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FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION.
III. TITANIUM SILICATES: THE CRYSTAL CHEMISTRY OF BARYTOLAMPROPHYLLITE

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ABSTRACT

The crystal structure of barytolamprophyllite, ideally $(BaK)\,Na_3\,Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$, *a* 19.8971(7), *b* 7.1165(3), *c* 5.4108(2) Å, β 96.676(2)°, *V* 760.96(3) Å^3, space group *C*2/*m*, *Z* = 2, $D_{calc.}$ 3.521 g.cm^{-3}, from Mt. Yukspor, Khibina alkaline massif, Kola Peninsula, Russia, has been refined to R_1 = 2.82% on the basis of 1175 unique reflections ($F_o > 4\sigma F$) collected on a Bruker AXS SMART APEX diffractometer with a CCD detector and Mo*K*α radiation. An electron-microprobe analysis gave (wt.%): SiO_2 29.31, Al_2O_3 0.16, Nb_2O_5 0.11, TiO_2 28.39, Fe_2O_3 0.49, FeO 2.66, MnO 2.42, MgO 0.26, CaO 0.88, SrO 4.11, BaO 16.37, K_2O 3.52, Na_2O 7.90, F 1.69, H_2O 0.77 (calculated from structure refinement), O=F –0.71, for a total of 98.33. The empirical formula is $(Ba_{0.88}\,K_{0.61}\,Sr_{0.33}\,Ca_{0.05}\,\square_{0.13})_{\Sigma 2.00}\,(Na_{2.09}\,Fe^{2+}{}_{0.30}\,Mn^{2+}{}_{0.28}\,Ca_{0.08}\,Mg_{0.05}\,\square_{0.20})_{\Sigma 3.00}\,(Ti_{2.91}\,Fe^{3+}{}_{0.05}\,Al_{0.03}\,Nb_{0.01})_{\Sigma 3.00}\,(Si_2O_7)_2\,O_2\,[F_{0.73}\,(OH)_{0.70}\,O_{0.57}]_{\Sigma 2.00}$, Z = 2, calculated on the basis of 4 Si *apfu*. The crystal structure of barytolamprophyllite can be described as a combination of two blocks, a TS (titanium silicate) block and an **I** (intermediate) block. The TS block consists of HOH sheets (H heteropolyhedral, O octahedral), which occur in 24 Ti disilicate minerals. In the TS block, there are six 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 (= $Ti_{1.97}Al_{0.03}$ *pfu*) is coordinated by five O atoms, with < M^H–O> = 1.914 Å; the $M^O(1)$ site (= $Ti_{0.94}\,Fe^{3+}{}_{0.05}\,Nb_{0.01}$ *pfu*) is coordinated by four O atoms and two OH groups, with <$M^O(1)$–O> = 1.993 Å; the $M^O(2)$ and $M^O(3)$ sites (= $Na_{1.00}$ and $Na_{1.09}\,Fe^{2+}{}_{0.30}\,Mn^{2+}{}_{0.28}\,Ca_{0.08}\,Mg_{0.05}\,\square_{0.20}$ *pfu*, respectively) are coordinated by six O atoms with <$M^O(2)$–O> = 2.441 Å, and four O atoms and two OH groups, with <$M^O(3)$–O> = 2.296 Å, respectively. The M^H square pyramid and (Si_2O_7) 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 (Si_2O_7) groups with $M^O(1–3)$ octahedra. The second or intermediate **I** block includes the [10]-coordinated A^P site (= $Ba_{0.88}\,K_{0.61}\,Sr_{0.33}\,Ca_{0.05}\square_{0.13}$ *pfu*) with <A^P–O> = 2.843 Å. The TS block and the **I** block (which ideally is a layer of Ba and K atoms) alternate along **a**. The ideal formula of barytolamprophyllite is $(BaK)\,Na_3\,Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$, *Z* = 2. The topology of its structure is identical to that of lamprophyllite, $(SrNa)\,Na_3\,Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$, and nabalamprophyllite, $Ba\,Na\,Na_3\,Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$. We explain why, for lamprophyllite, barytolamprophyllite and nabalamprophyllite, the chemical composition of the **I** block is of the form $(A^{2+}\,A^+)$ with a total charge of 3+, and the ideal formula of the minerals is $(A^{2+}A^+)\,Na_3\,Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$, where $A^{2+} = Sr^{2+}$, Ba^{2+}, Ca^{2+}; $A^+ = Na^+$, K^+.

Keywords: barytolamprophyllite, Ti disilicate minerals, structure refinement, electron-microprobe analysis, chemical formula, TS block, lamprophyllite, nabalamprophyllite.

SOMMAIRE

Nous avons affiné la structure cristalline de la barytolamprophyllite, de formule idéale $(BaK)\,Na_3\,Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$, *a* 19.8971(7), *b* 7.1165(3), *c* 5.4108(2) Å, β 96.676(2)°, *V* 760.96(3) Å^3, groupe spatial *C*2/*m*, *Z* = 2, $D_{calc.}$ 3.521 g.cm^{-3}, provenant du mont Yukspor, complexe alcalin de Khibina, péninsule de Kola, en Russie, jusqu'à un résidu R_1 de 2.82% en utilisant 1175 réflexions uniques ($F_o > 4\sigma F$) prélevées avec un diffractomètre Bruker AXS SMART APEX muni d'un détecteur CCD et avec un rayonnement Mo*K*α. Une analyse avec une microsonde électronique a donné (en %, poids): SiO_2 29.31, Al_2O_3 0.16, Nb_2O_5 0.11, TiO_2 28.39, Fe_2O_3 0.49, FeO 2.66, MnO 2.42, MgO 0.26, CaO 0.88, SrO 4.11, BaO 16.37, K_2O 3.52, Na_2O 7.90, F 1.69, H_2O 0.77 (calculé à partir de l'affinement de la structure), O=F –0.71, pour un total de 98.33. La formule empirique est $(Ba_{0.88}\,K_{0.61}\,Sr_{0.33}\,Ca_{0.05}\,\square_{0.13})_{\Sigma 2.00}\,(Na_{2.09}\,Fe^{2+}{}_{0.30}\,Mn^{2+}{}_{0.28}\,Ca_{0.08}\,Mg_{0.05}\,\square_{0.20})_{\Sigma 3.00}\,(Ti_{2.91}\,Fe^{3+}{}_{0.05}\,Al_{0.03}\,Nb_{0.01})_{\Sigma 3.00}\,(Si_2O_7)_2\,O_2\,[F_{0.73}\,(OH)_{0.70}\,O_{0.57}]_{\Sigma 2.00}$, Z = 2, calculé sur une base de 4 Si *apfu*. On peut décrire la structure de la barytolamprophyllite comme une combinaison de deux blocs, un bloc TS (silicate de titane) et un bloc **I** (intermédiaire). Le bloc TS contient des feuillets HOH (H hétéropolyèdres, O octaèdres), qui se retrouvent aussi dans 24 minéraux disilicatés de Ti. Dans le bloc TS, il y a six sites pour cations, un site *Si* à coordinence [4], avec <Si–O> = 1.631 Å, deux sites où dominent le Ti, un site M^H à coordinence [5], le site $M^O(1)$, à coordinence [6], et deux sites où dominent Na à coordinence [6], $M^O(2)$ et $M^O(3)$. Le site M^H (= $Ti_{1.97}Al_{0.03}$ *pfu*) est lié

