

FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION.
XVII. Fe^{3+} VERSUS Ti^{4+} : THE TOPOLOGY OF THE 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, $\text{Ba}_4\text{Ti}^{4+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OH})_2$

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ABSTRACT

The HOH layer is the main structural unit in the crystal structures of Fe^{3+} -disilicates ericssonite-2O, ideally $\text{Ba}_2\text{Fe}^{3+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, ferroericssonite, ideally $\text{Ba}_2\text{Fe}^{3+}_2\text{Fe}^{2+}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, and yoshimuraite, ideally $\text{Ba}_4\text{Ti}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OH})_2$, a TS-block mineral of Group II. The chemical compositions of the core part of the HOH layer in ericssonite-2O and ferroericssonite, $^{[5]}\text{Fe}^{3+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ and $^{[5]}\text{Fe}^{3+}_2\text{Fe}^{2+}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, are similar to the chemical composition of the core part of the HOH layer in yoshimuraite, $^{[5]}\text{Ti}^{4+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, except for the cation species at the [5]-coordinated M^{H} site in the H sheets: $^{[5]}\text{Fe}^{3+}$ and $^{[5]}\text{Ti}^{4+}$, respectively. Despite this similarity, the topology of the HOH layer in ericssonite-2O and ferroericssonite is different from that in yoshimuraite. In TS-block minerals, different distortions of M^{O} octahedra correspond to specific types of linkage of H and O sheets. Topological consideration of Fe^{3+} -disilicates ericssonite-2O and ferroericssonite and yoshimuraite, a TS-block mineral of Group II, shows that different topologies of the chemically identical HOH layer are due to a difference in the bond-valence contributions of Fe^{3+} and Ti^{4+} at the M^{H} site in the H sheet (*i.e.*, inability of Fe^{3+} to contribute sufficient bond-valence to the $\text{X}^{\text{O}}_{\text{M}}$ anion) and subsequent different distortions of M^{O} octahedra in the O sheet, where $\text{M}^{\text{O}} = \text{Mn}^{2+}$, Fe^{2+} .

Keywords: ericssonite-2O, ferroericssonite, yoshimuraite, TS block, structure topology

INTRODUCTION

To date, there are two known structures of Fe^{3+} -disilicate minerals: ericssonite-2O, $\text{Ba}_2\text{Mn}_4\text{Fe}^{3+}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ (Matsumura 1980), and ferroericssonite, $\text{Ba}_2\text{Fe}^{2+}_4\text{Fe}^{3+}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ (Kampf *et al.* 2011), (Table 1) which contain an HOH layer as the main structural unit. Here, the HOH notation of Ferraris *et al.* (1996) has been used. In ericssonite-2O and ferroericssonite, Mn^{2+} and Fe^{2+} are dominant cations in the central O (octahedral) sheet of the HOH layer; the two adjacent H (heteropolyhedral) sheets are composed of [5]-coordinated Fe^{3+} polyhedra and Si_2O_7 groups. Between the HOH layers, there is a distorted layer of Ba atoms (Fig. 1a). The HOH layer is the main structural unit in TS-block minerals (TS = Titanium-Silicate) (Sokolova 2006). We wish to understand how the presence of Fe^{3+} and Ti^{4+} affect the topology of the HOH layer. To do this, we will compare Fe^{3+} -disilicate minerals

ericssonite-2O and ferroericssonite with yoshimuraite, $\text{Ba}_4\text{Mn}_4\text{Ti}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OH})_2$ (McDonald *et al.* 2000), a TS-block mineral of Group II and the closest Ti^{4+} analogue of ericssonite-2O and ferroericssonite, with regard to the main structural unit in all three structures, the HOH layer. The chemical compositions of the core part of the HOH layer in ericssonite-2O and ferroericssonite, $^{[5]}\text{Fe}^{3+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ and $^{[5]}\text{Fe}^{3+}_2\text{Fe}^{2+}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, are similar to the chemical composition of the core part of the HOH layer in yoshimuraite, $^{[5]}\text{Ti}^{4+}_2\text{Mn}_4(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$, except for the cation species at the [5]-coordinated M^{H} sites in the H sheets: $^{[5]}\text{Fe}^{3+}$ and $^{[5]}\text{Ti}^{4+}$, respectively. Despite this similarity, the topology of the HOH layer in ericssonite-2O and ferroericssonite is different from that in yoshimuraite, *i.e.*, the two H sheets link to the central O sheet in different ways. In this paper, we consider the topologies of the HOH layer in ericssonite-2O, ferroericssonite, and yoshimuraite and explain why the occur-

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TABLE 1. FORMULAE* AND UNIT-CELL PARAMETERS OF ERICSSONITE-2O, FERROERICSSONITE, AND SELECTED MINERALS WITH THE TS BLOCK

