_{1.02}(\text{PO}_4)_{0.81}(\text{OH})_{0.51}\text{H}_2\text{O}_{0.17}]$.

Comments on phosphoinnelite and yoshimuraite

We wish to comment on some problems with two minerals related to innelite, phosphoinnelite (Pekov *et al.*, 2006) and yoshimuraite (McDonald *et al.*, 2000) (Table 1). These minerals are both titanium silicates with the TS block, and they belong to Group III (phosphoinnelite) and Group II (yoshimuraite).

Phosphoinnelite

For phosphoinnelite, the crystal structure is unknown. Pekov *et al.* (2006) described phos-

phoinnelite as a structural analogue of innelite, with $\text{P} > \text{S}$, reported a chemical analysis and gave empirical and simplified formulae for phosphoinnelite as follows: $(\text{Ba}_{3.59}\text{Sr}_{0.13}\text{K}_{0.01})_{\Sigma 3.73}(\text{Na}_{2.59}\text{Mg}_{0.21}\text{Mn}_{0.20}^{2+}\text{Ca}_{0.04})_{\Sigma 3.04}(\text{Ti}_{2.80}\text{Fe}_{0.26}^{3+}\text{Nb}_{0.07})_{\Sigma 3.13}(\text{Si}_{3.93}\text{Al}_{0.07})_{\Sigma 4.014}[(\text{P}_{1.11}\text{S}_{0.87})_{\Sigma 1.98}\text{O}_{7.96}](\text{O}_{2.975}\text{F}_{0.10})_{\Sigma 3.075}$ and $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4)_2(\text{SO}_4)_2(\text{O},\text{F})_3$, which both have 25 anions. The structure topology of innelite requires 26 anions p.f.u. (see Tables 4 and 5). Therefore the formulae of phosphoinnelite given above are not correct as they do not correspond to the structure topology of the innelite structure type. Table 12 gives the chemical analysis for phosphoinnelite (Pekov *et al.*, 2006) and the formula units calculated on 25 (taken from Pekov *et al.* (2006)) and 26 anions (this work). We modified the chemical analysis of phosphoinnelite, taking into consideration the structural information on innelite: (1) we calculated an H_2O content so that $\text{OH} + \text{F} = 2$ p.f.u. at the X_A^O site; (2) as in the formula unit of Pekov *et al.* (2006), $\text{Ti} + \text{Nb} + \text{Fe}^{3+} = 3.13$ a.p.f.u. (whereas the maximum possible Ti content is 3 a.p.f.u.), we recalculated Fe_2O_3 as $\text{Fe}_2\text{O}_3 + \text{FeO}$ so there is no cation excess at the Ti-dominant sites and Fe^{2+} substitutes for Na in the O sheet. This resulted in the following empirical formula: $(\text{Ba}_{3.61}\text{Sr}_{0.1320}\text{Ca}_{0.04}\text{K}_{0.01})_{\Sigma 3.79}(\text{Na}_{2.60}\text{Mg}_{0.21}\text{Fe}_{0.21}^{2+}\text{Mn}_{0.20}^{2+})_{\Sigma 3.22}(\text{Ti}_{2.81}\text{Nb}_{0.07}\text{Al}_{0.07}\text{Fe}_{0.05}^{3+})_{\Sigma 3}(\text{Si}_{3.95}\text{O}_{14})[(\text{P}_{1.11}\text{S}_{0.88})_{\Sigma 1.99}\text{O}_8]\text{O}_2(\text{OH}_{1.89}\text{F}_{0.10})_{\Sigma 1.99}$. In the latter formula unit, there is an excess of 0.22 a.p.f.u. for the alkali cations of the O sheet (3.22 vs 3 a.p.f.u.) and a vacancy of 0.21 p.f.u. at the $\text{A}^P + \text{B}^P$ sites: $(\text{Na}_{2.60}\text{Mg}_{0.21}\text{Fe}_{0.21}^{2+}\text{Mn}_{0.20}^{2+})_{\Sigma 3.22}$ and $(\text{Ba}_{3.61}\text{Sr}_{0.1320}\text{Ca}_{0.04}\text{K}_{0.01})_{\Sigma 3.79}$, respectively. However, it is not clear if Na substitutes for Ba at the $\text{A}^P + \text{B}^P$ sites; only structure refinement of phosphoinnelite can give us an answer. Our HRTEM data (see discussion above) show that it is extremely difficult to find an individual grain of innelite or phosphoinnelite as these minerals form intimate intergrowths. We suggest an ideal formula for phosphoinnelite (with 26 anions): $\text{Ba}_4\text{Ti}_2\text{Na}_3\text{Ti}(\text{Si}_2\text{O}_7)_2[(\text{PO}_4)(\text{SO}_4)]\text{O}_2(\text{OH})_2$, space group $P\bar{1}$, $Z = 1$.

