

FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION.
 IV. TITANIUM SILICATES: THE ORTHORHOMBIC POLYTYPE
 OF NABALAMPROPHYLLITE FROM THE LOVOZERO MASSIF,
 KOLA PENINSULA, RUSSIA

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ABSTRACT

The crystal structure of nabalamprophyllite-2O, an orthorhombic polytype of nabalamprophyllite, ideally (BaNa) Na₃ Ti₃ (Si₂O₇)₂ O₂ (OH)₂, *a* 19.564(2), *b* 7.1173(5), *c* 5.4144(4) Å, *V* 753.90(4) Å³, space group *Pnmn*, *Z* = 2, *D*_{calc.} 3.410 g.cm⁻³, from the Yubileynaya vein, Karnasurt Mountain, Lovozero alkaline massif, Kola Peninsula, Russia, has been refined to a *R*₁ of 5.1% on the basis of 669 unique reflections (*F*_o > 4σ*F*), collected on a Bruker P4 diffractometer with a CCD 4K Smart detector and MoKα radiation. An electron-microprobe analysis gave (wt.%): SiO₂ 29.79, Al₂O₃ 0.16, Nb₂O₅ 0.71, TiO₂ 27.85, Fe₂O₃ 1.05, MnO 3.52, MgO 0.20, CaO 0.15, SrO 6.09, BaO 16.55, K₂O 1.14, Na₂O 10.89, F 1.53, H₂O 0.99 (calculated from structure refinement), O=F -0.64, total 99.98. The empirical formula is (Ba_{0.87} Sr_{0.47} Na_{0.28} K_{0.20} Ca_{0.02} □_{0.16})_{Σ2} (Na_{2.56} Mn²⁺_{0.40} Mg_{0.04})_{Σ3} (Ti_{2.81} Fe³⁺_{0.11} Nb_{0.04} Al_{0.03})_{Σ3} (Si₂O₇)₂ [(OH)_{0.89} F_{0.65} O_{0.46}]_{Σ2}, *Z* = 2, calculated on the basis of 4 Si *apfu*. The crystal structure of nabalamprophyllite-2O can be described as a combination of a TS block and an I block. The TS (titanium silicate) block consists of HOH sheets (H: heteropolyhedral, O: octahedral), and occurs in 24 Ti disilicate minerals. In the TS block, there are five cation sites, a [4]-coordinated Si site with <Si-O> = 1.631 Å, two Ti-dominant sites, the [5]-coordinated M^H site and [6]-coordinated M^O(1) site, and two [6]-coordinated Na-dominant sites, M^O(2) and M^O(3). The M^H site (Ti_{1.97} Al_{0.03} *apfu*) is coordinated by five O atoms, with <M^H-O> = 1.91 Å; the M^O(1) site (Ti_{0.85} Fe³⁺_{0.11} Nb_{0.04} *apfu*) is coordinated by four O atoms and two OH groups, with <M^O(1)-O,OH> = 2.00 Å; the M^O(2) and M^O(3) sites (Na_{1.00} and Na_{1.56} Mn²⁺_{0.40} Ca_{0.08} Mg_{0.04} *apfu*, respectively) are coordinated by six O atoms with <M^O(2)-O> = 2.44 Å and four O atoms and two OH groups, with <M^O(3)-O,OH> = 2.30 Å, respectively. The M^H square pyramids and (Si₂O₇) groups constitute the H sheet. The M^O(1-3) octahedra form the close-packed O sheet. Linkage of H and O sheets occurs *via* common vertices of M^H square pyramids and (Si₂O₇) groups with M^O(1-3) octahedra. The I block includes the [10]-coordinated A^P sites (Ba_{0.87} Sr_{0.47} Na_{0.28} K_{0.20} Ca_{0.02} □_{0.16} *apfu*) with <A^P-O> = 2.82 Å. The TS block and the I block [which ideally is a layer of (BaNa) atoms] alternate along *a*. The ideal formula of nabalamprophyllite-2O is (BaNa) Na₃ Ti₃ (Si₂O₇)₂ O₂ (OH)₂, in accord with the general formula of nabalamprophyllite-2M, Ba Na Na₃ Ti₃ (Si₂O₇)₂ O₂ (OH)₂, space group *P2/m*, previously known as nabalamprophyllite. The structure topology of nabalamprophyllite-2O differs from that of nabalamprophyllite-2M in (1) disorder/order of the A^P cations in the I block, and (2) different stacking order of TS blocks. In nabalamprophyllite-2O, Ba and Na atoms are disordered at one A^P site; in nabalamprophyllite-2M, Ba and Na atoms are dominant each at one of two A^P sites. The difference in stacking order of TS blocks in nabalamprophyllite polytypes is identical to that in lamprophyllite-2O and lamprophyllite-2M. In Ti disilicates with the TS block, hainite, (Ca₃REE) Na (NaCa)Ti (Si₂O₇)₂ OF₃, and rinkite, (Ca₃REE) Na (NaCa)Ti (Si₂O₇)₂ OF₃, can be considered as polytypes.

Keywords: nabalamprophyllite-2O, Ti disilicate minerals, structure refinement, EMP analysis, chemical formula, TS block, lamprophyllite, polytype.