Mineral	Ideal formula	a (Å)	b (Å)	c (Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	**CN _{M^H}	Sp. gr.	Z	Ref.†
ericssonite-2O	Ba ₂ Mn ₄ Fe ³⁺ ₂ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	20.230	6.979	5.392				5	<i>Pnmm</i>	2	(1)
ferroericssonite	Ba ₂ Fe ²⁺ ₄ Fe ³⁺ ₂ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	20.346	7.0119	5.3879		94.874		5	<i>C2/m</i>	2	(2)
Group II, Ti = 2 apfu											
jinshajiangite	NaBaFe ²⁺ ₄ Ti ₂ (Si ₂ O ₇) ₂ O ₂ (OH) ₂ F	10.6785	13.786	20.700		94.937		6	<i>C2/m</i>	8	(3)
hejtmanite-P	Ba ₂ Mn ²⁺ ₄ Ti ₂ (Si ₂ O ₇) ₂ O ₂ (OH) ₄	5.361	6.906	12.556		119.8		6	<i>P2₁/m</i>	2	(4)
yoshimuraite	Ba ₄ Mn ²⁺ ₄ Ti ₂ (Si ₂ O ₇) ₂ (PO ₄) ₂ O ₂ (OH) ₂	5.386	6.999	14.748	95.50	93.62	89.98	5	<i>P1</i>	2	(5)
bussenite	Na ₂ Ba ₄ (Fe ²⁺ Na) ₂ Ti ₂ (Si ₂ O ₇) ₂ (CO ₃) ₂ O ₂ (OH) ₂ F ₂ (H ₂ O) ₂	5.399	7.016	16.254	102.44	93.18	90.10	6	<i>P1</i>	2	(6)
cámaraite***	NaBa ₃ Fe ²⁺ ₈ Ti ₄ (Si ₂ O ₇) ₄ O ₄ (OH) ₆ F	10.6965	13.7861	21.478	99.345	92.315	89.993	6	<i>C1</i>	4	(7)
Group III, Ti (+ Nb + Mg) = 3 apfu											
lamprophyllite-2M	Na ₃ (SrNa)Ti ₃ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.215	7.061	5.3719		96.797		5	<i>C2/m</i>	2	(8)
lamprophyllite-2O	Na ₃ (SrNa)Ti ₃ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.128	7.0799	5.3824				5	<i>Pnmm</i>	2	(8)
nabalampophyllite-2M	Na ₄ BaTi ₃ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.741	7.105	5.408		96.67		5	<i>P2/m</i>	2	(9)
nabalampophyllite-2O	Na ₃ (BaNa)Ti ₃ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.564	7.1173	5.414				5	<i>Pnmm</i>	2	(10)
barytolamprophyllite	Na ₃ (BaK)Ti ₃ (Si ₂ O ₇) ₂ O ₂ (OH) ₂	19.8971	7.1165	5.4108		96.676		5	<i>C2/m</i>	2	(11)
innelite-1T	Na ₂ M ²⁺ Ba ₄ Ti ₃ (Si ₂ O ₇) ₂ [(SO ₄) ₂ (PO ₄) ₂](OH)	5.4234	7.131	14.785	98.442	94.579	90.009	5	<i>P1</i>	1	(12)
innelite-1M	Na ₂ M ²⁺ Ba ₄ Ti ₃ (Si ₂ O ₇) ₂ [(SO ₄) ₂ (PO ₄) ₂](OH)	5.4206	7.125	29.314		94.698		5	<i>P2/c</i>	2	(12)
epistolite	Na ₄ □Nb ₂ Ti(Si ₂ O ₇) ₂ O ₂ (OH) ₂ (H ₂ O) ₄	5.460	7.170	12.041	103.63	96.01	89.98	6	<i>P1</i>	1	(13)
vuonnemite	Na ₁₁ Nb ₂ Ti(Si ₂ O ₇) ₂ (PO ₄) ₂ O ₃ F	5.4984	7.161	14.450	92.60	95.30	90.60	6	<i>P1</i>	1	(14)
bornemanite	Na ₇ BaTi ₂ Nb(Si ₂ O ₇) ₂ (PO ₄) ₂ O ₃ F	5.4587	7.1421	24.528	96.970	96.927	90.326	5,6	<i>P1</i>	2	(15)
kazanskyite	Na ₃ Ba□Ti ₂ Nb(Si ₂ O ₇) ₂ O ₂ (OH) ₂ (H ₂ O) ₄	5.4260	7.135	25.514	98.172	90.916	89.964	5,6	<i>P1</i>	2	(16)
nechelyustovite***	Na ₆ □Ba ₂ □Ti ₄ Nb ₂ (Si ₂ O ₇) ₄ O ₄ (OH) ₄ (H ₂ O) ₆	5.447	7.157	47.259	95.759	92.136	89.978	5,6	<i>P1</i>	2	(17)
Group IV, Ti (+ Mg + Mn) = 4 apfu											
murmanite	Na ₄ Ti ₄ (Si ₂ O ₇) ₂ O ₄ (H ₂ O) ₄	5.3875	7.0579	12.176	93.511	107.943	90.093	6	<i>P1</i>	1	(18)
lomonosovite	Na ₁₀ Ti ₄ (Si ₂ O ₇) ₂ (PO ₄) ₂ O ₄	5.4170	7.1190	14.487	99.957	96.711	90.360	6	<i>P1</i>	1	(18)
quadruphite	Na ₁₄ Ca ₂ Ti ₄ (Si ₂ O ₇) ₂ (PO ₄) ₄ O ₄ F ₂	5.4206	7.0846	20.3641	86.89	94.42	89.94	6	<i>P1</i>	1	(19)
sobolevite	Na ₁₃ Ca ₂ MnTi ₃ Mn(Si ₂ O ₇) ₂ (PO ₄) ₄ O ₃ F ₃	7.0755	5.4106	40.623		93.156		6	<i>Pc</i>	2	(20)
polyphite	Na ₁₈ Ca ₄ Ti ₄ (Si ₂ O ₇) ₂ (PO ₄) ₆ O ₄ F ₄	5.3933	7.0553	26.451	95.216	93.490	90.101	6	<i>P1</i>	1	(20)

*Ideal mineral formulae are from (Sokolova & Cámara 2013); for each Group, the content of Ti (+ Nb + Zr + Mg + Mn) (apfu) is given per (Si₂O₇)₂; for each mineral, the content of Ti (+ Nb + Mg + Mn) is shown in red; ** coordination number of the M^H cation; *** formula is given per (Si₂O₇)₄; M²⁺ = Mn, Fe²⁺, Mg, Ca.

† The most recent reference on the structure: (1) Matsubara (1980); (2) Kampf *et al.* (2011); (3) Sokolova *et al.* (2009); (4) Rastsvetaeva *et al.* (1991); (5) McDonald *et al.* (2000); (6) Zhou *et al.* (2002); (7) Cámara *et al.* (2009); (8) Krivovichev *et al.* (2003); (9) Rastsvetaeva & Chukanov (1999); (10) Sokolova & Hawthorne (2008); (11) Sokolova & Cámara (2008); (12) Sokolova *et al.* (2011); (13) Sokolova & Hawthorne (2004); (14) Ercit *et al.* (1998); (15) Cámara & Sokolova (2007); (16) Cámara *et al.* (2012); (17) Cámara & Sokolova (2009); (18) Cámara *et al.* (2008); (19) Sokolova & Hawthorne (2001); (20) Sokolova *et al.* (2005).

rence of Fe³⁺ and Ti⁴⁺ in the H sheets results in different topologies of the HOH layer in these structures.

