

THE CRYSTAL CHEMISTRY OF SILICATE MINERALS WITH CHAINS OF (TiO₆) OCTAHEDRA

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ABSTRACT

Chains of (TiO₆) octahedra occur in several crystal structures as fundamental building blocks, confirming the tendency of self-polymerization for (TiO₆) octahedra. There are two topologically distinct types of chains based on linkage of (TiO₆) octahedra, corner-sharing chains and edge-sharing chains. In this paper, we focus on the diversity of linkages between chains of (TiO₆) octahedra and (SiO₄) tetrahedra. In Ti-silicate structures based on chains of corner-sharing (Ti⁴⁺φ₆) octahedra, the chains are neither branched nor looped; they are topologically simple [Tiφ₅] chains. The chemical formulae of such structures may be written in a very general way as Na_{2a} (TiO)_a [Si_c O_{2(a+c)}] (H₂O)_n and Na_a (Ti{OH})_a [Si_c O_{2(a+c)}] (H₂O)_n, where *a* and *c* are integers. These are not arbitrary formulae; the bond topology is such that all anions obey the valence-matching principle. The formulae of batisite, narsarsukite, titanite, the minerals of the labuntsovite group and quartz (Ti-free) are in accord with this general formula. In structures based on chains of edge-sharing (Ti⁴⁺φ₆) octahedra, the chains may be simple, branched or looped, and there is usually another complicating factor to the bond topology: additional components [*e.g.*, (PO₄), Cl, ^[4]Al, Cr³⁺] are common. None of the resultant structures have cubic, hexagonal or trigonal symmetry. There are numerous silicate minerals containing chains of (TiO₆) octahedra. In contrast, layers of (TiO₆) octahedra are rare and occur only in four structure types, and frameworks of (TiO₆) octahedra are not known in silicate minerals.

Keywords: titanium silicates, (TiO₆) octahedron, chain, layer.

SOMMAIRE

La structure cristalline de plusieurs minéraux contiennent des chaînes d'octaèdres (TiO₆) comme module fondamental, ce qui confirme la tendance qu'ont ces octaèdres à se polymériser. Il faut distinguer deux types de chaînes topologiquement différents; dans un cas, les octaèdres partagent des coins, et dans l'autre, ils partagent des arêtes. Dans ce travail, nous évaluons la diversité d'agencements entre chaînes d'octaèdres (TiO₆) et de tétraèdres (SiO₄). Dans la structure de silicates de Ti dans lesquelles les octaèdres (Ti⁴⁺φ₆) partagent des coins, les chaînes sont ni branchées ou en boucle; ce sont des chaînes [Tiφ₅] topologiquement simples. On peut exprimer la formule chimique de telles structures d'une façon générale, Na_{2a} (TiO)_a [Si_c O_{2(a+c)}] (H₂O)_n et Na_a (Ti{OH})_a [Si_c O_{2(a+c)}] (H₂O)_n, dans laquelle *a* et *c* sont des nombres entiers. Il ne s'agit pas de formules quelconques. La topologie des liaisons est telle que tous les anions sont régis par le principe d'une concordance des valences de liaisons. La formule de la batisite, narsarsukite, titanite, les minéraux du groupe de la labuntsovite et le quartz (dépourvu de Ti) concordent avec cette formule générale. Dans les structures fondées sur des chaînes d'octaèdres (Ti⁴⁺φ₆) à arêtes partagées, les chaînes peuvent être simples, branchées ou en boucle, et il y a en général un autre facteur pour compliquer la topologie des liaisons: les composants additionnels [*e.g.*, (PO₄), Cl, ^[4]Al, Cr³⁺] sont répandus. Aucune de ces structures ne possède une symétrie cubique, hexagonale ou trigonale. Plusieurs minéraux silicatés contiennent des chaînes d'octaèdres (TiO₆). En revanche, les minéraux qui contiennent des couches d'octaèdres (TiO₆) sont rares et limitées à quatre types de structure; il n'y a aucun exemple d'un minéral silicaté contenant une trame d'octaèdres (TiO₆).

(Traduit par la Rédaction)

Mots-clés: silicates de titane, octaèdre (TiO₆), chaîne, couche.

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INTRODUCTION

Currently, the crystal structures of about 120 Ti–O compounds are known, half of them Ti silicates and half of them Ti oxides. Except for titanite, Ti silicates usually occur as accessory minerals and are less widespread than Ti-oxide minerals. Nevertheless, Ti silicates are fairly numerous, particularly compared to analogous sulfates, phosphates and arsenates: there are no Ti-sulfate minerals, one Ti-phosphate mineral and one Ti-arsenate mineral, although several Ti-silicate minerals also contain (PO₄) and (SO₄) groups. In minerals, Ti⁴⁺ is generally [6]-coordinated, and less commonly [5]-coordinated. In many Ti-silicate minerals, Ti ↔ Nb substitution is common (r [Ti⁴⁺] = 0.605, r [Nb⁵⁺] = 0.64 Å; Shannon 1976). Hence, when we refer to (TiO₆) octahedra, we include ({Ti,Nb}O₆) octahedra. In a crystal structure, (SiO₄) tetrahedra and (TiO₆) octahedra never share common edges; linkage of (TiO₆) and (SiO₄) groups involves only common vertices. If a (TiO₆) polyhedron contains a significant amount of M³⁺ cations, then edge-sharing between (MO₆) and (SiO₄) polyhedra becomes possible. There is one common feature of (TiO₆) and (SiO₄) polyhedra: they tend to self-polymerize (Pyatenko *et al.* 1976), forming one-, two- and three-dimensional linkages. Dimers of (TiO₆) octahedra, connected *via* common vertices or edges, occur in several silicate minerals, *e.g.*, astrophyllite: (K,Na)₃(Fe²⁺,Mn)₇Ti₂Si₈O₂₄(OH), leucosphenite: BaNa₄Ti₂B₂Si₁₀O₃₀. We will not consider them in this work, and will focus on more extensive polymerizations of (TiO₆) octahedra. Diversity in Ti-silicates results from two factors: (1) self-polymerization of (TiO₆) and (SiO₄) polyhedra, and (2) the dimensional similarity of motifs of polymerized (TiO₆) octahedra and (SiO₄) tetrahedra that allows these motifs to link together easily in a crystal structure. There are two types of self-linkage of (TiO₆) octahedra: (1) through a common vertex, and (2) through a common edge, each type of linkage producing a chain of (TiO₆) octahedra. Chains of (TiO₆) octahedra are fairly common, sheets of (TiO₆) octahedra are uncommon, and frameworks of (TiO₆) octahedra do not occur in structures of Ti-silicate minerals. Here, we examine this type of polymerization; we will not describe every Ti-silicate mineral, but will focus on those structures that exhibit the full diversity of the linkage of chains of (TiO₆) octahedra and different types of Si–O radicals. Our intention is to eventually produce a set of general formulae that generate all topologically and topochemically possible structures of Ti-silicate compounds.