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à cinq atomes d'oxygène, avec $<M^H–O>$ = 1.914 Å; le site $M°(1)$ (= $Ti_{0.94} Fe^{3+}_{0.05} Nb_{0.01}$ *pfu*) est lié à quatre atomes d'oxygène et deux groupes OH, avec $<M°(1)–O>$ = 1.993 Å; les sites $M°(2)$ et $M°(3)$ (= $Na_{1.00}$ et $Na_{1.09} Fe^{2+}_{0.30} Mn^{2+}_{0.28} Ca_{0.08} Mg_{0.05} \square_{0.20}$ *pfu*, respectivement) sont liés à six atomes d'oxygène avec $<M°(2)–O>$ = 2.441 Å, et quatre atomes d'oxygène et deux groupes OH, avec $<M°(3)–O>$ = 2.296 Å, respectivement. Une pyramide carrée M^H et les groupes (Si_2O_7) constituent le feuillet H. Les octaèdres M°(1–3) forment un feuillet O à empilement compact. Les agencements des feuillets H et O sont assurés par les coins communs des pyramides carrées M^H et des groupes (Si_2O_7) avec les octaèdres M°(1–3). Le second bloc, **I** ou intermédiaire, inclut le site A^P à coordinence [10] (= $Ba_{0.88} K_{0.61} Sr_{0.33} Ca_{0.05} \square_{0.13}$ *pfu*), avec $<A^P–O>$ = 2.843 Å. Le bloc TS et le bloc **I** (qui est idéalement un niveau d'atomes de Ba et K) alternent le long de **a**. La formule idéale de la barytolamprophyllite est $(BaK) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$, $Z = 2$. La topologie de sa structure est identique à celle de la lamprophyllite, $(SrNa) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$, et celle de la nabalamprophyllite, $Ba Na Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$. Nous expliquons pourquoi, dans le cas de la lamprophyllite, barytolamprophyllite et nabalamprophyllite, la composition chimique du bloc **I** prend la forme $(A^{2+} A^+)$ avec une charge totale de 3+, et la formule idéale de ces minéraux est $(A^{2+}A^+) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$, avec $A^{2+} = Sr^{2+}, Ba^{2+}, Ca^{2+}$; $A^+ = Na^+, K^+$.

(Traduit par la Rédaction)

Mots-clés: barytolamprophyllite, minéraux disilicatés de Ti, affinement de la structure, analyses à la microsonde électronique, formule chimique, bloc TS, lamprophyllite, nabalamprophyllite.

INTRODUCTION

Currently, the crystal structures of about 160 Ti minerals are known. Half of them are Ti silicates and half of them are Ti oxides. Except for titanite, Ti silicates usually occur as accessory minerals. Nevertheless, Ti silicates are fairly numerous, particularly compared to analogous sulfates, phosphates and arsenates: there are no Ti sulfate minerals, one Ti phosphate mineral, and one Ti arsenate mineral, although several Ti silicate minerals also contain (PO_4) and (SO_4) groups. Sokolova (2006) considered structural hierarchy and stereochemistry for twenty-four titanium disilicate minerals containing the TS block. In the Ti disilicate minerals, the TS block consists of HOH sheets, where H is a heteropolyhedral sheet including (Si_2O_7) groups, and O is a trioctahedral close-packed sheet. Sokolova (2006) established the relation between structure topology and chemical composition for these 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, called an intermediate (**I**) block, as it is intercalated between two TS blocks. In Groups I, II III and IV, Ti = 1, 2, 3 and 4 *apfu*, respectively. Six minerals belong to Group III. Three of these minerals have the same topology: lamprophyllite, $(SrNa) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$ [which has two polytypes, one with orthorhombic symmetry and the other with monoclinic symmetry, designated as lamprophyllite-2*O* and lamprophyllite-2*M* by Johnsen (1996)], barytolamprophyllite, $(BaK) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$, and nabalamprophyllite, $Ba Na Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$. Three minerals are of different topology: innelite, $Na_2 Ca Ba_4 Ti_3 (Si_2O_7)_2 (SO_4)_2 O_4$ (Chernov *et al.* 1971), epistolite, $Na_4 Ti Nb_2 (Si_2O_7)_2 O_2 (OH)_2 (H_2O)_4$ (Sokolova & Hawthorne 2004), and vuonnemite, $Na_{11} Ti Nb_2 (Si_2O_7)_2 (PO_4)_2 O_3 F$ (Ercit *et al.* 1998). These ideal formulae for the six minerals are written as presented by Sokolova (2006).

There are ambiguities with regard to the ideal formulae of lamprophyllite and barytolamprophyllite that we will address in this paper. There is also need to examine the crystal structure of barytolamprophyllite characterized by a complete chemical analysis. In this paper, the third in this series (Sokolova 2006, Sokolova & Cámara 2007), we present the crystal chemistry of barytolamprophyllite and explain why, for lamprophyllite, barytolamprophyllite and nabalamprophyllite, the chemical compositions of the **I** block must be presented in the form $(A^{2+} A^+)$ with a total charge of 3+, and the ideal formulae, as $(A^{2+}A^+) Na_3 Ti_3 (Si_2O_7)_2 O_2 (OH)_2$, where $A^{2+} = Sr^{2+}, Ba^{2+}, Ca^{2+}$; $A^+ = Na^+, K^+$. In response to a comment by one of the reviewers as to why did we do this work when the minerals have been so well characterized, we offer the following critical analysis.

PREVIOUS WORK

The first descriptions of lamprophyllite, barytolamprophyllite and nabalamprophyllite were published by Ramsay & Hackman (1894), Dudkin (1959) and Chukanov *et al.* (2004), respectively. The crystal structure of lamprophyllite was solved by Woodrow (1964), who gave the formula as (Ba,Ca,K) Na (Ti,Fe) Ti $Si_2 (O,OH,F)_9$, and the latest refinement of the structure is by Krivovichev *et al.* (2003), who gave the structural formula as $(Sr_{1.18} Na_{0.65} Ca_{0.12})_{\Sigma 1.96} Na (Na_{1.3}Mn_{0.36}Fe_{0.22}Mg_{0.12}) Ti_3 O_2 (Si_2O_7)_2 (OH)_2$. Rastsvetaeva & Chukanov (1999) reported the crystal structure of nabalamprophyllite (Table 1), and Chukanov *et al.* (2004) gave its ideal formula as $Ba (Na,Ba) \{Na_3 Ti [T_2 O_2 Si_4 O_{14}](OH,F)_2\}$. The crystal structure of barytolamprophyllite was solved by Peng *et al.* (1984), who gave the *crystallochemical* formula $(Ba,Sr,K)_2 Na Ti (Na,Fe^{2+})_2 (Ti,Fe^{3+})_2 [Si_2O_7]_2 O_2 (O,OH,F)_2$, Z =

