

From structure topology to chemical composition.

IX. Titanium silicates: revision of the crystal chemistry of lomonosovite and murmanite, Group-IV minerals

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ABSTRACT

The crystal structures of lomonosovite, ideally $\text{Na}_{10}\text{Ti}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_4$, $a = 5.4170(7)$ Å, $b = 7.1190(9)$ Å, $c = 14.487(2)$ Å, $\alpha = 99.957(3)^\circ$, $\beta = 96.711(3)^\circ$, $\gamma = 90.360(3)^\circ$, $V = 546.28(4)$ Å³, $D_{\text{calc.}} = 3.175$ g cm⁻³, and murmanite, ideally $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4(\text{H}_2\text{O})_4$, $a = 5.3875(6)$ Å, $b = 7.0579(7)$ Å, $c = 12.176(1)$ Å, $\alpha = 93.511(2)^\circ$, $\beta = 107.943(4)^\circ$, $\gamma = 90.093(2)^\circ$, $V = 439.55(2)$ Å³, $D_{\text{calc.}} = 2.956$ g cm⁻³, from the Lovozero alkaline massif, Kola Peninsula, Russia, have been refined in the space group $P\bar{1}$ ($Z = 1$) to R values of 2.64 and 4.47%, respectively, using 4572 and 2222 observed $|F_o| \geq 4\sigma(F)$ reflections collected with a single-crystal Bruker AXS SMART APEX diffractometer with a CCD detector and Mo- $K\alpha$ radiation. Electron microprobe analysis gave empirical formulae for lomonosovite $(\text{Na}_{9.50}\text{Mn}_{0.16}\text{Ca}_{0.11})_{\Sigma 9.77}(\text{Ti}_{2.83}^{4+}\text{Nb}_{0.51}\text{Mn}_{0.27}^{2+}\text{Zr}_{0.11}\text{Mg}_{0.11}\text{Fe}_{0.10}^{2+}\text{Fe}_{0.06}^{3+}\text{Ta}_{0.01})_{\Sigma 4.00}(\text{Si}_{2.02}\text{O}_7)_2(\text{P}_{0.98}\text{O}_4)_2(\text{O}_{3.50}\text{F}_{0.50})_{\Sigma 4}$, $Z = 1$, calculated on the basis of 26(O+F) a.p.f.u., and murmanite $(\text{Na}_{3.32}\text{Mn}_{0.15}\text{Ca}_{0.21}\text{K}_{0.05})_{\Sigma 3.73}(\text{Ti}_{3.08}^{4+}\text{Nb}_{0.51}\text{Mn}_{0.18}^{2+}\text{Fe}_{0.15}^{3+}\text{Mg}_{0.07}\text{Zr}_{0.01})_{\Sigma 4.00}(\text{Si}_{1.98}\text{O}_7)_2(\text{O}_{3.76}\text{F}_{0.24})_{\Sigma 4}(\text{H}_2\text{O})_4$, $Z = 1$, calculated on the basis of 22(O+F) a.p.f.u., with H₂O determined from structure refinement and $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratios obtained by Mössbauer spectroscopy. The crystal structures of lomonosovite and murmanite are a combination of a titanium silicate (TS) block and an intermediate (I) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral), and is characterized by a planar cell based on translation vectors, \mathbf{t}_1 and \mathbf{t}_2 , with $t_1 \sim 5.5$ and $t_2 \sim 7$ Å and $\mathbf{t}_1 \wedge \mathbf{t}_2$ close to 90°. The TS block exhibits linkage and stereochemistry typical for Group IV (Ti = 4 a.p.f.u.) of the Ti disilicate minerals: two H sheets connect to the O sheet such that two (Si₂O₇) groups link to Ti polyhedra of the O sheet adjacent along \mathbf{t}_1 . In murmanite and lomonosovite, the invariant part of the TS block is of composition $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4$. There is no evidence of vacancy-dominant cation sites or (OH) groups in the O sheet of lomonosovite or murmanite. In lomonosovite, the I block is a framework of Na polyhedra and P tetrahedra which gives 2[Na₃(PO)₄] p.f.u. In murmanite, there are four (H₂O) groups in the intermediate space between TS blocks. In lomonosovite, TS and I blocks alternate along \mathbf{c} . In murmanite, TS blocks are connected *via* hydrogen bonding. The H atoms were located and details of the hydrogen bonding are discussed.

KEYWORDS: lomonosovite, murmanite, crystal structure refinement, hydrogen bonding, EMP analysis, Mössbauer spectroscopy, chemical formula, Ti disilicate minerals, Group IV.

Introduction

MURMANITE was first mentioned by V. Ramsay in 1890 (Khalilov *et al.*, 1965a) under the name “mineral No. 3” from the Lovozero alkaline massif, Kola Peninsula, Russia, and Gutkova (1930) described murmanite, ideally $\text{Na}_2\text{MnTi}_3\text{Si}_2\text{O}_9(\text{H}_2\text{O})_n$, as a new mineral.

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Lomonosovite, $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9 \cdot \text{Na}_3\text{PO}_4$, from the Lovozero alkaline massif, was described by Gerasimovsky (1950) who stated that it forms a complete solid-solution series with murmanite. The relation between lomonosovite and murmanite was of great interest to many geologists working in the Kola Peninsula. However, murmanite was extremely difficult to analyse and its reported chemical formula changed with time as new data were accumulated.

Sokolova (2006) established the relation between structure topology and chemical composition for 24 Ti disilicate minerals and divided them into four groups, 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 atoms per formula unit (a.p.f.u.), respectively. The amount of Ti is very important for the hierarchy of structures of Ti disilicates, and each group is defined by its topology, chemical composition and stereochemistry; none of these factors can be ignored. The TS block is characterized by a planar cell based on translation vectors, \mathbf{t}_1 and \mathbf{t}_2 , with $t_1 \sim 5.5 \text{ \AA}$, $t_2 \sim 7 \text{ \AA}$ and $\mathbf{t}_1 \wedge \mathbf{t}_2$ close to 90° . Sokolova (2006) listed five minerals with known structures in Group IV: murmanite, lomonosovite, quadruphite, polyphite and sobolevite (Table 1). Each structure is a combination of TS and intermediate (I) blocks. In Group IV, the TS block exhibits linkage 3 where the (Si_2O_7) groups of two H sheets link to Ti octahedra of the O sheet adjacent along \mathbf{t}_1 . In Group IV, the general formula of the TS block is $\text{A}_2^{\text{P}}\text{M}_2^{\text{H}}\text{M}_4^{\text{O}}(\text{Si}_2\text{O}_7)_2\text{X}_4^{\text{O}}$. Ti ideally equals 4 a.p.f.u. Ti is dominant at two M^{H} sites in the H sheet and two M^{O} sites in the O sheet (except for Ti + Mn in the O sheet in sobolevite). Hence, $2M^{\text{O}} = \text{Ti}$, $2M^{\text{O}} = \text{Na}$ and subordinate Ca; $^{[6]}\text{M}^{\text{H}} = \text{Ti}$; $^{[5-8]}\text{A}^{\text{P}} = \text{Na}$ (A^{P} stands for peripheral (P) sites); anions $\text{X}_4^{\text{O}} = \text{primarily O}^{2-}$ with minor F^- . Sokolova (2006) considered the topology of lomonosovite and murmanite based on the latest structure work of Belov *et al.* (1977) and Khalilov (1989). However, the crystal structure and chemical formula of murmanite needed reconsideration and we felt that it was logical to add detailed stereochemistry to the well refined crystal structure of lomonosovite (Belov *et al.*, 1977). These issues prompted the present work on lomonosovite and murmanite. Following

Sokolova (2006), further work on the Ti disilicate minerals includes revision of the crystal structure and chemical formula of delindeite (Sokolova and Cámara, 2007), determination of the crystal structure of bornemanite (Cámara and Sokolova, 2007), revision of the chemical formula and crystal chemistry of barytolamprophyllite (Sokolova and Cámara, 2008a), structure work on an orthorhombic polytype of nabalamprophyllite (Sokolova and Hawthorne, 2008a), nacareniobsite-(Ce) (Sokolova and Hawthorne, 2008b), jinshajiangite (Sokolova *et al.*, 2009), mosandrite from the type locality (Sokolova and Cámara, 2008b) and this work on lomonosovite and murmanite.

Previous work

The first structure work on murmanite was done by Khalilov *et al.* (1965a). They reported triclinic symmetry, space group $P1$, $a = 5.50 \text{ \AA}$, $b = 7.00 \text{ \AA}$, $c = 11.94 \text{ \AA}$, $\alpha = 96^\circ$, $\beta = 101.43^\circ$, $\gamma = 88.92^\circ$, the main features of the structure topology, and gave the crystallochemical formula $\text{Na}_2\text{Mn}[\text{Ti}_2(\text{OH})_4(\text{Si}_2\text{O}_7)_2](\text{H}_2\text{O})_4$, $Z = 1$. Khalilov *et al.* (1965b) compared murmanite with the as yet structurally unknown epistolite (possible structure) and lomonosovite and emphasized the stability of the main structural unit, a titanium silicate (TS) block. In two books, Belov (1976) and Pyatenko *et al.* (1976) considered the TS block as a stable fragment, characteristic of several Ti-silicate structures. Rastsvetaeva *et al.* (1971) solved the crystal structure of lomonosovite and reported triclinic symmetry, space group $P1$, $a = 5.44 \text{ \AA}$, $b = 7.163 \text{ \AA}$, $c = 14.83 \text{ \AA}$, $\alpha = 99^\circ$, $\beta = 106^\circ$, $\gamma = 90^\circ$, detailed topology (to be discussed below), and an ideal formula $\text{Na}_5\text{Ti}_2[\text{Si}_2\text{O}_7][\text{PO}_4]\text{O}_2$, $Z = 2$. After this work on lomonosovite, it became clear that murmanite and lomonosovite have identical TS blocks but differ in stereochemistry and topology of the I block: (1) (H_2O) groups in murmanite, and (2) a framework of Na-polyhedra and P-tetrahedra giving 2 (Na_3PO_4) in lomonosovite. Rastsvetaeva *et al.* (1971) proposed a reaction leading to the formation of murmanite after lomonosovite: $\text{Na}_5\text{Ti}_2[\text{Si}_2\text{O}_7][\text{PO}_4]\text{O}_2 + 2\text{H}_2\text{O} = \text{Na}_2\text{Ti}_2[\text{Si}_2\text{O}_7](\text{OH})_4 + \text{Na}_3\text{PO}_4$. Belov *et al.* (1977) refined the crystal structure of lomonosovite in space group $P\bar{1}$ ($a = 5.49 \text{ \AA}$, $b = 7.11 \text{ \AA}$, $c = 14.50 \text{ \AA}$, $\alpha = 101^\circ$, $\beta = 96.43^\circ$, $\gamma = 90^\circ$) and wrote the reaction lomonosovite \rightarrow murmanite as follows: lomonosovite $\text{Na}_2\text{Ti}_2[\text{Si}_2\text{O}_7]\text{O}_2 \cdot \text{Na}_3\text{PO}_4 + n\text{H}_2\text{O} = \text{murmanite } \text{Na}_2\text{Ti}_2[\text{Si}_2\text{O}_7]\text{O}_2 \cdot n\text{H}_2\text{O} + \text{Na}_3\text{PO}_4$.