GENERAL STRUCTURAL PRINCIPLES FOR THE TS-BLOCK MINERALS

Currently, there are 35 titanium-disilicate minerals with known structures based on the TS (Titanium-Silicate) block [structures of 34 minerals have been

considered by Sokolova & Cámara (2013) + kolskyite (Cámara *et al.* 2013)]. For a description of the TS-block components, Sokolova (2006) and Sokolova & Cámara (2013) used the HOH notation of Ferraris *et al.* (1996). In the TS block, the O sheet is an array of close-packed M^O octahedra. The two adjacent H sheets are composed of [5-7]-coordinated M^H polyhedra and Si₂O₇ groups. There are two cation sites, A^P and B^P, on the periphery of the TS block. The A^P and B^P sites can occur in the

plane of the H sheet or be displaced out of the H sheet in the space between two TS blocks, *i.e.*, toward the intermediate (**I**) block. Sokolova (2006) wrote the general formula for the TS block with two identical H sheets as follows $A^P_2B^P_2M^H_2M^O_4(Si_2O_7)_2X_{4+n}$, where $X_{4+n} = X^O_4 + X^P_{M2} + X^P_{A2}$, X = anions, X^O = anions of the O sheet not bonded to Si atoms, $X^P_{M2} + X^P_{A2}$ = apical anions of M^H and A^P atoms, and n is the number of X^P anions: $n = 0, 2, 4$. The core part of the TS block, $M^H_2M^O_4(Si_2O_7)_2X^O_4$, is invariant. The TS block is characterized by a planar cell based on translation vectors, t_1 and t_2 , with $t_1 \sim 5.5$ and $t_2 \sim 7$ Å and $t_1 \wedge t_2$ close to 90° . There are four groups of structures (Sokolova 2006, Sokolova & Cámara 2013): each group of structures has a different linkage of H and O sheets in the TS block and different content and stereochemistry of Ti (+ Nb + Zr + Mg + Mn). In Group I, Ti (+ Nb + Zr) = 1 *apfu* and Ti occurs in the O sheet; linkage 1 occurs: two Si_2O_7 groups of two H sheets link to the *trans* edges of an M^O polyhedron of the O sheet (M^O = Na). In Group II, Ti = 2 *apfu* and Ti occurs in the H sheet; 2 M^H = Ti; linkage 2 occurs: Si_2O_7 groups link to two M^{2+} (= Fe^{2+} , Mn) octahedra of the O sheet adjacent along t_2 . In Group III, Ti (+ Nb + Mg) = 3 *apfu* and Ti occurs in the O and H sheets; linkage 1 occurs: Si_2O_7 groups link to the *trans* edges of an M^O octahedron of the O sheet (M^O = Ti); 1 M^O and 2 M^H = Ti. In Group IV, Ti (+ Mg + Mn) = 4 *apfu* and Ti occurs in the O and H sheets; linkage 3 occurs: Si_2O_7 groups link to two Ti octahedra of the O sheet adjacent along t_1 ; 2 M^O and 2 M^H = Ti. In the crystal structures of TS-block minerals, TS blocks either link directly or alternate with **I** blocks.

LINKAGE OF H AND O SHEETS IN ERICSSONITE-2O, FERROERICSSONITE, AND YOSHIMURAITE

The cation radii of Nb^{5+} [$^{16}0.64$ Å (Shannon 1976)], Ti^{4+} [$^{16}0.605$ and $^{15}0.51$ Å], and Fe^{3+} [$^{16}0.645$ and $^{15}0.58$ Å] are very similar. Where Nb^{5+} and Ti^{4+} substitute for each other, the topology of the TS block obeys the general principles for TS-block structures developed by Sokolova (2006).

However, where Fe^{3+} occurs at the M^H site in the H sheet, the general structural principles for TS-block structures of Sokolova (2006) do not hold: the topology of the HOH layer with $Fe^{3+} = 2$ *apfu* (Fig. 1a, ericssonite-2O) obeys linkage 1: two Si_2O_7 groups of two H sheets link to the *trans* edges of an octahedron of the O sheet. In yoshimuraite, the topology of the HOH layer obeys linkage 2 (as in Group II, where Ti = 2 *apfu*): two Si_2O_7 groups of two H sheets link to two octahedra of the O sheet adjacent along **b** (Fig. 1b). Hence the topology of the HOH layer with $Fe^{3+} = 2$ *apfu* exhibits the topology of linkage 1, as in Group III where Ti = 3 *apfu*, *e.g.*, in barytolamprophyllite, ideally (BaK) $Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$ (Sokolova & Cámara 2008) (Fig. 1c, Table 1).

STEREOCHEMISTRY OF Ti^{4+}

Sokolova (2006) showed that the topology and stereochemistry of the TS block are strongly related to the Ti (+ Nb) content. Where we refer to Ti, we mean a *Ti-dominant site*; this site may also contain Nb, Ta, Zr, Fe^{3+} , Mn, Mg, *etc.* The Ti(Nb)–O distances do not vary greatly within the M^O octahedron, but show a wide