CHAINS OF EDGE-SHARING (TiO₆) OCTAHEDRA

The two simplest types of chain of edge-sharing (TiO₆) octahedra are shown in Figures 1a and 1b. Both have the stoichiometry [TiO₄], but differ in the arrangement of adjacent octahedra (*i.e.*, they are geometrical

isomers). In Figure 1a, next-nearest-neighbor octahedra are in a *trans* configuration, and the resulting straight chain is a component of the structure of rutile; we designate this the *rutile chain*. In Figure 1b, next-nearest-neighbor octahedra are in a staggered configuration, and the resulting kinked chain is a component of the structure of brookite; we designate this the *brookite chain*. We will write the formulae of these chains in terms of the translationally symmetric fundamental building block: [TiO₄]^{4–} for the rutile chain, [Ti₂O₈]^{8–} for the brookite chain. The repeat distances along these two chains are ~2.8 Å for the rutile chain and ~5.6 Å for the brookite chain. These chains may be decorated either by other (TiO₆) octahedra, which link by vertex sharing, or chains may polymerize by vertex sharing to form ribbons or tunnels. Figure 1c shows a decorated brookite chain in which one of the two single-valence vertices of each octahedron in the chain links to a single (TiO₆) octahedron; the resultant formula is [Ti₄O₁₇]^{18–}, and the repeat distance remains ~5.6 Å; such chains can be designated as *branched chains* (Liebau 1985). Figure 1d shows a *looped chain* (Liebau 1985) formed by condensation of four rutile chains *via* sharing of octahedron vertices; the [Ti₄O₁₂]^{8–} tunnel has the repeat distance of the component [TiO₄] chains: ~2.8 Å. In the [Ti₄O₁₀(OH)₈]^{12–} cluster (Fig. 1e), each (TiO₆) octahedron shares three edges with other octahedra to form a vacant tetrahedron inside the cluster. In rutile, brookite and anatase, each (TiO₆) octahedron shares two, three and four edges, respectively, with adjacent octahedra. This cluster may be regarded as a derivative of the brookite structure because its constituent octahedra also share three edges with adjacent octahedra. Each cluster shares two common vertices with two adjacent clusters to form a [Ti₄O₁₀(OH)₄]^{8–} chain (Fig. 1e). Table 1 presents selected data for Ti-silicate minerals with chains of edge-sharing (TiO₆) octahedra.

Polyakovite-(Ce): REE₄MgCr³⁺₂Ti⁴⁺₂Si₄O₂₂

The main building unit of the polyakovite-(Ce) structure is a layer of octahedra parallel to (001) (Figs. 2a,b) (Popov *et al.* 2001). This layer consists of two distinct rutile-like chains of octahedra in which each octahedron shares two *trans* edges with adjacent octahedra; the first chain involves (TiO₆) octahedra, and the second chain involves (Cr³⁺O₆) octahedra. Ideally, the layer consists of regularly alternating [TiO₄]^{4–} and [Cr³⁺O₄]^{5–} chains that are connected through common vertices. Intercalated between these layers are heteropolyhedral chains of [Si₂O₇] groups and (MgO₆) octahedra that extend in the *a* direction. Two outer vertices of one tetrahedron of the [Si₂O₇] group link to the apical vertices of (TiO₆) octahedra (Figs. 2b, 3b). Regular arrangement of (TiO₆) and (Cr³⁺O₆) octahedra within the layer results in relatively large cages that contain the REE(1) and REE(2) sites (CN = [8] and [10], respectively). In a broad sense, polyakovite-(Ce) and perrierite-(Ce), ideally Ce₄Fe²⁺

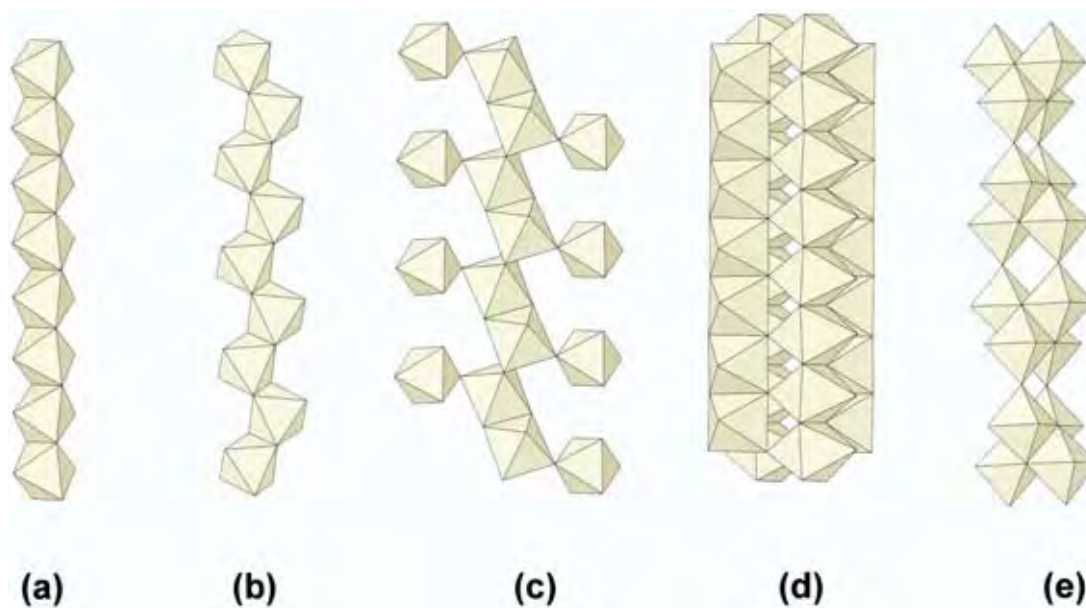


FIG. 1. Chains of edge-sharing (TiO₆) octahedra: (a) rutile [TiO₄]⁴⁻ chain, (b) brookite [Ti₂O₈]⁸⁻ chain, (c) branched [Ti₄O₁₇]¹⁸⁻ chain, (d) looped [Ti₄O₁₂]⁸⁻ chain, (e) looped [Ti₄O₁₀(OH)₄]⁸⁻ chain.

(Ti⁴⁺,Fe³⁺)₄ Si₄ O₂₂ (Gottardi 1960), are structural dimorphs, neglecting the compositional difference at the octahedrally coordinated sites. The principal difference between the two structure-types involves the linkage of (TiO₆) octahedra and [Si₂O₇] groups (Figs. 3a, b, Table 1). Between the layers, there are [6]-coordinated M(1) sites occupied by Mg, Fe²⁺, Zr or Ti⁴⁺, and [10–11]-coordinated A(1,2) sites occupied primarily by REE, Ca and Sr. On the basis of structure topology (Macdonald *et al.* 2002), chevkinite-group minerals can be divided into two groups: (1) chevkinite-(Ce), ideally (REE,Ca)₄ Fe²⁺ (Ti,Fe³⁺,Nb)₄ Si₄ O₂₂ (Sokolova *et al.* 2004), strontiochevkinite, ideally (Sr,REE)₄ Fe²⁺ (Ti⁴⁺,Fe³⁺) Si₄ O₂₂ (Haggerty & Mariano 1983), and polyakovite-(Ce) [all with β angles of ~101°], and (2) perrierite-(Ce), rengerite, ideally Sr₄ Zr Ti⁴⁺₄ Si₄ O₂₂ (Miyajima *et al.* 2001), and matsubaraite, ideally Sr₄ Ti⁴⁺₅ Si₄ O₂₂ (Miyajima *et al.* 2002) [all with β angles of ~113°]. Matsubaraite is the only mineral in which the M(1) site is occupied primarily by Ti⁴⁺.