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

Group	Mineral	Chemical formula	Structural formula		I block	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space group	Z	Ref.
			TS block	M ₄ ^O										
Group IV	Murmanite	Na ₂ Ti ₂	(Si ₂ O ₇) ₂ O ₄	(H ₂ O) ₄		5.3875	7.0579	12.1764	93.511	107.943	90.093	P $\bar{1}$	1	(1)
	Lomonosovite	Na ₂ Ti ₂	(Si ₂ O ₇) ₂ O ₄	Na ₆ (PO ₃) ₂		5.4170	7.1190	14.4869	99.957	96.711	90.360	P $\bar{1}$	1	(2)
	Quadruphite	Na ₂ Ti ₂	(Si ₂ O ₇) ₂ O ₄	Na ₈ Ca ₂ (PO ₄) ₄ F ₂		5.4206	7.0846	20.3641	86.89	94.42	89.94	P1	1	(3)
	Sobolevite	Na ₂ Ti ₂	(Si ₂ O ₇) ₂ O ₃ F	Na ₉ Ca ₂ Mn(PO ₄) ₄ F ₂		7.0755	5.4106	40.623		93.156		Pc	2	(4)
	Polyphite	Na ₂ Ti ₂	(Si ₂ O ₇) ₂ O ₄	Na ₁₄ Ca ₄ Mn(PO ₄) ₆ F ₄		5.3933	7.0553	26.451	95.216	93.490	90.101	P $\bar{1}$	1	(5)
	Epistolite	Na□Nb ₂	(Si ₂ O ₇) ₂ O ₂ (OH) ₂	(H ₂ O) ₄		5.460	7.170	12.041	103.63	96.01	89.98	P $\bar{1}$	1	(6)
	Vuonemite	Na ₂ Nb ₂	(Si ₂ O ₇) ₂ O ₃ F	Na ₆ (PO ₄) ₂		5.4984	7.161	14.450	92.60	95.30	90.60	P $\bar{1}$	1	(7)

* The structural formulae are presented as the sum of the titanium-silicate (TS) block, A₂M₂^HM₄^O(Si₂O₇)₂X₄^O, and the variable intermediate (I) block, in accord with Sokolova (2006); A^p = cations at the peripheral (P) sites; M^H = cations of the H sheet; M^O = cations of the O sheet; X₄^O = anions shared between O and H sheets. References (the latest reference on the structure is the numbered list of references): (1) this work, Khalilov (1989), Khalilov *et al.* (1965a), Rastsvetaeva and Andrianov (1986); (2) this work, Belov *et al.* (1977), Rastsvetaeva *et al.* (1971); (3) Sokolova and Hawthorne (2001), Sokolova *et al.* (1987a); (4) Sokolova *et al.* (2005), Sokolova *et al.* (1988); (5) Sokolova *et al.* (2005), Sokolova and Hawthorne (2004); (6) Sokolova and Hawthorne (2004); (7) Ereit *et al.* (1998), Drozdov *et al.* (1974).

Rastsvetaeva and Adrianov (1986) refined the crystal structure of murmanite with a different cell setting and reported a structure topology identical to that of Khalilov *et al.* (1965*a*). Khalilov (1989) refined the crystal structure of murmanite in space group $P1$, $a = 5.383 \text{ \AA}$, $b = 7.053 \text{ \AA}$, $c = 12.170 \text{ \AA}$, $\alpha = 93.16^\circ$, $\beta = 107.82^\circ$, $\gamma = 90.06^\circ$ and confirmed the topology previously described by Khalilov *et al.* 1965*a*. Khalilov (1989) gave the detailed structural formula $\{(\text{Na}, \square)(\text{Ti}, \text{Fe}, \text{Mn})[(\text{Na}, \text{Ca}, \text{K})(\text{Ti}, \text{Nb}, \text{Ta})\text{Si}_2\text{O}_7]\text{O}(\text{O}, \text{OH}, \text{F})\}(\text{H}_2\text{O})_2$, $Z = 2$ and the ideal chemical formula $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4(\text{H}_2\text{O})_4$, $Z = 1$. Khalilov (1989) also considered that the content of Mn^{2+} in murmanite had been overestimated in earlier publications. Although H atoms of (H_2O) groups were not located, Khalilov (1989) proposed a model for possible hydrogen bonding. In Group III ($\text{Ti} + \text{Nb} = 3 \text{ a.p.f.u.}$), there are two minerals, vuonnemite and epistolite, that are counterparts of lomonosovite and murmanite. Epistolite was originally described by Bøggild (1901) and vuonnemite was described by Bussen *et al.* (1973) who wrote its formula as $\text{Na}_4\text{TiNb}_2\text{Si}_4\text{O}_{17} \cdot 2\text{Na}_3\text{PO}_4$. Bussen *et al.* (1973) reported that “leaching of vuonnemite with water removes the Na_3PO_4 completely, leaving a residue that gives the X-ray pattern of epistolite”. The crystal structure of vuonnemite was solved in space group $P\bar{1}$ by Drozdov *et al.* (1974) who reported the details of structure topology and gave the following formulae: structural formula $\text{Na}_3\text{Ti}(\text{O}, \text{F})_2[\text{NaNbO}(\text{Si}_2\text{O}_7)]_2 \cdot 2\text{Na}_3\text{PO}_4$ and mineral formula $\text{Na}_{11}\text{Nb}_2\text{TiSi}_4\text{P}_2\text{O}_{25}\text{F}$. Unaware of the structure work of Drozdov *et al.* (1974), Ercit *et al.* (1998) solved and described the crystal structure of vuonnemite again. Their structure-refinement results are identical with the structure work of Drozdov *et al.* (1974). Sokolova and Hawthorne (2004) solved the crystal structure of epistolite, ideally $\text{Na}_4\text{Nb}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4$, and showed that murmanite and epistolite have TS blocks of different topology but identical I blocks of four H_2O groups. Sokolova and Hawthorne (2004) defined the structural formulae for murmanite and epistolite as $^{[8]}\text{Na}_2^{[6]}\text{Ti}_2\text{Na}_2\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{O}_2(\text{H}_2\text{O})_4$ and $^{[8]}\text{Na}\square^{[6]}\text{Nb}_2\text{Na}_3\text{Ti}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4$, respectively and related the two minerals by the substitution $\text{Nb}_2^{5+} + \square + (\text{OH})_2^- \rightleftharpoons \text{Ti}_3^{4+} + \text{O}_2^{2-}$. In accordance with the structure work of Khalilov (1989), they wrote the ideal formula for murmanite as $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4(\text{H}_2\text{O})_4$. Németh *et al.* (2005) reported Transmission Electron Microscopy

(TEM) and X-ray powder-diffraction data for murmanite and epistolite. However, they erroneously quoted the empirical formula of Sokolova and Hawthorne (2004) for epistolite as $\text{Na}_{1.12}\{\text{Na}_{2.63}\text{Ti}_{0.96}\text{Ca}_{0.27}\text{K}_{0.05}\text{Fe}^{3+}\text{Mn}_{0.04}\text{Ta}_{0.01}\}_{\Sigma 4}[(\text{Nb}_{1.92}\text{Ti}_{0.08})_{\Sigma 2}(\text{O}_2(\text{H}_2\text{O})_2)_{\Sigma 4}\text{Si}_4\text{O}_{14}](\text{OH}_{1.10}\text{F}_{0.55}\text{O}_{0.35})_{\Sigma 2} \cdot 2.19\text{H}_2\text{O}$.

Although ideal formulae for murmanite, $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4(\text{H}_2\text{O})_4$, and epistolite, $\text{Na}_4\text{Nb}_2\text{Ti}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4$, are now well established from the structure work of Khalilov (1989) and Sokolova and Hawthorne (2004), these formulae continued to be written incorrectly, e.g. murmanite, $(\text{Na}, \square)_2\{(\text{Na}, \text{Ti})_4[\text{Nb}_2(\text{O}, \text{H}_2\text{O})_4\text{Si}_4\text{O}_{14}](\text{OH}, \text{F})_2\}2\text{H}_2\text{O}$ and epistolite $(\text{Na}, \square)_2\{(\text{Na}, \text{Ti})_4[\text{Ti}_2(\text{O}, \text{H}_2\text{O})_4\text{Si}_4\text{O}_{14}](\text{OH}, \text{F})_2\}2\text{H}_2\text{O}$ (Németh *et al.* 2005); murmanite $\text{Na}_4\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4 \cdot 5\text{H}_2\text{O}$, and epistolite, $\text{Na}_5\text{TiNb}_2(\text{Si}_2\text{O}_7)_2(\text{F}, \text{O})_4 \cdot 5\text{H}_2\text{O}$ (Selivanova *et al.* 2008).

Experimental

Sample description

A pale-brown single crystal of lomonosovite was extracted from a very small sample (crushed grains) of bornemanite (#86957) obtained from the Fersman Mineralogical Museum. The crystals of murmanite used in this work are from the Yubileynaya pegmatite vein, Karnasut Mountain, Lovozero alkaline massif, and were obtained from the Royal Ontario Museum (sample # M46809) as small pink fragments.

Mössbauer spectroscopy

Transmission Mössbauer spectroscopy measurements were done on both minerals at room temperature (RT) using a $^{57}\text{Co}(\text{Rh})$ point source. The spectra were analysed using a Voigt-based quadrupole-splitting-distribution (QSD) method (Rancourt and Ping, 1991). The centre shift (CS) is given relative to $\alpha\text{-Fe}$ at RT. The small Fe content of both minerals necessitated long collection times: 12 days for lomonosovite and 22 days for murmanite. The RT Mössbauer spectrum of lomonosovite (Fig. 1*a*) was fitted to a model having two generalized sites, one for Fe^{2+} (solid-line spectrum) and one for Fe^{3+} (dashed-line spectrum). The RT spectrum of murmanite (Fig. 1*b*) was fitted to a model having two generalized sites for Fe^{3+} . The linewidth of the asymmetric elemental doublets of the QSD was allowed to vary during the fitting procedure. The refined hyperfine parameters are given in Table 2.