2. Two later refinements of the structure of minerals given the unapproved names "Ba-lamprophyllite" (Rastsvetaeva & Dorfman 1995) and "K-barytolamprophyllite" (Rastsvetaeva *et al.* 1995) confirmed the lamprophyllite-type structure, space group *C*2/*m*, $Z = 2$, and gave following structural formulae: $(Sr_{1.1}Ba_{0.9})\{Na(Na_{0.9}Mn^{2+}_{0.1})_2(Ti_{0.7}Mg_{0.3}(OH)_2\}\{[Si_2O_7]_2 \bullet (Ti_{0.7}Fe^{3+}_{0.3})_2O_2\}$ for "Ba-lamprophyllite" and $KBa\{Na[Na_{1.2}(Fe^{2+},Mn^{2+})_{0.8}] \bullet [Ti(O,OH)_2]\}\{[Si_2O_7]_2 Ti_2O_2\}$ for "K-barytolamprophyllite" (Table 1). We conclude that Rastsvetaeva & Dorfman (1995) and Rastsvetaeva *et al.* (1995) refined the crystal structures of lamprophyllite (Sr > Ba) and barytolamprophyllite (Ba > Sr), respectively, according to data presented by them. None of the three papers, Peng *et al.* (1984), Rastsvetaeva & Dorfman (1995), and Rastsvetaeva *et al.* (1995), contains results of a chemical analysis; empirical formulae were reported by Peng *et al.* (1984) and Rastsvetaeva *et al.* (1995): $(Ba_{1.05}Sr_{0.12}K_{0.53}Ca_{0.25}Na_{0.10})_{\Sigma 2.05}\,Na\,Ti\,(Na_{1.37}Fe^{2+}_{0.29}Mn_{0.20}Mg_{0.15})_{\Sigma 2.01}(Ti_{1.68}Fe^{3+}_{0.28}Mg_{0.05})_{\Sigma 2.01}[(Si_{3.83}Al_{0.18})_{\Sigma 4.01}O_{14}]\,O_2\,(O_{0.57}OH_{0.62}F_{0.68}Cl_{0.14})_{\Sigma 2.01}$ and $(K_{0.98}Ba_{0.84}Sr_{0.21})_{\Sigma 2.03}[Na(Na_{1.2}Fe_{0.41}Mn_{0.42}Ca_{0.27})_{\Sigma 2.3}(TiO_2)_{1.26}] \bullet [(Si_2O_7)_2Ti_2O_2]$, respectively.

Mandarino & Back (2004) gave the following formulae: lamprophyllite, $(Na,Mn,Ca,Fe)_3(Sr,Ba,K)_2(Ti,Fe)_3O_2(Si_2O_7)_2(O,OH,F)_2$; barytolamprophyllite, $(Na,K)_2(Ba,Ca,Sr)_2(Ti,Fe)_3(SiO_4)_4(O,OH)_2$. The formula for lamprophyllite has 12 cations, whereas the formula for barytolamprophyllite has 11 cations *pfu*. If they are isostructural, this is obviously not correct (as the presence of vacancies should also be recognized in a structural formula). Yakovenchuk *et al.* (2005) wrote the formulae of lamprophyllite and barytolamprophyllite as $(Sr,Ba,Na,Ca)_2Na(Na,Mn,Fe)_2Ti_3O_2[Si_2O_7]_2(OH)_2$ and $(Ba,Sr,Na,Ca)_2Na(Na,Mn,Fe)_2Ti_3O_2[Si_2O_7]_2(OH)_2$, respectively. Krivovichev *et al.* (2003) and Chukanov *et al.* (2004) stated that lamprophyllite and barytolamprophyllite have formulae $(Sr,Ba)_2Na_3Ti_3O_2(Si_2O_7)_2(OH)_2$ and $(Ba,Sr)_2Na_3Ti_3(Si_2O_7)_2O_2(OH)_2$; these formulae are not neutral, as they have an excess charge of +1 [note that Krivovichev *et al.* (2003) wrongly referred to the "Ba-lamprophyllite" of Rastvetaeva & Dorfman (1995) as barytolamprophyllite-2*M*]. Sokolova (2006) considered the structure work of Rastsvetaeva *et al.* (1995) as the latest structure work on barytolamprophyllite, $(KBa)Na_3Ti_3(Si_2O_7)_2O_2(OH)_2$; the latter ideal formula is neutral.

To summarize, (1) the crystal structure of barytolamprophyllite has never been done on a sample for which a chemical composition was given, and hence we do not know if the structure has ever been examined; (2) the chemical formulae of lamprophyllite and barytolamprophyllite quoted in Krivovichev *et al.* (2003) and Chukanov *et al.* (2004), *i.e.*, the latest works on the structure, are not neutral; they have an excess charge of +1, which is obviously wrong; (3) points (1) and (2) make it clear that there is an ambiguous situation with regard to the chemical formulae of the lamprophyllite group of minerals. We resolve this issue here.

EXPERIMENTAL

The crystals of barytolamprophyllite from Mt. Yuksporr, Khibina alkaline massif, Kola Peninsula, Russia, were kindly provided by Adriana and Renato Pagano, Milan, Italy, from their mineral collection (Collezione Mineralogica, sample #6270). These crystals were removed from a sample of delindeite originally obtained from A.P. Khomyakov and described in Khomyakov (1995).

Electron-microprobe analysis

One fragment of the crystal of barytolamprophyllite previously used for the structure refinement was analyzed with a Cameca SX–100 electron microprobe operating in wavelength-dispersion mode with an

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

Mineral	Formula	I block	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Sp. gr.	*Z*	Ref.
lamprophyllite-2*M*	$(SrNa)Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$	$(Sr_{1.18}Na_{0.65}Ca_{0.12})$	19.215	7.061	5.3719	96.797	*C*2/*m*	2	(1)
lamprophyllite-2*O*	$(SrNa)Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$	$(Sr_{1.18}Na_{0.65}Ca_{0.12})$	19.128	7.0799	5.3824		*Pnmn*	2	(1)
nabalamprophyllite	$Ba\,Na\,Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$	$(Ba_{1.30}Na_{0.50}K_{0.15}Sr_{0.05})$**	19.741	7.105	5.408	96.67	*P*2/*m*	2	(2)
barytolamprophyllite	$(BaK)Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$	$(Ba_{0.88}K_{0.61}Sr_{0.33}Ca_{0.05}\square_{0.13})$	19.8971	7.1165	5.4108	96.676	*C*2/*m*	2	(3)

* For each mineral, the structural formula is written in the form $A^P_2\,M^H_2\,M^O_4\,(Si_2O_7)_2\,X^O_4$ following Sokolova (2006).

** This composition is from the description of the new mineral species (Chukanov *et al.* 2004) rather than the structure work of Rastvetaeva & Chukanov (1999). Nabalamprophyllite is the only mineral with a lamprophyllite-type structure where there are two independent Ba- and Na-dominant A^P sites.

References (the latest reference on the structure): (1) Krivovichev *et al.* (2003), (2) Rastsvetaeva & Chukanov (1999), (3) this work.

The data for "Ba-lamprophyllite" (Rastsvetaeva & Dorfman 1995), *a* 19.744, *b* 7.099, *c* 5.409 Å, β 96.77°, space group *C*2/*m* and "K-barytolamprophyllite" (Rastsvetaeva *et al.* 1995), *a* 20.086, *b* 7.099, *c* 5.411 Å, β 96.65°, space group *C*2/*m*, are not included in the Table as there are no chemical data given in these papers. Sp. gr.: space group.

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: F: riebeckite; Na: jadeite; Ba: barite; Si, Ca: diopside; Fe: fayalite; Mn: spessartine; K: orthoclase; Ti: titanite; Zn: zircon; Nb: $BaNaNbO_4$; Mg: forsterite; Sr: strontianite; Al: andalusite. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The chemical composition of barytolamprophyllite is given in Table 2 and is the mean result of 10 point analyses.

The empirical formula is $(Ba_{0.88}\,K_{0.61}\,Sr_{0.33}\,Ca_{0.05}\,\square_{0.13})_{\Sigma 2.00}$ $(Na_{2.09}\,Fe^{2+}{}_{0.30}\,Mn^{2+}{}_{0.28}\,Ca_{0.08}\,Mg_{0.05}\,\square_{0.20})_{\Sigma 3.00}$ $(Ti_{2.91}\,Fe^{3+}{}_{0.05}\,Al_{0.03}\,Nb_{0.01})_{\Sigma 3.00}$ $(Si_2O_7)_2\,O_2$ $[F_{0.73}\,(OH)_{0.70}\,O_{0.57}]_{\Sigma 2.00}$, $Z = 2$, calculated on the basis of 4 Si *apfu*; the amount of (H_2O) was calculated from the structure refinement, the ideal formula is $(BaK)\,Na_3Ti_3\,(Si_2O_7)_2\,O_2\,(OH)_2$, in accord with Sokolova (2006).