SOMMAIRE

Nous avons affiné la structure cristalline de la nabalamprophyllite-2O, polytype orthorhombique de la nabalamprophyllite, de formule idéale (BaNa) Na₃ Ti₃ (Si₂O₇)₂ O₂ (OH)₂, *a* 19.564(2), *b* 7.1173(5), *c* 5.4144(4) Å, *V* 753.90(4) Å³, groupe spatial *Pnmn*, *Z* = 2, *D*_{calc.} 3.410 g.cm⁻³, provenant de la veine Yubileynaya, au mont Karnasurt, complexe alcalin de Lovozero, dans la péninsule de Kola en Russie, jusqu'à un résidu *R*₁ de 5.1% sur une base de 669 réflexions uniques (*F*_o > 4σ*F*) prélevées avec un diffractomètre Bruker P4 muni d'un détecteur CCD 4K Smart et avec rayonnement MoKα. Une analyse faite avec

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une microsonde électronique a donné SiO₂ 29.79, Al₂O₃ 0.16, Nb₂O₅ 0.71, TiO₂ 27.85, Fe₂O₃ 1.05, MnO 3.52, MgO 0.20, CaO 0.15, SrO 6.09, BaO 16.55, K₂O 1.14, Na₂O 10.89, F 1.53, H₂O 0.99 (calculé à partir de l'ébauche de la structure), O=F -0.64, pour un total de 99.98. La formule empirique est (Ba_{0,87} Sr_{0,47} Na_{0,28} K_{0,20} Ca_{0,02}□_{0,16})_{Σ2} (Na_{2,56} Mn²⁺_{0,40} Mg_{0,04})_{Σ3} (Ti_{2,81} Fe³⁺_{0,11} Nb_{0,04} Al_{0,03})_{Σ3} (Si₂O₇)₂ [(OH)_{0,89} F_{0,65} O_{0,46}]_{Σ2}, Z = 2, calculée sur une base de 4 Si *apfu*. On peut décrire la structure de la nabalamprophyllite-2O comme une combinaison des blocs TS et I. Le bloc TS (silicate de titane) et son module HOH (H: heteropolyédrique, O: octaédrique) se retrouvent dans 24 minéraux disilicatés de Ti. Dans ce bloc, il y a cinq sites pour cations, un site *Si* à coordinence [4], avec <Si-O> = 1.631 Å, deux sites à dominance de Ti, le site *M^H* à coordinence [5] et le site *M^O(1)* à coordinence [6], et deux sites remplis surtout par le Na, à coordinence [6], *M^O(2)* et *M^O(3)*. Le site *M^H* (Ti_{1,97} Al_{0,03} *apfu*) est coordonné par quatre atomes O et des groupes OH, avec <M^H-O> = 1.91 Å; le site *M^O(1)* contenant (Ti_{0,85} Fe³⁺_{0,11} Nb_{0,04} *apfu*) est coordonné par quatre atomes O et des groupes OH, avec <M^O(1)-O,OH> = 2.00 Å; les sites *M^O(2)* et *M^O(3)* (Na_{1,00} et Na_{1,56} Mn²⁺_{0,40} Ca_{0,08} Mg_{0,04} *apfu*, respectivement) sont coordonnés par six atomes O ayant <M^O(2)-O> = 2.44 Å et quatre atomes et deux groupes OH, avec <M^O(3)-O,OH> = 2.30 Å, respectivement. Les pyramides carrées *M^H* et les groupes (Si₂O₇) constituent la couche H. Les octaèdres *M^O(1-3)* forment un empilement compact d'atomes O. Les connexions entre les couches H et O sont assurées par les sommets communs des pyramides carrées *M^H* et des groupes (Si₂O₇) avec les octaèdres *M^O(1-3)*. Le bloc I inclut les sites *A^P* à coordinence [10] de composition (Ba_{0,87} Sr_{0,47} Na_{0,28} K_{0,20} Ca_{0,02}□_{0,16} *apfu*), avec <*A^P*-O> = 2.82 Å. Les blocs TS et I [ce dernier étant, idéalement une couche d'atomes (BaNa)] alternent le long de *a*. La formule idéale de la nabalamprophyllite-2O serait (BaNa) Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, en accord avec la formule générale de la nabalamprophyllite-2M, Ba Na Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, groupe spatial *P2/m*, que l'on considérerait autrefois simplement comme la nabalamprophyllite. La topologie structurale de la nabalamprophyllite-2O diffère de celle de la nabalamprophyllite-2M par (1) une relation d'ordre-désordre impliquant les cations *A^P* dans le bloc I, et (2) une différence dans la séquence d'empilement des blocs TS. Dans la nabalamprophyllite-2O, les atomes Ba et Na sont désordonnés sur un site *A^P*; dans la nabalamprophyllite-2M, les atomes Ba et Na sont dominants chacun dans un des deux sites *A^P*. La différence dans la séquence d'empilement des blocs TS dans ces deux polytypes de la nabalamprophyllite est identique à celle entre polytypes dans la lamprophyllite-2O et lamprophyllite-2M. Parmi les disilicates de Ti contenant le bloc TS, on pourrait considérer la hainite, (Ca₃REE) Na (NaCa)Ti (Si₂O₇)₂OF₃, et la rinkite, (Ca₃REE) Na (NaCa)Ti (Si₂O₇)₂OF₃, comme polytypes.

(Traduit par la Rédaction)

Mots-clés: nabalamprophyllite-2O, minéraux disilicatés de Ti, affinement de la structure, données de microsonde électronique, formule chimique, bloc TS, lamprophyllite, polytype.

INTRODUCTION

In the lamprophyllite group, there are three Ti disilicate minerals of the same topology with an ideal formula of the type (A²⁺A⁺) Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, where A²⁺ = Sr²⁺, Ba²⁺, Ca²⁺; A⁺ = Na⁺, K⁺; lamprophyllite: (SrNa) Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, barytolamprophyllite: (BaK) Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, and nabalamprophyllite: Ba Na Na₃Ti₃(Si₂O₇)₂O₂(OH)₂; the general and individual formulae are from Sokolova (2006). In the mineral formulae presented above, brackets indicate that atoms substitute for each other at one crystallographic (A) site, e.g., Na substitutes for Sr in lamprophyllite and K substitutes for Ba in barytolamprophyllite. Lack of brackets indicate that two atoms occupy two different A sites, e.g., Ba and Na order at the A(1) and A(2) sites (see below). The crystal structures of lamprophyllite and barytolamprophyllite were solved in space group *C2/m* by Woodrow (1964) and Peng *et al.* (1984), respectively. There were numerous speculations in the literature that lamprophyllite could be both monoclinic and orthorhombic (Gossner & Drexler 1935, Moore 1971, Peng & Chang 1965). For example, TEM observations and X-ray powder (Rietveld) data on lamprophyllite and barytolamprophyllite samples from the Gardiner Complex, East Greenland, reported by Johnsen (1996), showed that three polytypes could be identified: lamprophyllite-2M (*C2/m*), lamprophyllite-2O (*Pnmm*)

and barytolamprophyllite-2M (*C2/m*). Hence, Johnsen (1996) introduced a polytype nomenclature for the lamprophyllite group and described the main features of these structures. Structure work of Krivovichev *et al.* (2003) on lamprophyllite-2M and lamprophyllite-2O confirmed the findings of Johnsen (1996).