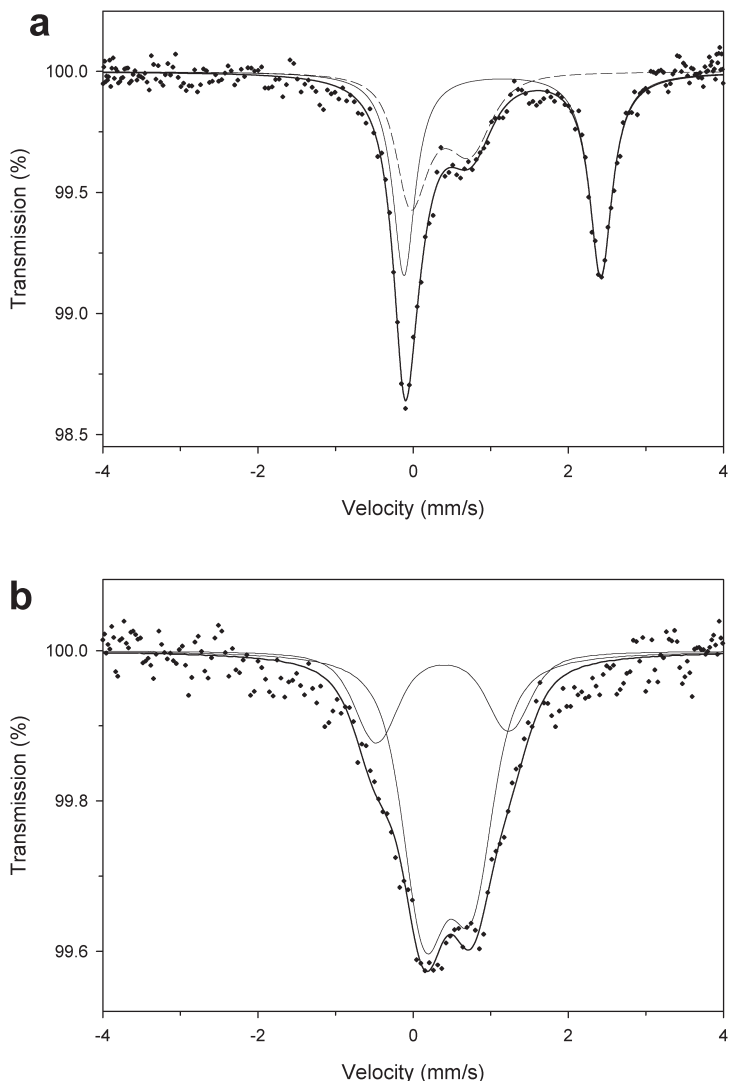


FIG. 1. Room-temperature Mössbauer spectra of lomonosovite (*a*) and murmanite (*b*) fitted using a Voigt-based quadrupole-splitting-distribution (QSD) method. Solid spectrum in (*a*): Fe²⁺, dashed spectra in (*a*): Fe³⁺.

The Fe³⁺/Fe_{tot} ratios were calculated assuming equal recoil-free fractions for Fe²⁺ and Fe³⁺. For the spectrum of murmanite, we also tried a model with a single generalized site for Fe³⁺, but the envelope showed systematic deviations from the spectral data.

Electron microprobe analysis

Single crystals of lomonosovite and murmanite previously used for the structure solution were

analysed with a Cameca SX100 electron microprobe operating in wavelength-dispersion mode using an accelerating voltage of 15 kV, a probe current of 15 nA, a beam size of 15 μm and count times on both peak and background positions of 20 s. The following X-ray lines and standards were used for the microanalysis (the analysing crystals are given in brackets): F-*Kα* (LTAP), F-bearing riebeckite; Na-*Kα* (TAP), albite; Mg-*Kα* (TAP), forsterite; Al-*Kα* (LTAP), andalusite; Si-*Kα* (TAP), diopside; P-*Kα* (LPET),

TABLE 2. Mössbauer parameters for lomonosovite and murmanite.

Sample		<CS> (mm/s)	<QS> (mm/s)	Rel. area (%)
Lomonosovite	Fe ²⁺	1.15(2)	2.54	58(3)
	Fe ³⁺	0.31(6)	0.7(3)	42(3)
Murmanite	Fe ³⁺ (I)	0.45(2)	0.61(5)	74(4)
	Fe ³⁺ (II)	0.38(6)	1.71(1)	26(4)

apatite; K-K α (LPET), orthoclase; Ca-K α (LPET), diopside; Ti(LLiF), titanite; Mn-K α (LLiF), spessartine; Fe-K α (LLiF), fayalite; Sr-L α (LPET), SrTiO₃; Zr-L α (LPET), zircon; Nb-L α (LPET), Ba₂NbNb₅O₁₅; Ba-L β (LLiF), baryte; Ta-L α (LLiF), MnNb₂Ta₂O₉. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou and Pichoir (1985). As murmanite is extremely unstable under the beam and the single crystal was a small thin plate (0.185 × 0.11 × 0.03 mm) (Table 3, analyses 2A and 2B), we used an additional larger grain (0.75 mm × 0.50 mm × 0.20 mm) from the same sample as a further check on the chemical composition (Table 3, analyses 3A and 3B), but we used the analysis of the grain used for the structure refinement in assigning site populations. In order to account for Na migration under the electron beam, Na was analysed first in the spectrometer with the TAP crystal, and a linear-decay model was obtained from counts at different times, which was then used to correct the Na counts. The chemical compositions of lomonosovite and murmanite are given in Table 3 and are the mean of 9 and 8 determinations, respectively.

The empirical formula for lomonosovite (Table 3) was calculated on the basis of 26 (O+F) anions: (Na_{0.50}Mn_{0.16}Ca_{0.11}) Σ _{9.77} (Ti_{2.83}Nb_{0.51}Mn_{0.27}Zr_{0.11}Mg_{0.11}Fe_{0.10}²⁺Fe_{0.06}³⁺Ta_{0.01}) Σ _{4.00}(Si_{2.02}O₇)₂(P_{0.98}O₄)₂(O_{3.50}F_{0.50}) Σ ₂, $D_{\text{calc.}} = 3.175 \text{ g.cm}^{-3}$, $Z = 1$ and it is in very close agreement with the ideal formula Na₂Ti₂Si₂O₉·Na₃PO₄ ($Z = 2$) = Na₁₀Ti₄(Si₂O₇)₂(PO₄)₂O₄, ($Z = 1$) given by Gerasimovsky (1950).

In both grains of murmanite, microprobe analysis detected P₂O₅: 0.56 wt.% and 0.51 wt.% in analyses 2A and 3A, respectively (Table 3). Gerasimovsky (1950) presented analytical data on lomonosovite and murmanite for a series of crystals that varied in colour from dark brown

(lomonosovite) through brown to pinkish-violet to yellow (murmanite). Figure 2 shows the relation between the P₂O₅ and SiO₂ contents (wt.%) of these crystals, with the contents of the ideal formulae for these minerals (shown as red squares) taken from Sokolova (2006). It is immediately apparent that there is a gradual chemical change from lomonosovite to murmanite that is reflected in the colour of the crystals (a simple admixture of discrete grains of ideal lomonosovite and murmanite would produce a powder of brown and yellow grains rather than a change in colour of the individual crystals). Karup-Møller (1986) reported that both Weissenberg and precession photographs of murmanite from the Ilímaussaq alkaline complex, Greenland show the presence of oriented intergrowths of lomonosovite in murmanite, estimated at 45% of the crystals examined. This is in accord with the presence of subsidiary peaks in the difference-Fourier map of the structure that suggest the presence of a minor amount (estimated as 3%) of an intergrown phase. Our structure refinement indicated that there is no individual site occupied by P in the crystal structure of murmanite, and we presume that the P content of 0.06 a.p.f.u. in murmanite is due to the presence of small quantities of oriented intergrowths of lomonosovite. Using the analysis of lomonosovite given in Table 3, 4.2 wt.% lomonosovite intergrown with murmanite will give a content of 0.56 wt.% P₂O₅ in murmanite (analysis 2A, Table 3). Thus 4.2 wt.% of lomonosovite was subtracted from murmanite analyses 2A (and 3.8%

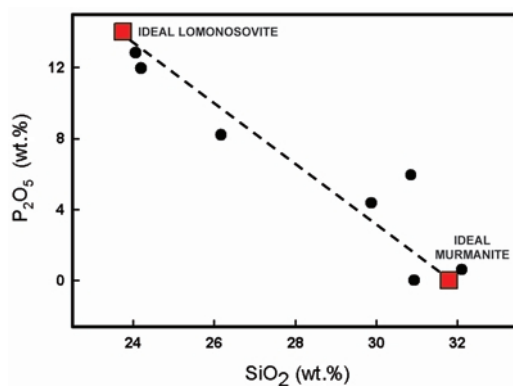


FIG. 2. Variation in P₂O₅ as a function of SiO₂ in dark brown (lomonosovite) through brown to pink and yellow crystals (murmanite) reported by Gerasimovsky (1950). The red squares are the ideal chemical compositions for lomonosovite and murmanite end-members from Sokolova (2006).

from analysis 3A, Table 3), and the results are given as analyses 2B and 3B in Table 3. The content of 4(H₂O) groups per formula unit (p.f.u.) was determined from structure refinement. The empirical formula for murmanite derived from analysis 2B is (Na_{3.32}Mn_{0.15}Ca_{0.21}K_{0.05})_{Σ3.73}(Ti_{3.08}⁴⁺Nb_{0.51}Mn_{0.18}²⁺Fe_{0.15}³⁺Mg_{0.07}Zr_{0.01})_{Σ4.00}(Si_{1.98}O₇)₂(O_{3.76}F_{0.24})_{Σ4}(H₂O)₄, $D_{\text{calc.}} = 2.956 \text{ g cm}^{-3}$, $Z = 1$, in close agreement with the ideal formula Na₄Ti₄(Si₂O₇)₂O₄(H₂O)₄ (Khalilov, 1989; Sokolova, 2006).

Crystal structure

Single-crystal X-ray diffraction data for lomonosovite and murmanite were collected with a Bruker AXS SMART APEX diffractometer with a CCD detector and Mo- $K\alpha$ radiation. An empirical absorption correction (*SADABS*, Sheldrick, 1998) was applied. The Bruker *SHELXTL* Version 5.1 system of programs (Sheldrick, 1997) was used for solution of the murmanite structure and refinement of both structures. In lomonosovite, the occupancies of the Ti-dominant and Na-dominant sites were refined with the scattering factors of Ti + Nb and Na, respectively, and both ionic and neutral scattering curves were used for O and Si atoms to refine their ionic and covalent components. In murmanite, the occupancies of the Ti-dominant and Na-dominant sites were refined with the scattering curves of Nb and Na, and neutral scattering curves were used for O and Si atoms. Scattering factors were taken from the International Tables for X-ray Crystallography (1992). The details of X-ray data collection and structure refinement are given in Table 4. A list of observed and calculated structure factors for lomonosovite and murmanite have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Lomonosovite

The intensities of 12104 reflections with $-8 \leq h \leq 8$, $-11 \leq k \leq 11$, $-23 \leq l \leq 23$ were collected with a frame width of 0.2° and a frame time of 5 s, out to $2\theta = 70.2^\circ$. The refined unit-cell parameters were obtained from 7479 reflections ($I > 10\sigma I$) and are given in Table 4. Using the atom coordinates of Belov *et al.* (1977), the structure of lomonosovite was refined in space group $P\bar{1}$, and converged to $R_1 = 2.64\%$ and a Goodness of Fit (GoF) of 1.066. Final atom parameters are given

in Table 5a, 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.

Murmanite

The intensities of 6546 reflections with $-7 \leq h \leq 7$, $-9 \leq k \leq 9$, $-17 \leq l \leq 17$ were collected with a frame width of 0.2° and a frame time of 5 s, out to $2\theta = 60.0^\circ$. The refined unit-cell parameters were obtained from 3345 reflections ($I > 10\sigma I$) and are given in Table 4. The crystal structure of murmanite was solved and refined in space group $P\bar{1}$. Four H atoms were located in the difference-Fourier map and inserted into the refinement with soft constraints $O_{\text{donor}}-\text{H} = 0.91 \text{ \AA}$ and $\text{H}-\text{H} = 1.50 \text{ \AA}$ in each H₂O group, and H-atom displacement parameters three times larger than those of the associated O_{donor} atoms.