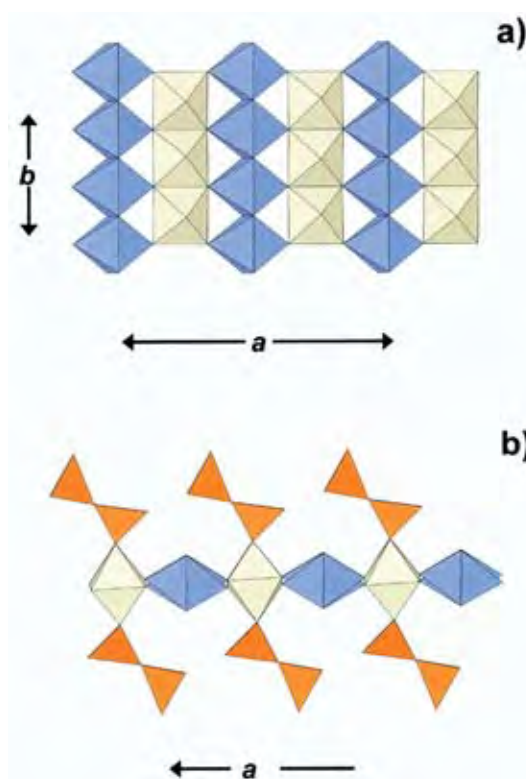


FIG. 2. The crystal structure of polyakovite-(Ce): (a) the layer of rutile-like [TiO₄]⁴⁻ and [CrO₄]²⁻ chains; (b) view of the layer with adjacent [Si₂O₇] groups down [010]. (TiO₆) octahedra are yellow, (CrO₆) octahedra are blue, and (SiO₄) tetrahedra are orange.

TABLE 1. SELECTED SILICATE MINERALS WITH CHAINS OF (TiO_6) OCTAHEDRA

Formula	a (Å)	b (Å)	c (Å)	β (°)	Z	Sp. gr.	Chain	Si-O radical	Ref.
<i>Chains of edge-sharing (TiO_6) octahedra</i>									
Polyakovite-(Ce) $(\text{REE}, \text{Ca})_4 (\text{Mg}, \text{Fe}^{2+}) (\text{Cr}, \text{Fe}^{3+})_2 (\text{Ti}^{4+}, \text{Nb})_2 (\text{Si}_2\text{O}_7)_2 (\text{Si}_2\text{O}_6)_2$	13.398	5.6974	11.042	100.539	2	C2/m	$[\text{TiO}_4]^{4-}$	$[\text{Si}_2\text{O}_7]^{6-}$ group	(1)
Vinogradovite $\text{Na}_5 \text{Ti}^{4+}_4 (\text{Si}, \text{Al}) \text{O}_{26} (\text{H}_2\text{O})_3$	24.49	8.657	5.203	100.2	2	C2/c	$[\text{Ti}_2\text{O}_6]^{8-}$	$[\text{Si}_2\text{O}_6]^{4-}$ & $[\text{Si}_4\text{O}_{10}]^{4-}$ chains	(2)
Murmanite* $\text{Na}_2 \text{Ti}^{4+}_2 \text{O}_2 [\text{Si}_2 \text{O}_7] (\text{H}_2\text{O})_2$	5.383	7.053	12.170	107.82	2	P1	$[\text{Ti}_4 \text{O}_{17}]^{18-}$	$[\text{Si}_2\text{O}_7]^{6-}$ group	(3)
Baotite $\text{Ba}_4 (\text{Ti}^{4+}, \text{Nb})_8 [\text{Si}_4 \text{O}_{13}] \text{O}_{16} \text{Cl}$	19.990	19.990	5.908		4	I4 ₁ /a	$[\text{Ti}_4 \text{O}_{12}]^{8-}$	$[\text{Si}_4\text{O}_{12}]^{8-}$	(4)
Sitinakite $\text{K Na}_2 \text{Ti}^{4+}_4 [\text{Si}_4 \text{O}_{12}] \text{O}_5 (\text{OH}) (\text{H}_2\text{O})_4$	7.819	7.819	12.099		2	P4 ₂ /mcm	$[\text{Ti}_4 \text{O}_{10} (\text{OH})_4]^{8-}$	$[\text{SiO}_4]^{4-}$ tetrahedron	(5)
<i>Chains of corner-sharing (TiO_6) octahedra</i>									
Batisite $\text{Ba Na}_2 \text{Ti}^{4+}_2 [\text{Si}_4\text{O}_{12}] \text{O}_2$	10.4	13.85	8.1		4	Ima2	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{Si}_4\text{O}_{12}]^{8-}$ chain	(6)
Narsarsukite $\text{Na}_4 \text{Ti}^{4+}_2 [\text{Si}_6\text{O}_{20}] \text{O}_2$	10.727	10.727	7.948		2	I4/m	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{Si}_6\text{O}_{20}]^{8-}$ chain	(7)
Titanite $\text{Ca Ti}^{4+} [\text{SiO}_4] \text{O}$	7.068	8.714	6.562	113.8	4	P2 ₁ /a	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{SiO}_4]^{4-}$ tetrahedron	(8)
Korobitsynite $\text{Na}_{6-x} \text{Ti}^{4+}_4 (\text{Si}_4\text{O}_{12})_2 (\text{O}, \text{OH})_4 (\text{H}_2\text{O})_8$	7.35	14.153	7.124		2	Pbam	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{Si}_4\text{O}_{12}]^{8-}$ ring	(9)
Lemleinite-(Ba) $\text{Na}_4 \text{K}_4 \text{Ba}_{6-x} \text{Ti}^{4+}_8 (\text{Si}_4\text{O}_{12})_4 (\text{O}, \text{OH})_8 (\text{H}_2\text{O})_8$	14.216	13.755	7.767	116.7	1	C2/m	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{Si}_4\text{O}_{12}]^{8-}$ ring	(10)
Zorite $\text{Na}_6 \text{Ti}^{4+}_4 (\text{Ti}^{4+}, \text{Nb})_4 (\text{Si}_6\text{O}_{17})_2 (\text{OH}, \text{O})_4 (\text{H}_2\text{O})_{10.5}$	23.241	7.238	6.955		1	Cmmm	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{Si}_6\text{O}_{17}]^{10-}$ chain	(11)
<i>Layers of (TiO_6) octahedra</i>									
Perrierite-(Ce) $(\text{REE}, \text{Ca})_4 (\text{Fe}^{2+}, \text{Ca}) (\text{Ti}^{4+}, \text{Al}, \text{Fe}^{3+})_2 \text{Ti}_2 [\text{Si}_2 \text{O}_7]_2 \text{O}_8$	13.61	5.62	11.63	113.5	2	C2/m	$[\text{TiO}_4]^{4-}$	$[\text{Si}_2\text{O}_7]^{6-}$ group	(12)
Chevkinite-(Ce) $(\text{REE}, \text{Ca})_4 (\text{Fe}^{2+}, \text{Mg}) \text{Fe}^{3+}_2 (\text{Ti}^{4+}, \text{Nb})_2 [\text{Si}_2 \text{O}_7]_2 \text{O}_8$	13.4319	5.7628	11.0914	100.629	2	C2/m	$[\text{TiO}_4]^{4-}$	$[\text{Si}_2\text{O}_7]^{6-}$ group	(13)
Fersmanite $(\text{Ca}, \text{Na})_4 (\text{Na}, \text{Ca})_4 (\text{Ti}^{4+}, \text{Nb})_4 (\text{Si}_2\text{O}_7)_2 \text{O}_8 \text{F}_3$	10.183	10.183	20.396	97.19	4	C2/c	$[\text{Ti}_2\text{O}_{10}]^{12-}$	$[\text{Si}_2\text{O}_7]^{6-}$ group	(14)
Lorenzenite $\text{Na}_2 \text{Ti}^{4+}_2 [\text{Si}_2 \text{O}_6] \text{O}_3$	8.713	5.233	14.487		4	PCcn	$[\text{Ti}_2 \text{O}_6]^{8-}$	$[\text{Si}_2\text{O}_6]^{4-}$ chain	(15)

* $\alpha = 93.16^\circ$, $\gamma = 90.06^\circ$

References: (1) Popov *et al.* (2001); (2) Kalsbeek & Ransbo (1992); (3) Khalilov (1989); (4) Nekrasov *et al.* (1969); (5) Sokolova *et al.* (1989); (6) Nikitin & Belov (1962); (7) Peacor & Buerger (1962); (8) Taylor & Brown (1976); (9) Rastvetaeva *et al.* (1997a); (10) Sandomirskii & Belov (1979); (11) Rastvetaeva *et al.* (1997b); (12) Gottardi (1960); (13) Sokolova *et al.* (2004); (14) Sokolova *et al.* (2002); (15) Sundberg *et al.* (1987).