Data collection and crystal-structure refinement

A single crystal of barytolamprophyllite was mounted on a Bruker AXS SMART APEX diffractometer equipped with graphite-filtered Mo*K*α X-radiation and a CCD detector. The intensities of 8747 reflections with $-27 < h < 27$, $-9 < k < 9$, $-7 < l < 7$ were collected to 59.86° 2θ using 20 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 5802 independent reflections. On the basis of 1185 unique observed reflections ($F_o > 4\sigma F$), the crystal structure of barytolamprophyllite was refined in the space group *C*2/*m* with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) to $R_1 = 2.8\%$ and a GoF of 1.12. 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, $M^{\circ}(1)$; $M^{\circ}(2)$, $M^{\circ}(3)$ and A^P sites were refined with the scattering curves of Ti; Na, Fe and Sr, respectively.

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF BARYTOLAMPROPHYLLITE

SiO_2	29.31	Si	4.00	Na	2.09
Nb_2O_5	0.11	Σ	4.00	Fe^{2+}	0.30
TiO_2	28.39			Mn^{2+}	0.28
Al_2O_3	0.16			Ca	0.08
Fe_2O_3	0.49	Ti^{4+}	1.97	Mg	0.05
FeO	2.66	Al	0.03	$\Sigma 3M^O$	1.80
MnO	2.42	$\Sigma 2M^H$	2.00		
MgO	0.26			Ba	0.88
CaO	0.88			K	0.61
SrO	4.11	Ti^{4+}	0.94	Sr	0.33
BaO	16.37	Fe^{3+}	0.05	Ca	0.05
K_2O	3.52	Nb	0.01	$\Sigma 2A^P$	1.87
Na_2O	7.90	$\Sigma 1M^O$	1.00		
F	1.69				
H_2O**	0.77			F^-	0.73
O=F	–0.71			$(OH)^-$	0.70
				O^{2-}	0.57
Total	98.33			$\Sigma 2X^O{}_A$	2.00

* formula contents on the basis of 4 Si^{4+} (*apfu*).
** calculated from structure refinement.

Details of the data collection and structure refinement are given in Table 3, final 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 table of structure factors may be obtained from the Depository of Unpublished Data, MAC web site [document Barytolamprophyllite CM46_403].

DESCRIPTION OF THE STRUCTURE

Cation sites

H sheet: In the crystal structure of barytolamprophyllite, 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 arranged in a square pyramid, with a $<M^H–O>$ distance of 1.914 Å (Table 5); this site is occupied by $Ti_{1.97}Al_{0.03}$ *pfu* (Table 6).

O sheet: The $M^{\circ}(1)$ site, $Ti_{0.94}Fe^{3+}{}_{0.05}Nb_{0.01}$, is coordinated by four O atoms and two anions (OH,F) (1), with a <M–O,OH> distance of 1.993 Å. There are two [6]-coordinated sites, primarily occupied by alkali cations. The $M^{\circ}(2)$ site is coordinated by O atoms and is fully occupied by Na, with a $<M^{\circ}(2)$ –O> distance of 2.441 Å. The $M^{\circ}(3)$ site, $Na_{1.09}Fe^{2+}{}_{0.30}Mn^{2+}{}_{0.28}Ca_{0.08}Mg_{0.05}\square_{0.20}$ *pfu*, is coordinated by four O atoms and two monovalent anions [which occur at the O(1) site; see discussion below], with a $<M^{\circ}(3)$–O> distance of 2.296 Å.

***I* block**: There is one A^P site, which is occupied by $Ba_{0.88}K_{0.61}Sr_{0.33}Ca_{0.05}\square_{0.13}$ *pfu*. There are ten A^P–O distances less than 3 Å (Table 5), and one longer distance, A^P–(O)(1) = 3.225 Å. We consider the A^P site as [10]-coordinated, with a $<{}^{[10]}A^P$–O> distance of 2.843 Å.

TABLE 3. MISCELLANEOUS REFINEMENT DATA FOR BARYTOLAMPROPHYLLITE

a (Å)	19.8971(17)	Absorption coefficient (mm^{-1})	6.10
b	7.1165(3)	*F*(000)	763.2
c	5.4108(2)	$D_{calc.}$ (g/cm^3)	3.521
β (°)	96.676(2)	Crystal size (mm)	0.03 × 0.10 × 0.16
V ($Å^3$)	760.96(3)	Radiation/ filter	Mo*K*α/graphite
Space group	*C*2/*m*	2θ range for data collection (°)	59.86
Z	2	*R*(int) (%)	2.9
Reflections collected		8747	
Independent reflections		1185	
$F_o > 4\sigma F$		1175	
Refinement method		Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$	
Goodness of fit on F^2		1.12	
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]		2.82	
R indices (all data) (%)		$R_1 = 2.87$, $wR_2 = 7.44$, Go*F* = 1.12	

Anion considerations

There are four anion sites, O(2)–O(5), occupied by O atoms that constitute the tetrahedral coordination of the Si atoms (Tables 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°(2) and two M°(3) (Tables 5, 7); this is the X°_{M} anion in the terminology of Sokolova (2006). The X°_{M} anion receives a bond-valence sum of 0.68 *vu* from M°(2) and two M°(3) cations (Table 7, Fig. 1a). To satisfy the bond-valence requirements of the X°_{M} atom, additional bond-valence (1.32 *vu*) is needed from the M^H cation. In fact, the M^H cation provides a bond valence of 1.42 *vu*, and the corresponding M^H–X°_{M} distance is very short, 1.686 Å (Table 5). This particular distance is in accord with the bond topology of Group III, where the bond length varies from 1.684 (lamprophyllite-2*M*) to 1.77 Å (epistolite) (Sokolova 2006). There is one site, O(1), which corresponds to 2 *apfu*. This is the X°_{A} site in the terminology of Sokolova (2006) (Fig. 1a). This site receives a bond-valence of 1.03 *vu* (Table 7), and hence is dominated by monovalent anions. The chemical analysis gives 0.73 *apfu* F (Table 2), and to satisfy the electroneutrality requirements, we assign $F_{0.73}OH_{0.70}O_{0.57}$ to this site. We label it O(1) for better comparison with the crystal structure of barytolamprophyllite (Rastsvetaeva *et al.* 1995) and lamprophyllite (Krivovichev *et al.* 2003). In minerals of Group III, the X°_{A} site ideally corresponds to $(OH)_2$ (Sokolova 2006).