At the last stages of the refinement, two peaks with magnitudes of 3 and 1.5 $e/\text{\AA}^3$ were found in the difference-Fourier map and were inserted into the structure model as the *Ti(1A)* and *Ti(1B)* sites, each with approximately the same *y*-coordinate as the Ti(1) atom in the basic structure. The displacement parameters of the *Ti(1A)* and *Ti(1B)* atoms were constrained to be equal to the displacement parameters of the Ti(1) atom. The refined occupancies of these subsidiary sites were 2 to 5% and the *Ti(1A)* and *Ti(1B)* sites are 0.44 and 0.64 \AA , respectively, from the *Ti(1)* site. These subsidiary peaks were attributed to the presence of an additional lomonosovite phase (cf. Karup-Møller 1986). We estimate the amount of this additional lomonosovite as ~3% of the volume of the crystal; note that this value is in accord with the proposal (see section on electron microprobe analysis) that the ~0.5 wt.% P₂O₅ in the analyses of murmanite (Table 3) is due to a intergrowth of 4.2 wt.% of lomonosovite. Such subsidiary diffraction peaks are a relatively common feature in TS-block structures, for example, bornemanite (Cámara and Sokolova, 2007) and nabalamprophyllite (Sokolova and Hawthorne, 2008a). Moreover, murmanite is often described as a transformation product of lomonosovite (Rastsvetaeva *et al.*, 1971; Belov *et al.*, 1977; Khomyakov, 1995). Thus, the presence of domains of lomonosovite in murmanite are quite probable.

The refinement converged to $R_1 = 4.47\%$ and a GoF = 1.116. Final atom parameters are given in Table 5b, selected interatomic distances and

TABLE 3. Chemical composition (wt.%) and unit formula (a.p.f.u.) for lomonosovite and murmanite.

	Lomonosovite				Murmanite							
	1	2A	2B [†]	3A	3B [†]	4	1	2A	2B [†]	3A	3B [†]	4
SiO ₂	23.28	29.90	28.92	29.90	29.02	30.74	Si	3.91	3.95	3.96	4.00	3.91
Nb ₂ O ₅	6.50	8.59	8.32	10.37	10.13	7.14						
Ta ₂ O ₅	0.21	n.d.	n.d.	n.d.	n.d.	0.53	Na	1.78	1.78	1.64	1.65	0.61
P ₂ O ₅	13.37	0.56	0.00	0.51	0.00	n.a.	Ca	0.14	0.15	0.15	0.15	0.19
TiO ₂	21.67	30.83	29.92	27.65	26.83	29.96	K	0.05	0.05	0.05	0.05	0.11
ZrO ₂	1.28	0.19	0.14	0.19	0.14	1.70	Σ2A ^P	1.97	1.98	1.84	1.85	0.91
Al ₂ O ₃	n.d.	n.d.	n.d.	0.32	0.32	n.d.						
Fe ₂ O ₃	0.46*	1.48*	1.46*	1.44*	1.42*	2.88	Ti	3.03	3.08	2.75	2.78	2.87
FeO	0.69	0.00	0.00	0.00	0.02	0.00	Nb	0.51	0.51	0.62	0.63	0.41
MnO	2.91	2.95	2.83	3.74	3.63	2.37	Mn	0.23	0.18	0.33	0.28	0.23
MgO	0.44	0.37	0.35	0.49	0.47	0.42	Fe ³⁺	0.15	0.15	0.14	0.15	0.28
CaO	0.57	1.45	1.43	1.44	1.42	2.82	Fe ²⁺	0.00	0.00	0.00	0.00	0.00
Na ₂ O	28.22	13.71	12.52	13.34	12.31	8.82	Mg	0.07	0.07	0.10	0.10	0.08
K ₂ O	n.d.	0.28	0.28	0.28	0.28	0.67	Al	n.d.	n.d.	0.05	0.05	n.d.
H ₂ O	n.a.	9.08**	8.77	8.97**	8.70	11.40	Ta	n.d.	n.d.	n.d.	n.d.	0.02
F	0.91	0.60	0.56	0.66	0.63	0.19	Zr	0.01	0.01	0.01	0.01	0.11
O=F	-0.38	-0.25	-0.24	-0.28	-0.27	-0.08	Σ[2M ^H +2M ^O (1)]	4.00	4.00	4.00	4.00	4.00
Total	100.13	99.74	95.26 ^{††}	99.02	95.05 ^{††}	99.56						
							Na	1.55	1.54	1.64	1.64	1.57
							Mn	0.10	0.15	0.09	0.14	0.03
							Ca	0.06	0.06	0.06	0.06	0.20
							Σ2M ^O (2)	1.71	1.75	1.79	1.84	1.80
							Na	0.15	0.00	0.10	0.00	0.00
							Mn	0.00	0.00	0.00	0.00	0.00
							Ca	0.00	0.00	0.00	0.00	0.00
							P	0.06	0.00	0.06	0.00	n.d.
							Σ[Na ₃ (PO ₄)]	0.06	0.00	0.06	0.00	0.00
							F	0.25	0.24	0.28	0.28	0.08
							H ₂ O	3.96	4.00	3.97	4.00	4.84
							Sum of anions	22.00	22.00	22.00	22.00	22.00

angles in Table 7, refined site-scattering values and assigned populations for selected sites in Table 9, bond-valence values in Table 11, and details of hydrogen bonding in Table 12.

Assignment of Mössbauer spectra

For lomonosovite, we observe two doublets with an area ratio of 0.58:0.42, which are assigned to Fe^{2+} and Fe^{3+} , respectively, in octahedral coordination at the *Ti*(1) and *Ti*(2) sites. Karup-Møller (1983) reported a Mössbauer spectrum of lomonosovite and was able to resolve two Fe^{2+} peaks. We attempted to fit two Fe^{2+} peaks to the spectrum but the data had insufficient resolution to do so. Consequently, we assigned Fe^{2+} equally to the *Ti*(1) and *Ti*(2) sites as suggested by the result of Karup-Møller (1986). The $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio obtained by Karup-Møller (1983) was 0.25, whereas the $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio obtained here is 0.38, and the latter value was used in the calculation of the empirical formula.

For murmanite, we observed two doublets with an area ratio of 0.76:0.24, both of which were assigned to Fe^{3+} in octahedral coordination at the *Ti*(1) and *Ti*(2) sites, as is to be expected in these structures. The *Ti*(1) and *Ti*(2) octahedra are quite distorted (Table 7) with RMS deviations from their mean bond lengths of 0.187 and 0.117, respectively. For more highly distorted coordinations, there is an inverse relation between the QS value and the distortion about the site (Ingalls, 1964). We assign the doublet with the smaller QS (Table 2) to Fe^{3+} at the *Ti*(1) site and the doublet with the larger QS (Table 2) to Fe^{3+} at the *Ti*(2) site; hence 0.11 Fe^{3+} a.p.f.u. is assigned to *Ti*(1) and 0.04 Fe^{3+} a.p.f.u. is assigned to *Ti*(2).

Description of the structure

Lomonosovite and murmanite belong to the Group-IV titanium disilicate minerals containing a TS block (Sokolova, 2006). Sokolova (2006) wrote the following general formula for the TS block within the planar cell (Group IV) $A_2^p M_2^H M_4^O (\text{Si}_2\text{O}_7)_2 X_{4+n}$, where M^O are cations of the O sheet, M^H are [6]-coordinated cations of the H sheet and A^P are cations at the peripheral (*P*) sites, $X_{4+n} = X_4^O + X_{M_2}^P + X_{A_2}^P$, where X_4^O anions are common vertices of M^O octahedra and two M^H and two A^P polyhedra (they are the X_M^O and X_A^O anions), and anions X_M^P and X_A^P belong to the M^H and A^P polyhedra on the outside of the TS

2,3: sample M4689; 2: single crystal used for structure refinement; 2A and 3A: analyses with 4.2 and 3.8% lomonosovite intergrowth;

2B and 3B: modified analyses 2A and 3A from which 4.2% and 3.8% of lomonosovite were subtracted;

4: average of three analyses for 'unaltered murmanite' (Khalilov 1989 from Vlasov et al. 1959) used for structure refinement by Khalilov (1989);

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

* calculated as Fe_2O_3 in accord with Mössbauer data;

** calculated from structure refinement: $\text{H}_2\text{O} = 4$ p.f.u.;

† excluding a lomonosovite component.

†† the total here is small because we have subtracted ~4% lomonosovite due to the presence of lomonosovite inclusions.

TABLE 4. Miscellaneous refinement data for lomonosovite and murmanite.

	Lomonosovite	Murmanite
a (Å)	5.4170(7)	5.3875(6)
b (Å)	7.1190(9)	7.0579(7)
c (Å)	14.487(2)	12.176(1)
α (°)	99.957(3)	93.511(2)
β (°)	96.711(3)	107.943(4)
γ (°)	90.360(3)	90.093(2)
V (Å ³)	546.28(4)	439.55(2)
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
Absorption coefficient (mm ⁻¹)	2.42	2.59
$F(000)$	505.1	390.0
$D_{\text{calc.}}$ (g/cm ³)	3.171	3.007
Crystal size (mm)	0.380 × 0.230 × 0.100	0.185 × 0.110 × 0.030
Radiation/filter	2Mo-K α /graphite	
2 θ -range for data collection (°)	70.21	60.03
$R(\text{int})$ (%)	2.24	2.70
Reflections collected	12104	6546
Independent reflections	4572	2547
$F_o > 4\sigma F$	4782	2222
Refinement method	Full-matrix least squares on F^2 , variable weights*	
Goodness of fit (GoF) on F^2	1.066	1.116
Final R (obs) (%)	2.64	4.47
$[F_o > 4\sigma F]$		
	$R_1 = 2.79$	$R_1 = 5.16$
R indices (all data) (%)	$wR^2 = 6.39$	$wR^2 = 11.29$
	$\text{GoF} = 1.066$	$\text{GoF} = 1.115$

* $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = [2F_c^2 + \max(F_o^2, O)]/3$

block (in the intermediate space between two TS blocks); n is the number of X^P anions: $n = 4$ in Group IV. The core of the TS block, $\mathbf{M}_2^H\mathbf{M}_4^O(\text{Si}_2\text{O}_7)_2\mathbf{X}_4$, is shown here in bold to highlight that the stoichiometry of this part of the TS block is invariant. There are two types of chains of edge-sharing octahedra within the O sheet: the Ti^O octahedra form a brookite-like $(\text{Ti}_2\text{O}_8)^{8-}$ chain, and the Na^O octahedra form a chain of the same topology. The O sheet is shown in Fig. 3a. The ratio Ti:Na equals 1:1 and the cations of the O sheet sum to Na_2Ti_2 a.p.f.u.. This is the maximum possible content of Ti in the O sheet of Ti disilicate minerals (Sokolova, 2006). In the H sheet, Ti-dominant M^H octahedra link to (Si_2O_7) groups and [8]-coordinated Na atoms occupy the A^P sites (Fig. 3b). In Group IV, linkage 3 occurs, and two (Si_2O_7) groups link to two next-nearest-neighbour Ti octahedra in a brookite-like chain (Fig. 3c). Each Ti octahedron links to two (Si_2O_7) groups, sharing one edge with

two tetrahedra of the first (Si_2O_7) group and a vertex with one tetrahedron of the second (Si_2O_7) group. The M^H (= Ti) octahedron shares a common vertex (the X_M^O anion) with three octahedra of the O sheet, two Na^O octahedra and one Ti^O octahedron (Fig. 3c).