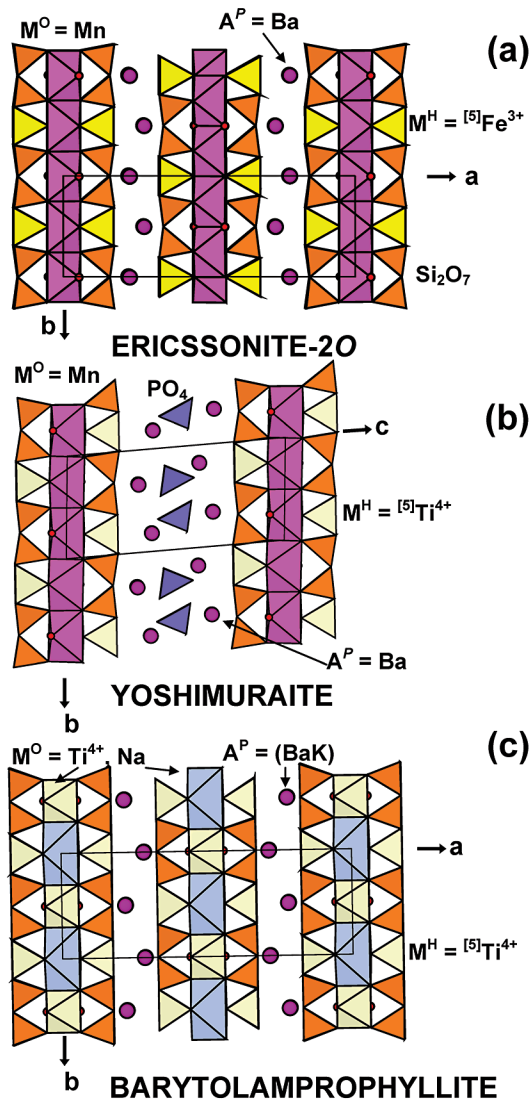


FIG. 1. General views of the crystal structures of (a) ericssonite-2O, (b) yoshimuraite, and (c) barytolamprophyllite. Mn, Ti, Fe^{3+} , Na, Si, and P polyhedra are magenta, pale yellow, yellow, blue, orange, and purple. Ba atoms and OH groups are shown as large raspberry and small red spheres.

range within the M^H polyhedron, *i.e.*, this polyhedron can be strongly distorted. Figure 2a shows the observed M^H -X distances as a function of bond valence incident at X (anion) from other cations. For Figure 2a, we used data of selected structures of TS-block minerals that

belong to Groups II, III, and IV where Ti occurs in the H sheet (Table 1). Figure 2b shows the environment of the [6]-coordinated M^H cation. Excluding the M^H cation, each X^O_M anion receives bond valence from three M^O cations of the O sheet, each X^{H}_{Si-M} anion receives bond

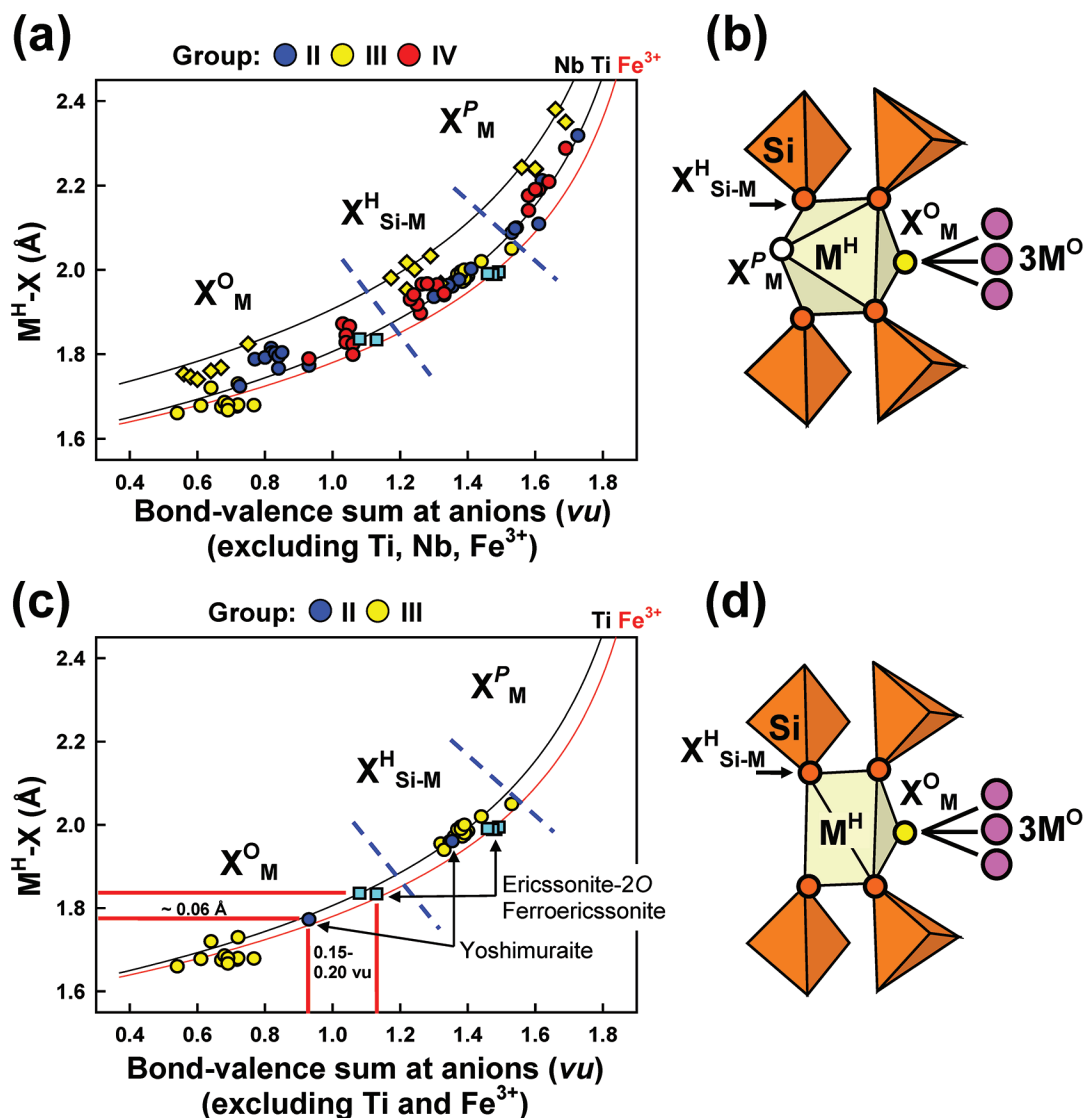


FIG. 2. The M^H -X distances (Å) versus bond-valence sums (excluding Ti, Nb, Fe^{3+}) for the [6]-coordinated M^H cation (a) and (excluding Ti and Fe^{3+}) for the [5]-coordinated M^H cation (c) at the X anions (vu), M^H = Ti, Nb, Fe^{3+} . The environment of the [6]-coordinated M^H cation (b) and [5]-coordinated M^H cation (d). Data for Group-II, Group-III, and Group-IV minerals (listed in Table 1) are shown as blue, yellow, and red circles (M^H = Ti) or diamonds (M^H = Nb). The data for ericssonite-2O and ferroericssonite are shown as turquoise squares. Dashed blue lines separate X^O_M , X^{H}_{Si-M} , and X^P_M data. Solid black and red lines show ideal bond-valence curves for Ti^{4+} , Nb^{5+} , and Fe^{3+} , respectively. In (b) and (d), M^H and Si polyhedra are pale yellow and orange; M^O cations and X^{H}_{Si-M} , X^P_M , and X^O_M anions are shown as large magenta and small orange, white, and yellow spheres. Modified from Sokolova (2006).