Polytypism is common in Ti disilicate minerals with the TS block. In this paper, we present the structure of the orthorhombic polytype of nabalamprophyllite as a continuation of our work on Ti disilicate minerals with the TS block [delindeite (Sokolova & Cámara 2007), barytolamprophyllite (Sokolova & Cámara 2008), nacareniobsite-(Ce) (Sokolova & Hawthorne 2008)]. The crystal of nabalamprophyllite-2O was taken from a sample of bornemanite from the Yubileynaya vein, Karnasurt Mountain, Lovozero alkaline massif, Kola Peninsula, Russia, purchased from D.I. Belakovsky.

PREVIOUS WORK

Chukanov *et al.* (2004) described a new member of the lamprophyllite group, nabalamprophyllite, from two localities in Russia: the Inagli alkaline-ultrabasic massif, Yakutia (holotype), and the Kovdor alkaline-ultrabasic massif, Kola Peninsula. Prior to the description of this new mineral, Rastsvetaeva & Chukanov (1999) had reported on the crystal structure of nabalamprophyllite using the name "a new high-

barium analogue of lamprophyllite with a primitive unit cell" (Table 1). They stated that the crystal structure of nabalamprophyllite has lower symmetry, $P2/m$, and is an ordered analogue of lamprophyllite and barytolamprophyllite. They gave structural and ideal formulae for nabalamprophyllite as $X^I\text{Ba} X^I(\text{Na}_{0.5}\text{Ba}_{0.3}\text{K}_{0.15}\text{Sr}_{0.05})_{\Sigma 1} \{^{VI}(\text{Na}_{2.75}\text{Mn}_{0.15}\text{Mg}_{0.05}\text{Ca}_{0.05})_{\Sigma 3} ^{VI}\text{Ti} [V(\text{Ti}_{1.7}\text{Fe}_{0.2}\text{Al}_{0.1})_{\Sigma 2} \text{O}_2 (\text{Si}_2\text{O}_7)_2] (\text{OH},\text{F})_2\}$ and $\text{Ba} (\text{Na},\text{Ba}) \{ \text{Na}_3\text{Ti} [\text{T}_2\text{O}_2\text{Si}_4\text{O}_{14}] (\text{OH},\text{F})_2\}$, respectively.

Sokolova (2006) considered structural hierarchy and stereochemistry for twenty-four titanium disilicate minerals containing the TS (titanium silicate) block, a trioctahedral central (O) sheet and two adjacent heteropolyhedral (H) sheets containing various polyhedra including (Si_2O_7) groups. Sokolova (2006) established the relation between structure topology and chemical composition for those minerals and divided them into four groups, characterized by different topology and stereochemistry of the TS block. Each group of structures has a different linkage of H and O sheets in the TS block and a different arrangement of Ti (= Ti + Nb) polyhedra. In a structure, the TS block can alternate with another block, which is an intermediate (I) block, as it is intercalated between two TS blocks. In Groups I, II III and IV, Ti equals 1, 2, 3 and 4 *apfu*, respectively. In Group III, there are six minerals. Sokolova (2006) showed that three minerals of Group III, lamprophyllite (two polytypes are designated as lamprophyllite-2O and lamprophyllite-2M; Table 1), barytolamprophyllite and nabalamprophyllite, have a TS block of composition $[\text{Na}_3\text{Ti}_3 (\text{Si}_2\text{O}_7)_2 \text{O}_2 (\text{OH})_2]^{3-}$. The interlayer cations constituting the I block must have a total charge of 3+ to satisfy the negative charge of the TS block (see ideal formulae above). In lamprophyllite

(Krivovichev *et al.* 2003) and barytolamprophyllite (Sokolova & Cámara 2008), the interlayer cations are disordered over one specific site, and they are (SrNa) and (BaK), respectively.

EXPERIMENTAL DETAILS

Electron-microprobe analysis

One fragment of the crystal of nabalamprophyllite-2O used by us for the structure refinement was analyzed with a Cameca SX-100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 10 μm , and count times on peak and background of 20 and 30 s for major and minor elements (<1 wt. %), respectively. The following standards and crystals were used for *K* or *L* X-ray lines: fluororibeckite: F, jadeite: Na, barite: Ba, diopside: Si, Ca, fayalite: Fe, spessartine: Mn, orthoclase: K, titanite: Ti, zircon: Zn, BaNaNbO₄: Nb, forsterite: Mg, strontianite: Sr, andalusite: Al. Data were reduced using the PAP procedure of Pouchou & Pichoir (1985). The chemical composition of nabalamprophyllite-2O is given in Table 2 and is the mean of 10 determinations.

The empirical formula is $(\text{Ba}_{0.87}\text{Sr}_{0.47}\text{Na}_{0.28}\text{K}_{0.20}\text{Ca}_{0.02}\square_{0.16})_{\Sigma 2} (\text{Na}_{2.56}\text{Mn}^{2+}_{0.40}\text{Mg}_{0.04})_{\Sigma 3} (\text{Ti}_{2.81}\text{Fe}^{3+}_{0.11}\text{Nb}_{0.04}\text{Al}_{0.03})_{\Sigma 3} (\text{Si}_2\text{O}_7)_2 [(\text{OH})_{0.89}\text{F}_{0.65}\text{O}_{0.46}]_{\Sigma 2}$, $Z = 2$, calculated on the basis of 4 Si *apfu*. The amount of (H_2O) was calculated from the structure refinement. The ideal formula is $(\text{BaNa}) \text{Na}_3\text{Ti}_3 (\text{Si}_2\text{O}_7)_2 \text{O}_2 (\text{OH})_2$, in accord with the general formula of nabalamprophyllite-2M, $\text{Ba} (\text{Na},\text{Ba}) \{ \text{Na}_3\text{Ti} [\text{T}_2\text{O}_2\text{Si}_4\text{O}_{14}] (\text{OH},\text{F})_2\}$ (Chukanov *et al.* 2004).