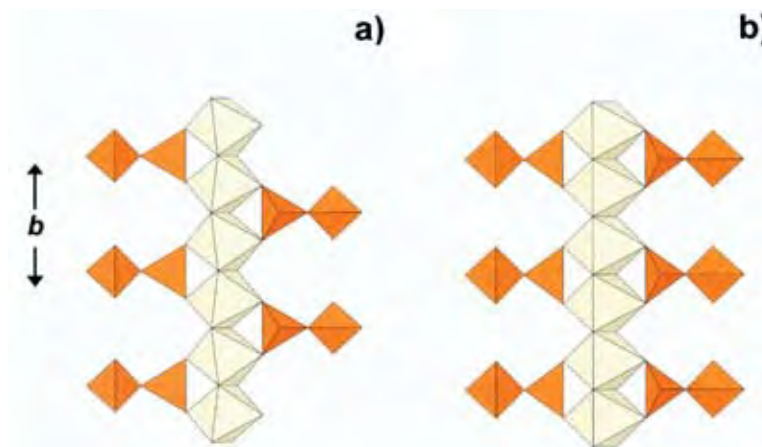


FIG. 3. Linkage of rutile-like $[\text{TiO}_4]^{4-}$ chains with (Si_2O_7) groups in the crystal structure of (a) polyakovite-(Ce) and (b) perrierite-(Ce). Legend as in Figure 2.

Ti^{4+} is an important constituent of the chevkinite-group minerals. The degree of polymerization of (TiO_6) octahedra is different for polyakovite-(Ce) and other minerals of this group: we can assume that chevkinite-(Ce), strontiochevkinite, perrierite-(Ce), rengerite and matsubaraite have a layer of (TiO_6) octahedra in their structure. We will consider this type of layer later.

Vinogradovite: $\text{Na}_5 \text{Ti}^{4+}_4 (\text{Si}_7\text{Al}) \text{O}_{26} (\text{H}_2\text{O})_3$

In the crystal structure of vinogradovite, (TiO_6) octahedra share common edges to form zig-zag brookite-like chains along $[001]$ (Fig. 4a) (Rastsvetaeva & Andrianov 1984, Kalsbeek & Rønso 1992). These chains are decorated by (NaO_6) octahedra and linked into a sheet parallel to (001) by *vinogradovite* $[\text{T}_4\text{O}_{10}]$ chains ($T = \text{Si}, \text{Al}$). There are actually two types of T -O chains in the crystal structure of vinogradovite: pyroxene-like $[\text{Si}_2\text{O}_6]$ chains and $[(\text{Si}, \text{Al})_4\text{O}_{10}]$ chains both occur, and both chains extend along $[001]$. Inspection of both T -O chains and the brookite-like chains (Figs. 4b, c) indicates how Si-O and Ti-O motifs can link to each other. Chains of tetrahedra and chains of octahedra link to form a framework with channels (along $[001]$, Fig. 4a) that contain disordered (H_2O) groups and Na atoms. An identical linkage of T -O chains and $[\text{Ti}_2\text{O}_8]^{8-}$ brookite-like chains occurs in the structure of

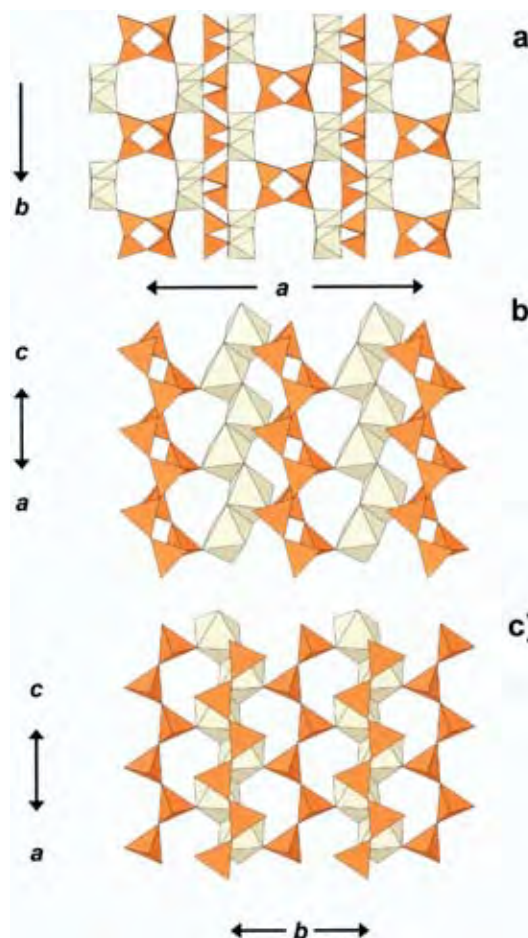


FIG. 4. Fragments of the crystal structure of vinogradovite: (a) mixed framework of (TiO_6) octahedra and (SiO_4) tetrahedra; (b) linkage of brookite-like $[\text{Ti}_2\text{O}_8]^{8-}$ chains and vinogradovite-like $[\text{T}_4\text{O}_{10}]$ chains, where $T = \text{Si}, \text{Al}$; (c) linkage of brookite-like $[\text{Ti}_2\text{O}_8]^{8-}$ chains and pyroxene-like $[\text{T}_2\text{O}_6]$ chains, where $T = \text{Si}, \text{Al}$. Legend as in Figure 2.

paravinogradovite, $\text{Na}_2 [\text{Ti}^{4+}_3 \text{Fe}^{3+} \{\text{Si}_2 \text{O}_6\}_2 \{\text{Si}_3 \text{AlO}_{10}\} (\text{OH})_4] \text{H}_2\text{O}$ (space group $P1$, a 5.2533(1), b 8.7411(3), c 12.9480(5) Å, α 70.466(1)° β 78.472(1)° γ 89.932(1)°, V 547.65(5) Å³, $Z = 1$) (Khomyakov *et al.* 2003). Paravinogradovite is chemically related to vinogradovite by the substitution $\square_3 + \text{Fe}^{3+} + (\text{OH})^{-}_4 + (\text{H}_2\text{O})_2 \leftrightarrow \text{Na}_3 + \text{Ti}^{4+} + \text{O}^{2-}_4 + \square_2$. The crystal structure of paravinogradovite is topologically identical to that of vinogradovite, except for the deficit of Na and complete order of Si and Al within vinogradovite-like $[\text{Si}_3\text{AlO}_{10}]^{5-}$ chains. The triclinic cell of paravino-

gradovite is related to the C -centered monoclinic cell of vinogradovite by the matrix transformation $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & -2 & 1 \end{pmatrix}$.