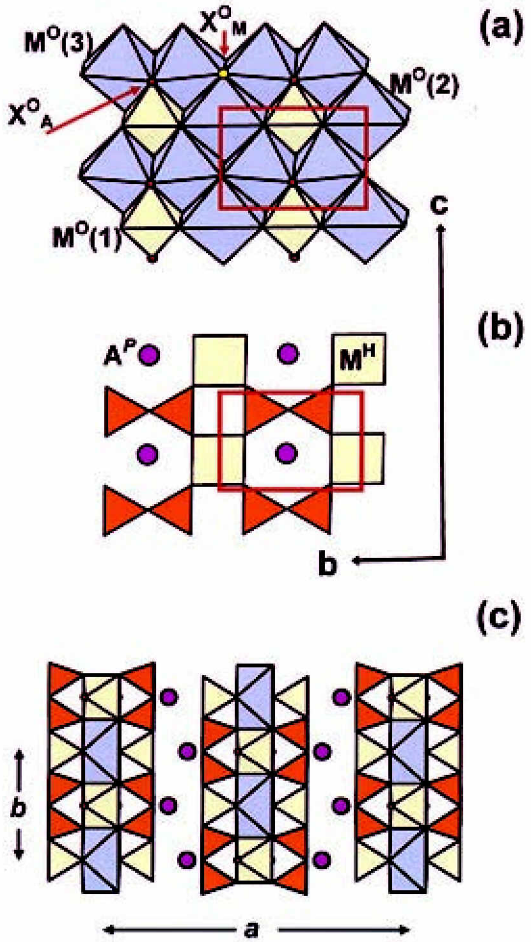

FIG. 1. The crystal structure of barytolamprophyllite: the O sheet (a) and the H sheet (b) of the TS block as viewed down [100]; general view of the crystal structure projected onto (001) (c). (SiO_4) tetrahedra are orange, Na octahedra are navy blue, Ti polyhedra, $^{[5]}M^H$ and $^{[6]}M^{\circ}(1)$, are yellow, the A^P atoms are shown as raspberry circles, the planar cell with translations $t_1 \approx 5.5$ Å and $t_2 \approx 7$ Å is shown in red.

Structure topology

In the crystal structure of barytolamprophyllite, the O sheet is of the form $M^{\circ}X^{\circ}_2$, where M° are cations and X° are anions (Fig. 1a). Structures with the TS block have 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, $\mathbf{t_1} \wedge \mathbf{t_2} \approx 90°$. This minimal cell contains 4 $[M^{\circ}X^{\circ}_2]$ (shown in red in Fig. 1a). In the H sheet, (SiO_4) tetrahedra link together to form (Si_2O_7) groups. These (Si_2O_7) groups and M^H square pyramids share common vertices to form the H sheet (Fig. 1b). The [10]-coordinated A^P cations are displaced from the plane of the H sheet and are located just above the centers of large voids in the H sheet (Fig. 1b). The H and O sheets link *via* common vertices of M°, Si and M^H polyhedra to form the TS block (Fig. 1c). There are two *TS* blocks per unit cell in the crystal structure of barytolamprophyllite (Fig. 1c). Along the **a** direction, the TS blocks alternate with layers of A^P atoms, which constitute the **I** block. The crystal structure of barytolamprophyllite is topologically identical to those of lamprophyllite and nabalamprophyllite.

CHEMICAL FORMULAE FOR LAMPROPHYLLITE, NABALAMPROPHYLLITE AND BARYTOLAMPROPHYLLITE

General formula

Sokolova (2006) wrote the following general formula for the TS block within the planar cell: $A^P_2\ B^P_2\ \mathbf{M^H_2\ M^{\circ}_4\ (Si_2O_7)_2\ X_{4+n}}$, where M° = cations of the O sheet, M^H = cations of the H sheet and A^P, B^P = cations at the peripheral (*P*) sites, $X_{4+n} = X^{\circ}_4 + X^P_{M2} + X^P_{A2}$, where X°_4 anions are common vertices of M° octahedra and two M^H and two A^P polyhedra (they are the X°_{M} and X°_{A} anions), and anions X^P_M and X^P_A belong to the M^H and A^P polyhedra on the outside of the TS block

TABLE 4. FINAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN BARYTOLAMPROPHYLLITE

Atoms	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
A^P	0.28240(2)	0	0.26285(6)	0.0158(2)	0.00744(18)	0.00770(19)	0	0.00154(12)	0	0.01030(13)
M^H	0.14603(3)	0	0.70520(11)	0.0103(3)	0.0069(3)	0.0047(3)	0	0.0014(2)	0	0.0073(2)
$M^O(1)$	0	½	0	0.0301(6)	0.0060(5)	0.0335(7)	0	−0.0225(5)	0	0.0253(3)
$M^O(2)$	0	0	0	0.0235(12)	0.0173(12)	0.0180(12)	0	0.0093(9)	0	0.0191(5)
$M^O(3)$	0	0.26016(15)	½	0.0230(6)	0.0135(5)	0.0141(5)	0	0.0053(4)	0	0.0166(3)
Si	0.13981(3)	0.28427(10)	0.20240(12)	0.0118(3)	0.0053(3)	0.0068(3)	0.0003(2)	0.0014(2)	−0.0001(2)	0.0079(2)
O(1)	0.44479(16)	0	0.2738(6)	0.0230(16)	0.0272(18)	0.0268(17)	0	0.0103(12)	0	0.0251(10)
O(2)	0.17024(10)	0.1883(3)	0.4639(3)	0.0182(9)	0.0101(9)	0.0091(8)	0.0023(7)	0.0012(7)	0.0004(7)	0.0125(4)
O(3)	0.17064(10)	0.1874(3)	0.9686(3)	0.0178(9)	0.0090(8)	0.0092(8)	−0.0028(6)	0.0033(7)	−0.0005(7)	0.0119(4)
O(4)	0.17175(14)	½	0.2170(5)	0.0142(12)	0.0060(11)	0.0107(12)	0	0.0015(9)	0	0.0103(5)
O(5)	0.05813(10)	0.2950(3)	0.1705(4)	0.0116(8)	0.0102(9)	0.0162(9)	0.0002(7)	0.0006(7)	0.0013(7)	0.0128(4)
O(6)	0.06071(15)	0	0.6672(6)	0.0121(13)	0.0356(18)	0.0133(13)	0	0.0025(10)	0	0.0202(7)

TABLE 5. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BARYTOLAMPROPHYLLITE

$M^O(1) - O(1)$	1.944(3)	×2	$M^O(2) - O(6)_a$	2.282(3)	×2
$M^O(1) - O(5)$	2.017(2)	×4	$M^O(2) - O(5)$	2.520(2)	×4
$\langle M^O(1) - O \rangle$	1.993		$\langle M^O(2) - O \rangle$	2.441	
$M^O(3) - O(5)$	2.249(2)	×2	$M^H - O(6)$	1.686(3)	
$M^O(3) - O(1)_b$	2.303(3)	×2	$M^H - O(2)$	1.969(2)	×2
$M^O(3) - O(6)$	2.335(2)	×2	$M^H - O(3)$	1.972(2)	×2
$\langle M^O(3) - O \rangle$	2.296		$\langle M^H - O \rangle$	1.914	
Si – O(5)	1.616(2)		$A^P - O(3)_b$	2.768(2)	×2
$Si - O(3)_a$	1.623(2)		$A^P - O(2)_b$	2.770(2)	×2
Si – O(2)	1.624(2)		$A^P - O(4)_d$	2.850(3)	
Si – O(4)	1.660(1)		$A^P - O(4)_b$	2.856(3)	
<Si – O>	1.631		$A^P - O(3)_h$	2.904(2)	×2
			$A^P - O(2)$	2.920(2)	×2
$Si - O(4) - Si_c$	135.3(2)		$\langle A^P - O \rangle$	2.843	

a: *x*, *y*, *z* – 1; b: –*x* + ½, –*y* + ½, –*z* + 1; c: *x*, –*y* + 1, *z*; d: –*x* + ½, –*y* + ½, –*z*.

[in the intermediate space (**I**) between two TS blocks]; n is the number of X^P anions: n = 0, 2, 4 depending on the coordination of the M^H site and the position of the A^P polyhedron relative to the adjacent TS block. The core of the TS block, $\mathbf{M^H_2\ M^O_4\ (Si_2O_7)_2\ X_4}$, is shown in bold; the stoichiometry of this part of the TS block is invariant.

