

The crystal chemistry of lamprophyllite-related minerals: a review

RAMIZA K. RASTSVETAeva^{1,*}, NIKITA V. CHUKANOV² and SERGEY M. AKSENOV^{1,3}

¹ Shubnikov Institute of Crystallography RAS, Moscow, 119333, Russia

*Corresponding author e-mail: rast@ns.crys.ras.ru

² Institute of Problems of Chemical Physics, Chernogolovka, Moscow region, 142432, Russia

³ St. Petersburg State University, St. Petersburg, 199034, Russia

Abstract: The crystal structures of the lamprophyllite-related minerals are based upon *HOH* modules consisting of a central octahedral *O* sheet sandwiched between two heteropolyhedral *H* sheets. The general crystal-chemical formula for these minerals can be written as $^{[10-11]}A_2 [^{[6]}M1^{[6]}M2^{[6]}M3X_2] [^{[5]}L_2(Si_2O_7)_2O_2]$, where the contents of the *O* and *H* sheets are given in square brackets in this order and *A* = Ba, Sr, K, Na.; *M1* = Na, Mn²⁺; *M2* = Na, Mn²⁺, Fe²⁺, Ca; *M3* = Ti, Mn²⁺, Mg, Fe³⁺, Fe²⁺; *L* = Ti, Fe³⁺; *X* = OH, O, F. According to the unit-cell parameters and symmetry, lamprophyllite-related minerals can be subdivided into five structure types: I (monoclinic polytypes, *C2/m*); II (orthorhombic polytypes, *Pnmm*), III (nabalamprophyllite, BaNa[Na₃Ti(OH)₂][Ti₂(Si₂O₇)₂O₂], monoclinic, *P2/m*, with an ordered arrangement of the interlayer Ba²⁺ and Na⁺ cations), IV (triclinic, *P1*) and V (triclinic, *P1*). The triclinic members (types IV and V) include schüllerite and its analogues, which differ from the lamprophyllite-group minerals *sensu stricto* in their symmetry and topology of the *HOH* modules. The end-member formulae of lamprophyllite-related minerals and the position of schüllerite in the ranks of heterophyllosilicates are discussed.

Key-words: chemical composition, crystal-chemical formulae, heterophyllosilicates, lamprophyllite-related minerals, OD structure, polytypism, schüllerite, topological features.

Introduction

The crystal structures of most layered silicate minerals are based upon two-dimensional layers consisting of different types of modules (Back & Mandarino, 2008; Belov, 1976; Ferraris *et al.*, 2004; Ferraris & Gula, 2005; Sokolova, 2006; Ferraris, 2008; Rastsvetaeva & Aksenov, 2011). Each module contains a central *O* (octahedral) sheet of edge-sharing *M*-centred octahedra linked to either one or two sheets of Si-centred tetrahedra (*T* sheets) or (in the case of heterophyllosilicates) two mixed *H* (heteropolyhedral) sheets containing Si-centred tetrahedra and *L*-centred octahedra or ‘semioctahedra’ (tetragonal pyramids). In heterophyllosilicates, the *O* and *H* sheets are connected *via* common O atoms to form *HOH* modules, which determine the values of two lattice parameters: ~ 5.4 Å and ~ 7.1 Å (most frequently designated as *a* and *b*). Heterophyllosilicates can formally be derived from pure phyllosilicates by replacing tetrahedral (*T*) sheets by mixed (heteropolyhedral) sheets containing either five- or six-coordinated *L* cations (Belov, 1976).

In heterophyllosilicates, SiO₄ tetrahedra usually form [Si₂O₇]⁶⁻ groups and the ratio *L*:(Si₂O₇) varies from 1:1 to 1:8. The stoichiometry of the heterophyllosilicates with *L*:(Si₂O₇) = 1:1 can be described by the general formula

$$A_2 \{ M_4 [L_2 X_{2+p} (Si_2O_7)_2] Y_2 \} W \quad (1)$$

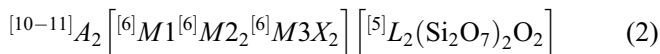
where *A* are low-field-strength interlayer cations (usually alkali and/or alkaline-earth metals), *M* are octahedral cations of the *O* sheet, *L* are cations with five- or six-fold coordination belonging to the *H* sheet, *X* and *Y* = O, F and OH; *W* are H₂O molecules and/or complex anions such as [PO₄]³⁻, [SO₄]²⁻ and [CO₃]²⁻; *p* = 0–2 (Ferraris & Gula, 2005). The value of *p* depends upon the coordination number of *L*. In the case of an octahedral coordination, the sixth corner can be either non-shared (*p* = 2) or shared with an octahedron from the adjacent layer (*p* = 1). If the coordination polyhedron of *L* is a square pyramid, then *p* = 0.

The most common *M* cations are Ti, Nb, Fe, Mn, Na, and Mg. In the minerals with a deficit of the octahedral cations, vacancy may be dominant in some octahedral sites as observed in delindeite, Ba₂[(Na,Ti)₄][Ti₂(O,OH)₂Si₄O₁₄](O,OH)₂(H₂O,OH)₂ (Ferraris *et al.*, 2001). The *L* site may contain Ti as well as Nb, Fe and Mn. According to Makovicky (1997), in a merotype series, one building module is permanent, whereas the second one (or third, fourth, *etc.*) is specific for each member of the series. A series is called ‘plesiotype’ when all its members share the same modules that, however, may slightly differ in their chemistry and configuration. The minerals that can be described using the general formula (1) are members of the bafertisite mero-plesiotype series (Ferraris & Gula, 2005). In most

heterophyllosilicate minerals, the *L* site is occupied by Ti. The presence of the *L* cations and (Si₂O₇) groups in the ratio of 1:1 is a distinguishing feature of the members of the bafertsite series. The topological features and the structural hierarchy of titanium disilicate minerals have been discussed elsewhere (Sokolova, 2006, 2012; Sokolova & Cámara, 2008, 2013).

The *HOH* module has a negative charge, and its chemical composition displays large variations. The change of the coordination number of the *L* site from six to five results in a decrease of the negative charge of the *H* sheet (Ferraris & Gula, 2005). The total charge of the *H* sheet also depends on the *L*: (Si₂O₇) ratio. The total negative charge of the *HOH* module decreases with the increase of the charge of the *M* cation, *e.g.* due to the replacement of Na⁺ by Fe²⁺ or Mn²⁺. In such minerals as epistolite, (Na, □)₂[(Na, Ti)₄][Nb₂(O, H₂O)₄Si₄O₁₄](OH, F)₂·2H₂O (Németh *et al.*, 2005), and murmanite, (Na, □)₂[(Na, Ti)₄][Ti₂(O, H₂O)₄Si₄O₁₄](OH, F)₂·2H₂O (Rastsvetaeva & Andrianov, 1986), formed as a result of leaching of interlayer cations (*e.g.* Lykova *et al.*, 2015a and b), the overall negative charge of the *HOH* module is relatively low.

The large family of bafertsite-series minerals includes lamprophyllite-related minerals with the general formula:



where *A* = Ba, Sr, K, Na, □; *M1* = Na, Ca, Mn²⁺; *M2* = Na, Mn²⁺, Fe²⁺, Ca; *M3* = Ti, Mn²⁺, Mg, Fe³⁺, Fe²⁺; *L* = Ti, Fe³⁺; *X* = OH, O, F (Rastsvetaeva & Aksenov, 2011; Chukanov *et al.*, 2012).

Two main specific features characterize the lamprophyllite-group minerals and related heterophyllosilicates: (i) the presence of the *HOH* modules containing *L* cations with fivefold coordination in the *H* sheet; (ii) the absence of interlayer *W* species (H₂O molecules and/or complex anions).

Heterophyllosilicates that belong to the lamprophyllite group of the bafertsite mero-plesiotype series are characterized by a rather wide structural and compositional diversity. According to the *Fleischer's Glossary of Mineral Species* (Back & Mandarino, 2008), the lamprophyllite group contains four mineral species: lamprophyllite, barytolamprophyllite, nabalamprophyllite and ericssonite. Unfortunately, in the last edition of this glossary (Back, 2014), ericssonite-2*M* and ericssonite-2*O* (isotypic with lamprophyllite-2*M* and lamprophyllite-2*O*, respectively) have not been included into the lamprophyllite group (Sokolova, 2006). On the other hand, delindeite and lileyite have been included into the group in the framework of the "TS-block supergroup" (TS = Titanium Silicate). However, it should be noted that delindeite differs from the lamprophyllite-group minerals in a number of important crystal-chemical features, including six-fold coordination of the *L* cations and the presence of interlayer H₂O molecules.

There is the problem of ambiguity in writing end-member formulae for lamprophyllite and barytolamprophyllite.

For example, the formulae (SrNa)Na₃Ti₃(Si₂O₇)₂O₂(OH)₂ and (BaK)Na₃Ti₃(Si₂O₇)₂O₂(OH)₂ accepted for these minerals (Sokolova & Cámara, 2008; Back, 2014), do not reflect strong predominance of Sr over Na and substantial predominance of Ba over K in the *A* site of most studied samples of lamprophyllite and barytolamprophyllite, respectively. The same problem arises with any other variant of the end-member formulae, as, *e.g.*, for lamprophyllite, (SrK)Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, Sr₂Na₃Ti₃(Fe³⁺Ti)(Si₂O₇)₂O₂(OH)₂, Sr₂Na₃Ti₃(Si₂O₇)₂O₂(OOH), and Sr₂Na₃Ti₃(Si₂O₇)₂O₂(OF). This problem is discussed in more detail below.

Recently, the lamprophyllite group has been complemented by several new mineral species and at present includes eight species approved by the IMA–CNMNC, as well as several potentially new minerals. In addition, for lamprophyllite, barytolamprophyllite and ericssonite, two polytypes are known: monoclinic 2*M* (space group *C2/m*) and orthorhombic 2*O* (space group *Pnmm*). In this contribution we discuss crystal-chemical relationships between the minerals of the lamprophyllite group and consider some new data in the framework of the "classical" nomenclature of heterophyllosilicates developed by Ferraris & Gula (2005) and Ferraris (2008) – *cf.*, *e.g.*, Sokolova (2006) and Sokolova & Cámara (2013).

Structure types: chemical composition, topological features, polytypism and crystal-chemical formulae

In the crystal structures of the lamprophyllite-related minerals, the shift of the *H* sheets with respect to the *O* sheet results in the topological changes of the *HOH* modules, whereas mutual shifts of the composite *HOH* modules in the *bc* plane result in the formation of 2*M*- and 2*O*-polytypes. Another source of crystal-chemical diversity is due to the ordering of the interlayer cations. All known lamprophyllite-related minerals can be subdivided into five structure types according to their chemical compositions, unit-cell parameters, topological features and symmetry (Tables 1–3). We provide below short descriptions of each type, together with historical notes on their studies.

Type I (lamprophyllite-2*M* type)

Among the minerals under consideration, members of the *lamprophyllite*–*barytolamprophyllite* solid-solution series are most widespread in nature. The most common 2*M* polytype of these minerals belongs to the structure type I and is characterized by a monoclinic unit cell (*a* ~ 19.21–20.34 Å, *b* ~ 7.01–7.10 Å, *c* ~ 5.34–5.41 Å, β ~ 94.8–96.8°) and the space group *C2/m* (Fig. 1). Originally, lamprophyllite and barytolamprophyllite were described as Sr- and Ba-dominant species, respectively (Dudkin, 1959; Dudkin *et al.*, 1964). Later crystal-structure studies established that large cations (Sr, Ba, K, Na and Ca) are located in the

Table 1. Unit-cell parameters and symmetry of all known mineral species and their polytypes within the lamprophyllite-group *sensu stricto*.