valence from one Si atom, and the X_M^P anion receives bond valence from the cations of the **I** block (if an **I** block is present). The Ti–X distances increase as the bond valence required to satisfy the valence-sum rule at the X anions decreases. The bond-valence curves for Ti^{4+} –O, Nb^{5+} –O, and Fe^{3+} –O (Brown 1981) are also shown in Figure 2a; the Ti^{4+} –O and Fe^{3+} –O curves are closer to each other than are the Ti^{4+} –O and Nb^{5+} –O curves. The Ti(Nb)–O bond-valence varies from ~ 0.34 to 1.53 *vu* (valence units), an extremely wide range of bond valence, with Ti(Nb)–O distances ranging from 2.38 (epistolite) to 1.66 Å (nechelyustovite). Figure 2a clearly shows three groups of M^H –O distances. The shortest distances are from the M^H cation to X_M^O (an anion common to the O and H sheets and not bonded to Si). Intermediate distances occur between the M^H cation and four X_{Si-M}^H anions of an Si_2O_7 group of the H sheet. The longest distances occur between the M^H cation and the X_M^P anion. The shortest M^H – X_M^O distances occur in Group III, where Ti^H is [5]-coordinated. The longest M^H – X_M^P distances occur in the crystal structure of epistolite, where Nb^{5+} is the dominant cation at the M^H site and is bonded to an H_2O group. Figure 2a shows that the main variation in bond valence (and corresponding distances) is associated with the X_M^O anion. The distortion of the M^H polyhedron allows Ti^H to satisfy the bond-valence requirements of the coordinating anions.

The M^H –O distances in ericssonite-2O and ferroericssonite (turquoise squares) fall within two groups of distances: the shortest distances from the M^H cation to X_M^O anion, and the intermediate distances between the M^H cation and four X_{Si-M}^H anions of an Si_2O_7 group of the H sheet (Fig. 2a). For more rigorous comparison, we consider structures with the [5]-coordinated M^H cation only: ericssonite-2O, ferroericssonite, and eight TS-block minerals (Fig. 2c). These TS-block minerals include yoshimuraite (Group II) and seven minerals of Group III: lamprophyllite, barytolamprophyllite, nabalamprophyllite, innelite, bornemanite, nechelyustovite, and kazanskyite. Figure 2d shows the environment of the [5]-coordinated M^H cation in the structures listed above. Excluding the M^H cation, each X_M^O anion receives bond valence from three M^O cations of the O sheet and each X_{Si-M}^H anion receives bond valence

from one Si atom. Note that distances and bond-valence contributions from the M^H cation to the X_{Si-M}^H anions of Si tetrahedra are approximately the same for TS-block minerals and ericssonite-2O and ferroericssonite (Fig. 2c). There is an insignificant difference in the M^H – X_M^O distances in yoshimuraite and ericssonite-2O and ferroericssonite: ~ 0.06 Å. However, the differences in bond-valence contribution to the X_M^O anion from the M^O cations of the O sheet in yoshimuraite and ericssonite-2O and ferroericssonite is significant: 0.20 *vu* (ericssonite-2O) and 0.15 *vu* (ferroericssonite) (Fig. 2c, Table 2).

DISTORTION OF OCTAHEDRA IN THE O SHEET

Consider the linkage of H and O sheets (Figs. 3a,c) and the corresponding distortion of M^O octahedra in the O sheet (Figs. 3b,d) for yoshimuraite and ericssonite-2O. In the TS block, each type of linkage of O and H sheets is associated with a specific type of distortion of the M^O octahedra in the O sheet (Sokolova 2006). In yoshimuraite, linkage 2 occurs: Si_2O_7 groups link to octahedra adjacent along t_2 (Fig. 3a). There are three types of anions in the O sheet: X_M^O (yellow sphere) is a common anion for three M^O cations and an M^H cation; X_{Si}^O (orange sphere) is a common anion for three M^O cations and a Si atom; X_A^O (blue sphere) is a common anion for three M^O cations and is an O atom of an OH group. In the O sheet, we identify two chains of octahedra, chain 1 and chain 2, along t_2 (Fig. 3b). In chain 1, each M^O octahedron shares anions with four Si tetrahedra and one M^H polyhedron (Fig. 3a,b). In chain 2, each M^O octahedron shares anions with two Si tetrahedra and two M^H polyhedra. Where an Si_2O_7 group links to the edge of an M^O octahedron, the latter edge contracts. In each M^O octahedron of chain 1, there are four long bonds to X_{Si}^O and two shorter bonds to the X_A^O and X_M^O anions. The shorter X_A^O – M^O – X_M^O distance is subparallel to t_1 , and four long bonds are in the plane perpendicular to t_1 . Therefore, in chain 1, an M^O octahedron is shortened along t_1 and elongated along t_2 . The M^O octahedra of two chains are the same size and they must distort in the same way in order to share edges and form the O sheet. Although M^O octa-

TABLE 2. BOND VALENCES* (*vu*) ON THE X_M^O ANION

Mineral	M^H	Bond-valence sum on the X_M^O anion	Contributions from specific cations	
			M^H	$3M^O$
yoshimuraite	$Ti^{4+}_{0.7}Fe^{3+}_{0.3}$	2.00	1.07	0.93
ericssonite-2O	Fe^{3+}	1.97	0.84	1.13
ferroericssonite	Fe^{3+}	1.89	0.81	1.08

*bond-valence values are from McDonald *et al.* (2000) for yoshimuraite and Kampf *et al.* (2011) for ferroericssonite; bond-valence values for ericssonite-2O have been calculated using bond-valence parameters of Brown (1981)