Sokolova (2006) wrote the general formula of lamprophyllite, barytolamprophyllite and nabalamprophyllite as $A^P_2\ M^H_2\ M^O_4\ (Si_2O_7)_2\ X^O_4$ (see Table 1), where A^P_2 represents the **I** block and $M^H_2\ M^O_4\ (Si_2O_7)_2\ X^O_4$ represents the TS block. In barytolamprophyllite, the total charge of the TS block [of ideal composition $Ti_2\ Na_3\ Ti\ (Si_2O_7)_2\ O_2\ (OH)_2$] is –3, and the **I** block has an ideal composition (BaK) with a total charge of +3. We thus write the ideal formula of barytolamprophyllite as $(BaK)Ti_2\ Na_3\ Ti\ (Si_2O_7)_2\ O_2\ (OH)_2$ or $(BaK)\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$. Note that this ideal formula is neutral. The ideal formulae of lamprophyllite, $(SrNa)\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$, and nabalamprophyllite, $Ba\ Na\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$, also are neutral.

Why, in several cases, have the ideal formulae for **lamprophyllite**, $(Sr,Ba)_2\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$, and **barytolamprophyllite** $(Ba,Sr)_2\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$, been written with an excess charge of +1? Let us examine the formula $(Sr,Ba)_2\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$. The aggregate charge of the fixed part of the formula, $Na_3\ Ti_2\ (Si_2O_7)_2\ O_2\ (OH)_2$ is $1^+ \times 3 + 4^+ \times 3 + 2^- \times 2 + 4^+ \times 4 + 2^- \times 14 + 1^- \times 2 = 3^-$. A stable structure *must* accord with the electroneutrality principle, and hence the aggregate charge of the alkali and alkaline-earth part of the formula must have a net charge of 3^+. To write the formula as $(Sr,Ba)_2$ violates the electroneutrality principle, as $(Sr,Ba)_2$ has a net charge of 4^+. Inspection of Table 2 indicates that monovalent cations form a major part of the A^P site: 0.61 K. The properties of an end-member include the following requirements: (1) the end-member formula must be fixed, and (2) the structure must show the maximum degree of order consonant with the electroneutrality principle. For barytolamprophyllite examined here, the resulting end-member formula is $(BaK)\ Na_3\ Ti\ (Si_2O_7)_2\ O_2\ (OH)_2$.; the parentheses indicate that Ba and K occupy the same site, but there is no comma, as their relative amounts in the end-member are fixed by the electoneutrality principle.

Reconsideration of the analytical data

Consider the chemical data for lamprophyllite and barytolamprophyllite, taken from literature (Table 8). There are the first analytical data on these minerals, compiled by Anthony *et al.* (1995): Dana (1899), Vlasov (1966) for lamprophyllite, and Dudkin (1959) and Peng & Chang (1965) for barytolamprophyllite. Comparatively recent analyses were done by Johnsen *et al.* (1994) for lamprophyllite and barytolamprophyllite. Three analyses were done on samples used for crystal-structure refinement: lamprophyllite (Krivovichev *et al.* 2003), barytolamprophyllite (this work) and nabalam-

TABLE 6. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR BARYTOLAMPROPHYLLITE

Site	Site-scattering	Site population	Calculated site-scattering	$\langle X–\varphi\rangle_{calc.}$* Å	$\langle X–\varphi\rangle_{obs}$ Å
$^{[10]}A^P$	77.2(2)	0.88 Ba + 0.61 K + 0.33 Sr + 0.05 Ca + 0.13 □	74.4	2.886	2.843
$^{[5]}M^H$	43.0(2)	1.97 Ti + 0.03 Al	43.7	1.890	1.914
$M^O(1)$	22.0(1)	0.94 Ti + 0.05 Fe^{3+} + 0.01 Nb	22.4	1.975	1.993
$M^O(2)$	11.0(1)	1.00 Na	11.0	2.400	2.441
$M^O(3)$	30.5(2)	1.09 Na + 0.30 Fe^{2+} + 0.28 Mn^{2+} + 0.08 Ca + 0.05 Mg + 0.20 □	30.0	2.304	2.296
O(1)	17.0	0.73 F + 0.70 OH + 0.57 O	16.7		

* ionic radii for $^{[4]}O^{2-}$, $^{[4]}OH^-$, $^{[4]}F^-$, Ti, Nb, Al, Mg, Mn^{2+}, Fe^{2+}, Fe^{3+}, Na, Ba, Sr, K are from Shannon (1976); φ: unspecified anion.

TABLE 7. BOND-VALENCE* TABLE (*vu*) FOR BARYTOLAMPROPHYLLITE

Atom	Si	A^P	M^H	$M^O(1)$	$M^O(2)$	$M^O(3)$	Σ
O(1)				$0.63^{\times 2}\downarrow$		$0.20^{\times 2}\downarrow\rightarrow$	1.03
O(2)	1.02	$0.20^{\times 2}\downarrow$ $0.14^{\times 2}\downarrow$	$0.64^{\times 2}\downarrow$				2.00
O(3)	1.02	$0.20^{\times 2}\downarrow$ $0.14^{\times 2}\downarrow$	$0.63^{\times 2}\downarrow$				1.99
O(4)	$0.92^{\times 2}\rightarrow$	$0.16^{\times 2}\downarrow$					2.16
O(5)	1.04			$0.56^{\times 4}\downarrow$	$0.17^{\times 4}\downarrow$	$0.25^{\times 2}\downarrow$	2.02
O(6)			1.42		$0.26^{\times 2}\downarrow$	$0.21^{\times 2}\downarrow\rightarrow$	2.10
Total	4.00	$^{[10]}$1.68	3.96	3.50	1.20	1.32	
Aggr. charge	4.00	1.59	3.99	3.96	1.00	1.23	

* Bond-valence parameters are from Brown (1981).

prophyllite (Chukanov *et al.* 2004). We have calculated chemical formulae for these nine samples on the basis of 4 Si *apfu* and have assigned site populations for groups of atoms in accord with the lamprophyllite-type structure. In compositions (1) and (6), the sum of cations is in excess of the number of available sites by 0.5 *apfu*; therefore, these analyses contain significant errors. The sum of the anions (ideally 18) is lower in many cases and is close to 18.7 *pfu* in composition (6). Although the results in Table 8 are not very accurate, we can still see that: (1) the two A^P sites include A^{2+} and A^+ cations; (2) at the A^P site, divalent cations are slightly dominant over monovalent cations.

We now modify our calculation of the formulae, taking into account the crystal chemistry of the lamprophyllite structure-type (Sokolova 2006): (1) monovalent anions are dominant at the X^O_A site, giving 2 *apfu*, and the content of H_2O in the chemical composition can be calculated from the equation, F + OH = 2 *apfu*; (2) the Ti-dominant $M^O(1)$ site is invariably fully occupied and can contain Ti, Nb, Fe^{3+} and Al; (3) Fe^{2+} occurs at one of the 3 M^O sites in the O sheet; (4) all anion sites are fully occupied, and the sum of the anions must be 18 *apfu*. We discard compositions (1) and (6) of Dana (1889) and Peng & Chang (1965), respectively (Σ cations = 12.54 and 12.50 instead of 12.00 *apfu*), neglect any content of Cl (as there is no site suitable for this anion in the crystal structure), and reconsider the Fe^{3+}/Fe^{2+} values. Modified compositions are given in Table 9. Consideration of the unit formulae gives us certain information necessary to write ideal formulae and chemical formulae in general.

(1) At the two A^P sites, both divalent (Ba, Sr, Ca) and monovalent (K, Na) cations are present; divalent cations are dominant over monovalent cations; the total charge of two A^P cations is invariably less than +3.5.