Mineral	Unit-cell parameters				Sp. Gr.	References
	<i>a</i> , Å	<i>b</i> , Å	β , °	<i>c</i> , Å		
<i>Type I</i>						
Lamprophyllite-2 <i>M</i>	19.215(5)	7.061(2)	96.797(4)	5.3719(15)	<i>C2/m</i>	Krivovichev <i>et al.</i> , 2003
Fluorlamprophyllite-2 <i>M</i>	19.255(2)	7.0715(7)	96.794(2)	5.3807(6)	<i>C2/m</i>	Andrade <i>et al.</i> , 2014
"Oxylamprophyllite"-2 <i>M</i>	19.431–19.489	7.086–7.086	96.75–96.75	5.386–5.392	<i>C2/m</i>	Saf'yanov <i>et al.</i> , 1983 Rastsvetaeva <i>et al.</i> , 1990
Barytolamprophyllite-2 <i>M</i>	19.744–19.897	7.099–7.117	96.68–96.77	5.409–5.411	<i>C2/m</i>	Rastsvetaeva & Dorfman, 1995; Sokolova & Cámara, 2008
<i>K-analogue of barytolamprophyllite-2M</i>	20.086(8)	7.099(3)	96.65(3)	5.411(1)	<i>C2/m</i>	Rastsvetaeva <i>et al.</i> , 1995
"Fluor-barytolamprophyllite-2 <i>M</i> "	19.83–19.96	7.07–7.09	96.5–96.7	5.39–5.43	<i>C2/m</i>	Peng & Zhang, 1965; Peng <i>et al.</i> , 1984; Akimenko <i>et al.</i> , 2015
Ericssonite-2 <i>M</i>	20.42	7.03	95.5	5.34	<i>C2/m</i>	Moore, 1971
Ferroericssonite-2 <i>M</i>	20.3459(10)	7.0119(3)	94.874(7)	5.3879(4)	<i>C2/m</i>	Kampf <i>et al.</i> , 2011
Lileyite-2 <i>M</i>	19.905(1)	7.098(1)	96.349(5)	5.405(1)	<i>C2/m</i>	Chukanov <i>et al.</i> , 2012
Emmerichite-2 <i>M</i>	19.9601(3)	7.0989(1)	96.367(1)	5.4074(1)	<i>C2/m</i>	Chukanov <i>et al.</i> , 2014; Aksenov <i>et al.</i> , 2014
<i>Type II</i>						
Lamprophyllite-2 <i>O</i>	19.128(4)	7.0799(14)		5.3824(11)	<i>Pnmm</i>	Krivovichev <i>et al.</i> , 2003
Barytolamprophyllite-2 <i>O</i> *	19.564(2)	7.1173(5)		5.4144(4)	<i>Pnmm</i>	Sokolova & Hawthorne, 2008
Ericssonite-2 <i>O</i> **	20.23–20.32	6.98–7.03		5.34–5.39	<i>Pnmm</i>	Moore, 1971; Matsubara, 1980
<i>Type III</i>						
Nabalamprophyllite-2 <i>M</i>	19.741(5)	7.105(4)	96.67(1)	5.408(2)	<i>P2/m</i>	Rastsvetaeva & Chukanov, 1999

Note: Mineral names not approved by the IMA CNMNC are italicized.

Here and in next table:

*In Sokolova & Hawthorne (2008), the 2*O* polytype of barytolamprophyllite is erroneously named "orthorhombic polytype of nabalamprophyllite".

**Orthoericssonite is discredited, since it corresponds to the orthorhombic polytype of ericssonite (Williams *et al.*, 2011).

Table 2. Dominant components in crystallographic sites of lamprophyllite-group minerals *sensu stricto*.

Mineral	Sites						References
	A/A'	M1	M2	M3	L/L'	X/X'	
<i>Type I</i>							
Lamprophyllite-2M	Sr	Na	Na	Ti	Ti	OH	Krivovichev <i>et al.</i> , 2003
Fluorlamprophyllite-2M	Sr	Na	Na	Ti	Ti	F	Andrade <i>et al.</i> , 2014
"Oxylamprophyllite-2M"	Sr	Na	Na	Ti	Ti	O	Rastsvetaeva <i>et al.</i> , 1990
Barytolamprophyllite-2M	Ba	Na	Na	Ti	Ti	OH	Rastsvetaeva & Dorfman, 1995; Sokolova & Cámara, 2008
<i>K-analogue of barytolamprophyllite-2M</i>	K	Na	Na	Ti	Ti	OH	Rastsvetaeva <i>et al.</i> , 1995
"Fluorobarytolamprophyllite-2M"	Ba	Na	Na	Ti	Ti	F	Peng & Zhang, 1965; Peng <i>et al.</i> , 1984; Akimenko <i>et al.</i> , 2015
Ericssonite-2M	Ba	Mn ²⁺	Mn ²⁺	Mn ²⁺	Fe ³⁺	OH	Moore, 1971
Ferroicssonite-2M	Ba	Fe ²⁺	Fe ²⁺	Fe ²⁺	Fe ³⁺	OH	Kampf <i>et al.</i> , 2011
Lilleyite-2M	Ba	Na	Na	Mg	Ti	F	Chukanov <i>et al.</i> , 2012
Emmerichite-2M	Ba	Na	Na	Fe ³⁺	Ti	F	Chukanov <i>et al.</i> , 2014; Aksenov <i>et al.</i> , 2014
<i>Type II</i>							
Lamprophyllite-2O	Sr	Na	Na	Ti	Ti	OH	Krivovichev <i>et al.</i> , 2003
Barytolamprophyllite-2O	Ba	Na	Na	Ti	Ti	OH	Sokolova & Hawthorne, 2008
Ericssonite-2O	Ba	Mn ²⁺	Mn ²⁺	Mn ²⁺	Fe ³⁺	OH	Matsubara, 1980
<i>Type III</i>							
Nabalamprophyllite-2M	Ba/Na	Na	Na	Ti	Ti/Ti	OH/O	Rastsvetaeva & Chukanov, 1999

Table 3. Unit-cell parameters, symmetry and dominant site components in the schüllerite-like structures (types IV, V).

Mineral	Unit-cell parameters					Sites			
	<i>a</i> (Å) / α (°)	<i>b</i> (Å) / β (°)	<i>c</i> (Å) / γ (°)	Space group	A/A'	M1/M2	M2'/M3	L/L'	X/X'
Schüllerite	5.4027(7) 99.816(1)	7.066(4) 99.624(1)	10.2178(1) 90.084(1)	<i>P</i> 1	Ba/Ba	Na/Mn ²⁺	Fe ²⁺ /Fe ³⁺	Ti/Ti	O/F
Fe ²⁺ -analogue of schüllerite	5.4061(1) 99.86(1)	7.0416(6) 99.78(1)	10.2077(7) 89.98(1)	<i>P</i> 1	Ba/Ba	Na/Ca	Fe ²⁺ /Mg	Ti/Ti	O/F
Mg-rich schüllerite-like mineral	5.396(1) 99.73(3)	7.071(1) 99.55(3)	10.226(2) 90.09(3)	<i>P</i> 1	Ba	Na	Mg	Ti	F
									Sokolova <i>et al.</i> , 2013

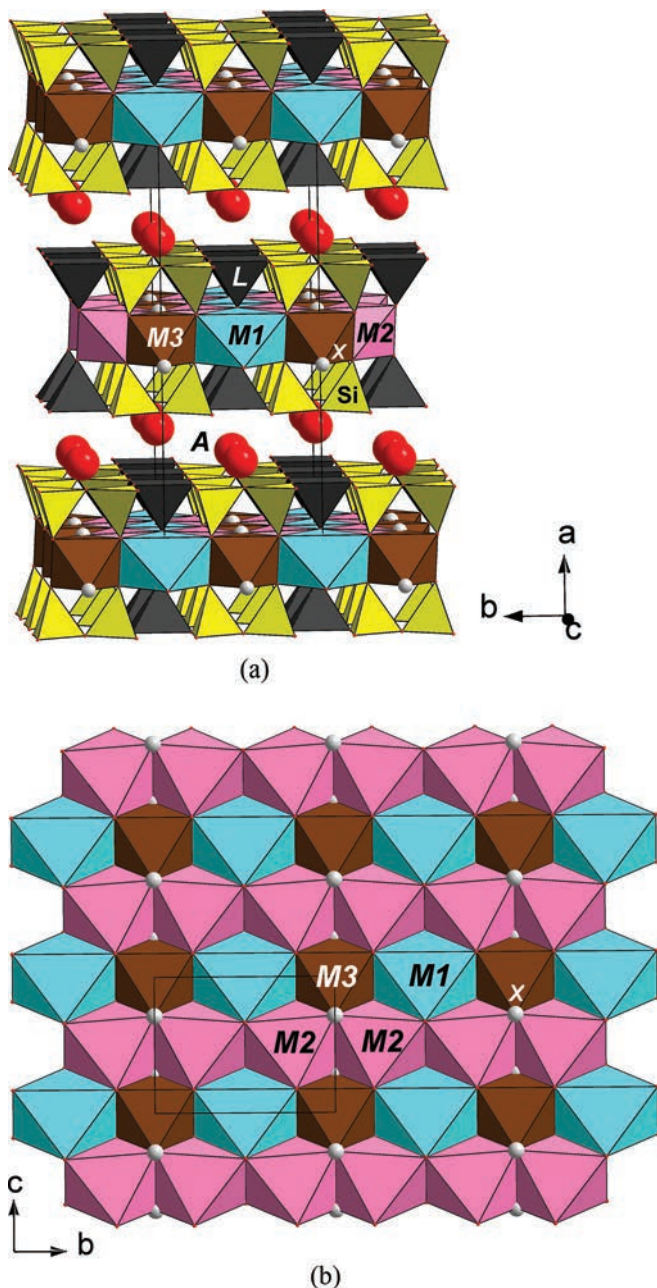
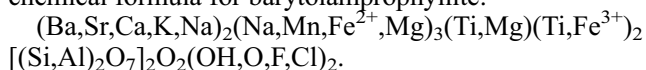


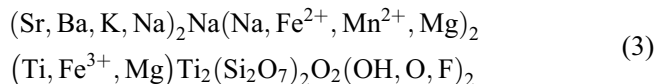
Fig. 1. Site designation in monoclinic (space group $C2/m$) lamprophyllite-related minerals belonging to the type I: general view (a) and O sheet (b). (online version in colour)

interlayer space between the HOH blocks. In addition, heterovalent substitutions are typical for the M and X sites. Taking into account these variations, Rastsvetaeva and Dorfman (1995) suggested the following general crystal-chemical formula for barytolamprophyllite:

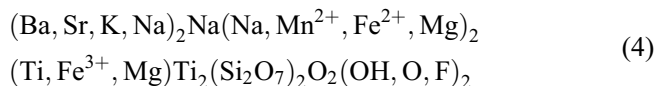


However, according to the available chemical data, this formula seems to be excessively detailed. Most reliable reported compositions correspond to $\text{Al} < 0.1$ atom per formula unit (*apfu*), $\text{Ca} < 0.2$ *apfu*, and Cl below the

detection limit. Recent structural and chemical studies (Krivovichev *et al.*, 2003; Sokolova & Cámara, 2008; Sokolova & Hawthorne, 2008) do not indicate any noticeable amounts of Fe in the L site. Therefore, on the basis of available structural data and chemical analyses (Johnsen *et al.*, 1994; Zaitsev & Kogarko, 2002; Azarova, 2004; Chukanov *et al.*, 2004), the following general crystal-chemical formulae can be suggested:

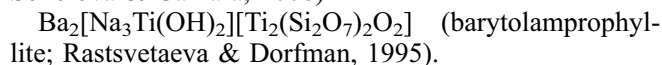
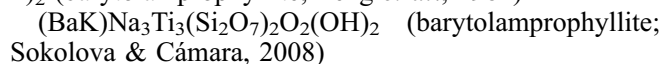
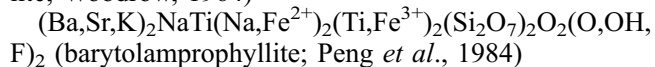
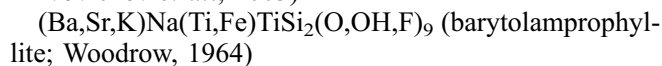
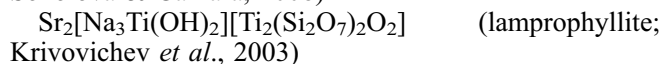
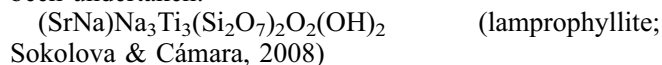


for lamprophyllite and



for barytolamprophyllite. These formulae contain the dominant and most important subordinate components in different cationic and anionic sites.

Numerous attempts to simplify the end-member formulae of lamprophyllite and barytolamprophyllite have been undertaken:



We note that all these formulae either do not conform to the real compositional and structural features of these minerals and/or are not charge-balanced. In particular, the formulae suggested by Sokolova & Cámara (2008) do not reflect the predominance of Sr and Ba in the A sites of lamprophyllite and barytolamprophyllite, respectively. In addition, most of them do not reflect the presence of Mn^{2+} , Fe^{2+} and Mg^{2+} in the $M2$ site (indeed, the total content of $\text{Mn}^{2+} + \text{Fe}^{2+} + \text{Mg}$ in lamprophyllite and barytolamprophyllite is typically between 0.6 and 1.0 *apfu*). In addition, it has been demonstrated that not only Na , but also K can be the main charge-balancing monovalent cation in the A site (Rastsvetaeva *et al.*, 1990; Zaitsev & Kogarko, 2002; Belyaevskaya & Borutsky, 1993).