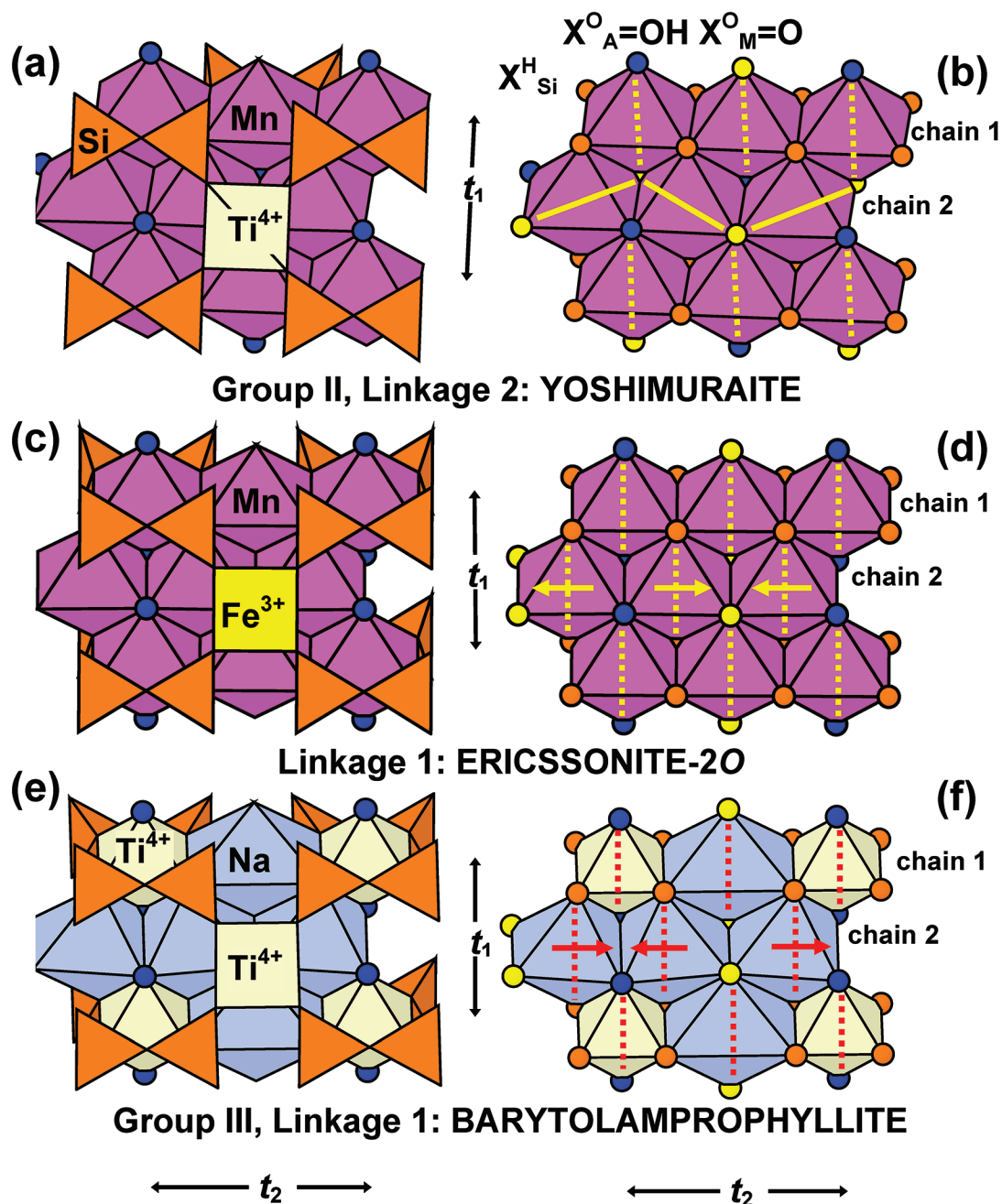


FIG. 3. Distortion of M^O octahedra in the O sheet of yoshimuraite, ericssonite-2O and, barytolamprophyllite: (a) linkage 2 in Group II, yoshimuraite; (b) the O sheet in yoshimuraite; (c) linkage 1 in ericssonite-2O; (d) the O sheet in ericssonite-2O; (e) linkage 1 in Group III, barytolamprophyllite; (f) the O sheet in barytolamprophyllite. Anions of the O sheet are shown as orange (X^O_{Si}), yellow (X^O_M), and blue (X^O_A) spheres. The Mn^{2+} , Na, Ti^{4+} , and Fe^{3+} polyhedra are magenta, blue, pale yellow, and yellow; Si tetrahedra are orange. Directions of shortening and elongation of M^O octahedra are shown by dashed and solid yellow (yoshimuraite and ericssonite-2O) and red (barytolamprophyllite) lines. Within an octahedron, the possible directions of displacement of a cation toward anions with low bond-valence sums are shown by yellow (yoshimuraite and ericssonite-2O) and red (barytolamprophyllite) arrows.

hedra in chain 2 do not share their edges with Si_2O_7 groups, an M^{O} octahedron (chain 2) must contract along $\mathbf{t}_1$ and elongate along $\mathbf{t}_2$, as does an M^{O} octahedron in chain 1. Inspection of the structures of Group II shows that $\text{M}^{\text{O}}(2)-\text{X}^{\text{O}}_{\text{M}}$ bonds are the longest in the M^{O} octahedron in chain 2, and these octahedra are elongate along $\text{X}^{\text{O}}_{\text{M}}-\text{M}^{\text{O}}(\text{chain } 2)-\text{X}^{\text{O}}_{\text{M}}$ (yellow circles in Fig. 3b). Thus with linkage 2, the arrangement of the $\text{X}^{\text{O}}_{\text{M}}$ anions allows the two types of M^{O} octahedra to be similarly distorted, and chain 2 has the same periodicity as chain 1, as required for an O sheet to occur.