(2) The sum of cations at three Ti-dominant sites (2 M^H + M^O) is 3 *apfu*, and the total charge is invariably more than +11.5.

(3) At the three M^O sites, Na^+ is the dominant cation, Na > 2 *apfu*. The total charge varies from +3.75 to +3.13.

(4) The total charge of cations [4 Si + 2 A^P + Ti-dominant (2 M^H + M^O) + Na-dominant 3 M^O] varies from +34.81 to +34.21. The total charge of anions results from 14 O atoms [of (SiO_4) tetrahedra], 2 O atoms (2 X^O_M) and 2 X^O_A anions. The 16 O atoms give aggregate charge of –32. The bond-valence sum at the two X^O_A anions varies from +2.81 to +2.21 *vu*, with a mean value of +2.53 *vu*. To satisfy the electroneutrality of the unit formula, we assign OH, F and O to the two X^O_A sites. Our assignments show that monovalent anions are always dominant at the two X^O_A sites (Table 9).

We can now more accurately calculate the content of H_2O in each case and make a final calculation of the unit formula. In Table 10, the sums of the cations vary from 12.05 to 11.67 *apfu* (ideally 12), and the sums of the anions vary from 17.97 to 18.04 *apfu* (ideally 18). This is a very good convergence and shows that the chemical formulae have been calculated appropriately. Note that in composition (4) (Dudkin 1959), Sr > Ba *apfu*, and therefore this mineral is Ba-rich lamprophyllite,

TABLE 8. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) OF LAMPROPHYLLITE, BARYTOLAMPROPHYLLITE AND NABALAMPROPHYLLITE§

mineral	lamprophyllite Sr > Ba					barytolam-prophyllite Ba > Sr			nabalam-prophyllite
sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	30.40	30.93	31.29	32.2	30.95	28.53	29.9	29.31	28.75
Nb_2O_5	–	0.16	–	0.43	–	–	–	0.11	–
TiO_2	27.48	27.14	29.27	30.30	28.15	26.6	28.68	28.39	27.8
Al_2O_3	–	0.56	0.10	–	0.22	1.12	0.04	0.16	0.44
Fe_2O_3	3.87	1.36	–	–	0.89	2.72	–	0.49	0.78
FeO	1.97	2.31	0.66	2.08	4.15	2.63	1.27	2.66	–
MnO	2.33	3.46	3.54	3.49	1.05	1.75	1.60	2.42	1.10
MgO	0.25	0.40	0.33	0.66	0.86	1.00	1.03	0.26	0.34
CaO	1.41	2.48	0.62	0.84	1.64	1.70	0.26	0.88	0.36
SrO	14.58	14.12	14.89	16.43	7.99	1.47	3.48	4.11	0.65
BaO	1.25	3.49	5.05	0.49	10.51	17.24	20.06	16.37	24.12
K_2O	2.31	1.26	0.65	0.45	1.82	3.10	0.94	3.52	0.94
Na_2O	12.35	10.64	11.34	12.38	9.8	9.52	11.99	7.90	11.14
F	1.82	1.10	–	–	1.45	1.60	–	1.69	1.18
CL	–	–	–	–	0.04	0.51	–	–	–
H_2O	–	0.56	–	–	0.99	0.70	–	0.77**	1.83
O=F	–0.77	–0.46			–0.61	–0.67		–0.71	–0.50
O=Cl					–0.01	–0.12			
Total	99.25	99.51	97.74	99.75	99.89	99.4	99.25	98.33	98.93
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Ba	0.06	0.18	0.25	0.02	0.53	0.95	1.05	0.88	1.32
Sr	1.11	1.06	1.10	1.18	0.60	0.12	0.27	0.33	0.05
Ca	0.10	0.17	0.05	0.12	0.12	0.13	0.04	0.05	–
ΣA^{P2+}	1.27	1.41	1.40	1.32	1.25	1.20	1.36	1.26	1.37
K	0.39	0.21	0.11	0.07	0.30	0.55	0.16	0.61	0.17
Na	0.44	0.47	0.36	0.66	0.13	0.33	0.52	–	0.50
ΣA^{P+}	0.83	0.68	0.47	0.73	0.43	0.88	0.68	0.61	0.67
$\Sigma 2A^{P}$	2.10	2.09	1.87	2.05	1.68	2.07	2.04	1.87	2.04
Ti	2.72	2.64	2.81	2.83	2.74	2.81	2.89	2.91	2.91
Nb	–	0.01	–	0.02	–	–	–	0.01	–
Fe^{3+}	0.38	0.13	–	–	0.09	0.29	–	0.05	0.08
Al	–	0.09	0.02	–	0.03	0.19	0.01	0.03	0.07
$\Sigma 3(2M^{H}+M^{O})$	3.10	2.87	2.83	2.85	2.86	3.29	2.90	3.00	3.06
Na	2.71	2.20	2.45	2.32	2.15	2.26	2.59	2.09	2.51
Fe^{2+}	0.22	0.25	0.07	0.22	0.45	0.31	0.14	0.30	–
Mn^{2+}	0.26	0.38	0.38	0.37	0.12	0.21	0.18	0.28	0.13
Ca	0.10	0.17	0.04	–	0.11	0.13	–	0.08	0.05
Mg	0.05	0.08	0.06	0.12	0.17	0.21	0.21	0.05	0.07
$\Sigma 3M^{O}$	3.34	3.08	3.00	3.03	3.00	3.12	3.12	2.80	2.76
F^-	0.76	0.45	–	–	0.59	0.71	–	0.73	0.52
$(OH)^-$	–	0.48	–	–	0.85	0.66	–	0.70	1.70
Cl^-	–	–	–	–	0.01	0.12	–	–	–
ΣX^-	0.76	0.93	–	–	1.45	1.49	–	1.43	2.22
Σcations	12.54	12.03	11.70	11.93	11.70	12.50	12.05	11.67	11.86
Σanions	18.06	17.82	17.07	17.27	17.85	18.68	17.30	17.98	18.23

* formula contents on a basis of 4 Si *apfu*.

** H_2O content calculated from results of structure refinement, $2X^{O}_{A}$ (*apfu*) = 0.73F + 0.70OH + 0.57O.

Sources: (1) Dana (1899), (2) Vlasov (1966), (3) Johnsen *et al.* (1994): sample MM55312, (4) Krivovichev *et al.* 2003, (5) Dudkin (1959): sample 1, (6) Peng & Chang (1965), (7) Johnsen *et al.* (1994): sample NM6004/8B, (8) this work, (9) Chukanov *et al.* (2004). § The chemical data reported here are as presented in the original articles.