Lomonosovite

Cation sites

The structure of lomonosovite consists of two blocks (TS and **I**) stacked along [001]. We describe the cation sites of the TS block (O and H sheets, peripheral sites) and the cation sites of the **I** block.

The O sheet

There are two cations sites coordinated by O atoms: the Ti-dominant site, $Ti(2)$, with $\langle \text{Ti}(2)-\text{O} \rangle = 2.013$ Å, and the Na-dominant site, $Na(2)$, with $\langle \text{Na}(2)-\text{O} \rangle = 2.468$ Å (Tables 6, 8).

TABLE 5a. Final atom coordinates and displacement parameters (\AA^2) for lomonosovite.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ti(1)	0.16618(3)	0.92849(2)	0.21810(1)	0.00720(8)	0.00757(8)	0.00951(8)	0.00179(5)	0.00135(5)	0.00042(5)	0.00803(5)
Ti(2)	0.77151(4)	0.38667(3)	-0.00770(1)	0.01771(10)	0.01111(9)	0.00982(9)	0.00161(6)	0.00013(6)	0.00247(6)	0.01302(6)
Si(1)	0.66652(6)	0.20422(5)	0.17702(2)	0.00813(15)	0.00652(15)	0.00755(15)	0.00152(10)	0.00122(10)	0.00007(10)	0.00734(10)
Si(2)	0.64975(6)	0.64040(5)	0.19841(2)	0.00819(15)	0.00614(14)	0.00644(14)	0.00092(10)	0.00051(10)	0.00011(10)	0.00697(9)
P	0.17814(6)	0.22491(4)	0.43221(2)	0.01012(14)	0.00799(14)	0.00866(14)	0.00056(9)	0.00141(10)	0.00022(9)	0.00901(9)
Na(1)	0.17183(12)	0.41851(9)	0.23393(4)	0.0170(3)	0.0217(3)	0.0139(3)	0.0035(2)	0.0006(2)	-0.0037(2)	0.01759(18)
Na(2)	0.75658(12)	0.88235(9)	-0.00370(6)	0.0126(3)	0.0159(3)	0.0356(4)	-0.0045(3)	-0.0052(3)	0.0029(2)	0.0231(2)
Na(3)	0.67740(11)	0.97076(8)	0.36205(4)	0.0222(3)	0.0142(2)	0.0181(3)	-0.00057(18)	-0.00070(19)	-0.00028(18)	0.01881(15)
Na(4)	0.67504(14)	0.45798(9)	0.39770(5)	0.0267(4)	0.0161(3)	0.0186(3)	0.0011(2)	0.0008(2)	0.0033(2)	0.02085(19)
Na(5)	0.23789(14)	0.74012(9)	0.41534(5)	0.0312(4)	0.0155(3)	0.0203(3)	0.0058(2)	0.0055(3)	0.0024(2)	0.0218(2)
O(1)	0.67330(19)	0.42899(12)	0.23057(7)	0.0233(5)	0.0064(4)	0.0098(4)	0.0015(3)	0.0019(3)	0.0017(3)	0.0132(2)
O(2)	0.63916(19)	0.19579(14)	0.06524(6)	0.0156(4)	0.0144(4)	0.0081(4)	0.0013(3)	0.0007(3)	0.0009(3)	0.0129(2)
O(3)	0.9287(2)	0.12230(16)	0.21347(8)	0.0174(5)	0.0180(5)	0.0215(5)	0.0035(4)	-0.0036(4)	0.0091(4)	0.0194(3)
O(4)	0.4366(2)	0.10347(16)	0.21026(8)	0.0213(6)	0.0208(5)	0.0240(6)	0.0009(4)	0.0098(4)	-0.0112(4)	0.0219(3)
O(5)	0.59482(19)	0.60837(14)	0.08374(6)	0.0182(5)	0.0128(4)	0.0067(4)	0.0015(3)	0.0004(3)	-0.0006(3)	0.0127(2)
O(6)	0.90590(18)	0.75276(15)	0.24541(7)	0.0121(4)	0.0178(5)	0.0126(4)	0.0024(3)	0.0011(3)	-0.0066(3)	0.0143(2)
O(7)	0.41669(17)	0.73437(14)	0.24916(7)	0.0105(4)	0.0132(4)	0.0111(4)	0.0011(3)	0.0010(3)	0.0047(3)	0.0117(2)
O(8)	0.12981(19)	0.83454(15)	0.09180(7)	0.0144(5)	0.0195(5)	0.0089(4)	0.0001(3)	0.0011(3)	-0.0025(3)	0.0146(3)
O(9)	0.0880(2)	0.42270(13)	0.07013(7)	0.0203(5)	0.0113(4)	0.0108(4)	0.0024(3)	0.0024(3)	0.0004(3)	0.0140(2)
O(10)	0.23599(19)	0.03479(13)	0.36655(7)	0.0175(5)	0.0092(4)	0.0112(4)	-0.0003(3)	0.0024(3)	0.0026(3)	0.0128(2)
O(11)	0.90049(19)	0.22363(16)	0.44212(8)	0.0119(4)	0.0196(5)	0.0247(5)	0.0011(4)	0.0065(4)	0.0009(3)	0.0187(3)
O(12)	0.2497(2)	0.39967(14)	0.39089(8)	0.0272(6)	0.0104(4)	0.0176(5)	0.0036(3)	0.0047(4)	-0.0026(4)	0.0181(3)
O(13)	0.3294(2)	0.23068(16)	0.52885(8)	0.0273(6)	0.0173(5)	0.0133(5)	0.0008(4)	-0.0059(4)	0.0014(4)	0.0202(3)

Table 5b. Final atom coordinates and displacement parameters (\AA^2) for murmanite.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ti(1)	0.41614(19)	0.32516(10)	0.2405(2)	0.0095(3)	0.0140(3)	0.0182(7)	0.0027(3)	0.0052(4)	0.0007(2)	0.0136(2)
Ti(2)	0.27783(11)	0.88695(8)	0.50472(5)	0.0189(3)	0.0157(3)	0.0252(3)	0.0030(2)	0.0073(2)	0.00195(19)	0.0197(2)
Si(1)	0.92177(17)	0.05009(13)	0.25961(8)	0.0115(4)	0.0108(4)	0.0199(5)	0.0025(3)	0.0055(3)	0.0000(3)	0.0138(2)
Si(2)	0.94748(18)	0.62237(13)	0.27519(9)	0.0135(4)	0.0106(4)	0.0222(5)	0.0028(3)	0.0062(4)	0.0008(3)	0.0152(2)
Na(1)	0.3843(3)	0.8278(2)	0.19944(15)	0.0231(9)	0.0226(9)	0.0316(10)	0.0010(6)	0.0095(7)	0.0011(6)	0.0255(5)
Na(2)	0.7374(3)	0.6117(3)	0.49032(17)	0.0245(10)	0.0211(10)	0.0453(13)	0.0108(8)	0.0205(8)	0.0080(7)	0.0277(7)
O(1)	0.1367(7)	0.1365(5)	0.2105(3)	0.0421(18)	0.050(2)	0.0249(15)	-0.0031(14)	0.0150(14)	-0.0315(16)	0.0382(8)
O(2)	0.6368(6)	0.1309(5)	0.2023(3)	0.0301(16)	0.049(2)	0.0267(16)	-0.0043(14)	-0.0012(13)	0.0274(15)	0.0377(8)
O(3)	0.0014(5)	0.9327(4)	0.5987(2)	0.0144(11)	0.0172(12)	0.0214(12)	0.0025(9)	0.0075(9)	0.0010(9)	0.0171(5)
O(4)	0.8993(6)	0.8248(4)	0.2163(3)	0.0397(17)	0.0119(12)	0.0260(14)	0.0008(10)	0.0077(12)	0.0015(11)	0.0264(6)
O(5)	0.6701(7)	0.5178(5)	0.2395(3)	0.0386(18)	0.048(2)	0.0367(18)	-0.0006(15)	0.0132(15)	-0.0331(16)	0.0411(9)
O(6)	0.0615(5)	0.6659(4)	0.4145(2)	0.0208(13)	0.0181(12)	0.0242(13)	0.0027(10)	0.0061(10)	0.0023(10)	0.0212(5)
O(7)	0.1633(7)	0.5200(5)	0.2294(3)	0.0354(17)	0.044(2)	0.0365(18)	-0.0035(14)	0.0078(14)	0.0278(15)	0.0395(9)
O(8)	0.5306(5)	0.3005(4)	0.3940(2)	0.0163(12)	0.0225(13)	0.0228(13)	0.0041(10)	0.0060(10)	-0.0003(10)	0.0204(5)
O(9)	0.5033(5)	0.8939(4)	0.4131(2)	0.0152(11)	0.0161(12)	0.0226(13)	0.0023(9)	0.0061(9)	0.0007(9)	0.0178(5)
O(10)H ₂ O	0.2815(7)	0.3373(5)	0.0436(3)	0.049(2)	0.0324(17)	0.0302(17)	0.0058(13)	0.0096(15)	0.0069(15)	0.0375(8)
O(11)H ₂ O	0.2528(7)	0.7255(5)	0.0060(3)	0.0365(18)	0.0380(18)	0.0343(18)	0.0087(14)	0.0115(14)	0.0012(15)	0.0359(7)
H(1)	0.305(10)	0.277(7)	-0.020(3)	0.0450(40)						
H(2)	0.152(5)	0.423(4)	0.026(4)	0.0450(40)						
H(3)	0.244(11)	0.5988(17)	-0.013(4)	0.04305(0)						
H(4)	0.290(11)	0.79(5)	-0.047(3)	0.04305(0)						
Ti(1A)	0.389(2)	0.3251(14)	0.2036(15)	0.009(3)	0.0140(3)	0.0182(3)	0.0027(7)	0.0052(3)	0.0007(4)	0.0136(10)
Ti(1B)	0.455(5)	0.325(3)	0.294(4)	0.009(3)	0.0140(3)	0.0182(3)	0.0027(7)	0.0052(3)	0.0007(4)	0.0136(10)

CRYSTAL CHEMISTRY OF LOMONOSOVITE AND MURMANITE

TABLE 6. Selected interatomic distances (Å) and angle (°) in lomonosovite.