Consider bond valences on the $\text{X}^{\text{O}}_{\text{M}}$ anion in yoshimuraite, ericssonite-2O, and ferroericssonite. In yoshimuraite, the $\text{X}^{\text{O}}_{\text{M}}$ anion receives 1.07 *vu* from Ti^{4+} at the M^{H} site, with $\text{Ti}^{4+}-\text{X}^{\text{O}}_{\text{M}} = 1.773 \text{ \AA}$, and it needs 0.93 *vu* from the M^{O} cations of the O sheet (Table 2). From the M^{O} cations, the $\text{X}^{\text{O}}_{\text{M}}$ anion receives the following bond-valence contributions: $(0.23 + 0.27) \text{ vu}$ from two M^{O} (chain 2) + 0.43 vu from M^{O} (chain 1) = 0.93 vu . There are two $\text{M}^{\text{O}}-\text{X}^{\text{O}}_{\text{M}}$ bond-lengths of 2.338 and 2.279 $\text{\AA}$ (McDonald *et al.* 2000) along $\text{X}^{\text{O}}_{\text{M}}-\text{M}^{\text{O}}(\text{chain } 2)-\text{X}^{\text{O}}_{\text{M}}$; they are the longest bond-lengths in the M^{O} octahedra. Hence in yoshimuraite, the arrangement of the $\text{X}^{\text{O}}_{\text{M}}$ sites allows the two types of M^{O} octahedra to be similarly distorted, chain 2 has the same periodicity as chain 1, and linkage 2 occurs (Fig. 3a).

In ericssonite-2O (and ferroericssonite), the $\text{X}^{\text{O}}_{\text{M}}$ anion receives 0.84 (0.81) *vu* from Fe^{3+} at the M^{H} site, with $\text{Fe}^{3+}-\text{X}^{\text{O}}_{\text{M}} = 1.834$ (1.836) $\text{\AA}$ (Figs. 3c,d), and needs 1.13 (1.08) *vu* from the M^{O} cations of the O sheet, *i.e.*, 0.20 (0.32) *vu* more than the $\text{X}^{\text{O}}_{\text{M}}$ anion in yoshimuraite (Table 2, Fig. 2c). In ericssonite-2O, the $\text{X}^{\text{O}}_{\text{M}}$ anion receives the following bond-valence contributions from the M^{O} cations: $0.33 \times 2 \text{ vu}$ from two M^{O} cations (chain 2) + 0.47 vu from one M^{O} cation (chain 1) = 1.13 vu . In ericssonite-2O, there are two $\text{M}^{\text{O}}-\text{X}^{\text{O}}_{\text{M}}$ distances of 2.192 $\text{\AA}$ (Matsubara 1980) along $\text{X}^{\text{O}}_{\text{M}}-\text{M}^{\text{O}}(\text{chain } 2)-\text{X}^{\text{O}}_{\text{M}}$; these distances are not the longest distances within M^{O} octahedra, they are similar to the other bond-lengths that range from 2.074 to 2.266 $\text{\AA}$. In ericssonite-2O, the Mn (= M^{O}) octahedra shorten in the $\mathbf{t}_1$ direction in both chains of octahedra and the Mn atoms shift toward the $\text{X}^{\text{O}}_{\text{M}}$ anions in chain 2 (Fig. 3d). The same scheme applies to ferroericssonite. Hence the distortions of the octahedra in the O sheet of ericssonite-2O and ferroericssonite are identical to those in barytolamprophyllite [Figs. 3e,f; after Sokolova (2006)], a Group-III TS-block mineral ($\text{Ti} = 3 \text{ apfu}$). These specific distortions are characteristic of linkage 1 of the O and H sheets in Group-III minerals: Si_2O_7 groups link to *trans* edges of the same octahedron in the O sheet (Figs. 3c,e). Therefore, the HOH layers in ericssonite-2O and ferroericssonite ($\text{Fe}^{3+} = 2 \text{ apfu}$) exhibit topology characteristic of the TS block in Group-III minerals ($\text{Ti} = 3 \text{ apfu}$) (Fig. 1c).

SUMMARY

(1) In ericssonite-2O and ferroericssonite, the $\text{X}^{\text{O}}_{\text{M}}$ anion receives a smaller bond-valence contribution from [5]-coordinated Fe^{3+} at the M^{H} site in the H sheet (compared to [5]-coordinated Ti^{4+} in yoshimuraite) and hence needs a larger contribution from the M^{O} cations of the O sheet.

(2) To provide this larger bond-valence contribution to the $\text{X}^{\text{O}}_{\text{M}}$ anion in ericssonite-2O and ferroericssonite, the M^{O} octahedra in the O sheet must distort differently from the M^{O} octahedra in yoshimuraite.

(3) In TS-block minerals, different distortions of M^{O} octahedra correspond to specific types of linkage of H and O sheets (Sokolova 2006). In ericssonite-2O and ferroericssonite and yoshimuraite, H and O sheets link in different ways and topologies of the HOH layer obey linkage 1 in ericssonite-2O and ferroericssonite and linkage 2 in yoshimuraite.

We conclude that different topologies of the chemically identical HOH layer in Fe^{3+} -disilicates ericssonite-2O and ferroericssonite and yoshimuraite, a TS-block mineral of Group II, are due to the difference in the bond-valence contributions of Fe^{3+} and Ti^{4+} in the H sheet and the subsequent different distortions of M^{O} octahedra in the O sheet, where $\text{M}^{\text{O}} = \text{Mn}^{2+}, \text{Fe}^{2+}$.

ACKNOWLEDGEMENTS

ES and FC are grateful to Frank C. Hawthorne for critically reading this manuscript; his comments significantly improved our English. FC thanks Frank C. Hawthorne for supporting two visiting research periods at Winnipeg (2008, 2013) and the Italian CNR for a grant of the Short-term Mobility Program 2008.