Murmanite: $\text{Na}_2 \text{Ti}_2 \text{O}_2 [\text{Si}_2\text{O}_7] (\text{H}_2\text{O})_2$

The principal building unit of the murmanite structure is a Ti-silicate block (TS); these blocks stack along $[001]$ with weak hydrogen bonding between them (Khalilov 1989). The TS block consists of a central sheet of octahedra and two adjacent sheets of heteropolyhedra containing $(\text{Ti}\phi_6)$ octahedra, (Si_2O_7) groups and $(\text{Na}\phi_8)$ polyhedra where ϕ represents any anion (Fig. 5a). There are two types of chains of edge-sharing octahedra within the central sheet: (TiO_6) octahedra form a brookite-like $(\text{Ti}_2\text{O}_8)^{8-}$ chain (cf. Fig. 1b) and (NaO_6) octahedra form a chain of the same topology (Fig. 5b). The (TiO_6) octahedra of the central sheet link to $(\text{Ti}\phi_6)$ octahedra of the adjacent sheets of heteropolyhedra to produce a branched chain with mixed edge- and corner-sharing of (TiO_6) octahedra (cf. Figs. 1c and 5c). Each (TiO_6) octahedron of the central sheet shares two *cis* vertices with vertices of two (SiO_4) tetrahedra of the $[\text{Si}_2\text{O}_7]$ group in one adjacent sheet, and one vertex with an (SiO_4) tetrahedron of the $[\text{Si}_2\text{O}_7]$ group in the other adjacent sheet. By analogy with Liebau's classification of silicates (Liebau 1985), we call this $[\text{Ti}_4\text{O}_{17}]^{18-}$ chain a branched chain. Pyatenko *et al.* (1976) called this chain a *lomonosovite* chain when they identified it in lomonosovite, $\text{Na}_{10} \text{Ti}^{4+}_4 [\text{Si}_2\text{O}_7]_2 [\text{PO}_4]_2 \text{O}_4$ (Rastvetaeva *et al.* 1971). This chain occurs in the structures of the silicophosphate minerals of the lomonosovite group: lomonosovite, quadruphite, $\text{Na}_{14} \text{Ca}_2 \text{Ti}^{4+}_4 (\text{Si}_2\text{O}_7)_2 (\text{PO}_4)_4 \text{O}_4 \text{F}_2$ (Sokolova & Hawthorne 2001), polyphite, $\text{Na}_{17} \text{Ca}_3 \text{Mg} (\text{Ti}^{4+}, \text{Mn}^{2+})_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_6 \text{O}_2 \text{F}_6$ (Sokolova *et al.* 1987), and sobolevite, $\text{Na}_{11} (\text{Na}, \text{Ca}) (\text{Mg}, \text{Mn}^{2+}) \text{Ti}^{4+}_4 [\text{Si}_2\text{O}_7]_2 (\text{PO}_4)_4 \text{O}_3 \text{F}_3$ (Sokolova *et al.* 1988). In the silicophosphate structures, TS blocks (Fig. 5a) stack along $[001]$ with intervening blocks (AC) of alkali cations.

Baotite: $\text{Ba}_4 (\text{Ti}^{4+}, \text{Nb})_8 [\text{Si}_4\text{O}_{12}] \text{O}_{16} \text{Cl}$

In the crystal structure of baotite, $[\text{Si}_4\text{O}_{12}]^{8-}$ rings and looped $[\text{Ti}_4\text{O}_{12}]^{8-}$ chains (Fig. 1d) form a mixed tetrahedron–octahedron framework (Nekrasov *et al.* 1969). Figure 6a shows the corner-sharing linkage of the $[\text{Ti}_4\text{O}_{12}]^{8-}$ and $[\text{Si}_4\text{O}_{12}]^{8-}$ components. The edge of an (SiO_4) tetrahedron is just the right length to bridge adjacent O atoms along a rutile chain. The c parameter, 5.908 Å, is double the c cell parameter of rutile because of the arrangement of $[\text{Si}_4\text{O}_{12}]^{8-}$ rings in the $[001]$ direction (Fig. 6b).

Sitinakite: $\text{K Na}_2 \text{Ti}^{4+}_4 [\text{SiO}_4]_2 \text{O}_5 (\text{OH}) (\text{H}_2\text{O})_4$

Sitinakite is a zeolite-type Ti-silicate with tetragonal symmetry (Sokolova *et al.* 1989) in which (TiO_6)

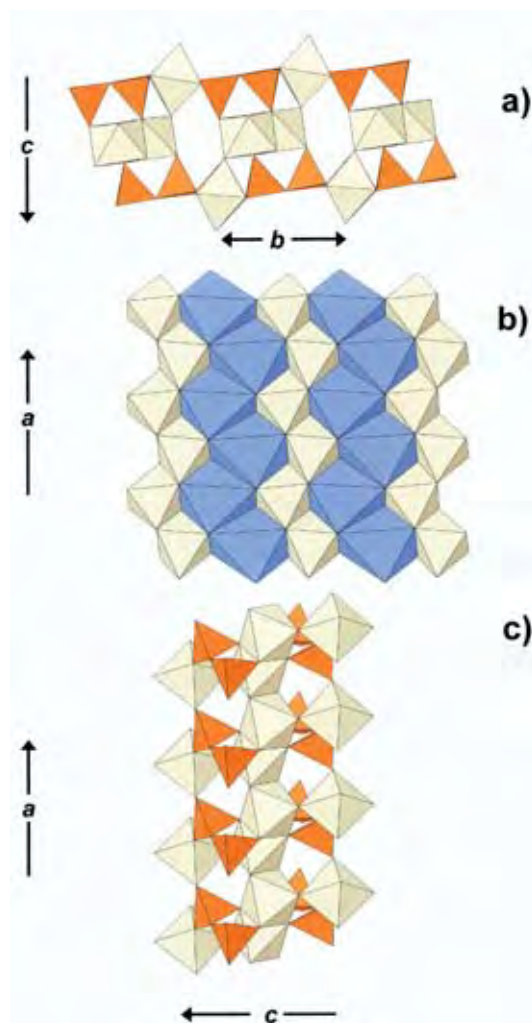


FIG. 5. Fragments of the crystal structure of murmanite. Linkage of brookite-like $[\text{Ti}_2\text{O}_8]^{8-}$ chains of the Ti-silicate block with (TiO_6) octahedra and $[\text{Si}_2\text{O}_7]$ groups of the adjacent Ti-silicate sheets: (a) viewed down $[100]$, (b) general view of the central sheet of octahedra, (c) linkage of a branched chain $[\text{Ti}_4\text{O}_{17}]^{18-}$ with $[\text{Si}_2\text{O}_7]$ groups. Legend as in Figure 2, except for (NaO_6) octahedra, which are blue.

octahedra and (SiO₄) tetrahedra form a mixed framework with large (~5.7 Å in diameter) one-dimensional eight-membered channels that extend along [001] (Fig. 7a). The channels are filled with disordered Na and K atoms and (H₂O) groups. Within this framework, (TiO₆) octahedra form a looped [Ti₄O₁₀(OH)₄]⁸⁻ chain with both edge- and corner-sharing between octahedra. In this chain, [Ti₄O₁₀(OH)₈]¹²⁻ clusters link to each other through common *trans* vertices (Figs. 1e, 7b) that are the (OH)⁻ groups of the cluster. Each (TiO₆) octahedron shares three edges with other (TiO₆) octahedra to form a vacant tetrahedron at the core of the cluster. An (SiO₄) tetrahedron shares two vertices with two (TiO₆) octahedra of the same cluster.