Si(1)–O(4)	1.596(1)	Si(2)–O(6)	1.614(1)	P–O(11)a	1.528(1)
Si(1)–O(2)	1.599(1)	Si(2)–O(7)	1.625(1)	P–O(13)	1.531(1)
Si(1)–O(3)	1.606(1)	Si(2)–O(5)	1.629(1)	P–O(12)	1.537(1)
Si(1)–O(1)	1.651(1)	Si(2)–O(1)	1.652(1)	P–O(10)	1.570(1)
<Si(1)–O>	1.613	<Si(2)–O>	1.630	<P–O>	1.542
Ti(1)–O(8)	1.824(1)	Ti(2)–O(9)d	1.928(1)	Si(1)–O(1)–Si(2)	136.64(6)
Ti(1)–O(3)b	1.897(1)	Ti(2)–O(8)c	1.936(1)		
Ti(1)–O(4)c	1.943(1)	Ti(2)–O(9)e	1.952(1)		
Ti(1)–O(6)a	1.997(1)	Ti(2)–O(2)	2.034(1)		
Ti(1)–O(7)	2.012(1)	Ti(2)–O(5)e	2.158(1)		
Ti(1)–O(10)	2.141(1)	Ti(2)–O(5)	2.180(1)		
<Ti(1)–O>	1.969	<Ti(2)–O>	2.013		
Na(1)–O(12)	2.299(1)	Na(2)–O(2)e	2.251(1)	Na(3)–O(11)c	2.229(1)
Na(1)–O(9)	2.369(1)	Na(2)–O(8)d	2.374(1)	Na(3)–O(13)g	2.314(1)
Na(1)–O(3)a	2.435(1)	Na(2)–O(2)c	2.403(1)	Na(3)–O(10)c	2.443(1)
Na(1)–O(7)	2.566(1)	Na(2)–O(9)e	2.417(1)	Na(3)–O(7)	2.445(1)
Na(1)–O(4)	2.663(1)	Na(2)–O(8)f	2.670(1)	Na(3)–O(6)	2.530(1)
Na(1)–O(1)a	2.697(1)	Na(2)–O(5)	2.696(1)	Na(3)–O(4)c	2.738(1)
Na(1)–O(1)	2.723(1)	<Na(2)–O>	2.468	<Na(3)–O>	2.450
Na(1)–O(6)a	2.780(1)				
<Na(1)–O>	2.565	<Na(4)–O(11)	2.214(1)	Na(5)–O(11)g	2.252(1)
		<Na(4)–O(13)g	2.289(1)	Na(5)–O(10)c	2.326(1)
		<Na(4)–O(12)	2.326(1)	Na(5)–O(13)g	2.384(1)
		<Na(4)–O(1)	2.393(1)	Na(5)–O(12)	2.391(1)
		<Na(4)–O>	2.305	Na(5)–O(7)	2.692(1)
				<Na(5)–O>	2.409

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

The H sheet

The Ti(1) ($=M^H$) site is occupied primarily by Ti (Tables 6, 8) and is coordinated by O atoms. The Ti–O distances vary from 1.824 to 2.141 Å with $\langle \text{Ti}(1)\text{--O} \rangle = 1.969$ Å. There are two tetrahedrally coordinated sites occupied by Si, with a grand $\langle \langle \text{Si--O} \rangle \rangle$ distance of 1.622 Å.

The peripheral (P) sites

The [8]-coordinated Na(1) ($=A^P$) site is occupied solely by Na ($\text{Na}_{1.95}\square_{0.05}$ a.p.f.u.), with $\langle \text{Na}(1)\text{--O} \rangle = 2.565$ Å.

The I block.

There is one P site tetrahedrally coordinated by O atoms, with $\langle \text{P--O} \rangle = 1.542$ Å. There are three sites occupied primarily by Na: the [6]-coordinated Na(3) site and the [4]-coordinated Na(4) site are occupied primarily by Na with minor Ca and Mn, respectively; the [5]-coordinated Na(5) site is occupied solely by Na (Table 8). Three Na sites

are coordinated by O atoms with $\langle \text{Na}(3,4,5)\text{--O} \rangle = 2.450, 2.305$ and 2.409 Å, respectively. The cation sum of the I block gives Na_6P_2 a.p.f.u.

Anion considerations

Table 10 lists the bond valence values at all anions, 1.84–2.38 v.u. (valence units), which indicate that all anions are O atoms. In Group IV, the O sheet is of the form $\text{M}_4^{\text{O}} \text{X}_8^{\text{O}}$. Four X^{O} anions belong to (Si_2O_7) groups and they are O atoms, O(2) and O(5), giving O_4 a.p.f.u. (Table 5a). Five O(1,3,4,6,7) anions belong to (Si_2O_7) groups in the H sheet; they are O atoms giving O_{10} a.p.f.u. Table 10 gives 2.05 and 1.84 v.u. for O(8) [$=\text{X}_M^{\text{O}}$] and O(9) [$=\text{X}_A^{\text{O}}$] anions which receive bond valence from two Ti atoms and two Na atoms. The X_M^{O} site receives bond valence from Ti(1) in the H sheet, and from Ti(2) and two Na(2) atoms in the O sheet, and it is fully occupied by O atoms. The X_A^{O} atom receives bond valence from two Ti(2) atoms and

TABLE 7. Selected interatomic distances (Å) and angle (°) in murmanite.

Si(1)–O(1)a	1.594(3)	Si(2)–O(5)	1.589(3)
Si(1)–O(2)	1.600(3)	Si(2)–O(7)a	1.593(3)
Si(1)–O(4)b	1.637(3)	Si(2)–O(4)	1.623(3)
Si(1)–O(3)c	1.642(3)	Si(2)–O(6)a	1.626(3)
<Si(1)–O>	1.618	<Si(2)–O>	1.608
Ti(1)–O(8)	1.799(4)	Ti(2)–O(9)	1.888(3)
Ti(1)–O(7)	1.918(3)	Ti(2)–O(8)c	1.938(3)
Ti(1)–O(5)	1.930(3)	Ti(2)–O(9)d	1.965(3)
Ti(1)–O(1)	1.941(3)	Ti(2)–O(6)	1.999(3)
Ti(1)–O(2)	1.944(3)	Ti(2)–O(3)e	2.123(3)
Ti(1)–O(10)H ₂ O	2.288(3)	Ti(2)–O(3)	2.154(3)
<Ti(1)–φ>	1.970	<Ti(2)–O>	2.011
Na(1)–O(11)H ₂ O	2.310(4)	Na(2)–O(6)a	2.254(3)
Na(1)–O(9)	2.494(3)	Na(2)–O(8)c	2.366(3)
Na(1)–O(2)f	2.526(4)	Na(2)–O(6)c	2.422(3)
Na(1)–O(7)	2.574(4)	Na(2)–O(9)	2.439(3)
Na(1)–O(1)f	2.575(4)	Na(2)–O(8)	2.512(3)
Na(1)–O(5)	2.660(4)	Na(2)–O(3)e	2.714(3)
Na(1)–O(4)g	2.683(4)	<Na(2)–O>	2.451
Na(1)–O(4)	2.719(4)		
<Na(1)–φ>	2.568	Si(1)–O(4)–Si(2)	137.4(2)

φ = unspecified anion, O, H₂O, F;

a: x+1, y, z; b: x, y–1, z; c: –x+1, –y+1, –z+1; d: –x+1, –y+2, –z+1; e: –x, –y+2, –z+1; f: x, y+1, z; g: x–1, y, z.

one Na(2) atom in the O sheet and an Na(1) atom in the H sheet (Fig. 3c). Note that the sum of bond valences at O(9) is smaller than at O(8). The *Ti*(2) site is of composition $Ti_{1.31}Mn_{0.22}Nb_{0.20}Zr_{0.11}Mg_{0.11}Fe_{0.05}^{2+}$ and has a significant content of divalent cations: $Mn_{0.22}Mg_{0.11}Fe_{0.05}^{2+}$, i.e. M^{2+} equals 0.38 a.p.f.u. Therefore the bond-valence contribution from the two *Ti*(2) sites to the O(9) site is smaller than that from the *Ti*(1) + *Ti*(2) sites to the O(8) site, 1.43 v.u. vs. 1.71 v.u.. Substitution of M^{2+} for Ti requires substitution of F for O: $Ti^{4+} + O^{2-} \rightarrow M^{2+} + F^-$. To satisfy the electroneutrality principle, Mn^{2+} substitutes for Na^+ elsewhere in the structure. Hence, F enters the O(9) site which is of composition $(O_{1.50}F_{0.50})$. Note that the amount of F at the O(9) site correlates with amount of M^{2+} at the *Ti*(2) site, 0.38 a.p.f.u.. Ideally, O(8) and O(9) sites give O_4 a.p.f.u.. Four O(10–13) anions belong to a (PO_4) group and give O_8 a.p.f.u.. The total number of anions is thus O_{26} a.p.f.u. We write the ideal formula of lomonosovite as $Na_{10}Ti_4(Si_2O_7)_2(PO_4)_2O_4$, $Z = 1$.

Structure topology

The crystal structure of lomonosovite is an alternation of the TS block (described above) and the **I** block (Fig. 4a). In the **I** block, there are two **I** layers. Each layer consists of [4]- to [6]-coordinated Na polyhedra and (PO_4) tetrahedra. In the **I** layer, Na polyhedra share edges and corners, whereas (PO_4) tetrahedra share vertices with Na polyhedra. These two layers are parallel to (001) and are related by an inversion centre. Alternating TS and **I** blocks along **c** build up the crystal structure of lomonosovite (Fig. 4a). All features of structure topology are as described by Belov *et al.* (1977).

Murmanite

Previously, the crystal structure of murmanite was solved in space group *P1* (Khalilov *et al.*, 1965a; Khalilov, 1989). Here, we present a new model of the crystal structure of murmanite in space group $P\bar{1}$ which is in accord with overall topology of the

TABLE 8. Refined site-scattering (e.p.f.u.) and assigned site-populations (a.p.f.u.) for lomonosovite**>

1	Site**	2	Refined site scattering	Site population	Calculated site scattering	$\langle X-\phi \rangle_{\text{calc.}}^*$ (Å)	$\langle X-\phi \rangle_{\text{obs.}}$ (Å)
Ti(1)	M ^H		52.1(1)	1.52 Ti + 0.05 Mn ²⁺ + 0.31 Nb + 0.06 Fe ³⁺ + 0.01 Ta + 0.05 Fe ²⁺	51.0	2.004	1.969
Ti(2)	M ^O (1)		50.8(1)	1.31 Ti + 0.22 Mn ²⁺ + 0.20 Nb + 0.11 Zr + 0.11 Mg + 0.05 Fe ²⁺	49.5	2.026	2.013
[8]Na(1)***	A ^P		21.84(8)	1.95 Na + 0.05 □	21.45	2.590	2.565
Na(2)	M ^O (2)		21.88(8)	1.95 Na + 0.05 □	21.45	2.426	2.468
Na(3)			23.29(1)	1.89 Na + 0.11 Ca	23.00	2.402	2.450
[4]Na(4)			21.86(8)	1.71 Na + 0.16 Mn ²⁺ + 0.13 □	22.81	2.349	2.305
[5]Na(5)			22.11(8)	2.00 Na	22.00	2.383	2.409

* ionic radii from Shannon (1976); φ = unspecified anion (O, H₂O and minor F);

** 1: in accord with atom sites of Belov *et al.* (1977) used in this work;

2: in accord with terminology of Sokolova (2006); each site gives 2 a.p.f.u.;

*** coordination number is shown in brackets for a non-octahedral site.

TABLE 9. Refined site-scattering (e.p.f.u.) and assigned site-populations (a.p.f.u.) for murmanite*.