On the basis of structural data for one uncommon sample with $\text{K}_{0.61}$ from the Khibiny alkaline massif, Sokolova and Cámara (2008) suggested for barytolamprophyllite the formula $(\text{BaK})\text{Na}_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$. In our opinion, this formula does not reflect the real composition of this mineral. In minerals belonging to the lamprophyllite–barytolamprophyllite series, the

total content of Ba + Sr is typically between 1.2 and 1.4 *apfu*, and, in most (about 90 %) of the samples, the K content is less than 0.5 *apfu* (Figs 2–4). Only four samples with K > 0.57 *apfu* are known; three of them originate from hyper-potassic associations of the Murun massif, Siberia, Russia (Konev *et al.*, 1996; note that the Murun alkaline complex is characterized by a high K content and a strong differentiation of K and Na between different rocks) and one sample (with $K_{0.61}$) originates from the Khibiny alkaline complex (Sokolova & Cámara, 2008). The only known but incompletely investigated K-dominant sample “K-barytolamprophyllite” (with K: Ba: Sr = 48: 42: 10) was

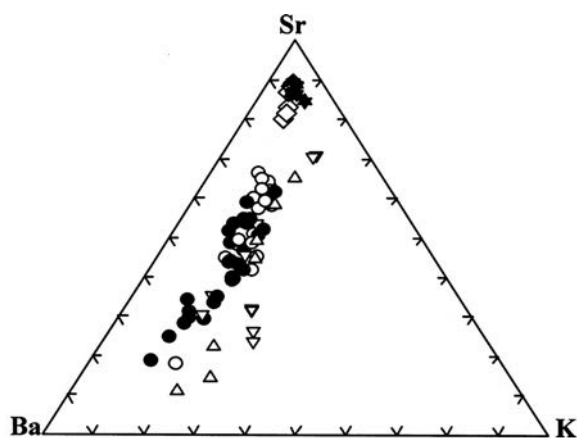


Fig. 2. Relative contents of Ba, Sr and K (apfu) in lamprophyllite and barytolamprophyllite from different rocks of Khibiny and from lujavrites of Lovozero (squares) alkaline massifs, Kola peninsula (after Azarova, 2004).

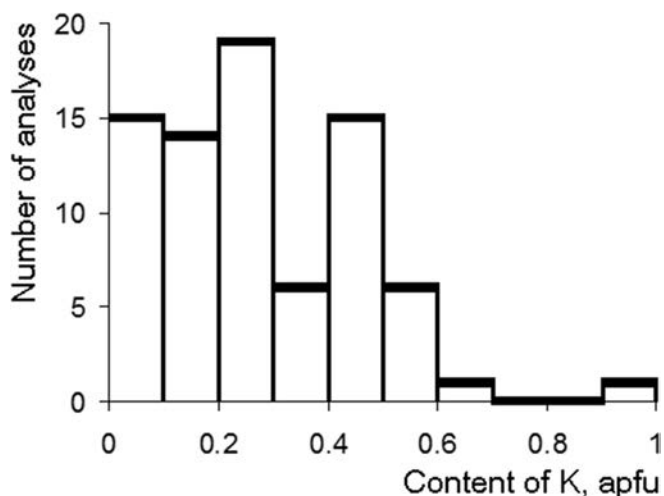


Fig. 3. The distribution of K content in lamprophyllite and barytolamprophyllite from alkaline massifs worldwide (after Chukanov *et al.*, 2004; Zaitsev & Kogarko, 2002; Azarova, 2004).

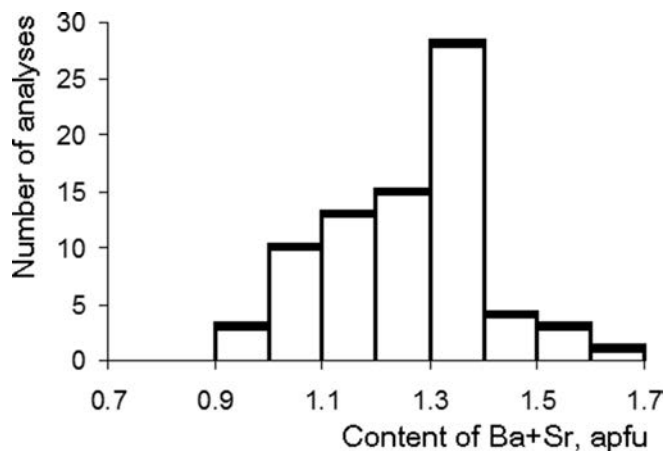


Fig. 4. The distribution of the Ba+Sr content in lamprophyllites from alkaline massifs worldwide (after Chukanov *et al.*, 2004; Zaitsev & Kogarko, 2002; Azarova, 2004).

discovered in the Murun alkaline massif (Rastsvetaeva *et al.*, 1995).

In addition to the heterovalent substitutions in the *A* site, there are wide heterovalent substitutions in the *M1*, *M2*, *M3* and *X* sites. Consequently, for lamprophyllite, along with the end-member formula $(\text{SrNa})\text{Na}_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ suggested by Sokolova and Cámara (2008), one may suggest the formulae $\text{Sr}_2\text{Na}_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2[\text{O}(\text{OH})]$ and $\text{Sr}_2\text{Na}_3\text{Fe}^{3+}\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$. If subordinate components such as Ba, Ca, Fe^{2+} , Mg, Mn and F are not taken into account, the real composition of lamprophyllite may be considered as intermediate between these three end-members.

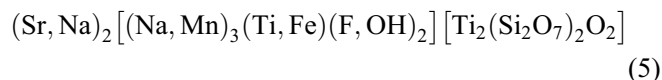
In most known samples, monovalent anions such as $(\text{OH})^-$ or, more rarely, F^- , dominate over O in the *X* site. Among seven samples studied by Sokolova and Cámara (2008), five samples are OH-dominant, one is F-dominant and one is O-dominant. As it follows from the above discussion, the formulae of lamprophyllite and barytolamprophyllite cannot be adequately and unambiguously idealized by the end-member compositions with integer coefficients and only one component in each site for the following reasons:

- (i) there are different ways of writing the idealized end-member formulae, and there are no obvious reasons to prefer one formula at the expense of the other;
- (ii) any simplified formula with integer coefficients does not reflect the real composition of the mineral: the formula $(\text{SrNa})\text{Na}_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ does not reflect the predominance of Sr in the *A* site; the formula $\text{Sr}_2\text{Na}_3\text{Ti}(\text{Fe}^{3+}\text{Ti})(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ does not reflect the predominance of Ti in the *L* site; the formula $\text{Sr}_2\text{Na}_3\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OOH})$ does not reflect the predominance of OH in the *X* site, *etc.*;

- (iii) every formula with only one component in each site is not charge-balanced.

The X anion site in the lamprophyllite-related minerals is shared between two $M2$ and one $M3$ octahedra (Fig. 1). Depending on the nature of cations present in these octahedra, the X site can be occupied by OH, F or O. For example, in lileite, the X site is occupied by F.

Fluorlamprophyllite, the F-dominant analogue of lamprophyllite, was found recently in the Poços de Caldas alkaline massif, Minas Gerais, Brasil, in association with natrolite, aegirine, analcime, nepheline, and microcline (Andrade *et al.*, 2014). The formula suggested for this mineral is $\text{Na}_3(\text{SrNa})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$. As in the case of lamprophyllite, this formula does not reflect the real chemical composition of the mineral and, in particular, the population of the A site. For example, the cotype material deposited in the RRUFF Project collection (deposition number R130421; see <http://rruff.info/>) has the following empirical formula $(\text{Sr}_{1.35}\text{Na}_{0.33}\text{Ca}_{0.15}\text{K}_{0.08})(\text{Na}_{2.30}\text{Mn}_{0.54}\text{Mg}_{0.16})(\text{Ti}_{2.63}\text{Fe}_{0.24}\text{Al}_{0.03})\text{Si}_{3.89}\text{O}_{16}[\text{F}_{1.15}(\text{OH})_{0.85}]$. A more adequate formula of fluorlamprophyllite could be written as follows:



Ericssonite, $\text{Ba}_2[\text{Mn}^{2+}_4(\text{OH})_2][\text{Fe}^{3+}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$ (Moore, 1971; Matsubara, 1980), and *ferroericssonite*, $\text{Ba}_2[\text{Fe}^{2+}_4(\text{OH})_2][\text{Fe}^{3+}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$ (Kampf *et al.*, 2011), are isotypic to the corresponding polytypes from the lamprophyllite–barytolamprophyllite series. Chemical analytical data on ericssonite-2*M* and ericssonite-2*O* from Långban, Sweden, under the names ericssonite and orthoericssonite (Moore, 1971), respectively, are in agreement with the idealized crystal-chemical formula $\text{Ba}_2\text{Mn}^{2+}_2\text{Mn}^{2+}_2\text{Mn}^{2+}_2\text{Fe}^{3+}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$. Merging the Mn^{2+} -dominant M -sites, the formula of ericssonite can be written as $(\text{Ba}, \text{Sr})_2(\text{Mn}^{2+}_4\text{Fe}^{2+})_4(\text{Fe}^{3+}, \text{Ti})_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH}, \text{O})_2$. Ferroericssonite was found at the Big Greek, Fresno Country, as well as at the Trumbull Peak, Mariposa Country, California, USA, and is a Fe^{2+} -analogue of ericssonite (Kampf *et al.*, 2011).

Sokolova and Cámara (2014) compared the crystal structures of ericssonite-2*O*, ferroericssonite and yoshimuraite, ideally $\text{Ba}_4\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OH})_2$, in terms of the topology of the *HOH* module. The authors explain topological differences between the *HOH* modules in yoshimuraite and minerals of the ericssonite–ferroericssonite series by the inability of Fe^{3+} (unlike Ti^{4+}) to contribute sufficient bond-valence to the X site, which results in different degrees of distortion of the M -octahedra. However, in general, there is no direct relation between the nature of the 5-coordinated cation of the H sheet and the topology of the *HOH* block. For example, barytolamprophyllite with Ti^{4+} in the 5-coordinated site has the same topology as ericssonite.

Besides ferroericssonite and fluorlamprophyllite, the lamprophyllite group contains two minerals discovered

recently in the pneumatolytic associations related to alkali basalts of the Eifel paleovolcanic area: *lileite*, $\text{Ba}_2[(\text{Na}, \text{Fe}, \text{Ca})_3\text{MgF}_2][\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$ (Chukanov *et al.*, 2012), and *emmerichite*, $\text{Ba}_2[\text{Na}_3\text{Fe}^{3+}_2\text{F}_2][\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$ (Chukanov *et al.*, 2014; Aksenov *et al.*, 2014).

Lileite and emmerichite are isotypic to the 2*M* polytypes of lamprophyllite, barytolamprophyllite, ericssonite and ferroericssonite. The detailed crystal-chemical formulae of lileite and emmerichite are $(\text{Ba}, \text{K}, \text{Sr})_2[\text{Na}(\text{Na}, \text{Fe}, \text{Ca}, \text{Mn})_2(\text{Mg}, \text{Fe})\text{F}_2][\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$ and $(\text{Ba}, \text{Sr}, \text{K})_2[(\text{Na}, \text{Ca})(\text{Na}, \text{Fe}^{2+}, \text{Mn}, \text{Mg})_2(\text{Fe}^{3+}, \text{Mg})(\text{F}, \text{O})_2][(\text{Ti}, \text{Nb}, \text{Fe}^{3+})_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$, respectively, where the contents of the O and H sheets are given in square brackets.

Emmerichite is the analogue of lileite with $\text{Fe}^{3+} > \text{Mg}$ in the octahedral $M3$ site. The predominance of Fe^{3+} in the $M3$ site was first found in ericssonite and subsequently in ferroericssonite, but, unlike emmerichite, these minerals contain Fe^{3+} in the 5-coordinated L site.