TABLE 1. STRUCTURAL FORMULAE* AND UNIT-CELL PARAMETERS FOR SELECTED MINERALS WITH THE TS BLOCK

Mineral	Formula					<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Space group	<i>Z</i>	Ref.
	A^P_2	M^H_2	M^O_4	$(\text{Si}_2\text{O}_7)_2$	X^O_4							
nabalamprophyllite-2M**	BaNa	Ti ₂	Na ₃ Ti	$(\text{Si}_2\text{O}_7)_2$	$\text{O}_2(\text{OH})_2$	19.741	7.105	5.408	96.67	<i>P2/m</i>	2	(1)
nabalamprophyllite-2O	(BaNa)	Ti ₂	Na ₃ Ti	$(\text{Si}_2\text{O}_7)_2$	$\text{O}_2(\text{OH})_2$	19.564	7.1173	5.414		<i>Pnmm</i>	2	(2)
lamprophyllite-2M	(SrNa)	Ti ₂	Na ₃ Ti	$(\text{Si}_2\text{O}_7)_2$	$\text{O}_2(\text{OH})_2$	19.215	7.061	5.3719	96.797	<i>C2/m</i>	2	(3)
lamprophyllite-2O	(SrNa)	Ti ₂	Na ₃ Ti	$(\text{Si}_2\text{O}_7)_2$	$\text{O}_2(\text{OH})_2$	19.128	7.0799	5.3824		<i>Pnmm</i>	2	(3)
hainite***	$[\text{Ca}_2(\text{REE},\text{Y})]$		$\text{Na}(\text{NaCa})\text{Ti}$	$(\text{Si}_2\text{O}_7)_2$	OF_3	9.6079	5.7135	7.3198	101.077	$P\bar{1}$	1	(4)
rinkite	(Ca_3REE)		$\text{Na}(\text{NaCa})\text{Ti}$	$(\text{Si}_2\text{O}_7)_2$	OF_3	7.437	5.664	18.843	101.4	<i>P2₁/c</i>	2	(5)

* For each mineral, the structural formula is written in the form $A^P_2 M^H_2 M^O_4 (\text{Si}_2\text{O}_7)_2 X^O_4$, where M^O represents the cations of the O sheet, M^H , the cations of the H sheet, A^P , the cations at the peripheral (P) sites, and X^O_4 , the anions that are common vertices of M^O octahedra and two M^H and two A^P polyhedra; they are the X^O_w and X^O_s anions (they belong to both sheets). ** This composition is from the description of a new mineral (Chukanov *et al.* 2004) rather than the structure work of Rastsvetaeva & Chukanov (1999). *** $\alpha = 89.916$, $\gamma = 100.828^\circ$. References (the latest reference on the structure): (1) Rastsvetaeva & Chukanov (1999), (2) this work, (3) Krivovichev *et al.* (2003), (4) Christiansen *et al.* (2003), (5) Galli & Alberti (1971); for rinkite, the latest reference is Rastsvetaeva *et al.* (1991), but we use the structure data of Galli & Alberti (1971).

Data collection and crystal-structure refinement

A single crystal of nabalamprophyllite-2O was mounted on a Bruker P4 diffractometer with a CCD 4K Smart detector and MoK α radiation. The intensities of reflections were collected to 60.01° 2 θ using 30 s per 0.2° frame, and an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 3) were obtained from 5627 reflections with $I > 10\sigma I$. As there were hardly any observed reflections at high 2 θ , refinement of the structure was based on 4433 intensities of reflections with $2\theta \leq 50^\circ$ and $-23 \leq h \leq 23$, $-7 \leq k \leq 8$, $-6 \leq l \leq 6$. On the basis of 669 unique observed reflections ($F_o > 4\sigma F$), the crystal structure of nabalamprophyllite-2O was refined using the atom coordinates of lamprophyllite-2O (Krivovichev *et al.* 2003) in the space group $Pn\bar{m}n$ with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) to $R_1 = 5.1\%$ and a GoF of 1.26. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). The R indices are given in Table 3, and are expressed as percentages. Site occupancies for the M^H and $M^O(1)$, $M^O(2)$ and $M^O(3)$ and A^P sites were refined with the scattering curves of Ti, Na and Ba, respectively. At the last stages of the refinement, six peaks with magnitudes from 6 to 1.8 e \AA^{-3} were found in the difference-Fourier map; they were labeled A^P_m , $M^O(1)_m$, $M^O(2)_m$, $M^O(3)_m$

and Si_m sites, each with approximately the same x coordinate as the namesake atom in the basic structure model. These subsidiary peaks were attributed to the presence of nabalamprophyllite-2M domains. Refined site-occupancies of subsidiary positions vary from 8 to 14%; we can estimate the presence of 2M domains as approximately 10% of the volume of the crystal. The shifts of the subsidiary peaks along the c axis are 1.54 Å for the cations of the O sheet, and 2.4 Å for the cations of the H sheet and the A^P cations. Similar subsidiary positions were reported for the lamprophyllite-2O structure due to the stacking faults common for the 2O polytype (Krivovichev *et al.* 2003).

Details of the data collection and structure refinement are given in Table 3, final atom and subsidiary atom parameters are given in Table 4, selected interatomic distances and angles in Table 5, refined site-scattering values and assigned populations for selected sites in Table 6 and bond-valence values in Table 7. A structure-factor table is available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Nabalamprophyllite-2O CM46_1323].