CHAINS OF CORNER-SHARING (TiO₆) OCTAHEDRA

The two types of chains of corner-sharing (TiO₆) octahedra are shown in Figures 8a and 8b. Topologi-

cally, they are identical and have the stoichiometry [TiO₅]. There is a difference in values of the Ti–O–Ti angle along a chain. For the extended chain (Fig. 8a), ∠ Ti–O–Ti is ideally 180°, whereas for the zig-zag chain (Fig. 8b), ∠ Ti–O–Ti is about 141°. The extended chain is a component of the structure of perovskite, CaTi⁴⁺O₃; we designate this the *perovskite* chain. The kinked chain is a component of the structure of titanite, CaTi⁴⁺SiO₅, and we designate this the *titanite* chain. The repeat distance along the perovskite chain is ~4.0 Å and corresponds to the size of one (TiO₆) octahedron. The repeat distance along the titanite chain is ~7.1 Å and corresponds to two (TiO₆) octahedra. In terms of the

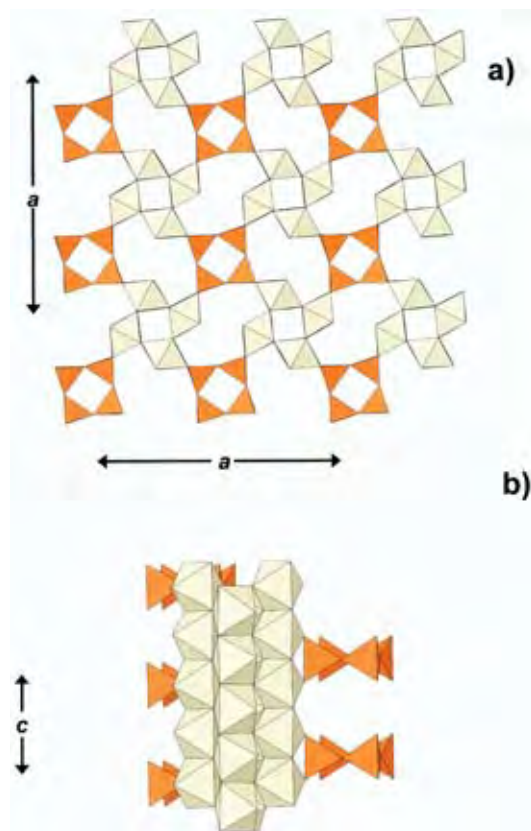


FIG. 6. Fragments of the crystal structure of baotite: (a) linkage of [Si₄O₁₂]⁸⁻ rings and [Ti₄O₁₂]⁸⁻ chains projected onto (001), and (b) a looped [Ti₄O₁₂]⁸⁻ chain. Legend as in figure 2.

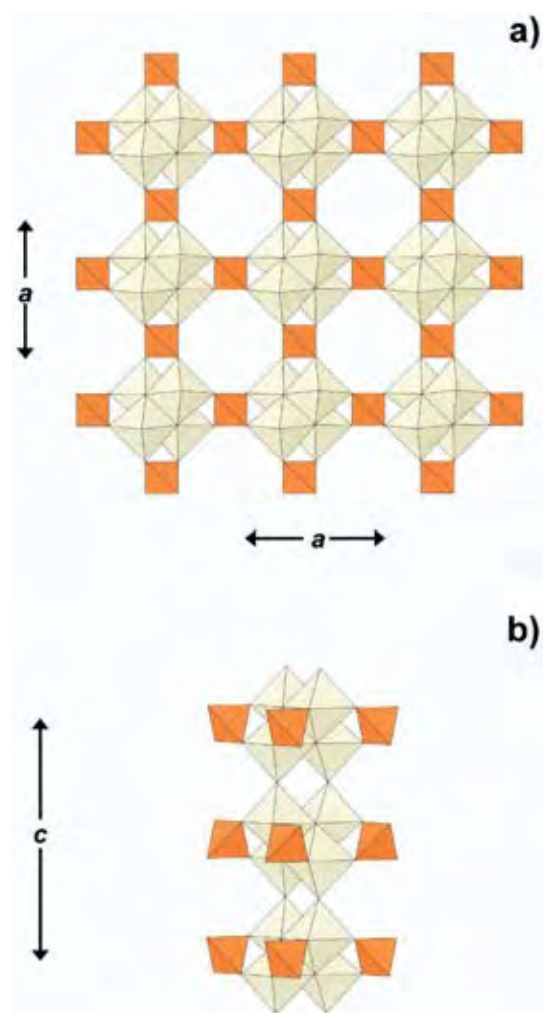


FIG. 7. Fragments of the crystal structure of sitinakite: (a) mixed octahedron-tetrahedron framework projected onto (001); (b) linkage of a [Ti₄O₁₀(OH)₄]⁸⁻ chain and (SiO₄) tetrahedra. Legend as in Figure 5.

translationally symmetric fundamental building blocks, the formulae of these chains are $[\text{TiO}_5]^{6-}$ for the perovskite chain and $[\text{Ti}_2\text{O}_{10}]^{12-}$ for the titanite chain. As yet, there are no examples of decoration of perovskite or titanite chains by other (TiO_6) octahedra in the crystal structures of silicate minerals.

Batisite: $\text{Ba Na}_2 \text{Ti}^{4+}_2 [\text{Si}_4\text{O}_{12}] \text{O}_2$

The crystal structure of batisite, ideally $\text{Ba Na}_2 \text{Ti}^{4+}_2 [\text{Si}_4\text{O}_{12}] \text{O}_2$, contains extended chains of (TiO_6) octahedra (Nikitin & Belov 1962). Figure 9a shows these chains viewed “end on” and their linkage to (SiO_4) tetrahedra. The linkage of $[\text{TiO}_5]$ chains and $[\text{Si}_4\text{O}_{12}]$ chains is shown in Figure 9b: each $[\text{Si}_2\text{O}_7]$ group is linked to two (TiO_6) octahedra, and the anion separations match exactly. The topology of the mixed octahedron–tetrahedron framework in batisite is identical to that of its K-dominant analogue, shcherbakovite, ideally $\text{K}_2 \text{Na Ti}^{4+}_2 [\text{Si}_4\text{O}_{12}] \text{O}(\text{OH})$; in cavities of the framework, there are three types of cages of different size. In batisite, they contain a [9]-coordinated Ba site and [8]- and [6]-coordinated Na sites, whereas in shcherbakovite, they contain [9]- and [8]-coordinated K sites and a [6]-coordinated Na site (Uvarova *et al.* 2003).

Narsarsukite: $\text{Na}_4 \text{Ti}^{4+}_2 [\text{Si}_8\text{O}_{20}] \text{O}_2$

Narsarsukite is a Ti-silicate of tetragonal symmetry and known for the $[\text{Si}_8\text{O}_{20}]^{8-}$ silicate chain that occurs only in this structure (Pyatenko & Pudovkina 1960, Peacor & Buerger 1962). Straight $[\text{TiO}_5]^{6-}$ chains and $[\text{Si}_8\text{O}_{20}]^{8-}$ chains extend along (001) and link to form a

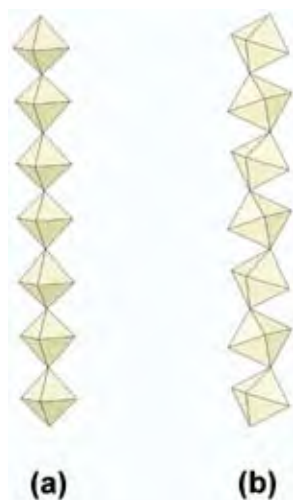


FIG. 8. Chains of corner-sharing (TiO_6) octahedra: (a) perovskite $[\text{TiO}_5]^{6-}$ chain; (b) titanite $[\text{Ti}_2\text{O}_{10}]^{12-}$ chain.

mixed tetrahedron–octahedron framework (Figs. 10a, b). The $[\text{Si}_8\text{O}_{20}]^{8-}$ chain can be described as a sequence of $[\text{Si}_4\text{O}_{12}]^{8-}$ rings linked together in the c direction to form a tube. Peacor & Buerger (1962) defined the Si–O chain as $[\text{Si}_4\text{O}_{10}]^{4-}$, whereas we designate the repeat unit as $[\text{Si}_8\text{O}_{20}]^{8-}$ in accord with the c repeat. Each $[\text{TiO}_5]^{6-}$ chain links to four $[\text{Si}_8\text{O}_{20}]^{8-}$ chains, and each $[\text{Si}_8\text{O}_{20}]^{8-}$ chain links to four $[\text{TiO}_5]^{6-}$ chains. In the interstices of the framework, cages contain [7]-coordinated Na sites.