Type II (lamprophyllite-2*O* type)

The type II includes 2*O*-polytypes of three mineral species crystallizing in the *Pnmm* space group ($a \sim 19.13$ – 20.32 Å, $b \sim 6.98$ – 7.12 Å, $c \sim 5.34$ – 5.41 Å; Table 1): *lamprophyllite-2O* (Johnsen, 1996; Krivovichev *et al.*, 2003), *barytolamprophyllite-2O* (Rastsvetaeva & Dorfman, 1995; Sokolova & Cámara, 2008; Sokolova & Hawthorne, 2008) and *ericssonite-2O* (Moore, 1971; Matsubara, 1980). *Ericssonite-2O* from Långban, Sweden, was initially described under the name “orthoericssonite” (Moore, 1971) and is characterized by the idealized crystal-chemical formula $\text{Ba}_2[\text{Mn}^{2+}_4(\text{OH})_2][\text{Fe}^{3+}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$. *Ericssonite-2O* from the Hijikozu mine, Iwate prefecture, Japan (Matsubara, 1980) contains substantial amounts of Sr, Fe^{2+} and Ti substituting for Ba, Mn^{2+} and Fe^{3+} , respectively.

The symmetry operations that relate equivalent *HOH* modules in different polytypes were analyzed by Krivovichev *et al.* (2003), Ferraris *et al.* (2004) and Sokolova & Hawthorne (2008). These authors have found two symmetry operations (2_1 -axes and n -plane), whereas Belokoneva *et al.* (2015) reported the possibility of a third operation, resulting in another space group (see below). The analysis done by Belokoneva *et al.* (2015) was based upon the OD (order-disorder) analysis, which is a useful tool to describe the crystal structures of the lamprophyllite-related minerals and predict new polytypes (Dornberger-Schiff, 1964; Đurovič, 1997; Belokoneva, 2005).

The lamprophyllite-related minerals belong to the OD family consisting of two different kinds of layers. The first layer is the *HOH* module, which is non-polar and is characterized by the local symmetry operation λ -PO $P(1)2/m(1)$ (Fig. 5), where PO stands for a partial operation valid only for a part of the structure (block, rod, module, etc) and λ -POs means that the operations transform the part of the structure into itself. The second layer corresponds to the interlayer A -cations. The local symmetry group of the interlayer is $P(2)n(2_1)m(2_1)m$ (Ferraris *et al.*,

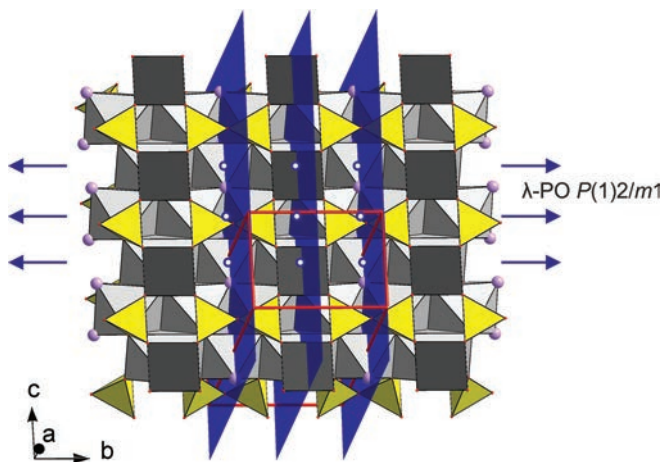


Fig. 5. The local symmetry (λ -PO $P(1)2/m1$) of the *HOH* module in the structure of lamprophyllite-related minerals. (online version in colour)

2004) and it is higher than that of the *HOH* module. This group is never realized in the whole structure.

In the lamprophyllite-related minerals, *HOH* modules can be multiplied by two σ -partial operations, which transform a layer into the adjacent one: σ -PO $P2_1/m$ in the $2M$ -polytype (Fig. 6a) and σ -PO $Pnm2_1$ in the $2O$ -polytype (Fig. 6b). Both these groups are subgroups of $Pnmm$. These polytypes are MDO polytypes, which means that each pair of the *HOH* modules is related by a single set of σ -operations (only by $P2_1/m$ or by $Pnm2_1$, Fig. 6).

In general, the structures of these polytypes are characterized by the following symmetry groupoids (Belokoneva *et al.*, 2015): λ -PO $P(1)2/m1$ (brackets show the direction perpendicular to the layers) and σ -PO $[P12_1/m1 \parallel Pnm2_1]$, where the double line indicates the possibility of both operations.

Different polytypes with partially ordered structures are predicted using the above symmetry groupoids through combination of different σ -POs in a single structure. The hypothetical crystal structure of lamprophyllite-4O (space group $Pnmm$) can be formed by the sequential alternation of the 2_1 -axes along a : $\langle \dots, 2_{1y}, 2_{1z}, 2_{1y}, 2_{1z}, \dots \rangle$ (Fig. 7), where 2_{1y} -axes belong to σ -PO $P2_1/m$ and 2_{1z} -axes belong to σ -PO $Pnm2_1$, respectively. The lamprophyllite-6M polytype with the sequence $\langle \dots, 2_{1y}, 2_{1y}, 2_{1z}, 2_{1y}, 2_{1y}, 2_{1z}, \dots \rangle$ and $a \sim 58 \text{ \AA}$ would possess a monoclinic symmetry. More complex polytypes are also possible up to structures with completely disordered layer stacking along the a axis.

In the triclinic crystal structure of schüllerite, the local symmetry of the *HOH* module is λ -PO $P\bar{1}$. The *HOH* modules are also related by inversion centres, and the symmetry groupoid is simpler than that for lamprophyllite: λ -PO $P\bar{1}$ and σ -PO $P\bar{1}$ (Fig. 8).

Inversion centre as a symmetry operation is present in the disordered schüllerite-like mineral with the space group $P\bar{1}$ (Sokolova *et al.*, 2013) whereas, in ordered minerals, with the schüllerite structure and the space

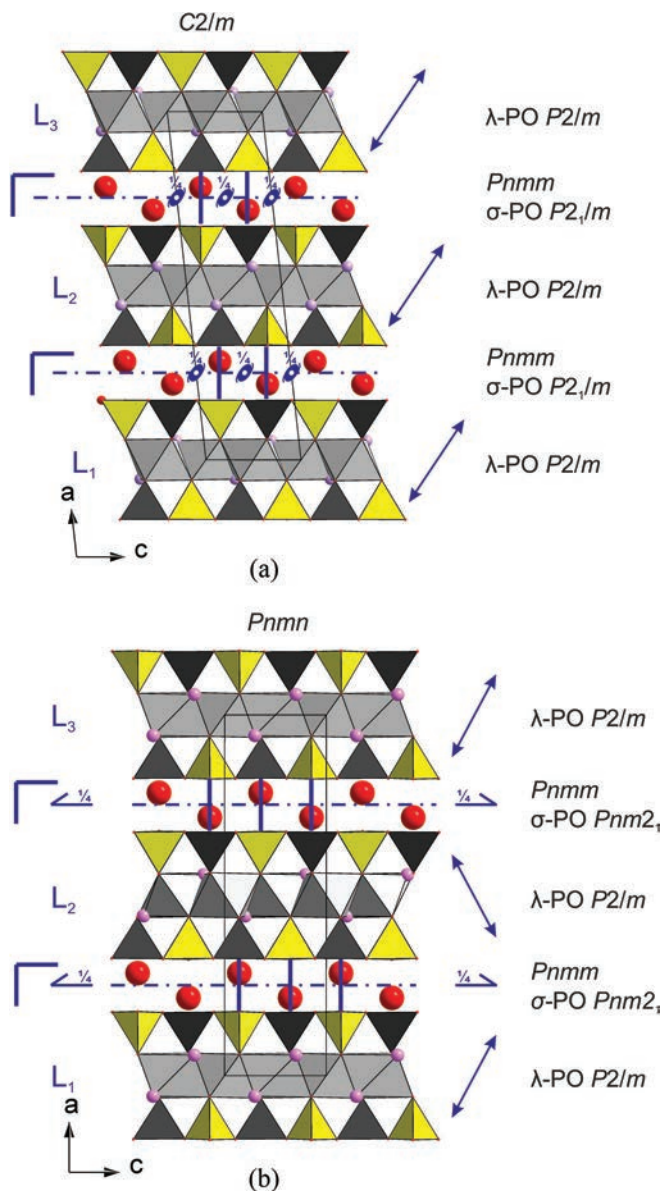


Fig. 6. The monoclinic (a) and the orthorhombic (b) MDO polytypes for lamprophyllite-related minerals. The action of 2_{1y} - and 2_{1z} -axes leads to the different orientation of Si_2O_7 groups in the *HOH* module (blue arrows) (after Belokoneva *et al.*, 2015). (online version in colour)

group $P1$ (Rastsvetaeva *et al.*, 2011, 2014), it is realized only as a pseudo-symmetry operation.

Type III (nabalamprophyllite type)

This type is represented by *nabalamprophyllite*, $\text{BaNa}[\text{Na}_3\text{Ti}(\text{OH})_2][\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$ (Rastsvetaeva & Chukanov, 1999; Chukanov *et al.*, 2004), a mineral species from the peralkaline pegmatites of the Inagli alkaline massif, South Yakutiya, Russia. For this mineral the only known polytype is $2M$, which is characterized by the monoclinic unit

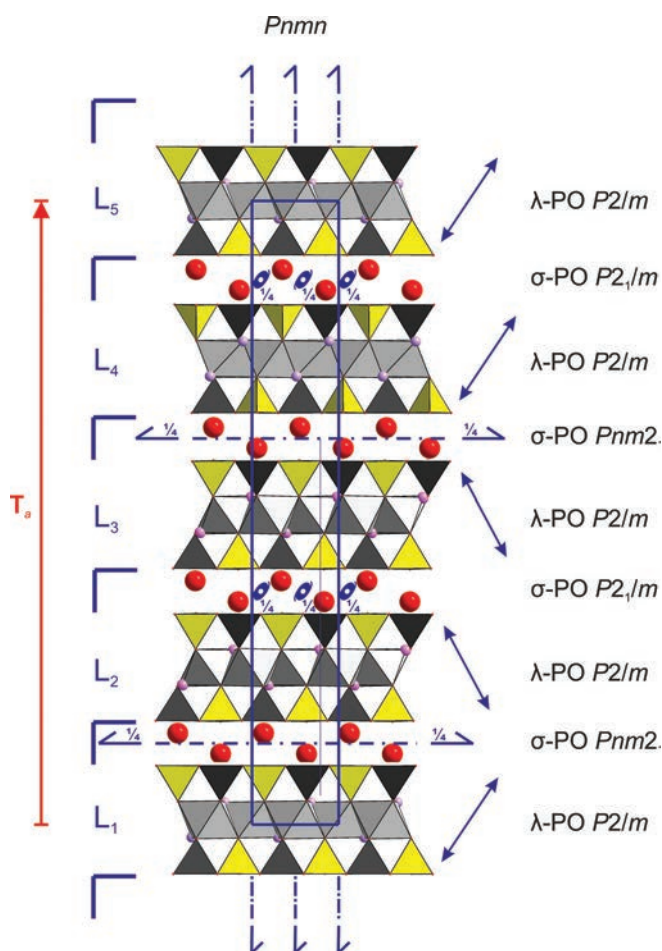


Fig. 7. The predicted hypothetical structure of "lamprophyllite-4O" with $a \sim 39$ Å (after Belokoneva *et al.*, 2015). (online version in colour)

cell ($a = 19.741$ Å, $b = 7.105$ Å, $c = 5.408$ Å, $\beta = 96.67^\circ$). Compared to barylamlamprophyllite, nabamlamprophyllite has a lower symmetry (space group $P2/m$) with Na and Ba ordered in the two interlayer sites, $A1$ and $A2$ (Fig. 9). The $A1$ site is occupied by Ba, whereas the $A2$ site is generally Na-dominant and is split into three subsites, $A2'$, $A2''$ and $A2'''$. The composition of the $A2'$ site is $\text{Ba}_{0.33}\text{Na}_{0.30}\text{K}_{0.12}\text{Sr}_{0.05}$. The $A2''$ and $A2'''$ subsites are at 0.64(5) and 0.67(4) Å from $A2'$ and contain $\text{Na}_{0.10}$ each.

Type IV (schüllerite type) and Type V (centrosymmetrical analogues of schüllerite)

The type IV is represented by *schüllerite*, ideally $\text{Ba}_2[\text{NaMnFe}^{2+}\text{Fe}^{3+}\text{F}_2][\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2]$, (Table 3, Fig. 10), a lamprophyllite-like heterophyllosilicate mineral discovered in the Löhley basalt quarry, Eifel volcanic region, Germany (Chukanov *et al.*, 2011; Rastsvetaeva *et al.*, 2011).