DESCRIPTION OF THE STRUCTURE

Cation sites

We describe cation sites in the crystal structure of nabalamprophyllite-2O and compare them with corresponding sites in the crystal structure of nabalamprophyllite-2M (Rastvetaeva & Chukanov 1999). Note that the crystal structure of nabalamprophyllite-2M has lower symmetry, $P2/m$ (maximum equipoint rank of 4), than all other minerals of the lamprophyllite group, lamprophyllite ($Pn\bar{m}n$ and $C2/m$), barytolamprophyllite ($C2/m$) and nabalamprophyllite-2O ($Pn\bar{m}n$), all of which have space groups of maximum equipoint rank of 8. Therefore, the number of individual sites in

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF NABALAMPROPHYLLITE-2O

Sample**	(1)	(2)	(1)	(2)
SiO ₂	29.79	28.75	Si	4.00
Nb ₂ O ₅	0.71	—	Ba	0.87
TiO ₂	27.85	27.80	Sr	0.47
Al ₂ O ₃	0.16	0.44	Na	0.28
Fe ₂ O ₃ ***	1.05	0.20	K	0.20
FeO****	0.00	0.52	Ca	0.02
MnO	3.52	1.10	Σ2A ^P	1.84
MgO	0.20	0.34	2A ^P charge	+3.16
CaO	0.15	0.36	Ti	2.81
SrO	6.09	0.65	Nb	0.04
BaO	16.55	24.12	Fe ²⁺	0.11
K ₂ O	1.14	0.94	Al	0.03
Na ₂ O	10.89	11.14	Σ3(2M ^H + M ^O)	2.99
F	1.53	1.18	Na	2.56
H ₂ O****	0.99	1.19	Fe ²⁺	0.00
O=F	-0.64	-0.50	Mn ²⁺	0.40
			Ca	—
			Mg	0.04
			Σ3M ^O	3.00
			F ⁻	0.65
			(OH) ⁻	0.89
			O ²⁻	0.46
			Σ2X _A ^O	2.00
			Σ cations	11.82
			Σ anions	18.02
Total	99.98	98.23		

* formula contents on a basis of 4 Si⁴⁺ (*apfu*); ** (1) nabalamprophyllite-2O (this work), (2) nabalamprophyllite-2M (Chukanov *et al.* 2004). *** The ratio Fe²⁺/Fe³⁺ was recalculated on the basis of crystal topology. **** Calculated from structure refinement.

TABLE 3. MISCELLANEOUS DATA CONCERNING THE STRUCTURE REFINEMENT OF NABALAMPROPHYLLITE-2O

Unit-cell parameters	a 19.564(2), b 7.1173(5), c 5.4144(4) Å
Space group, Z	$Pn\bar{m}n$, 2
Absorption coefficient	6.34 mm ⁻¹
$F(000)$	729.6
D_{calc}	3.410 g/cm ³
Crystal size	0.80 × 0.60 × 0.15 mm
Radiation/filter	MoK α /graphite
2 θ range for data collection	49.99° (60.01)° θ
$R(int)$	3.6%
Reflections collected	4433
Independent reflections	730
$F_o > 4\sigma F^*$ reflections	669
Refinement method	Full-matrix least-squares on F^2 , fixed weights proportional to $1/\sigma F_o^2$
Goodness of fit on F^2	1.26
Final $R(obs)$ $F_o > 4\sigma F^*$	5.1%
R indices (all data)	$R_1 = 5.4\%$, $WR_2 = 15.2\%$, GoF = 1.26

* used for the structure refinement.

TABLE 4. FINAL ATOM COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR NABALAMPROPHYLLITE-2O

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
A ^P	0.21647(7)	0	0.6442(2)	0.0150(8)	0.0060(8)	0.0074(8)	0	0.0002(5)	0	0.0095(6)
M ^H	0.35220(13)	0	0.1436(4)	0.0064(13)	0.0018(13)	0.0037(14)	0	-0.0003(9)	0	0.0040(8)
M ^O (1)	0	0	0	0.026(2)	0.007(2)	0.036(3)	0	-0.026(2)	0	0.0228(13)
M ^O (2)	½	0	½	0.025(5)	0.017(4)	0.018(5)	0	-0.008(4)	0	0.020(2)
M ^O (3)	½	0.2610(6)	0	0.013(3)	0.006(2)	0.007(2)	0	-0.0030(18)	0	0.0085(16)
Si	0.14125(13)	0.2162(4)	0.1428(5)	0.0071(14)	0.0007(15)	0.0050(15)	0.0002(10)	-0.0005(10)	0.0018(10)	0.0043(8)
O(1)(OH)	0.0568(7)	0	0.700(2)	0.012(7)	0.017(6)	0.032(7)	0	0.006(5)	0	0.020(3)
O(2)	0.3274(3)	0.1864(9)	0.3933(12)	0.011(3)	0.001(3)	0.010(3)	-0.003(3)	0.001(3)	-0.003(3)	0.0073(15)
O(3)	0.3280(3)	0.1868(9)	0.8881(12)	0.012(3)	0.000(3)	0.010(3)	0.004(3)	0.003(3)	-0.002(3)	0.0071(15)
O(4)	0.1727(7)	0	0.145(2)	0.012(7)	0.000(5)	0.013(6)	0	0.005(5)	0	0.008(3)
O(5)	0.0587(4)	0.2049(10)	0.1455(12)	0.006(3)	0.007(4)	0.014(4)	-0.001(3)	0.001(3)	-0.001(3)	0.0087(17)
O(6)	0.4382(5)	0	0.1435(18)	0.009(5)	0.027(7)	0.010(5)	0	-0.001(4)	0	0.015(3)
A ^P _m *	0.2167(9)	0	0.069(3)	0.060(12)	0.013(8)	0.024(9)	0	-0.005(7)	0	0.032(7)
M ^H _m	0.3522(14)	0	0.575(5)	0.033(16)	0.010(16)	0.030(16)	0	-0.001(11)	0	0.024(11)
M ^O (1) _m	0.004(3)	0	0.719(10)	0.08(3)	0.02(2)	0.05(3)	0	0.02(2)	0	0.051(19)
M ^O (2) _m	0.500(4)	0	0.214(15)	0.06(5)	0.01(4)	0.01(5)	0	0.02(4)	0	0.03(3)
M ^O (3) _m	0.5000(18)	0.264(5)	0.718(6)	0.043(19)	0.008(18)	0.027(19)	-0.001(14)	-0.006(14)	0.005(14)	0.026(12)
Si _m	0.1429(14)	0.783(4)	0.586(6)	0.029(16)	0.017(16)	0.043(16)	-0.006(12)	0.005(11)	-0.008(11)	0.030(11)

*_m : subsidiary atom positions related to nabalamprophyllite-2M with site occupancy ~10%.