Titanite: $\text{Ca Ti}^{4+} \text{O}(\text{SiO}_4)$

The second type of corner-sharing $[\text{TiO}_5]^{6-}$ chain occurs in titanite, $\text{Ca Ti}^{4+} \text{O}(\text{SiO}_4)$ (Taylor & Brown 1976). The linkage of zig-zag $[\text{Ti}_2\text{O}_{10}]^{12-}$ chains and

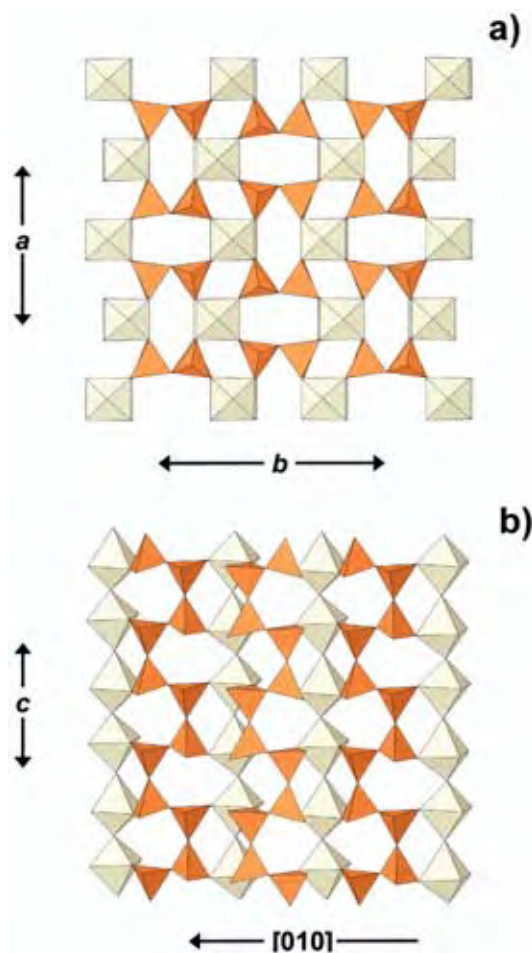


FIG. 9. Fragments of the crystal structure of batisite: (a) mixed octahedron–tetrahedron framework projected onto (001); (b) linkage of linear $[\text{TiO}_5]^{6-}$ chains and $[\text{Si}_4\text{O}_{12}]^{8-}$ chains.

(SiO₄) tetrahedra is shown in Figures 11a,b. The [TiO₅]⁶⁻ chains extend along [100], and (SiO₄) tetrahedra share vertices with four (TiO₆) octahedra of three different chains. There are [7]-coordinated Ca sites in the interstices of the octahedron–tetrahedron framework.

Korobitsynite: $\text{Na}_{8-x}\text{Ti}^{4+}_4(\text{Si}_4\text{O}_{12})_2(\text{O},\text{OH})_4(\text{H}_2\text{O})_8$

Over the last five years, there has been extensive work on the nomenclature of the labuntsovite-group (LG) minerals (Chukanov *et al.* 1999, 2002). The labuntsovite-group minerals, either Ti⁴⁺- or Nb-dominant, adopt orthorhombic or monoclinic structures. We chose korobitsynite (Rastsvetaeva *et al.* 1997a) as an orthorhombic Ti-dominant representative of the labuntsovite-group minerals (nenadkevichite subgroup).

In the crystal structure of korobitsynite, [Ti₂O₁₀]¹²⁻ titanite chains extend along [100] and are connected by [Si₄O₁₂]⁸⁻ rings into an octahedron–tetrahedron framework (Figs. 12a, b). Each [Ti₂O₁₀]¹²⁻ chain links to four [Si₄O₁₂]⁸⁻ rings, and each [Si₄O₁₂]⁸⁻ ring links to four [Ti₂O₁₀]¹²⁻ chains (*cf.* Figs. 10a, 12a). There are Na atoms and H₂O groups in the interstices of the framework. Nenadkevichite, $\text{Na}_{8-x}\text{Nb}_4(\text{Si}_4\text{O}_{12})_2(\text{O},\text{OH})_4(\text{H}_2\text{O})_8$, is a Nb-dominant analogue of korobitsynite (Perrault *et al.* 1973, Rastsvetaeva *et al.* 1994).

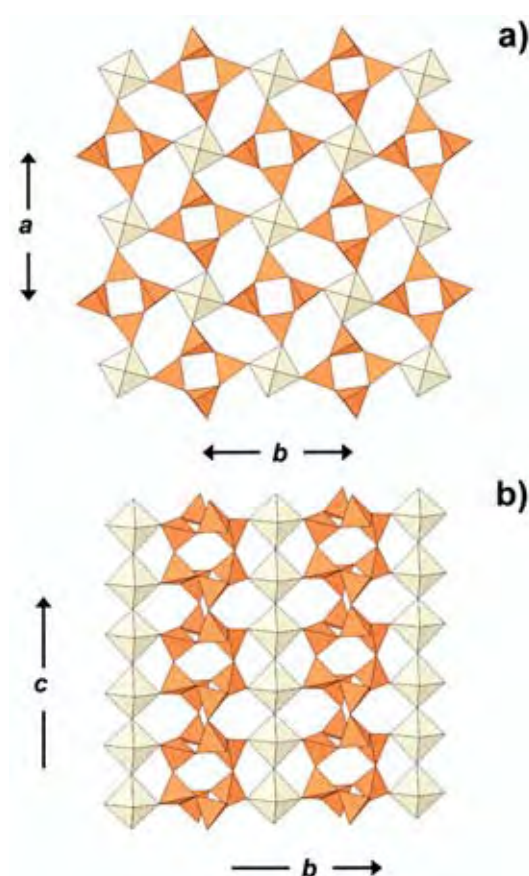


FIG. 10. Fragments of the crystal structure of narsarsukite: (a) mixed octahedron–tetrahedron framework projected onto (001); (b) linkage of perovskite (TiO₅)⁶⁻ chains and [Si₈O₂₀]⁸⁻ chains. Legend as in Figure 2.