In heterophyllosilicates, including minerals of the lamprophyllite group, the (Si_2O_7) groups are strongly distorted due to their bonding both to large interlayer

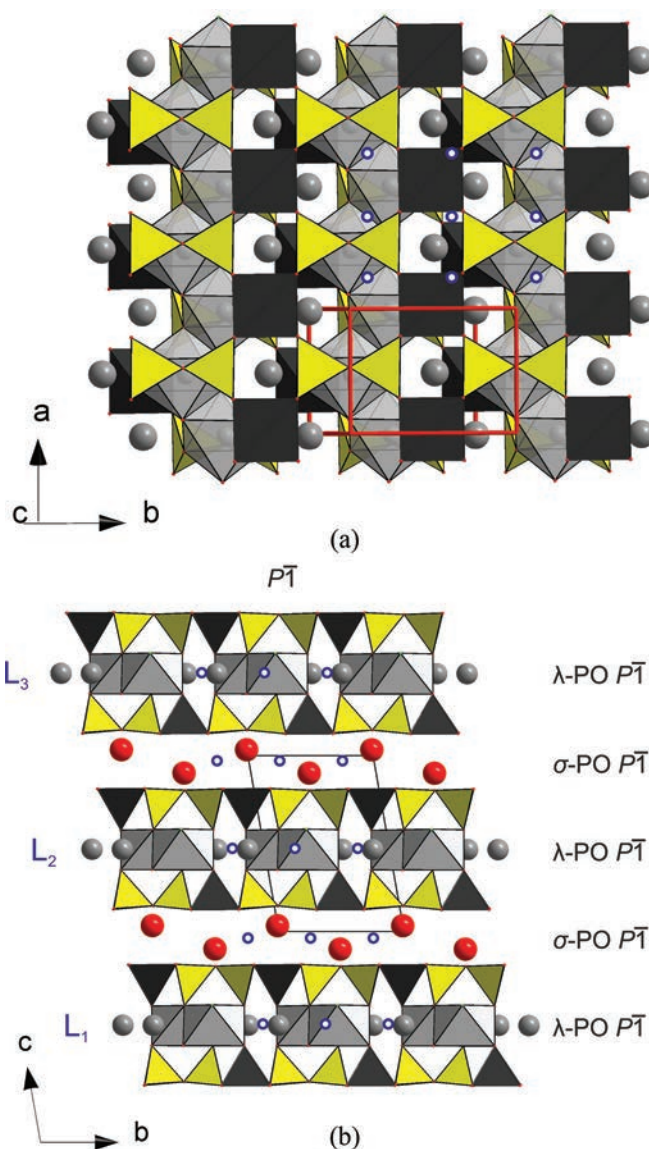


Fig. 8. The local symmetry ($\lambda\text{-PO } P\bar{1}$) of the *HOH* module in the structure of *schüllerite* (a) and reproduction of *HOH* modules by ($\sigma\text{-PO } P\bar{1}$) (b) (after Belokoneva *et al.*, 2015). For the best visualization of the *O* sheet, only Fe(Mg)-centred octahedra are drawn, whereas Na and Mn cations are shown by grey spheres. The large cations of the *A* layer (Ba, Sr, K) are shown as red spheres. (online version in colour)

cations such as Ba, Sr, and K, and small *M* octahedra occupied by Ti in lamprophyllite, Mg in lileite, Fe^{3+} in emmerichite and ericssonite, *etc.* As a consequence, in all these minerals, the connection between the *H* and *O* sheets can be realized in different ways, resulting in the formation of topologically different *HOH* modules. Ferraris & Gula (2005) provided the following reason for the mutual shifts of the adjacent *H*- and *O*-sheets in bafertsite-series heterophyllosilicates: "An oxygen atom shared between *H* and *O* sheets is bonded to four cations: three belonging to the *O*-sheet and one to the *H*-sheet.

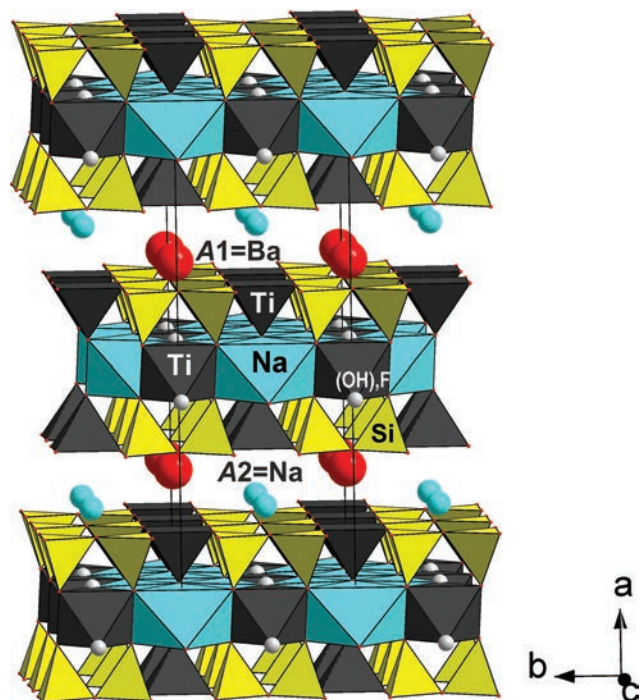


Fig. 9. The crystal structure of nabalamprophyllite (Rastsvetaeva & Chukanov, 1999). (online version in colour)

Because of bond valence balance, even an O^{2-} anion cannot be bonded at the same time to four high-charge cations like Si^{4+} and Ti^{4+} or Nb^{5+} ; consequently, constraints are derived not only to the composition, but also to the topology of the *HOH* module. Thus, to reach a suitable bond-valence balance, [...] a different connectivity between the *H* and *O* sheets is established.”

All lamprophyllite-related minerals listed in Table 1 are characterized by the same topological type of the *HOH* modules, with *H* sheets connected to the *trans* edges of the same octahedron of the *O* sheet, and the Si_2O_7 groups situated opposite to each other, whereas, in schüllerite, the *H* sheets are shifted with respect to the *O* sheet along the *b* axis.

Despite the topological differences, the unit-cell commensurability of schüllerite and other lamprophyllite-related minerals favours their epitactic intergrowths and interstratifications. Regular intergrowths of schüllerite with lileyste and emmerichite are frequently observed (Chukanov *et al.*, 2011, 2014; Rastsvetaeva *et al.*, 2014). In most cases, the interface between two intergrowing minerals is abrupt, but sometimes continuous change in the chemical composition is observed across the interface (Rastsvetaeva *et al.*, 2014), which indicates a possible interstratification of different *HOH* modules. The possibility of regular interstratification of schüllerite-type and lileyste-type *HOH* modules is confirmed by the X-ray diffraction data analysis (Rastsvetaeva *et al.*, 2014).

The position of schüllerite in the taxonomy of heterophyllosilicates is uncertain. In accordance with the topological approach by Sokolova (2006), lamprophyllite,

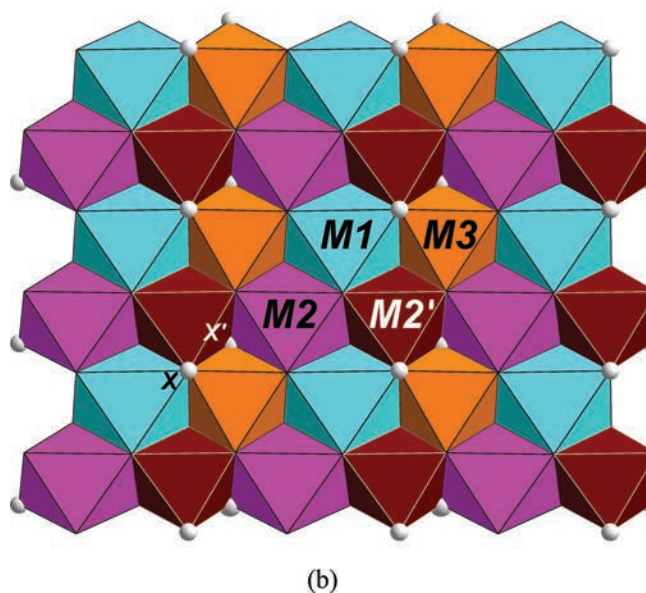
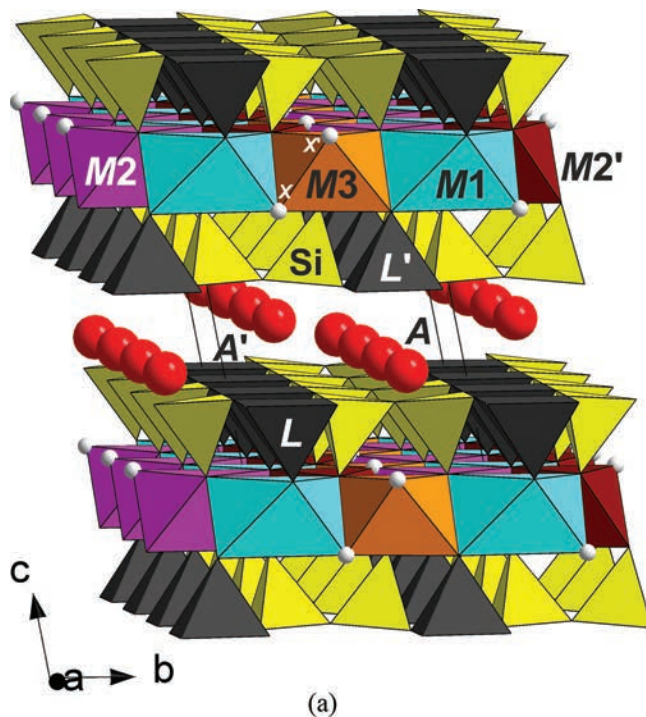


Fig. 10. The crystal structure of schüllerite (Rastsvetaeva *et al.*, 2011; Chukanov *et al.*, 2011): general view (a) and *O* sheet (b). (online version in colour)

barytolamprophyllite, nabalamprophyllite and lileyste should be in the group III that contain minerals with different coordinations of the *L* site and different components of the interlayer space (H_2O , SO_4^{2-} , PO_4^{3-}): innelite, epistolite, vunnemite, bornemanite, kazanskyite, nechelystovite and delindeite. On the other hand, schüllerite was included (Sokolova & Cámara, 2013) into the group IV together with minerals having sixfold coordination of the *L* site and additional *W*-components

(PO_4^{3-} groups or H_2O molecules) in the interlayer (murmantite, calcimurmantite (Lykova *et al.*, 2016), lomonosovite, quadruphite, sobolevite and polyphite). We consider the topological type of the *HOH* module as being of a minor importance compared to stoichiometry and cation coordination (Rastsvetaeva *et al.*, 2011; Chukanov *et al.*, 2011; Rastsvetaeva *et al.*, 2014; Aksenov *et al.*, 2014). According to the specific features of its crystal structure, schüllerite is closely related to the lamprophyllite-group minerals.

The possibility of three topologically different *HOH* modules in the bafertisite-series minerals (lamprophyllite, lomonosovite and bafertisite) was first established by Rastsvetaeva (1991). At present, only two of them have been found in lamprophyllite-related minerals: without (Fig. 11a) and with a shift of *H* sheets relative to each other in schüllerite (Rastsvetaeva *et al.*, 2011) (Fig. 11b). We predict the existence of lamprophyllite-related minerals with the third kind of topology, like that in bafertisite (Guan Ya-Xian *et al.*, 1963; Fig. 11c), where the *H* sheet is shifted along the *b* axis.

Despite the revision of the crystal structure of schüllerite by Sokolova *et al.* (2013), the holotype sample of this mineral definitely has an acentric structure, and a substantial predominance of Fe^{3+} over Fe^{2+} was established by crystal-structure refinements and a direct X-ray spectroscopic method. Taking into account the statistics of the $|E^2-1|$ distribution of normalized structure amplitudes after Wilson (the experimental value is 0.798 *vs.* 0.904 for centrosymmetric and 0.886 for acentric structures), the schüllerite structure should be considered as acentric. During the refinement in the acentric space group *P1*, no correlations of isotropic and anisotropic displacement parameters between cations related with a pseudo-centre were observed. In the crystal structure of schüllerite, the *O* layer contains four symmetrically non-equivalent octahedra of the *M1*, *M2*, *M2'*, and *M3* sites occupied predominantly by Na, Mn, Fe^{2+} , and Fe^{3+} , respectively. The *H* sheet contains two five-fold coordinated sites occupied by Ti (the *L* and *L'* polyhedra) and two types of Si_2O_7 groups. Ba, Sr, and K occupy two Ba-dominant sites (*A* and *A'*) in the interlayer space (Fig. 10a). The crystal-chemical formula of schüllerite resulting from the structure refinement is (*Z* = 1): $(\text{Ba}_{0.6}\text{Sr}_{0.3}\text{K}_{0.1})\text{Ba}[\text{Na}(\text{Mn}_{0.5}\text{Ca}_{0.4}\text{Na}_{0.1})(\text{Fe}^{2+}_{0.6}\text{Mg}_{0.25}\text{Fe}^{3+}_{0.15})(\text{Fe}^{3+}_{0.55}\text{Mg}_{0.45})\text{OF}][(\text{Ti}_{0.7}\text{Nb}_{0.2}\text{Fe}^{3+}_{0.1})(\text{Ti}_{0.6}\text{Al}_{0.2}\text{Mg}_{0.2})(\text{Si}_2\text{O}_7)_2\text{O}_2]$. The site assignment is provided in Table 4.