TABLE 5. SELECTED ATOMIC DISTANCES (Å) AND ANGLES (°) FOR NABALAMPROPHYLLITE-2O

M ^H - O(6)	1.68(1)	M ^O (1) - O(1)a *	1.97(1) ×2	M ^O (2) - O(6)	2.28(1) ×2
M ^H - O(2)	1.955(7) ×2	M ^O (1) - O(5)	2.017(7) ×4	M ^O (2) - O(5)	2.520(7) ×4
M ^H - O(3)a	1.976(7) ×2	<M ^O (1) - O,OH>	2.00	<M ^O (2) - O>	2.44
<M ^H - O>	1.91				
		Si - O(3)c	1.613(7)	A ^P - O(2)d	2.745(7) ×2
M ^O (3) - O(5)b	2.250(7) ×2	Si - O(5)	1.617(7)	A ^P - O(3)c	2.765(7) ×2
M ^O (3) - O(1)b	2.302(9) ×2	Si - O(2)c	1.638(7)	A ^P - O(4)e	2.84(1)
M ^H - O(3)a	2.348(7) ×2	Si - O(4)	1.657(5)	A ^P - O(4)	2.84(1)
<M ^O (3) - O,OH>	2.300	<Si - O>	1.631	A ^P - O(3)	2.877(7) ×2
				A ^P - O(2)	2.883(7) ×2
		Si - O(4) - Si f	136.5(8)	<A ^P - O>	2.82

*O(1) = (OH)_{0.45}F_{0.32}O_{0.23}, ideally (OH).

a: x, y, z - 1; b: x + ½, -y + ½, -z + ½; c: -x + ½, -y + ½, z - ½; d: x + ½, y - ½, z + ½; e: x, y, z + 1; f: x, -y, z.

nabalamprophyllite-2M is twice that of the other four structures listed above.

H sheet: In the crystal structure of nabalamprophyllite-2O, there is one tetrahedrally coordinated site occupied by Si with a <Si-O> distance of 1.631 Å. There is one [5]-coordinated Ti-dominant site, M^H, coordinated by five O atoms, with a <M^H-O> distance of 1.91 Å (Table 5); this site is occupied mainly by Ti: Ti_{1.97}Al_{0.03} apfu (Table 6). In nabalamprophyllite-2M, all corresponding sites are very similar to those in nabalamprophyllite-2O: there are two Si sites and two [5]-coordinated Ti-dominant M^H sites with <Si-O> distances of 1.634 and 1.618 Å and with <M^H-O> distances of 1.92 and 1.91 Å, respectively.

O sheet: In the crystal structure of nabalamprophyllite-2O, the M^O(1) site, Ti_{0.94}Fe³⁺_{0.05}Nb_{0.01}, is coordinated by four O atoms and ideally two (OH) groups (see discussion below) with a <M^O(1)-O,OH> distance of 2.00 Å. There are two [6]-coordinated sites primarily occupied by alkali cations. The M^O(2) site is coordinated by O atoms and is fully occupied by Na, with a <M^O(2)-O> distance of 2.44 Å. The M^O(3) site, Na_{1.09}Fe²⁺_{0.30}Mn²⁺_{0.28}Ca_{0.08}Mg_{0.05}□_{0.20} apfu, is coordinated by six O atoms and two (OH) groups with a <M^O(3)-O,OH> distance of 2.300 Å. In nabalamprophyllite-2M, all corresponding sites are identical to those in nabalamprophyllite-2O: M^O(1) → Ti(2) and Ti(2) with mean distances of 1.98 and 2.00 Å, respectively; M^O(2)

TABLE 6. REFINED SITE-SCATTERING VALUES (*apfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR NABALAMPROPHYLLITE-2O

Site	Site-scattering	Site population ***	Calculated site-scattering	$\langle X-\phi \rangle_{\text{calc}}^*$ Å	$\langle X-\phi \rangle_{\text{obs}}^*$ Å
$^{10}A^p$	75.6(8)	0.87 Ba + 0.47 Sr + 0.28 Na + 0.20 K + 0.02 Ca + 0.16 □	73.9	2.83	2.82
$^{8}M^h$	44.0(2)	1.97 Ti + 0.03 Al	43.7	1.89	1.91
$M^o(1)$	22.0(1)	0.85 Ti + 0.11 Fe ³⁺ + 0.04 Nb	23.2	1.98	2.00
$M^o(2)$	11.0(4)	1.00 Na	11.0	2.40	2.44
$M^o(3)$	27.8(5)	1.56 Na + 0.40 Mn + 0.04 Mg	27.6	2.341	2.300
(OH,F)(1)	—	0.89 OH + 0.65 F + 0.46 O	—	—	—

* ionic radii for $^{10}O^{2-}$, $^{11}OH^-$, $^{14}F^-$, Ti, Nb, Al, Mg, Mn²⁺, Fe²⁺, Fe³⁺, Na, Ba, Sr, K are from Shannon (1976).

TABLE 7. BOND-VALENCE (*vu*)^{*} TABLE FOR NABALAMPROPHYLLITE-2O

	Si	M ^h	M ^o (1)	M ^o (2)	M ^o (3)	A ^p	Σ
O(1)			0.64 ^{x2}		0.25 ^{x2; x2, →}		1.14
O(2)	0.98	0.66 ^{x2;}				0.20 ^{x2;} 0.14 ^{x2;}	1.98
O(3)	1.05	0.62 ^{x2;}				0.19 ^{x2;} 0.15 ^{x2;}	2.01
O(4)	0.93 ^{x2, →}					0.16 0.16	2.18
O(5)	1.03		0.56 ^{x2;}	0.17 ^{x2;}	0.27 ^{x2;}		2.03
O(6)		1.44		0.26 ^{x2;}	0.23 ^{x2; x2, →}		2.16
Total	3.99	4.00	3.52	1.20	1.50	1.68	
Aggregate charge	4.00	3.99	3.93	1.00	1.22	1.60	

* Bond-valence parameters from Brown (1981).