Yoshimuraite

The latest structure work on yoshimuraite was done by McDonald *et al.* (2000). Yoshimuraite, $\text{Ba}_4\text{Ti}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OH})_2$, is a Group-II mineral. In yoshimuraite, the I block is topologically identical to that of innelite with $\text{P} > \text{S}$

TABLE 12. Chemical composition (wt.%) and unit formula (a.p.f.u.) for innelite (this work) and phosphoinnelite (Pekov *et al.*, 2006).

Oxide	Innelite	– Phosphoinnelite –		Formula unit	Innelite	– Phosphoinnelite –	
		(1)	(2)			(1)	(2)
SO ₃	6.03	5.29	5.29	S	1.02	0.87	0.88
Nb ₂ O ₅	0.18	0.74	0.74	P	0.81	1.11	1.11
P ₂ O ₅	4.24	5.93	5.93	Σ(S+P)	1.83	1.98	1.99
TiO ₂	17.50	16.88	16.88				
SiO ₂	17.76	17.83	17.83	Si	4.01	3.93	3.95
Al ₂ O ₃	0.06	0.27	0.27	Al	0	0.07	0
Fe ₂ O ₃	0	1.55	0.30	ΣSi	4.01[4]	4.00[4]	3.95[4]
FeO	0.89	0	1.13				
MnO	1.98	1.07	1.07	Ti	2.97	2.80	2.81
MgO	0.43	0.64	0.64	Fe ³⁺	0	0.26	0.05
BaO	44.59	41.60	41.60	Nb	0.02	0.07	0.07
SrO	0.48	0.99	0.99	Al	0.02	0	0.07
CaO	0.40	0.15	0.15	Σ~Ti	3.01[3]	3.13[3]	3.00[3]
K ₂ O	0.00	0.04	0.04				
Na ₂ O	4.95	6.06	6.06	Na	2.16	2.59	2.60
H ₂ O	1.22*	0	1.28	Mn ²⁺	0.38	0.20	0.20
F	0.30	0.14	0.14	Fe ²⁺	0.17	0.27	0.21
O=F	–0.13	–0.06	–0.06	Mg	0.15	0.21	0.21
Total	100.88	99.12	100.28	Ca	0.10	0.04	0
				ΣM ^O	2.96[3]	3.31[3]	3.22[3]
				Ba	3.94	3.59	3.61
				K	0	0.01	0.01
				Sr	0.06	0.13	0.13
				Na	0	0	0
				Ca	0	0	0.04
				Σ2A ^P + 2B ^P	4.00[4]	3.73[4]	3.79[4]
				Σ cations	15.81	16.51	15.91
				OH	0.99	0	1.89
				F	0.21	0.14	0.10
				Σ2X _A ^O **	1.20**	0.14	1.99
				H ⁺ ***	0.85	0	0
				Total H ⁺	1.84	0	1.89

(1) taken from Pekov *et al.* (2006) where the unit formula was calculated on 25 anions; (2) = (1) modified: Fe₂O₃ 1.55 wt.% → Fe₂O₃ 0.30 + FeO 1.13 wt.%; H₂O = 1.28 wt.% so that OH + F ~2 p.f.u.

n.a. = not analysed; n.d. = not detected

maximum content for a specific cation group is given in [], e.g. [4] = 4 a.p.f.u.