1	Site**	2	Refined site scattering	Site population	Calculated site scattering	$\langle X-\phi \rangle_{\text{calc.}}^*$ (Å)	$\langle X-\phi \rangle_{\text{obs.}}$ (Å)
Ti(1)**	M ^H		44.5(2)	1.67 Ti + 0.22 Nb + 0.11 Fe ³⁺	48.6	1.972	1.970
Ti(2)	M ^O (1)		48.7(2)	1.40 Ti + 0.29 Nb + 0.19 Mn + 0.07 Mg + 0.04 Fe ³⁺ + 0.01 Zr	49.7	2.017	2.011
[8]Na(1)***	A ^P		22.0(2)	1.78 Na + 0.15 Ca + 0.05 K + 0.02 □	23.5	2.540	2.568
Na(2)	M ^O (2)		20.3(2)	1.55 Na + 0.14 Mn + 0.06 Ca + 0.25 □	21.7	2.468	2.451

* ionic radii from Shannon (1976); φ = unspecified anion (O, H₂O and minor F);

** 1: atom sites used in this work;

2: in the terminology of Sokolova (2006); each site gives 2 a.p.f.u.;

*** coordination number is shown in brackets for a non-octahedral site.

TABLE 10. Bond-valence (v.u.)* table for lomonosovite.

Atom	Si(1)	Si(2)	P	Ti(1)	Ti(2)	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Σ
O(1)	0.95	0.94				0.12 0.12			0.20		2.38
O(2)	1.09				0.56		0.26 0.20				2.11
O(3)	1.07			0.81		0.19					2.07
O(4)	1.09			0.71		0.13		0.12			2.05
O(5)		1.00			0.41 0.39		0.12				1.92
O(6)		1.04		0.62		0.11		0.17			1.94
O(7)		1.01		0.60		0.15		0.20		0.13	2.09
O(8)				0.99	0.72		0.21 0.13				2.05
O(9)					0.74 0.69	0.21	0.20				1.84
O(10)			1.14	0.43				0.20		0.24	2.01
O(11)			1.29					0.29	0.27	0.27	2.12
O(12)			1.25			0.25			0.22	0.21	1.93
O(13)			1.27					0.25	0.24	0.21	1.97
Total	4.20	3.99	4.95	4.16	3.51	1.28	1.12	1.23	0.93	1.06	
Aggregate charge	4.00	4.00	5.00	4.08	3.72	0.98	0.98	1.06	1.01	1.00	

* Bond-valence parameters from Brown (1981);

O(9) = X_A^O equals (O_{1.50}F_{0.50}) p.f.u., aggregate charge equals -1.75.

TABLE 11. Bond-valence table (v.u.)* for murmanite.

Atom	Si(1)	Si(2)	Ti(1)	Ti(2)	Na(1)	Na(2)	H(1)	H(2)	H(3)	H(4)	Σ
O(1)	1.08		0.71		0.16						1.95
O(2)	1.06		0.71		0.17					0.10	2.04
O(3)	0.95			0.45 0.41		0.11					1.92
O(4)	0.96	1.00			0.13 0.12		0.07				2.28
O(5)		1.09	0.73		0.14						1.96
O(6)		0.99		0.61		0.24 0.17					2.01
O(7)		1.08	0.75		0.16						2.00
O(8)			0.99	0.72		0.19 0.15					2.05
O(9)				0.82 0.67	0.18	0.17					1.84
O(10)(H ₂ O)			0.31				0.86	0.86	0.12		2.15
O(11)(H ₂ O)					0.26		0.07	0.07 ^{x2?}	0.88	0.90	2.25
Total	4.05	4.16	4.20	3.68	1.32	0.79	1.0	1.0	1.0	1.0	
Aggregate charge	4.00	4.00	4.04	3.89	1.07	0.98					

* Bond-valence parameters from Brown (1981);

O(9) = X_A^O equals (O_{1.75}F_{0.25}) p.f.u., aggregate charge equals -1.88.

TABLE 12. Hydrogen bonding in murmanite.

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$\angle DHA$ (°)
$O(10)H_2O-H(1)\cdots O(11)(H_2O)a$	0.91(1)	2.33(5)	2.785(5)	110(4)
$O(10)H_2O-H(1)\cdots O(4)a$	0.91(1)	2.36(3)	3.150(5)	145(4)
$O(10)H_2O-H(2)\cdots O(11)(H_2O)$	0.91(1)	2.25(3)	2.802(5)	119(2)
$O(10)H_2O-H(2)\cdots O(11)(H_2O)b$	0.91(1)	2.33(3)	2.782(5)	111(2)
$O(11)H_2O-H(3)\cdots O(10)(H_2O)$	0.91(1)	2.00(3)	2.802(5)	147(4)
$O(11)H_2O-H(4)\cdots O(2)a$	0.91(1)	2.14(2)	3.009(5)	160(4)

a: $-x+1, -y+1, -z$; b: $-x, -y+1, -z$.

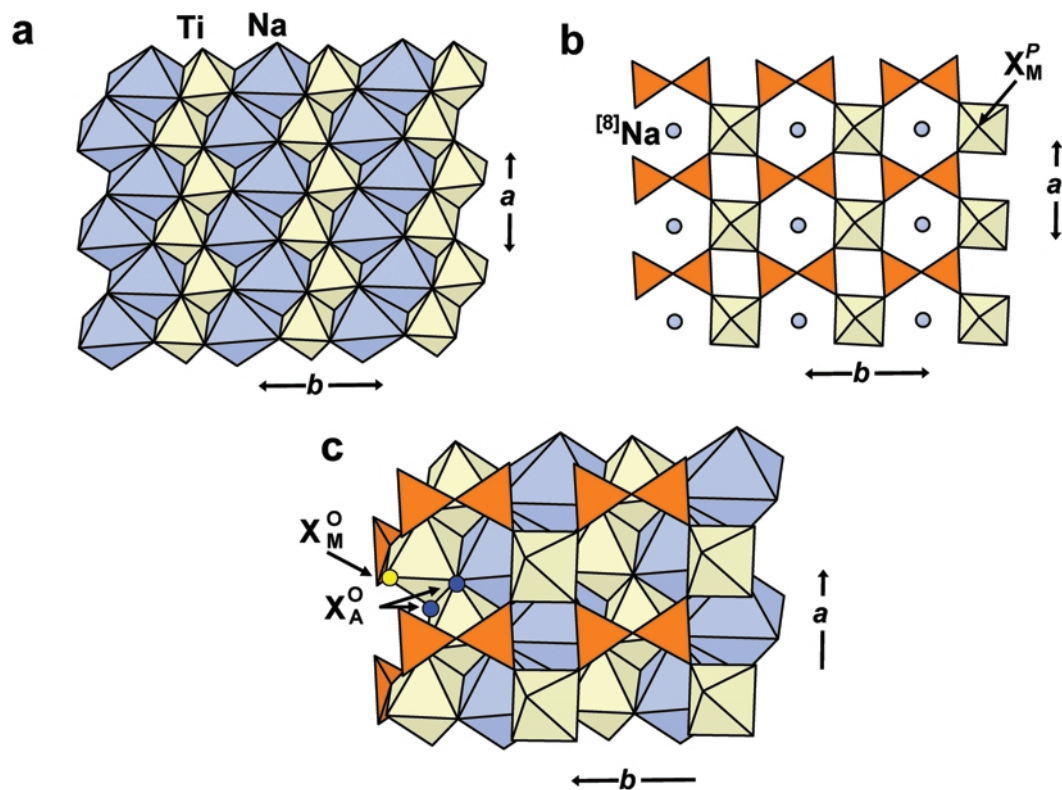


FIG. 3. The TS block in lomonosovite and murmanite viewed down [001]: the close-packed octahedral (O) sheet (a); the heteropolyhedral H sheet (b); linkage of O and H sheets (c). (SiO₄) tetrahedra are orange; Ti⁴⁺-dominant polyhedra are yellow; Na-octahedra are navy blue; [8]-coordinated Na atoms are shown as navy blue spheres. X_M^P = O in lomonosovite and (H₂O) in murmanite, X_M^O and X_A^O anions are shown as yellow and blue circles.

structure reported by Khalilov (1989). The structure of murmanite consists of TS blocks stacked along [001].

Cation sites

The O sheet

Two cation sites are coordinated by O atoms: the Ti-dominant site, *Ti(2)*, of composition $\text{Ti}_{1.40}\text{Nb}_{0.29}\text{Mn}_{0.19}\text{Mg}_{0.07}\text{Fe}_{0.04}^{3+}\text{Zr}_{0.01}$ with $\langle\text{Ti}(2)\text{--O}\rangle = 2.011 \text{ \AA}$, and the Na-dominant site, *Na(2)*, with $\langle\text{Na}(2)\text{--O}\rangle = 2.451 \text{ \AA}$ (Tables 6, 8).

The H sheet

The *Ti(1)* ($=M^H$) site is occupied primarily by Ti (Tables 7, 9) and is coordinated by five O

atoms and one H_2O group, O(10). The $\text{Ti}(1)\text{--O}$ distances vary from 1.799 to 2.288 \AA with $\langle\text{Ti}(1)\text{--O}\rangle = 1.970 \text{ \AA}$; the longest distance is from Ti(1) to H_2O (Table 7). There are two tetrahedrally coordinated sites occupied by Si, with a grand $\langle\text{Si--O}\rangle$ distance of 1.613 \AA .

The peripheral (P) sites

The *Na(1)* ($=A^P$) site is coordinated by seven O atoms and one H_2O group, O(11), and is occupied primarily by Na with subordinate Ca and minor K; $\langle\text{Na}(1)\text{--O}\rangle = 2.568 \text{ \AA}$.

We emphasize that in murmanite, there are no vacant cation sites; all cation sites are occupied at 88–100% [cf. formula of murmanite by Németh *et al.* (2005)].

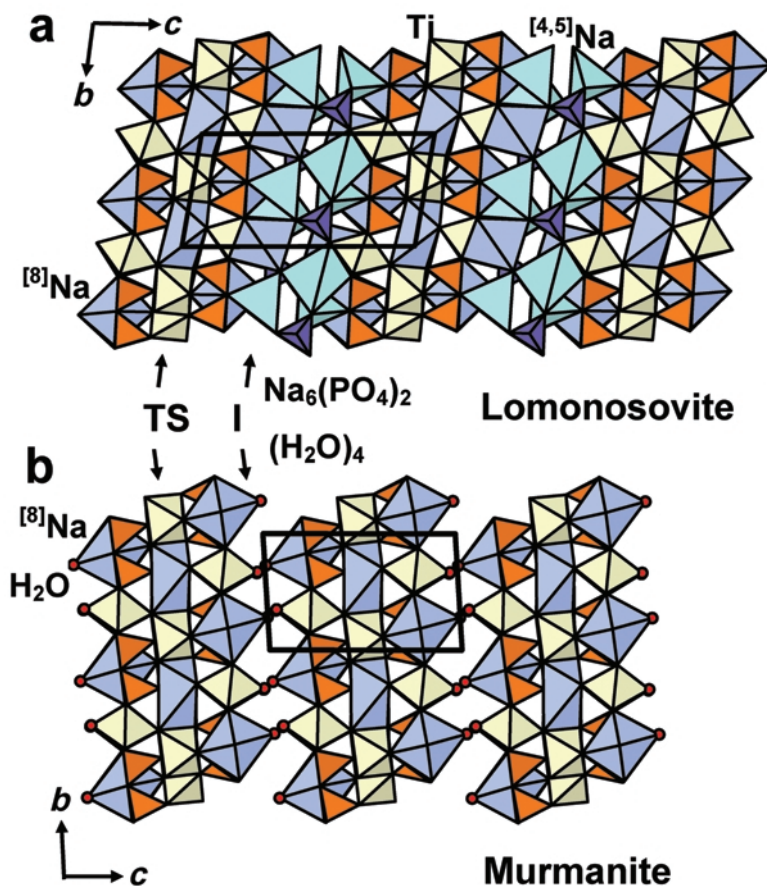


FIG. 4. General view of the crystal structure of lomonosovite (a) and murmanite (b) projected onto (100). Legend as in Fig. 2, [8]-coordinated Na-polyhedra are navy blue; [4,5]-coordinated Na polyhedra in the I block of lomonosovite are turquoise, H_2O groups are shown as red spheres. The unit cell is shown by thick black lines. Titanium silicate and intermediate blocks are labelled TS and I, respectively.