→ Na(1) and Na(1)' with mean distances of 2.45 and 2.42 Å, respectively; M^o(3) → M(3) and M(3)' with mean distances of 2.30 and 2.31 Å, respectively.

I block: There is one A^p site, which is occupied by Ba_{0.87}Sr_{0.47}Na_{0.28}K_{0.20}Ca_{0.02}□_{0.16} apfu with $\langle A^p-O \rangle = 2.82$ Å. The aggregate charge at the A^p site is +3.2 (see aggregate charge of +1.6, 1 apfu in Table 7) or, ideally, +3. At the A^p site, Ba²⁺ > (Sr²⁺ + Ca²⁺), Na⁺ > K⁺, and we write the ideal composition of this site as (BaNa) with a charge of +3, which is in close accord with the aggregate charge in the empirical formula. Although Sr²⁺ > Na at the A^p site, the actual charge at the site, +3.2, does not allow us to write its ideal composition as (BaSr) with a total charge of +4. There are ten A^p-O distances less than 3 Å (Table 5), and one longer distance, A^p-O(1) = 3.14(1) Å. We consider the A^p site as being [10]-coordinated, with a $\langle [^{10}]A^p-O \rangle$ distance of 2.82 Å. In nabalamprophyllite-2M, there are four A^p sites. There are two [11]-coordinated A^p sites: the Ba site is occupied by 2.0 Ba with $\langle Ba-O \rangle = 2.83$, and the M(1) site is occupied by Ba_{0.66}Na_{0.60}K_{0.24}Sr_{0.10}□_{0.40} with $\langle M(1)-O \rangle = 2.87$ Å; there are two sites 20% occupied by Na, Na(2) and Na(3) (Rastsvetaeva

& Chukanov 1999). Chukanov *et al.* (2004) considered the M(1), Na(2) and Na(3) sites as an aggregate site and redefined the composition of the M(1) site as Na_{1.00}Ba_{0.66}K_{0.24}Sr_{0.10}. The aggregate charge of the I block is +3.37 (Table 2), and it can be written ideally as BaNa (Sokolova 2006). [The lack of parentheses indicates that Ba and Na are dominant at two crystallographically distinct A sites (each gives 1 apfu), and do not substitute for each other at one A site.]

Anion considerations

There are six anion sites. The four sites O(2)–O(5) are occupied by O atoms, which constitute the tetrahedral coordination of the Si atoms (Tables 4, 5, 7). There is one O site, O(6), which is the common anion for the M^h polyhedron and three octahedra of the O sheet: M^o(2) and two M^o(3) (Table 7). The O(1) site receives a bond-valence of 1.14 *vu* (Table 7), and hence is dominated by monovalent anions. The chemical analysis gives F 0.65 apfu (Table 2), and to satisfy the electroneutrality requirements, we assign OH_{0.89}F_{0.65}O_{0.46} to this site. As monovalent anions are dominant at this site and OH > F, the site is ideally (OH)₂.

Structure topology

In the Ti disilicate minerals (Sokolova 2006), the TS block consists of HOH sheets, where H represents a heteropolyhedral sheet including (Si₂O₇) groups, and O represents a trioctahedral close-packed sheet. In the crystal structure of nabalamprophyllite-2O, the O sheet is of the form M^oX^oO₂, where M^o are cations and X^o are anions. Structures with the TS block have a characteristic two-dimensional minimal cell in the plane of the O sheet with $t_1 \approx 5.5$ and $t_2 \approx 7.1$ Å, $\mathbf{t}_1 \wedge \mathbf{t}_2 \approx 90^\circ$, and this minimal cell contains 4 [M^oX^oO₂]. In the H sheet, the (SiO₄) tetrahedra link together to form (Si₂O₇) groups. The (Si₂O₇) groups and [5]-coordinated M^h polyhedra share common vertices to form the sheet

as in Ti disilicate minerals. The [10]-coordinated A^P cations are shifted from the plane of the H sheet and are located just above the centers of large voids in the H sheet. The H and O sheets link *via* common vertices of M^H , Si and M^O polyhedra to form the TS block. There are two TS blocks per unit cell in the crystal structure of nabalamprophyllite-2O (Fig. 1a). Along the *a* direction, the TS blocks alternate with layers of A^P atoms, which constitute the I (intermediate) block. Adjacent HOH layers are related by an *n* glide plane parallel to (100) or by the 2_1 screw axis parallel to [010] (or both). The crystal structure of nabalamprophyllite-2O is topologically identical to that of lamprophyllite-2O (Krivovichev *et al.* 2003).

RELATED POLYTYPES

Nabalamprophyllite-2M

Because of the discovery of nabalamprophyllite-2O, we consider the previously described nabalamprophyllite (Chukanov *et al.* 2004) a monoclinic polytype, *i.e.*, nabalamprophyllite-2M (Table 1, Fig. 1b). There is, however, an ambiguous situation with nabalamprophyllite-2M. Figure 1 shows a general view of the crystal structures of nabalamprophyllite-2M and lamprophyllite-2M. The relation between lamprophyllite-2O and lamprophyllite-2M was discussed in detail by Krivovichev *et al.* (2003). They pointed out that (1) *in the 2O polytype, adjacent HOH layers are related by an *n* glide plane parallel to (100) and by a 2_1 screw axis parallel to [001]*; (2) *in the 2M polytype, adjacent HOH*

blocks are related by a C-translation and a 2_1 screw axis perpendicular to [010] (both these operations do not change the layer orientation). We assume that a misprint occurred in the last statement and we read it: (2) *in the 2M polytype, adjacent HOH blocks are related by the C-translation and the 2_1 screw axis perpendicular to [100] (both these operations do not change the layer orientation)* (Fig. 1c). When we compare Figures 1a and 1c, we can see that TS blocks (HOH blocks) are related by elements of symmetry, *e.g.*, an *n* glide plane and a 2_1 screw axis. In nabalamprophyllite-2M (Rastsvetaeva & Chukanov 1999), (1) adjacent TS blocks are distinct and are *not* related by any elements of symmetry, and (2) Ba and Na are ordered at two distinct A^P sites. The occurrence of nabalamprophyllite-2O (in which Ba and Na are disordered at one A^P site) suggests that there is a possibility of finding nabalamprophyllite-2M with $C2/m$ symmetry where Ba and Na are disordered at one A^P site, similar to lamprophyllite-2M with $C2/m$ symmetry, where Sr and Na are disordered at one A^P site (Krivovichev *et al.* 2003).