* calculated from structure refinement

** monovalent anions of the O sheet

*** content of H⁺ from (OH)_{0.51} + (H₂O)_{0.17} in the I block (see text).

(Table 13) and the TS block is of different topology and chemistry. In the TS block, the O sheet is composed of Mn octahedra and the topology of the TS block is defined by linkage 2 (Sokolova, 2006) (Fig. 6). For yoshimuraite, McDonald *et al.* (2000) reported an empirical

formula calculated on 13 anions and we present it here in a doubled form, based on 26 anions: (Ba_{3.90}Sr_{0.56})_{Σ4.46}(Mn_{3.28}²⁺Fe_{0.98}Mg_{0.06})_{Σ4.32}(Ti_{1.56}Fe_{0.44}³⁺)_{Σ2.00}O₂(Si₂O₇)₂[(P_{0.92}S_{0.68}Si_{0.34})_{Σ1.94}O₈](OH)₂, space group *P* $\bar{1}$, *Z* = 1 (valence was not assigned to Fe in the O sheet). The latter formula

CRYSTAL STRUCTURES OF INNELITE-1T AND INNELITE-2M

TABLE 13. Chemical composition (wt.%) and unit formula (a.p.f.u.) for yoshimuraite.

Oxide	(1)	(2)	Formula unit	(1)	(2)
SO ₃	3.92	3.92	S	0.71	0.70
P ₂ O ₅	4.21	4.21	P	0.86	0.85
TiO ₂	8.12	8.12	Σ(S+P)	1.57	1.55
SiO ₂	17.00	17.00			
Fe ₂ O ₃	8.04	3.06	Si	4.12[4]	4.04[4]
FeO	0	4.48			
MnO	15.15	15.15	Ti	1.48	1.45
MgO	0.18	0.18	Fe ³⁺	0.52	0.55
BaO	39.08	39.08	Σ~Ti	2.00[2]	2.00[2]
SrO	3.01	3.01			
H ₂ O*	1.23	2.40	Mn ²⁺	3.11	3.05
Total	99.94	100.61	Fe ²⁺	0	0.89
			Fe ³⁺	0.95	0
			Mg	0.07	0.06
			ΣM ^O	4.13[4]	4.00[4]
			Ba	3.71	3.64
			Sr	0.42	0.42
			Σ2A ^P + 2B ^P	4.13[4]	4.06[4]
			Σ cations	15.95	15.65
			OH		
			[O sheet]	1.99	2.00
			[I block]	0	1.80
			Total H ⁺	1.99	3.80

(1) McDonald *et al.* (2000); (2) modified in this work.

n.a. = not analysed; n.d. = not detected;

maximum content for a specific cation group is given in [], e.g. [4] = 4 a.p.f.u.

*calculated from structure refinement.

has an excess charge of 1.16⁺ (Fe_{0.98}²⁺ in the O sheet) or 2.14⁺ (Fe_{0.98}³⁺ in the O sheet), and the sums of the two cation groups are too high: 2A^P + 2B^P = 4.46 and 4M^O = 4.32 *vs* the maximum allowed value of 4.00 a.p.f.u. A corresponding chemical analysis from McDonald *et al.* (2000) is presented in Table 13 where all Fe is given as Fe₂O₃ (analysis (1)). Calculation of the formula unit based on analysis (1) gives the empirical formula: (Ba_{3.71}Sr_{0.42})Σ_{4.13}(Mn_{3.11}²⁺Fe_{0.95}³⁺Mg_{0.07})Σ_{4.13}(Ti_{1.48}Fe_{0.52}³⁺)Σ₂O₂(Si₂O₇)₂[(P_{0.86}S_{0.71}Si_{0.12})Σ_{1.69}O₈](OH)_{1.99} which is neutral. However, the structure refinement results of McDonald *et al.* (2000) indicate that (1) cation radii for octahedra in the O sheet are ≥0.83 Å, and therefore Fe³⁺ does not occur in the O sheet; we must assign Fe²⁺ to the O sheet; and (2) mean bond-lengths of the *T* site in the **I** block vary from 1.47 to 1.52 Å which is in accord with S-P disorder and excludes Si as a