The crystal structure of a Fe^{2+} , Mg-dominant analogue of schüllerite with $\text{Fe}^{2+} > \text{Fe}^{3+}$ and the general formula $\text{Ba}_2\text{Ti}_2\text{Na}(\text{Ca}, \text{Mn})(\text{Fe}^{2+}, \text{Fe}^{3+})\text{Mg}[\text{Si}_2\text{O}_7]_2\text{O}_2(\text{O}, \text{F})\text{F}$ was reported by Rastsvetaeva *et al.* (2014). The mineral was found in a late pneumatolytic association related to alkali basalts in the Kahlenberg quarry, Eifel, Germany. This mineral differs from schüllerite in the lower Na content (0.85 instead of 1.05 *apfu*) and the high contents of Fe (1.8 *versus* 1.46 *apfu*) and Ca (0.43 *versus* 0.3 *apfu*). The $|E^2-1|$ Wilson statistics indicated the absence of an inversion centre (space group *P1*) as in the holotype sample of

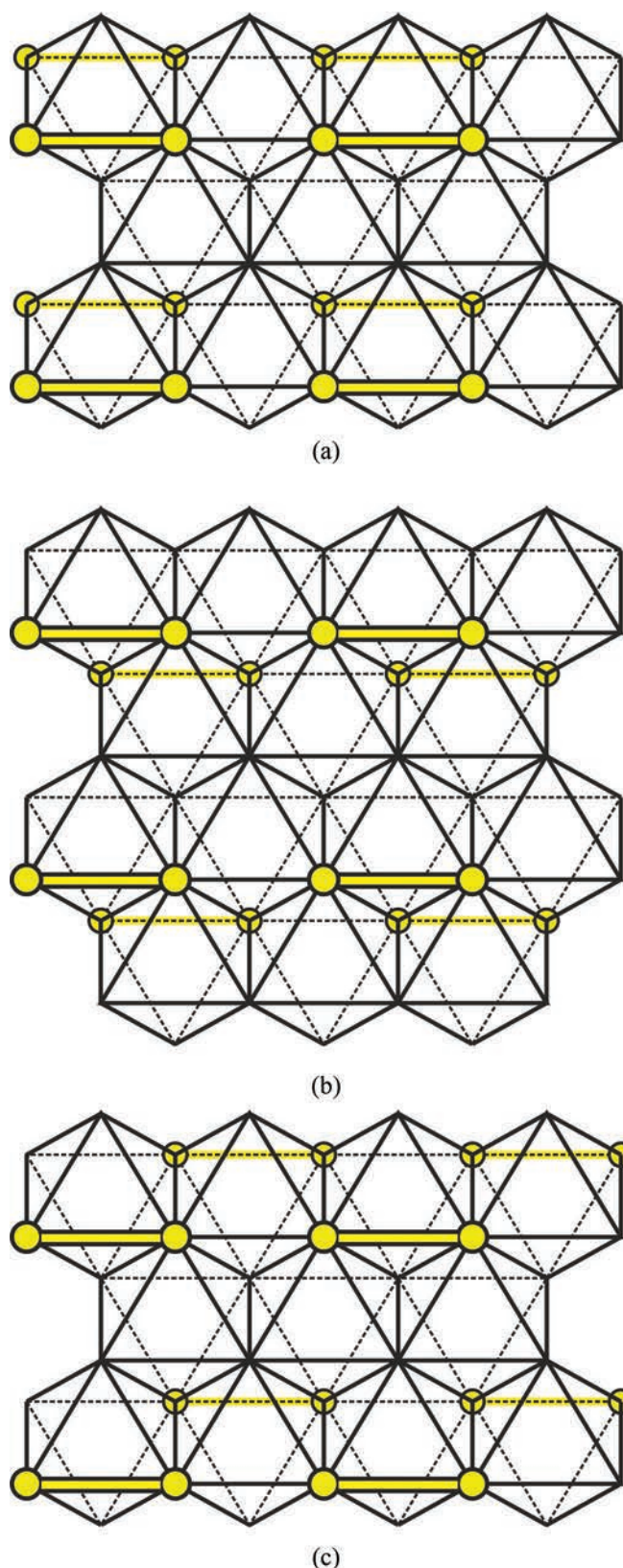


Fig. 11. Schematic representation of the *O* sheets and the positions of the Si_2O_7 groups (circles correspond to the O atoms) in the structures of lamprophyllite (a), schüllerite (b) and bafertisite (c) (after Rastsvetaeva, 1991; and Sokolova, 2006). (online version in colour)

Table 4. Site populations and average bond lengths [Å] in coordination polyhedra for schüllerite-type minerals

Site	Schüllerite		Fe ²⁺ -Mg-dominant analogue of schüllerite		Mg-rich schüllerite-like mineral	
	Composition (Z = 1)	<d>, Å	Composition (Z = 1)	<d>, Å	Composition (Z = 1)	<d>, Å
A	0.6Ba + 0.3Sr + 0.1K	2.872	0.6Ba + 0.3Sr + 0.1K	2.869	1.57Ba + 0.14Sr + 0.14K + 0.15	2.842
A'	1.0Ba	2.873	1.0Ba	2.854		
L	0.7Ti + 0.2Nb + 0.1Fe ³⁺	1.938	0.6Ti + 0.3Fe ³⁺ + 0.1Nb	1.922	1.67Ti + 0.21Fe ³⁺ + 0.09Nb + 0.02Zr + 0.01Al	1.928
L'	0.6Ti + 0.2Al + 0.2Mg	1.925	0.8Ti + 0.2Al	1.947		
M1	1.0Na	2.299	0.85Na + 0.15Ca	2.27	1.10Na + 0.43Ca + 0.3Mn + 0.17Fe ²⁺	2.313
M2	0.5Mn + 0.4Ca + 0.1Na	2.295	0.5Ca + 0.5Mn	2.25		
M2'	0.6Fe + 0.25Mg + 0.15Fe	2.169	1.0(Fe ²⁺ , Fe ³⁺)	2.18	0.79Mg + 0.71Fe ²⁺ + 0.33Na + 0.17 Fe ³⁺	2.150
M3	0.55Fe + 0.45Mg	2.160	0.6Mg + 0.4Fe ²⁺	2.22		

Note: A-site corresponds to A1; A' - A2; L - M1; L' - M2; M1 - M3; M2 - M4; M2' - M6 and M3 - M5 in the low-symmetry structures of schüllerite (Rastsvetaeva *et al.*, 2011; Chukanov *et al.*, 2011) and Fe²⁺-analogue of schüllerite (Rastsvetaeva *et al.*, 2014). In the high-symmetry structure of the Mg-rich schüllerite-like mineral (Sokolova *et al.*, 2013), the sites ^[10]A^P, ^[5]M^H, ^[6]M^P(2) and ^[6]M^P(1) correspond to the following pairs of sites in schüllerite, respectively: A + A', L + L', M1 + M2 and M2' + M3.

schüllerite. The minerals with the schüllerite-type topology of the HOH module (*i.e.* the holotype sample of schüllerite, the Fe²⁺, Mg-dominant analogue of schüllerite and the sample investigated by Sokolova *et al.*, 2013) are the only representatives of the family of lamprophyllite-related minerals with triclinic symmetry.

The second occurrence (Kahlenberg) of a mineral with the schüllerite-type structure confirms initial conclusions concerning the cation-ordering mechanism reported by Rastsvetaeva *et al.* (2011). The crystal-chemical formula of this mineral can be written as (Z = 1): (Ba_{0.6}Sr_{0.3}K_{0.1})Ba[(Na_{0.85}Ca_{0.15})(Ca_{0.5}Mn_{0.5})(Fe²⁺, Fe³⁺)_{1.0}(Mg_{0.6}Fe²⁺_{0.4})(O,F)][(Ti_{0.6}Fe³⁺_{0.3}Nb_{0.1})(Ti_{0.8}Al_{0.2})(Si₂O₇)₂O₂]. The predominance of Fe²⁺ over Fe³⁺ is supported by the average octahedral bond lengths: the mean <M3–O> and <M2'–O> distances are 2.160 Å and 2.169 Å in schüllerite from Löhley (holotype) versus 2.22 Å and 2.18 Å in the Fe²⁺-analogue of schüllerite from Kahlenberg, respectively (Table 4).

The crystal structure of the third schüllerite-like mineral was reported by Sokolova *et al.* (2013). Two grains of this mineral from the type locality of the Eifel volcanic region, Germany, were obtained from an American mineral collector. The exact locality for this specimen was not given and its identity with schüllerite had not been explained. It is noteworthy that the Ba-dominant lamprophyllite-related minerals from the Eifel region are very diverse in composition and crystal-chemical features, including the F-analogue of barytolamprophyllite, lileyite, emmerichite and insufficiently investigated schüllerite-type minerals. However, after the discovery of schüllerite, many specimens of lamprophyllite-like minerals from the Eifel region retained in private collections were renamed as “schüllerite”. The chemical composition of the sample investigated by Sokolova *et al.* (2013) differs from that of the holotype schüllerite by the predominance of Fe²⁺ over Fe³⁺ and by the high Na content: 1.43 *apfu* versus 1.05 *apfu* and 0.85 *apfu* in schüllerite-type samples studied earlier (Table 4). The Fe²⁺: Fe³⁺ ratio was estimated from the Mössbauer spectrum and the structure was refined in the space group *P*1̄ with four non-equivalent cationic positions (^[10]A^P, ^[5]M^H- and two ^[6]M^O-sites). As a result, the following crystal-chemical formula was obtained: (Ba_{1.57}Sr_{0.14}K_{0.14}□_{0.15})(Na_{1.10}Ca_{0.43}Mn_{0.30}Fe²⁺_{0.17})(Mg_{0.79}Fe²⁺_{0.71}Na_{0.33}Fe³⁺_{0.17})(Ti_{1.67}Fe³⁺_{0.21}Nb_{0.09}Zr_{0.02}Al_{0.01})Si_{3.95}O_{15.93}F_{2.07}. Unfortunately, the Mössbauer spectrum was not of a sufficient quality (due to the scarce amount of available material) to verify the presence of two kinds of Fe²⁺ and two kinds of Fe³⁺, as well as the distribution of these cations over different sites. The presence of Na and Fe³⁺ in the same site seems questionable, because of the differences in their cationic radii and charges. The revised ideal structural formula Na₂Ba₂Mg₂Ti₂(Si₂O₇)₂O₂F₂ suggested for schüllerite by Sokolova *et al.* (2013) might actually refer to another mineral, different from schüllerite both in its chemical composition and symmetry. This (or these) mineral(s) need(s) further investigations.

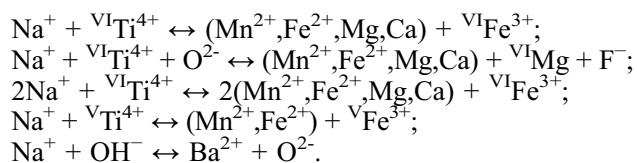
The high degree of cation ordering, the deficit of Ti and the absence of OH groups are typical not only for

schüllerite, but also for other lamprophyllite-related minerals from the pneumatolytic parageneses hosted by the Eifel alkali basalts (such as lileyite and emmerichite). These specific features can be explained by the combination of different genetic factors including magma outgassing, high temperatures of crystallization and high oxygen fugacity (Chukanov *et al.*, 2008) as well as heterovalent substitutions in octahedral sites.