REFERENCES

- BROWN, I.D. (1981) The bond valence method: an empirical approach to chemical structure and bonding. In *Structure and Bonding in Crystals II* (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, New York, United States (1–30).
- CÁMARA, F. & SOKOLOVA, E. (2007) From structure topology to chemical composition. VI. Titanium silicates: the crystal structure and crystal chemistry of bornemanite, a group III Ti-disilicate mineral. *Mineralogical Magazine* **71**, 593–610.
- CÁMARA, F. & SOKOLOVA, E. (2009) From structure topology to chemical composition. X. Titanium silicates: the crystal structure and crystal chemistry of nechelyustovite, a group III Ti-disilicate mineral. *Mineralogical Magazine* **73**, 887–897.
- CÁMARA, F., SOKOLOVA, E., HAWTHORNE, F.C., & ABDU, Y. (2008) From structure topology to chemical composition. IX. Titanium silicates: revision of the crystal chemistry of

- lomonosovite and murmanite, Group-IV minerals. *Mineralogical Magazine* **72**, 1207–1228.
- CÁMARA, F., SOKOLOVA, E., & NIETO, F. (2009) Cámaraité, $\text{Ba}_3\text{NaTi}_4(\text{Fe}^{2+}, \text{Mn})_8(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH}, \text{F})_7$. II. The crystal structure and crystal chemistry of a new group-II Ti-disilicate mineral. *Mineralogical Magazine* **73**, 855–870.
- CÁMARA, F., SOKOLOVA, E., & HAWTHORNE, F.C. (2012) Kazanskyite, $\text{Ba}\square\text{TiNbNa}_3\text{Ti}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4$, a Group-III Ti-disilicate mineral from the Khibiny alkaline massif, Kola Peninsula, Russia: description and crystal structure. *Mineralogical Magazine* **76**, 473–492.
- CÁMARA, F., SOKOLOVA, E., ABDU, Y.A., HAWTHORNE, F.C., & KHOMEYAKOV, A.P. (2013) Kolskyite, $(\text{Ca}\square)\text{Na}_2\text{Ti}_4(\text{Si}_2\text{O}_7)_2\text{O}_4(\text{H}_2\text{O})_7$, a Group-IV Ti-disilicate mineral from the Khibiny alkaline massif, Kola Peninsula, Russia: description and crystal structure. *Canadian Mineralogist* **51**(6), 921–936.
- ERCIT, T.S., COOPER, M.A., & HAWTHORNE, F.C. (1998) The crystal structure of vuonnemite, $\text{Na}_{11}\text{Ti}^{4+}\text{Nb}_2(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_3(\text{F}, \text{OH})$, a phosphate-bearing sorosilicate of the lomonosovite group. *Canadian Mineralogist* **37**, 1311–1320.
- FERRARIS, G., IVALDI, G., KHOMEYAKOV, A.P., SOBOLEVA, S.V., BELLUSO, E., & PAVESE, A. (1996) Nafertisite, a layer titanosilicate member of a polysomatic series including mica. *European Journal of Mineralogy* **8**, 241–249.
- KAMPE, 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. *Canadian Mineralogist* **49**, 587–594.
- KRIVOVICHEV, S.V., ARMBRUSTER, T., YAKOVENCHUK, V.N., PAKHOMOVSKY, YA. A., & MEN'SHIKOV, YU. P. (2003) Crystal structures of lamprophyllite-2M and lamprophyllite-2O from the Lovozero alkaline massif, Kola peninsula, Russia. *European Journal of Mineralogy* **15**, 711–718.
- MATSUBARA, S. (1980) The crystal structure of orthoericssonite. *Mineralogical Journal* **10**, 107–121.
- MCDONALD, A.M., GRICE, J.D., & CHAO, G.Y. (2000) The crystal structure of yoshimuraite, a layered Ba–Mn–Ti silicophosphate, with comments of five-coordinated Ti^{4+} . *Canadian Mineralogist* **38**, 649–656.
- RASTSVETAeva, R.K. & CHUKANOV, N.V. (1999) Crystal structure of a new high-barium analogue of lamprophyllite with a primitive unit cell. *Doklady Chemistry* **368**, 228–231.
- RASTSVETAeva, R.K., TAMAZYAN, R.A., SOKOLOVA, E.V., & BELAKOVSKII, D.I. (1991) Crystal structures of two modifications of natural Ba, Mn-titanosilicate. *Soviet Physics, Crystallography* **36**, 186–189.
- SHANNON, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica A* **32**, 751–767.
- SOKOLOVA, E. (2006) From structure topology to chemical composition. I. Structural hierarchy and stereochemistry in titanium disilicate minerals. *Canadian Mineralogist* **44**, 1273–1330.
- SOKOLOVA, E. & CÁMARA, F. (2008) From structure topology to chemical composition. III. Titanium silicates: crystal chemistry of barytolamprophyllite. *Canadian Mineralogist* **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. *Canadian Mineralogist* **51**(6), 861–891.
- SOKOLOVA, E. & HAWTHORNE, F.C. (2001) The crystal chemistry of the $[\text{M}_3\text{O}_{11-14}]$ trimeric structures: from hyperagapaitic complexes to saline lakes. *Canadian Mineralogist* **39**, 1275–1294.
- SOKOLOVA, E. & HAWTHORNE, F.C. (2004) The crystal chemistry of epistolite. *Canadian Mineralogist* **42**, 797–806.
- SOKOLOVA, E. & HAWTHORNE, F.C. (2008) From structure topology to chemical composition. IV. Titanium silicates: the orthorhombic polytype of nabalamprophyllite from Lovozero massif, Kola Peninsula, Russia. *Canadian Mineralogist* **46**, 1323–1331.
- SOKOLOVA, E., HAWTHORNE, F.C., & KHOMEYAKOV, A.P. (2005) Polyphite and sobolevite: revision of their crystal structures. *Canadian Mineralogist* **43**, 1527–1544.
- SOKOLOVA, E., CÁMARA, F., HAWTHORNE, F.C., & ABDU, Y. (2009) From structure topology to chemical composition. VII. Titanium silicates: the crystal structure and crystal chemistry of jinshajiangite. *European Journal of Mineralogy* **21**, 871–883.
- SOKOLOVA, E., CÁMARA, F., & HAWTHORNE, F.C. (2011) From structure topology to chemical composition. XI. Titanium silicates: crystal structures of innelite-1T and innelite-2M from the Inagli massif, Yakutia, Russia and the crystal chemistry of innelite. *Mineralogical Magazine* **75**, 2495–2518.
- ZHOU, H., RASTSVETAeva, R.K., KHOMEYAKOV, A.P., MA, Z., & SHI, N. (2002) Crystal structure of new micalike titanosilicate—bussenite, $\text{Na}_2\text{Ba}_2\text{Fe}^{2+}(\text{TiSi}_2\text{O}_7)(\text{CO}_3)\text{O}(\text{OH})(\text{H}_2\text{O})$. *F. Crystallography Reports* **47**, 43–46.

Received March 15, 2014. Accepted April 11, 2014.