possible substituent for P and S. Therefore the *T* site is occupied by P, S and vacancy and gives (based on analysis (1)) ~P_{0.86}S_{0.71}□_{0.43} p.f.u. Earlier in this paper, we showed that in the innelite structure, the absence of P and S atoms at the *T* sites requires substitution of O atoms by OH groups (Fig. 5), and we apply the same mechanism for yoshimuraite, otherwise two TS blocks are not connected to each other and the structure cannot exist. We modified the chemical analysis taking into account the occurrence of Fe²⁺ in the O sheet and substitution of OH groups for O atoms in the **I** block where a vacancy of 0.45 p.f.u. corresponds to 0.45 × 4 = 1.80 OH p.f.u. [chemical analysis (2), Table 13] and recalculated the formula unit on 26 anions p.f.u. The unit formula (2) (Table 13) is as follows: (Ba_{3.64}Sr_{0.42})Σ_{4.06}(Mn_{3.05}²⁺Fe_{0.89}³⁺Mg_{0.06})Σ_{4.00}(Ti_{1.45}Fe_{0.55}³⁺)Σ₂(Si_{2.02}O₇)₂[(P_{0.85}S_{0.70}□_{0.45})Σ₂O_{6.20}(OH)_{1.80}](OH)₂. This

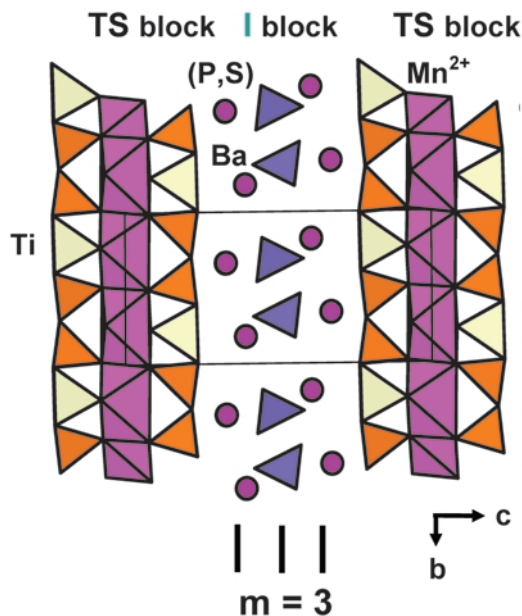


FIG. 6. The crystal structure of yoshimuraite projected onto (100). Legend as in Fig. 3; Ba atoms at the A^P and B^P sites are shown as raspberry-coloured spheres, (P,S) tetrahedra are purple, Mn^{2+} tetrahedra are magenta. The three vertical lines show the positions of cation layers ($m = 3$) in the I block.

formula is neutral, does not show a large excess of cations in the O sheet, ($Mn_{3.05}^{2+}Fe_{0.89}Mg_{0.06}$) $\Sigma_{4.00}$, and I block, ($Ba_{3.64}Sr_{0.42}$) $\Sigma_{4.06}$, and corresponds to the structure-refinement results of McDonald *et al.* (2000). In accord with McDonald *et al.* (2000), the ideal formula of yoshimuraite is $Ba_4Ti_2Mn_4(Si_2O_7)_2(PO_4)_2O_2(OH)_2$.

Summary

(1) The chemical composition of innelite has been revised and its ideal formula is as follows $Ba_4Ti_2Na_2M^{2+}Ti(Si_2O_7)_2[(SO_4)(PO_4)]O_2[O(OH)]$, where $M^{2+} = Mn, Fe^{2+}, Mg, Ca$.

(2) Innelite, space group $P1$ (Kravchenko *et al.*, 1961; Chernov *et al.*, 1971) is a triclinic polytype, innelite-1T, and has been refined in space group $P\bar{1}$. A new monoclinic polytype of innelite, innelite-2M, has been described with the space group $P2_1/c$; $c_{2M} = 2c_{1T}$.

(3) Intergrowth of innelite-1T and innelite-2M polytypes has been shown by transmission electron spectroscopy.

(4) For both polytypes, the number of anions is 26 p.f.u. and it remains 26 p.f.u. whether the T sites in the I block are occupied by S and P or they are vacant.

(5) There are two substitutions in the O sheet of the TS block: $Na^+ \rightleftharpoons M^{2+}$ at the M^O sites adjacent to the X_A^O site and $OH^- \rightleftharpoons O^{2-}$ at the X_A^O site, and these couple as follows: $Na^+ + OH^- \rightleftharpoons M^{2+} + O^{2-}$.

(6) There are two substitutions in the I block: $T(S,P) \rightleftharpoons T\Box$ at the T sites and $O^{2-} \rightleftharpoons OH^-$ at the anion sites which coordinate the T sites; they couple as follows: $T(S,P) + O^{2-} \rightleftharpoons T\Box + OH^-$.

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