Anion considerations

As the TS blocks are identical in lomonosovite and murmanite, anion considerations for these two minerals are similar, except for outer anions of the TS block (the X_M^P and X_A^P sites, Fig. 2*b*). Table 11 lists bond-valence values at all anions. Atoms O(1)–O(9) are O atoms, with bond-valence sums varying from 2.28 v.u. at the O(4) bridge oxygen of the (Si₂O₇) group to 1.84 v.u. at O(9) [= X_A^O]. These atoms give O₁₈ p.f.u. Table 11 gives 2.05 and 1.84 v.u. for the O(8) [= X_M^O] and O(9) [= X_A^O] anions which receive bond valence from two Ti atoms and two Na atoms (note the same values occur for O(8) [= X_M^O] and O(9) [= X_A^O] in lomonosovite). Following the above discussion and in accord with the substitution: $Ti^{4+} + O^{2-} \rightarrow M^{2+} + F^-$, we assign (O_{1.76}F_{0.24}) p.f.u. to the O(9) site in murmanite. The amount of F at the O(9) site correlates with amount of M^{2+} at the Ti(2) site, 0.26 a.p.f.u. There are two atoms, O(10) (= X_M^P) and O(11) (= X_A^P), which have bond-valence sums of 0.31 [from Ti(1)] and 0.26 v.u. [from Na(1)]; these are the O atoms of (H₂O) groups. In total, O(10) + O(11) give (H₂O)₄ p.f.u. Bond-valence considerations indicate that there are no OH groups in the crystal structure of murmanite [cf. formula of murmanite by Németh *et al.* (2005)]. Therefore, the total number of anions is twenty two – O₁₈(H₂O)₄ a.p.f.u.

We may express the ideal formula of murmanite as Na₄Ti₄(Si₂O₇)₂O₄(H₂O)₄, $Z = 1$, in exact agreement with the ideal formula of Khalilov (1989) and Sokolova (2006).

Structure topology

There is one unique TS block in the unit cell of murmanite (Fig. 4*b*). Two adjacent TS blocks do not link directly; they repeat along **c** and are connected by hydrogen bonds between (H₂O)–(H₂O) groups and (H₂O)–O atoms of adjacent TS blocks.

Hydrogen bonding in murmanite

The H atoms of the (H₂O) groups were located in the difference-Fourier map (Table 5*b*) and Table 12 gives all information on the arrangement of hydrogen bonds in murmanite. There are four hydrogen bonds involving two (H₂O) groups and two O_{acceptor} atoms and these hydrogen bonds connect two TS blocks (Table 12, Fig. 5*a,b*). Each (H₂O) group is a ligand of a Ti(1) atom

[O(10)] or a Na(1) atom [O(11)]; thus the O atom of each (H₂O) group is bonded to one cation. Two H atoms attached to the O(10) atom each form bifurcated bonds: H(1) forms hydrogen...acceptor bonds to O(11) and O(4), and H(2) forms hydrogen...acceptor bonds to two symmetrically distinct O(11) atoms. Therefore, the H₂O group [O(10)] forms hydrogen...acceptor bonds to three other H₂O groups [O(11)] and an O(4) atom (Fig. 5*a*). The DHA angle varies from 110 to 145° (Table 12). Two H atoms attached to the O(11) atom each form a single hydrogen bond: H(3) forms a hydrogen...acceptor bond to O(10), and H(4) forms a hydrogen...acceptor bond to O(2). The value of the DHA angle varies from 147 to 160° (Table 12). Hydrogen bonds range from 2.00 to 2.33 Å and the mean *D* (donor)–*A* (acceptor) distance is 2.888 Å, corresponding to weak hydrogen bonding. Hydrogen bonds form a band that extends along **a**, and all hydrogen bonds link adjacent TS blocks (Fig. 5*b*). We suggest that the arrangement of hydrogen bonds in murmanite can be applicable to the epistolite structure where it was not possible to locate hydrogen atoms directly (Sokolova and Hawthorne 2004).

On the relation between lomonosovite and murmanite

This work shows that: (1) the TS blocks in lomonosovite and murmanite have identical topology and stereochemistry: $A_2^P M_2^H M_4^O$ (Si₂O₇)₂X₄ = Na₂Ti₂(Na₂Ti₂)_{Σ=4}(Si₂O₇)₂O₄ = Na₄Ti₄(Si₂O₇)₂O₄ and (2) lomonosovite and murmanite have **I** blocks of different topology and stereochemistry: $2 \times [Na_3(PO_4)]$ and (H₂O)₄, respectively. Our work agrees with the relation between lomonosovite and murmanite: lomonosovite Na₂Ti₂[Si₂O₇]O₂ × Na₃ PO₄ + *n*H₂O = murmanite Na₂Ti₂ [Si₂O₇]O₂*n*H₂O + Na₃ PO₄ (Belov *et al.*, 1977). The latter relation can be modified to relate vuonnemite and epistolite in the form vuonnemite Na₅Nb₂Ti[Si₂O₇]₂O₃(F,OH) × (Na₃PO₄)₂ + *n*H₂O = epistolite (Na₄,□)Nb₂Ti [Si₂O₇]O₂(OH,F)₂*n*H₂O + (Na₃PO₄)₂. Note that these are algebraic relations between chemical formulae, not chemical reactions.

Summary

- (1) The crystal structures of lomonosovite and murmanite are a combination of a titanium silicate (TS) block and an intermediate (**I**) block.
 - (a) The TS block exhibits linkage and stereochemistry typical of Group IV (Ti =

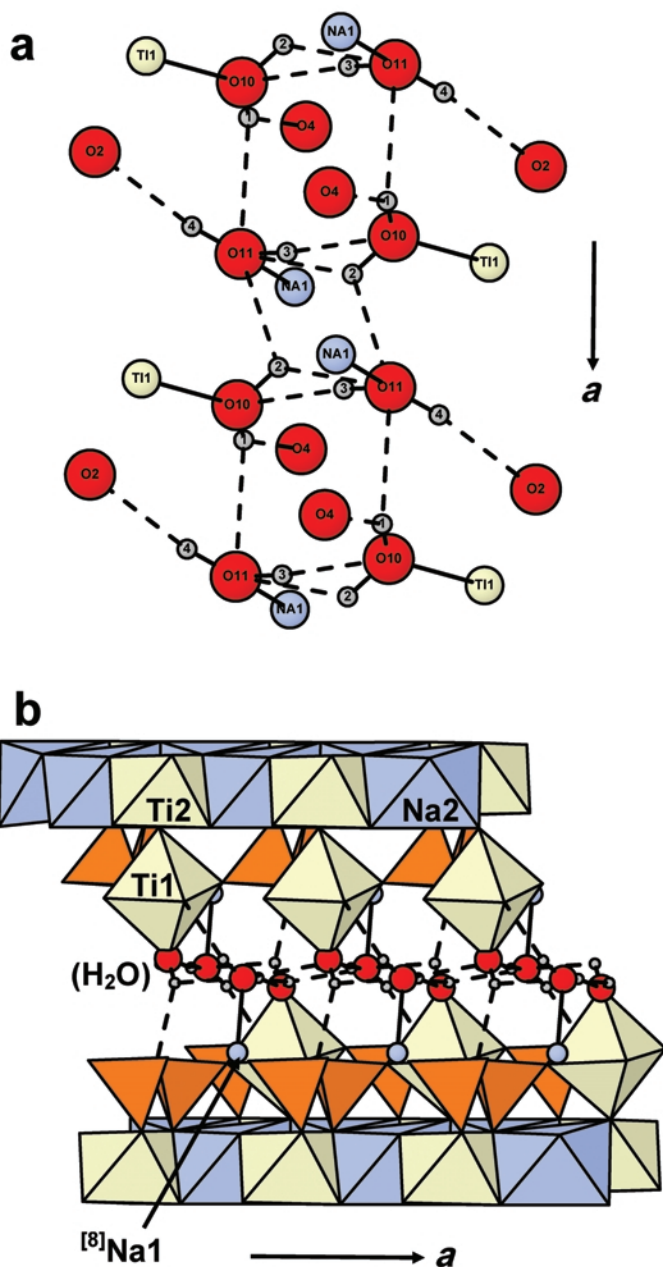


FIG. 5. Hydrogen bonding in murmanite: (a) a general scheme of hydrogen bonding; (b) xz projection of the crystal structure. Legend as in Figs 2 and 3; O atoms of H₂O groups, O(10) and O(11), and H atoms are shown as large red and small grey spheres, [8]-coordinated Na(1) atoms are shown as blue spheres, bonds Na(1)–O(11) and O_{donor}–H atom are shown as black solid lines and hydrogen bonds H...O (acceptor) are shown as dashed lines. In (a), O(2) and O(4) atoms (acceptors) are shown as large red spheres, Ti(1) atoms are shown as yellow spheres and bonds Ti(1)–O(10) are shown as solid black lines.

4 a.p.f.u.) Ti-disilicate minerals: two H sheets connect to the O sheet such that two (Si₂O₇) groups link to Ti polyhedra of the O sheet adjacent along **t**₁. In murmanite and lomonosovite, the TS blocks have the same chemical composition, bond topology and stereochemistry Na₄Ti₄(Si₂O₇)₂O₄.

(b) In lomonosovite, the **I** block is a framework of Na polyhedra and P tetrahedra, which gives 2 [Na₃(PO)₄] p.f.u. In murmanite, the **I** block is an arrangement of (H₂O) groups which gives (H₂O)₄ p.f.u. In lomonosovite, TS and **I** blocks alternate along **c**. In murmanite, TS blocks are connected *via* hydrogen bonding.

(2) There is no evidence for vacancy-dominant cation sites or (OH) sites in the TS blocks of lomonosovite and murmanite.

(3) The end-member formula for lomonosovite is Na₁₀Ti₄(Si₂O₇)₂(PO₄)₂O₄, Z = 1 and is in complete agreement with the work of Belov *et al.* (1977). The end-member formula for murmanite is Na₄Ti₄(Si₂O₇)₂O₄(H₂O)₄, Z = 1, in agreement with the work of Khalilov (1989).

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