TABLE 9. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) OF LAMPROPHYLLITE, BARYTOLAMPROPHYLLITE AND NABALAMPROPHYLLITE§

mineral	lamprophyllite Sr > Ba				barytolam-prophyllite Ba > Sr		nabalam-prophyllite
sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Fe_2O_3†	2.62	0.73	1.58	2.32	1.00	0.49	0.20
FeO†	1.18	–	0.66	2.86	0.37	2.66	0.52
H_2O**	1.80	2.35	2.41	1.63	2.24	0.77	1.60
O=F	–0.46	–	–	–0.61	–	–0.71	–0.50
Total	100.87	100.16	102.32	100.64	101.59	98.33	98.64
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Ba	0.18	0.25	0.02	0.53	1.05	0.88	1.32
Sr	1.06	1.11	1.18	0.60	0.27	0.33	0.05
Ca	0.17	0.05	0.06	0.10	0.04	0.05	–
ΣA^{P2+}	1.41	1.41	1.26	1.23	1.36	1.26	1.37
K	0.21	0.11	0.07	0.30	0.16	0.61	0.17
Na	0.40	0.39	0.61	0.30	0.54	–	0.50
ΣA^{P+}	0.61	0.50	0.68	0.60	0.70	0.61	0.67
$\Sigma 2A^{P}$	2.02	1.91	1.94	1.83	2.06	1.87	2.04
$2A^{P}$ charge	+3.40††	+3.32	+3.20	+3.06	+3.32	+3.13	+3.34
Ti	2.66	2.81	2.83	2.74	2.89	2.91	2.91
Nb	0.01	–	0.02	–	–	0.01	–
Fe^{3+}	0.26	0.07	0.15	0.23	0.10	0.05	0.02
Al	0.09	0.02	–	0.03	0.01	0.03	0.07
$\Sigma 3(2M^{H}+M^{O})$	3.02	3.00	3.00	3.00	3.00	3.00	3.00
$(2M^{H}+M^{O})$ charge	+11.66	+11.51	+11.87	+11.74	+11.89	+11.93	+11.91
Na	2.27	2.42	2.37	2.16	2.57	2.09	2.51
Fe^{2+}	0.13	–	0.07	0.31	0.04	0.30	0.06
Mn^{2+}	0.38	0.38	0.37	0.12	0.18	0.28	0.13
Ca	0.17	0.04	0.06	0.13	–	0.08	0.05
Mg	0.08	0.06	0.12	0.17	0.21	0.05	0.07
$\Sigma 3M^{O}$	3.03	2.90	2.99	2.89	3.00	2.80	2.82
$3M^{O}$ charge	+3.75	+3.38	+3.61	+3.62	+3.43	+3.51	+3.13
Total charge of cations	+34.81	+34.21	+34.68	+34.43	+34.64	+34.57	+34.38
BVS‡ at $2X^{O}_{A}$	+2.81	+2.21	+2.68	+2.43	+2.64	+2.57	+2.38
F^-	0.45	–	–	0.59	–	0.73	0.52
$(OH)^-$	0.74	1.79	1.32	0.99	1.33	0.70	1.10
O^{2-}	0.81	0.21	0.68	0.41	0.67	0.57	0.38
$\Sigma 2X^{O}_{A}$	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Σcations	12.03	11.70	11.93	11.70	12.05	11.67	11.86

§ As is made clear in these footnotes, the chemical data from original papers have been modified.

* wt.% of SiO_2, Nb_2O_5, TiO_2, Al_2O_3, MnO, MgO, CaO, SrO, BaO, K_2O, Na_2O and F are the same as in Table 8, formula contents on a basis of 4 Si *apfu*.

** H_2O content is calculated in accord with F + OH = 2 *apfu*, except for this work (6).

† The ratio Fe^{3+}/Fe^{2+} was recalculated from the crystal-topology basis (see text).

†† Where sum of cations exceeds the multiplicity of a site (or a group of sites), the charge is normalized to the multiplicity of a site (or a group of sites).

‡ bond-valence sum. Sources: (1) Vlasov (1966), (2) Johnsen *et al.* (1994): sample MM55312, (3) Krivovichev *et al.* 2003, (4) Dudkin (1959): sample 1, (5) Johnsen *et al.* (1994): sample NM6004/8B, (6) this work, (7) Chukanov *et al.* (2004).

not barytolamprophyllite [note that Krivovichev *et al.* (2003) erroneously referred to Dudkin (1959) as the author of the first description of *a Ba-analogue of lamprophyllite, barytolamprophyllite*]. Note also that in composition (7) (Table 8) [= composition (5) (Tables 9, 10)] (Johnsen et al. 1994), K < Na *apfu* at the AP site, and therefore this mineral is actually nabalamprophyllite, not barytolamprophyllite.

On the ideal formulae of lamprophyllite, nabalamprophyllite and barytolamprophyllite

We showed above (Tables 9, 10) that the total charge at three Ti-dominant sites, $[2M^{H} + M^{O}(1)]$, is invariably more than +11.5 (ideally +12), and that the ideal composition of three Ti-dominant sites is Ti_3. In every case, Na is dominant at three M^{O} sites $[M^{O}(2) + 2\,M^{O}(3)]$,

TABLE 10. CHEMICAL COMPOSITION (wt.%) AND FINAL UNIT-FORMULA* (*apfu*) FOR LAMPROPHYLLITE, BARYTOLAMPROPHYLLITE AND NABALAMPROPHYLLITE

mineral	lamprophyllite Sr>Ba				barytolamprophyllite, Ba>Sr		nabalamprophyllite
sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)
H_2O**	0.86	2.1	1.59	1.14	1.5	0.77	1.19
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Nb	0.01	–	0.02	–	–	0.01	–
Ti	2.64	2.81	2.83	2.74	2.89	2.91	2.91
Al^{3+}	0.09	0.02	0	0.03	0.01	0.03	0.07
$Fe^{3+\dagger}$	0.26	0.07	0.15	0.23	0.10	0.05	0.02
Fe^{2+}	0.13	–	0.07	0.31	0.04	0.30	0.06
Mn^{2+}	0.38	0.38	0.37	0.12	0.18	0.28	0.13
Mg	0.08	0.06	0.12	0.17	0.21	0.05	0.07
Ca	0.34	0.09	0.11	0.23	0.04	0.13	0.05
Sr	1.06	1.10	1.18	0.60	0.27	0.33	0.05
Ba	0.18	0.25	0.02	0.53	1.05	0.88	1.32
K	0.21	0.11	0.07	0.30	0.16	0.61	0.17
Na	2.67	2.81	2.98	2.46	3.11	2.09	3.01
F	0.45	–	–	–	–	0.73	0.52
H^+	0.74	1.79	1.32	0.98	1.34	0.70	1.10
Σ cations	12.03	11.70	11.93	11.70	12.05	11.67	11.86
Σanions	18.01	18.00	18.01	17.97	18.02	17.98	18.04

Note that the chemical data from original papers have been modified, as explained here. * The wt.% values are the same as in Table 9; formula contents are calculated on a basis of 4 Si^{4+} apfu; ** H_2O content was calculated on the basis of electroneutrality requirements. † Fe^{3+}/Fe^{2+} was calculated as in Table 9.
Columns: (1) Vlasov (1966), (2) Johnsen *et al.* (1994), sample MM55312, (3) Krivovichev *et al.* 2003, (4) Dudkin (1959), sample 1, (5) Johnsen *et al.* (1994), sample NM6004/8B, (6) This work, (7) Chukanov *et al.* (2004).

Na > 2 *apfu* (Tables 9, 10), and we can write the ideal composition of the three M° sites as Na_3. Monovalent anions, OH + F, are invariably dominant at the two X°_A sites, and we can write the ideal composition of the two X°_A anions as $(OH)_2$. So far, we can write the ideal formula as $A^P_2\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$, which leaves us with A^P_2 to assign with a total charge of +3. Note that nabalamprophyllite is the only mineral with lamprophyllite-type structure in which there are two independent Ba- and Na-dominant A^P sites. The observed total charge of the two A^P cations is in every case less than +3.5 (Tables 9, 10) and ideally is +3; therefore, we write the ideal composition of the two A^P sites as $(A^{2+}\ A^+)$. This gives us the ideal formula $(A^{2+}\ A^+)\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$ for

lamprophyllite	$A^{2+}\ A^+ = (SrNa)$,
barytolamprophyllite	$A^{2+}\ A^+ = (BaK)$,
nabalamprophyllite	$A^{2+}\ A^+ = (BaNa)$,

and suggests another possible composition: $(SrK)\ Na_3\ Ti_3\ (Si_2O_7)_2\ O_2\ (OH)_2$.

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