The crystal-chemical role of sodium in lamprophyllite-related minerals

Among lamprophyllite-related minerals, lamprophyllite is the most widespread species and one of the most important concentrators of Sr in peralkaline rocks and related pegmatites. Except for fluorlamprophyllite, all other minerals related to lamprophyllite are Ba-dominant. They are characterized by the variable Na content: from ~ 0 *apfu* in ericssonite and ferroericssonite to ~ 3 *apfu* in nabalamprophyllite (Table 5). The Na content has an obvious geochemical origin and a crystal-chemical importance. Indeed, Na-free ericssonite and ferroericssonite occur in metasomatic and metamorphic formations with a low Na activity. In contrast, barium lamprophyllite-related minerals with relatively low Na contents (from 1 to 2 *apfu*) are known only in pneumatolytic associations related to the alkaline basalts of the Eifel paleovolcanic region, Germany, where lamprophyllite and barytolamprophyllite are absent. Barytolamprophyllite with 2.4–2.7 *apfu* Na occurs in peralkaline intrusive rocks and pegmatites. Nabalamprophyllite characterized by the highest content of Na (2.95 *apfu* on average) is known only in peralkaline pegmatites, where it crystallized at the stage of the highest Na activity (Chukanov *et al.*, 2004; Moiseev & Chukanov, 2006).

In the series of Ba-dominant lamprophyllite-related minerals, the increase in Na content is achieved by the progressive substitution of divalent cations, which requires charge compensation in other sites according to the following heterovalent substitution schemes:



It is important to note that the schüllerite-type topology of the *HOH* module is realized only in a narrow interval of Na contents: from 0.85 *apfu* for the Fe^{2+} -analogue of schüllerite (Rastsvetaeva *et al.*, 2014) to 1.44 *apfu* for the schüllerite-like mineral described by Sokolova *et al.* (2013), through 1.05 *apfu* in schüllerite.

According to the chemical composition, there are three types of cation distribution in the *O* sheet in the lamprophyllite-related minerals. In Na-poor ericssonite and ferroericssonite, the *O* sheet consists of homogeneous bands of edge-sharing octahedra (Mn- and Fe-centred, respectively) running along the *b* axis. In minerals with the highest Na

Table 5. Chemical composition and symmetry of Ba-dominant lamprophyllite-related minerals.

Mineral	Simplified formulae	Na ₂ O content, wt.%*	Number of Na atoms per 4 Si atoms in the empirical formula	Space group	References
Nabalamprophyllite	BaNa[Na ₃ Ti(OH) ₂][Ti ₂ (Si ₂ O ₇) ₂ O ₂]	11.14	2.95	<i>P2/m</i>	Rastsvetaeva & Chukanov, 1999
Barytolamprophyllite	(Sr,Ba,K) ₂ [Na(Na,Mn ²⁺) ₂ (Ti,Fe ³⁺)(OH) ₂][Ti ₂ (Si ₂ O ₇) ₂ O ₂]	Typically, 9–10	2.3–2.7	<i>C2/m</i>	Rastsvetaeva & Dorfman, 1995; Sokolova & Cámara, 2008; Azarova, 2004
Lileyite	Ba ₂ [(Na,Fe,Ca) ₃ MgF ₂][Ti ₂ (Si ₂ O ₇) ₂ O ₂]	6.75	1.89	<i>C2/m</i>	Chukanov <i>et al.</i> , 2012
Emmerichite	Ba ₂ [Na ₃ Fe ³⁺ F ₂][Ti ₂ (Si ₂ O ₇) ₂ O ₂]	5.44	1.54	<i>C2/m</i>	Chukanov <i>et al.</i> , 2014; Aksenov <i>et al.</i> , 2014
Mg-rich schüllerite-like mineral	Na ₂ Ba ₂ (Mg,Fe ²⁺) ₂ Ti ₂ (Si ₂ O ₇) ₂ O ₂ F ₂	4.97	1.44	<i>P1</i>	Sokolova <i>et al.</i> , 2013
Schüllerite	(Ba,Sr,K) ₂ [NaMn ²⁺ Fe ²⁺ (Fe ³⁺ ,Mg)(F,O) ₂][Ti ₂ (Si ₂ O ₇) ₂ O ₂]	3.55	1.05	<i>P1</i>	Rastsvetaeva <i>et al.</i> , 2011; Chukanov <i>et al.</i> , 2011
Fe ²⁺ -analogue of schüllerite	Ba ₂ [NaMn ²⁺ Fe ²⁺ (F,O) ₂][Ti ₂ (Si ₂ O ₇) ₂ O ₂]	2.90	0.85	<i>P1</i>	Rastsvetaeva <i>et al.</i> , 2014
Ericssonite	Ba ₂ [Mn ²⁺ ₄ (OH) ₂][Fe ³⁺ ₂ (Si ₂ O ₇) ₂ O ₂]	~ 0	~ 0	<i>C2/m</i>	Moore, 1971; Matsubara, 1980
Ferroericssonite	Ba ₂ [Fe ²⁺ ₄ (OH) ₂][Fe ³⁺ ₂ (Si ₂ O ₇) ₂ O ₂]	~ 0	~ 0	<i>Pmmn</i>	Kampf <i>et al.</i> , 2011

*For all minerals except barytolamprophyllite, sodium contents of holotype samples are given.

contents, the ...*Na-Na-Na-Na*... bands of Na-centred octahedra alternate with the mixed ...*Na-Ti-Na-Ti*...bands in lamprophyllite and the ...*Na-Mg-Na-Mg*... bands in lileite. An intermediate case is realized in the schüllerite-type structures, where the ...*Na-Fe³⁺-Na-Fe³⁺*... and ...*Mn-Fe²⁺-Mn-Fe²⁺*... bands alternate. In the Fe²⁺-analogue of schüllerite, the bands are ...*Na-Mg-Na-Mg*... and ...*Ca-Fe²⁺-Ca-Fe²⁺*... (or ...*Mn-Fe²⁺-Mn-Fe²⁺*...). In the centrosymmetric schüllerite-type mineral reported by Sokolova *et al.* (2013), both bands are of the ...*Na-Mg-Na-Mg*... type.

In silicates with large cations such as Na and Ca, the main structural unit is the Si₂O₇ group with an Si-O-Si angle of *ca.* 180° due to its geometric commensurability with the Ca (Na)-centred polyhedra (Belov, 1976). In lamprophyllite, barytolamprophyllite, lileite and emmerichite, the Si₂O₇ group is bonded to larger Ba- or Sr-centred polyhedra on one side and to smaller Ti-, Mg- or Fe³⁺-centred octahedra on the other side. As a result, the Si-O-Si angle is reduced to 140°. In schüllerite, small octahedra occupied by Ti, Mg, Fe³⁺ and Fe²⁺ are not isolated from each other and form chains within the *O* sheet. Owing to this, mutual shifts of the *O*- and *H*-sheets are possible, which result in the change of topology of the *HOH* module. In Na-free lamprophyllite-group minerals such as ericssonite and ferroericssonite, all octahedra are nearly equal, and the lamprophyllite-type topology is realized.

The chemical composition and the symmetry of barium lamprophyllite-related minerals including schüllerite are given in Table 5 in order of decreasing Na content.

Conclusions

The family of lamprophyllite-related minerals is rather large and comprises eight valid and several potential mineral species belonging to five structure types differing in the topology of *HOH* modules and the ordering of interlayer cations. In addition, the shifts of the *HOH* modules with respect to each other can result in different polytypes. At present, 2*M*- and 2*O*-polytypes are known, but the existence of other polytypes can be predicted by means of the OD analysis.

The general crystal-chemical formulae were suggested: (Sr,Ba,K,Na)₂Na(Na,Fe²⁺,Mn²⁺,Mg)₂(Ti,Fe³⁺,Mg)Ti₂(Si₂O₇)₂O₂(OH,O,F)₂ for lamprophyllite, (Ba,Sr,K,Na)₂Na(Na,Mn²⁺,Fe²⁺,Mg)₂(Ti,Fe³⁺,Mg)Ti₂(Si₂O₇)₂O₂(OH,O,F)₂ for barytolamprophyllite and (Sr,Na)₂[(Na,Mn)₃(Ti,Fe)(F,OH)₂][Ti₂(Si₂O₇)₂O₂] for fluorlamprophyllite. Any simplification of the above formulae, like (SrNa)Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, (SrK)Na₃Ti₃(Si₂O₇)₂O₂(OH)₂, Sr₂Na₃Ti(Fe³⁺Ti)(Si₂O₇)₂O₂(OH)₂, Sr₂Na₃Ti₃(Si₂O₇)₂O₂(OOH), or Sr₂Na₃Ti₃(Si₂O₇)₂O₂(OF) (in the case of lamprophyllite), does not reflect real compositions of these minerals.

The nomenclature and the systematics of lamprophyllite-group minerals have not been approved by the IMA–CNMNC, and the classification position of schüllerite is still uncertain. However, it is obvious that, by its structural

features, schüllerite is very close to lamprophyllite-group minerals and could be included into the lamprophyllite group, or into a supergroup that includes the lamprophyllite group *sensu stricto*. We consider topological features of schüllerite as a secondary criterion because, as discussed above, the topology of the *HOH* module depends on the chemical composition of the *O* sheet (primarily, on the Na content). The minerals with schüllerite-type topology and unit cell, *i.e.* a Mg-rich schüllerite-like mineral (Sokolova *et al.*, 2013) and a Fe²⁺,Mg-dominant analogue of schüllerite, are potentially new mineral species and need further investigation. There are no reasons for the revision of the formula of schüllerite, at least until reinvestigation of the holotype sample will provide any new data.

Acknowledgements: This study was supported by the Russian Foundation for Basic Research (grants Nos. 14-05-31150 mol_a; 16-35-00537 mol_a and 14-05-00190-a) and the Foundation of the President of the Russian Federation (-grants Nos. MK-4990.2014.5 and NSh-1072.2014.5). The authors thank anonymous referees for useful comments and suggestions, and Sergey Krivovichev for handling the manuscript.

References

- Akimenko, M.I., Aksenov, S.M., Sorokhtina, N.V., Kogarko, L.N., Kononkova, N.N., Rastsvetaeva, R.K., Rozenberg, K.A. (2015): Variations in the chemical composition of lamprophyllite group minerals and the crystal structure of fluorine-rich barytolamprophyllite from new peralkaline dyke. *Crystallogr. Rep.*, **60**, 821–830.
- Aksenov, S.M., Rastsvetaeva, R.K., Chukanov, N.V. (2014): The crystal structure of emmerichite Ba₂(Na,Mg)₃Fe³⁺Ti₂(Si₂O₇)₂O₂F₂, a new lamprophyllite-group mineral. *Z. Kristallogr.*, **229**(1), 1–7.
- Andrade, M.B., Yang, H., Downs, R.T., Färber, G., Contreira Filho, R.R., Evans, S.H., Loehn, C.W., Schumer, B.N. (2014): Fluorlamprophyllite, IMA 2013-102. CNMNC newsletter No. 19, February 2014, page 166. *Mineral. Mag.*, **78**, 165–170.
- Azarova, Y.V. (2004): Genesis and typomorphism of lamprophyllite – barytolamprophyllite series minerals from lujavritemalignite complex of Khibiny massif. *New Data Miner.*, **39**, 65–70.
- Back, M.E. (2014): Fleischer's glossary of mineral species. The Mineralogical Record Inc., Tucson, 420 p.
- Back, M.E. & Mandarino, J.A. (2008): Fleischer's glossary of mineral species. The Mineralogical Record Inc., Tucson, 344 p.
- Belokoneva, E.L. (2005): Borate crystal chemistry in terms of the extended OD theory: topology and symmetry analysis. *Crystallogr. Rev.*, **11**, 151–198.
- Belokoneva, E.L., Topnikova, A.P., Aksenov, S.M. (2015): Topology-symmetry structural law for natural titanosilicates micas and related heterophyllosilicates on the base of extended OD-theory, structure prediction. *Crystallogr. Rep.*, **60**, 1–15.
- Belov, N.V. (1976): Essays on Structural Mineralogy. Nedra, Moscow, 344. (in Russian).
- Belyaevskaya, G.P. & Borutsky, B.E. (1993): The correspondence between real chemical composition and crystal structure of