Hainite and rinkite

There have been recent studies on polytypic relations in Ti disilicate minerals (Christiansen *et al.* 1999, Christiansen & Rønso 2000) and new structure work on Group-I minerals (as defined by Sokolova 2006): götzenite, hainite, seidozerite, grenmarite, kochite and rosenbuschite (Christiansen *et al.* 2003) and rinkite. Sokolova & Hawthorne (2008) studied the crystal structure of another mineral from Group I, nacareniob-

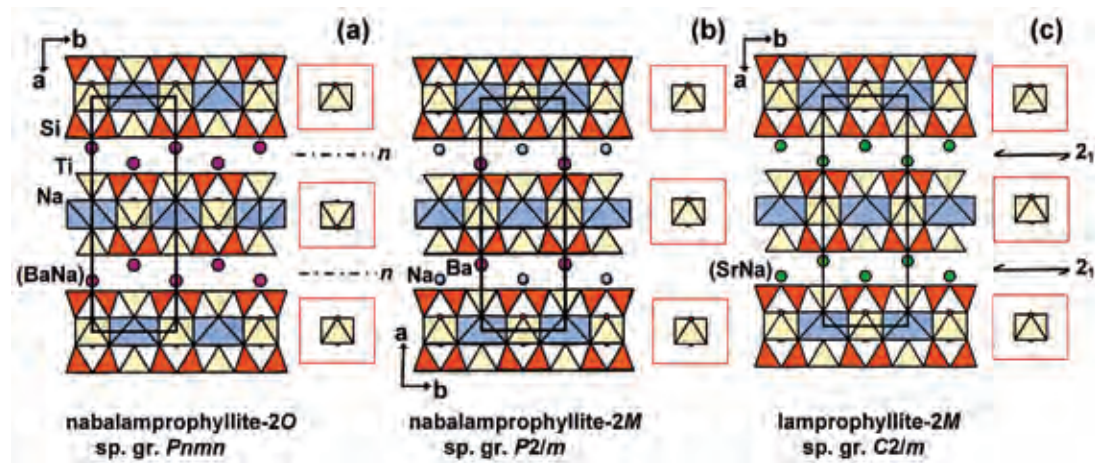


FIG. 1. General view of the crystal structure of nabalamprophyllite-2O (a), nabalamprophyllite-2M (b), and lamprophyllite-2M (c), projected onto (001). The (SiO_4) tetrahedra are shown in orange, Na octahedra in navy blue, and the Ti polyhedra, $^{15}M^H$ and $^{16}M^O(1)$, in yellow; the A^P atoms are shown as raspberry circles in (a), raspberry and blue circles in (b), and green circles in (c). The right side of each diagram shows the orientation of the $M^O(1)$ octahedron in the O sheet of the TS block. Elements of symmetry that relate TS blocks along *a* are (a) a n_x glide plane, shown as dash-dotted black lines, and (c) a 2_1 screw axis, shown as double-headed solid black lines.

site-(Ce), a Nb analogue of rinkite. They showed that nacareniobsite-(Ce) has space group $P2_1/c$, which is in accord with the rinkite structure by Galli & Alberti (1971). We consider hainite and rinkite (see Table 1) as another example of a polytypic relation. Both minerals share the ideal formula $(Ca_3REE) Na (NaCa) Ti (Si_2O_7)_2 OF_3$ (Sokolova 2006), and the topology of the TS block is identical, as they both belong to Group I. Hainite and rinkite have an O sheet of the form Na (NaCa) Ti OF_3 and an H sheet of the form $(Ca_3REE) Ti (Si_2O_7)_2$ (including A^P sites). In hainite, there is one TS block per unit cell and adjacent TS blocks are related by an inversion center (the O sheet orientation does not change). In rinkite, there are two TS blocks per unit cell, and adjacent TS blocks are related by the 2_1 screw axis parallel to [100] (the O sheet orientation changes). Hainite and rinkite can be considered as $1T$ (triclinic) and $2M$ (monoclinic) polytypes, respectively.

SUMMARY

(1) An orthorhombic polytype of nabalamprophyllite has been described with the space group $Pnmm$, nabalamprophyllite-2O, ideally $(BaNa) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$. In the I block, Ba and Na are disordered at one unique A^P site. The crystal structure is identical to that of lamprophyllite-2O.

(2) Previously known nabalamprophyllite (Rastsvetaeva & Chukanov 1999, Chukanov *et al.* 2004) is a monoclinic polytype, nabalamprophyllite-2M, ideally $BaNa Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$, space group $P2/m$. In the I block, Ba and Na are ordered at two distinct A^P sites.

(3) There is a possibility of finding a monoclinic polytype of nabalamprophyllite-2M with $C2/m$ symmetry where Ba and Na are disordered at one A^P site (analogous to lamprophyllite-2M).

(4) Hainite and rinkite, both ideally $(Ca_3REE) Na (NaCa)Ti (Si_2O_7)_2 OF_3$, are $1T$ (triclinic) and $2M$ (monoclinic) polytypes, respectively.

ACKNOWLEDGEMENTS

We are very grateful to Mark Cooper, who found the orthorhombic polytype of nabalamprophyllite. We thank reviewers Joel Grice and Sergey Krivovichev, and Major Editor Robert F. Martin, for their useful comments. FCH was supported by a Canada Research Chair and Major Equipment, Discovery and Major Facilities Access grants from the Natural Sciences and Engineering Research Council of Canada, and Innovation Grants from the Canada Foundation for Innovation.

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Received November 19, 2007, revised manuscript accepted July 15, 2008.