- lamprophyllite. *Doklady Akademii Nauk*, **328**(1), 90–93, (in Russian).
- Chukanov, N.V., Moiseev, M.M., Pekov, I.V., Lazebnik, K.A., Rastsvetaeva, R.K., Zayakina, N.V., Ferraris, G., Ivaldi, G. (2004): Nabalamprophyllite $\text{Ba}(\text{Na},\text{Ba})\{\text{Na}_3\text{Ti}[\text{Ti}_2\text{O}_2\text{Si}_4\text{O}_{14}](\text{OH},\text{F})_2\}$, a new layered lamprophyllite-group mineral from the alkaline-ultrabasic massifs Inagli and Kovdor, Russia. *Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva*, **133** (1), 59–72, (in Russian).
- Chukanov, N.V., Pekov, I.V., Rastsvetaeva, R.K., Aksenov, S.M., Zador, A.E., Van, K.V., Blass, G., Schüller, W., Ternes, B. (2012): Lileyite, $\text{Ba}_2(\text{Na},\text{Fe},\text{Ca})_3\text{MgTi}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, a new lamprophyllite-group mineral from the Eifel volcanic area, Germany. *Eur. J. Mineral.*, **24**, 181–188.
- Chukanov, N.V., Rastsvetaeva, R.K., Aksenov, S.M., Blass, G., Pekov, I.V., Belakovskiy, D.I., Tschörtner, J., Schüller, W., Ternes, B. (2014): Emmerichite, $\text{Ba}_2\text{Na}(\text{Na},\text{Fe}^{2+})_2(\text{Fe}^{3+},\text{Mg})\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, a new lamprophyllite-group mineral from the Eifel paleovolcanic region, Germany. *New Data on Minerals*, **49**, 5–13.
- Chukanov, N.V., Rastsvetaeva, R.K., Britvin, S.N., Virus, A.A., Belakovskiy, D.I., Pekov, I.V., Aksenov, S.M., Ternes, B. (2011): Schüllerite, $\text{Ba}_2\text{Na}(\text{Mn},\text{Ca})(\text{Fe}^{3+},\text{Mg},\text{Fe}^{2+})_2\text{Ti}_2(\text{Si}_2\text{O}_7)_2(\text{O},\text{F})_4$, a new mineral species from the Eifel volcanic district, Germany. *Geology of Ore Deposits*, **53**, 767–774.
- Chukanov, N.V., Rozenberg, K.A., Rastsvetaeva, R.K., Möckel, S. (2008): New data on titanium-rich biotite: A problem of “wodanite”. *New Data on Minerals*, **43**, 72–77.
- Dornberger-Schiff, K. (1964): Grundzüge einer theorie der OD-strukturen aus schichten. *Abhandlungen der deutschen Akademie der Wissenschaften zu Berlin. Klasse für Chemie, Geologie und Biologie*, **3**, 1–107.
- Dudkin, O.B. (1959): On barium lamprophyllite. *Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva*, **88**, 713–715. (in Russian).
- Dudkin, O.B., Kozyreva, L.V., Pomerantseva, N.G. (1964): Mineralogy of apatite localities of Khibiny Tundras. Nauka, Moscow-Leningrad, 236 p. (in Russian).
- Đurovič, S. (1997): Fundamentals of the OD theory. *EMU Notes in Mineralogy*, **1**, 3–28.
- Ferraris, G. (2008): Modular structures – the paradigmatic case of the heterophyllosilicates. *Z. Kristallogr.*, **223**, 76–84.
- Ferraris, G. & Gula, A. (2005): Polysomatic aspects of microporous minerals - heterophyllosilicates, palysepioles and rhodesite-related structures. *Rev. Mineral. Geochem.*, **57**, 69–104.
- Ferraris, G., Ivaldi, G., Pushcharovsky, D.Y., Zubkova, N.V., Pekov, I.V. (2001): The crystal structure of delindeite, $\text{Ba}_2\{(\text{Na},\text{K},\square)_3(\text{Ti},\text{Fe})[\text{Ti}_2(\text{O},\text{OH})_4\text{Si}_4\text{O}_{14}](\text{H}_2\text{O},\text{OH})_2\}$, a member of the meroplesiotype bafertisite series. *Can. Mineral.*, **39**, 1307–1316.
- Ferraris, G., Makovický, E., Merlino, S. (2004): Crystallography of Modular Materials. IUCr/Oxford University Press, Oxford, 370 p.
- Guan, Y.-X., Simonov, V.I., Belov, N.V. (1963): The crystal structure of bafertisite, $\text{BaFe}_2\text{TiO}[\text{Si}_2\text{O}_7](\text{OH})_2$. *Dokl. Akad. Nauk SSSR*, **149**, 123–126. (in Russian).
- Johnsen, O. (1996): TEM observations and X-ray powder data on lamprophyllite polytypes from gardiner complex, East Greenland. *N. Jb. Miner. Mh.*, **1996**, 407–417.
- Johnsen, O., Nielsen, T.F.D., Rønsbo, J.G. (1994): Lamprophyllite and barytolamprophyllite from the Tertiary Gardiner complex, East Greenland. *N. Jb. Miner. Mh.*, **1994**, 328–336.
- Kampf, A.R., Roberts, A.C., Venance, K.E., Dunning, G.E., Walstrom, R.E. (2011): Ferroericssonite, the Fe^{2+} analogue of ericssonite, from Eastern Fresno County, California, U.S.A. *Can. Mineral.*, **49**, 587–594.
- Konev, A.A., Vorobiev, E.I., Lazebnik, K.A. (1996): Mineralogy of Murun alkaline massif. Siberian Branch of Russian Academy of Sciences, Novosibirsk, 222 p.
- Krivovichev, S.V., Armbruster, T., Yakovenchuk, V.N., Pakhomovsky, Y.A., Men'shikov, Y.P. (2003): Crystal structures of lamprophyllite-2M and lamprophyllite-2O from the Lovozero alkaline massif, Kola peninsula, Russia. *Eur. J. Mineral.*, **15**, 711–718.
- Lykova, I.S., Pekov, I.V., Chukanov, N.V., Belakovskiy, D.I., Yapaskurt, V.O., Zubkova, N.V., Britvin, S.N., Giester, G. (2016): Calciomurmanite, $(\text{Na},\square)_2\text{Ca}(\text{Ti},\text{Mg},\text{Nb})_4[\text{Si}_2\text{O}_7]_2\text{O}_2(\text{OH},\text{O})_2(\text{H}_2\text{O})_4$, a new mineral from the Lovozero and Khibiny alkaline complexes, Kola Peninsula, Russia. *Eur. J. Mineral.*, **28**, 835–845.
- Lykova, I.S., Pekov, I.V., Zubkova, N.V., Chukanov, N.V., Yapaskurt, V.O., Chervonnaya, N.A., Zolotarev, A.A. (2015a): Crystal chemistry of cation-exchanged forms of epistolite-group minerals. Part I. Ag- and Cu-exchanged lomonosovite and Ag-exchanged murmanite. *Eur. J. Mineral.*, **27**, 535–549.
- Lykova, I.S., Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Chervonnaya, N.A., Zolotarev, A.A., Giester, G. (2015b): Crystal chemistry of cation-exchanged forms of epistolite-group minerals. Part II. Vigrishinite and Zn-exchanged murmanite. *Eur. J. Mineral.*, **27**, 669–682.
- Makovicky, E. (1997): Modularity – different types and approaches. *EMU Notes in Mineralogy*, **1**, 315–344.
- Matsubara, S. (1980): The crystal structure of orthoericssonite. *Mineral. J.*, **10**, 107–121.
- Moiseev, M.M. & Chukanov, N.V. (2006): Mineralogy of alkaline pegmatites and hydrothermalites of the Kovdor massif. *New Data on Minerals*, **41**, 56–70.
- Moore, P.B. (1971): Ericssonite and orthoericssonite. Two new members of the lamprophyllite group from Långban, Sweden. *Lithos*, **4**, 137–145.
- Németh, P., Ferraris, G., Radnóczy, G., Ageeva, O.A. (2005): TEM and X-ray study of syntactic intergrowths of epistolite, murmanite and shkatulkalite. *Can. Mineral.*, **43**, 973–987.
- Peng, Z. & Zhang, J. (1965): New varieties of lamprophyllite-barytolamprophyllite and orthorhombic lamprophyllite. *Sci. Sin.*, **14**, 1827–1840.
- Peng, Z., Zhang, J., Shu, J. (1984): The crystal structure of barytolamprophyllite. *Kexue Tongbao*, **29**, 237–241.
- Rastsvetaeva, R.K. (1991): *Crystal chemistry of sulfates and silicates with mixed radicals*. D. Sc. Thesis. Leningrad State University. Leningrad, 44 p. (in Russian).
- Rastsvetaeva, R.K. & Aksenov, S.M. (2011): Crystal chemistry of silicates with three-layer TOT and HOH modules of layered, chainlike, and mixed types. *Crystallogr. Rep.*, **56**, 910–934.
- Rastsvetaeva, R.K. & Andrianov, V.I. (1986): New data on the crystal structure of murmanite. *Sov. Phys. Crystallogr.*, **31**, 44–48.
- Rastsvetaeva, R.K. & Chukanov, N.V. (1999): Crystal structure of a new high-barium analogue of lamprophyllite with a primitive unit cell. *Doklady Chem.*, **368**, 228–231.
- Rastsvetaeva, R.K. & Dorfman, M.D. (1995): Crystal structure of Ba-lamprophyllite in the isomorphous lamprophyllite-barytolamprophyllite series. *Crystallogr. Rep.*, **40**, 951–954.

- Rastsvetaeva, R.K., Aksenov, S.M., Chukanov, N.V. (2011): Crystal structure of schüllerite, a new mineral of the heterophyllosilicate family. *Doklady Chem.*, **437**, 90–94.
- Rastsvetaeva, R.K., Aksenov, S.M., Chukanov, N.V., Lykova, I.S., Verin, I.A. (2014): Iron-rich schüllerite from Kalenberg (Eifel, Germany): crystal structure and relation to the lamprophyllite-group minerals. *Crystallogr. Rep.*, **59**, 955–961.
- Rastsvetaeva, R.K., Evsyunin, V.G., Konev, A.A. (1995): Crystal structure of K-barytolamprophyllite. *Crystallogr. Rep.*, **40**, 472–474.
- Rastsvetaeva, R.K., Sokolova, M.N., Gusev, A.I. (1990): Refined crystal structure of lamprophyllite. *Mineral. Zh.*, **5**, 25–28. (in Russian).
- Saf'yanov, Y.N., Vasil'eva, N.O., Golovachev, V.P., Kuz'min, E.A., Belov, N.V. (1983): Crystal structure of lamprophyllite. *Dokl. Akad. Nauk SSSR*, **269**, 117–120.
- Sokolova, E. (2006): From structure topology to chemical composition. I. Structural hierarchy and stereochemistry in titanium disilicate minerals. *Can. Mineral.*, **44**, 1273–1330.
- Sokolova, E. (2012): Further developments in the structure topology of the astrophyllite-group minerals. *Mineral. Mag.*, **76**(4), 863–882.
- Sokolova, E. & Cámara, F. (2008): From structure topology to chemical composition. III. Titanium silicates: The crystal chemistry of barytolamprophyllite. *Can. Mineral.*, **46**, 403–412.
- Sokolova, E. & Cámara, F. (2013): From structure topology to chemical composition. XVI. New developments in the crystal chemistry and prediction of new structure topologies for titanium disilicate minerals with the TS block. *Can. Mineral.*, **51**, 861–891.
- Sokolova, E. & Cámara, F. (2014): From structure topology to chemical composition. XVII. Fe^{3+} versus Ti^{4+} : the topology of HOH layer in ericssonite-2O, $\text{Ba}_2\text{Fe}^{3+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, ferroericssonite, $\text{Ba}_2\text{Fe}^{3+}_2\text{Fe}^{2+}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, and yoshimuraite, $\text{Ba}_4\text{Ti}^{4+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OH})_2$. *Can. Mineral.*, **52**, 569–576.
- Sokolova, E. & Hawthorne, F.C. (2008): From structure topology to chemical composition. IV. Titanium silicates: the orthorhombic polytype of nabalamprophyllite from the Lovozero massif, Kola Peninsula, Russia. *Can. Mineral.*, **46**, 1323–1331.
- Sokolova, E., Hawthorne, F.C., Abdu, Y. (2013): From structure topology to chemical composition. XV. Titanium silicates: revision of the crystal structure and chemical formula of schüllerite, $\text{Na}_2\text{Ba}_2\text{Mg}_2\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$, from the Eifel volcanic region, Germany. *Can. Mineral.*, **51**, 715–725.
- Williams, P.A., Hatert, F., Pasero, M., Mills, S.J. (2011): IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) Newsletter No. 7. New minerals and nomenclature modifications approved in 2010. *Mineral. Mag.*, **75**, 27–31.
- Woodrow, P.J. (1964): Crystal structure of lamprophyllite. *Nature*, **204**, 375.
- Zaitsev, V.A. & Kogarko, L.N. (2002): Compositions of minerals of the lamprophyllite group from alkaline massifs worldwide. *Geochem. Int.*, **40**, 313–322.

Received 24 November 2014

Modified version received 5 March 2016

Accepted 20 April 2016