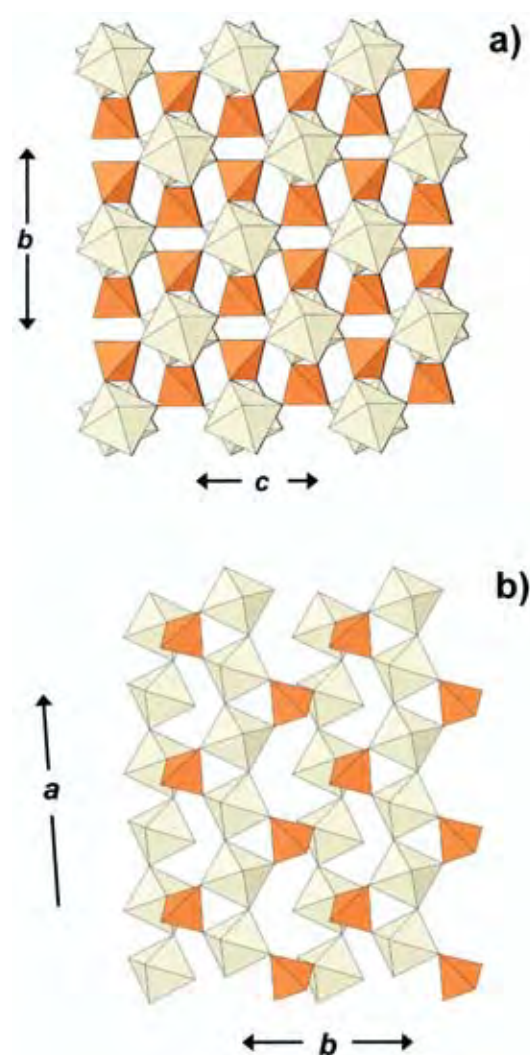


FIG. 11. Fragments of the crystal structure of titanite: (a) mixed octahedron–tetrahedron framework projected onto (010); (b) linkage of squiggly korobitsynite (Ti₂O₁₀)¹²⁻ chains and (SiO₄) tetrahedra. Legend as in Figure 2.

Lemmleinite-Ba: $\text{Na}_4\text{K}_4\text{Ba}_{2-x}\text{Ti}^{4+}_8$
 $(\text{Si}_4\text{O}_{12})_4(\text{O},\text{OH})_8(\text{H}_2\text{O})_8$

We chose lemmleinite-Ba (Rastsvetaeva *et al.* 1997b) as a monoclinic Ti-dominant representative of the labuntsovite group (LG) of minerals (labuntsovite and lemmleinite subgroups). In the structure of monoclinic LG minerals (space group $C2/m$), there is an additional octahedrally coordinated site ($D = \text{Mn}^{2+}$, Fe^{2+} , Mg , Zn , $\square$), the so-called *linking octahedron* connecting every two $[\text{TiO}_5]$ zig-zag chains in a layer parallel to (010) (Fig. 13a); note that the D site can be either occupied or vacant. The linkage of $[\text{TiO}_5]$ chains and $[\text{Si}_4\text{O}_{12}]^{8-}$ groups is shown in Figure 13b. Lowering of symmetry results in new structure-types in the monoclinic LG minerals (space group Cm), *e.g.*, kuzmenkoite-Mn, $\text{K}_4\text{Mn}^{2+}_2\text{Ti}^{4+}_8(\text{Si}_4\text{O}_{12})_4(\text{OH})_8(\text{H}_2\text{O})_n$, $10 < n < 12$ (Rastsvetaeva *et al.* 2000) and gutkovaite-Mn, $\text{Ca}_2\text{K}_4\text{Mn}^{2+}_2\text{Ti}^{4+}_8(\text{Si}_4\text{O}_{12})_4(\text{OH})_8(\text{H}_2\text{O})_n$, $n = 10$ (Rastsvetaeva *et al.* 2001).

Chukanov *et al.* (2002) stated that (1) the symmetry of the LG minerals depends on the configuration of the chains of octahedra, and that (2) chains are straight in the structure of orthorhombic members and corrugated in the structure of monoclinic members. Figure 14 shows that there is an infinite titanite $[\text{M}_2\text{O}_{10}]$ chain in both orthorhombic and monoclinic structures. The $\angle M-O-M$ is $\sim 137^\circ$ for the orthorhombic structure (Fig. 15a) and $\sim 135.5^\circ$ for the monoclinic structure (Fig. 14b); Figures 12b and 13b also illustrate this quite clearly. The topology of the chain is identical in both structures, *i.e.*, that involving the linkage of (MO_6) octahedra and the linkage of (MO_6) octahedra and (SiO_4) tetrahedra of four-membered rings. The only difference is the presence of additional (DO_6) octahedra in the monoclinic structure (Fig. 14b).

Zorite: $\text{Na}_6\text{Ti}^{4+}(\text{Ti}^{4+},\text{Nb})_4(\text{Si}_6\text{O}_{17})_2$
 $(\text{OH},\text{O})_4(\text{OH})(\text{H}_2\text{O})_{10.5}$

Zorite has an OD (order-disorder) type of structure: Ti, Si, Na and O (including OH) sites are partly occu-

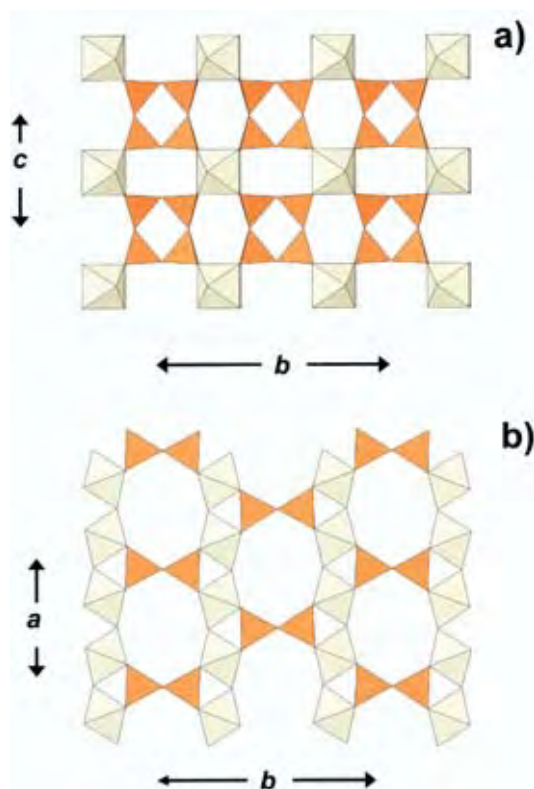


FIG. 12. Fragments of the crystal structure of korobitsynite: (a) mixed octahedron-tetrahedron framework projected onto (100); (b) linkage of titanite $(\text{Ti}_2\text{O}_{10})^{12-}$ chains and four-membered rings $[\text{Si}_4\text{O}_{12}]$. Legend as in Figure 2.

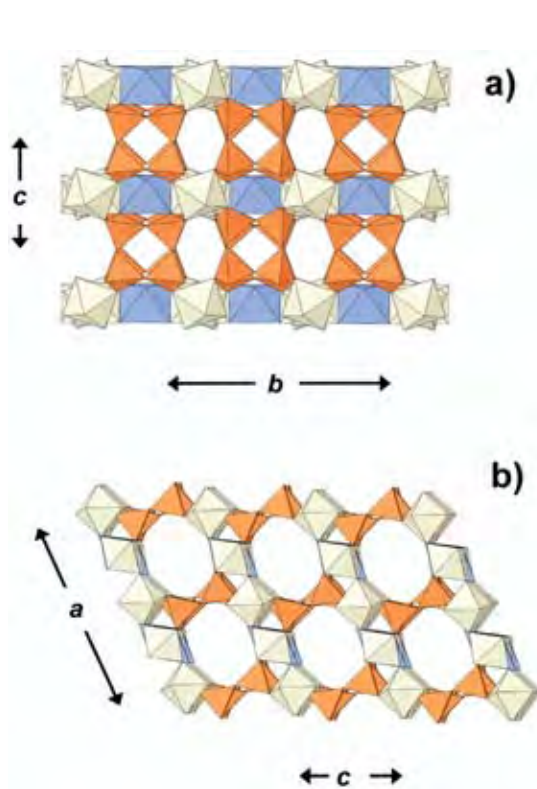


FIG. 13. Fragments of the crystal structure of lemmleinite-Ba: (a) a fragment of the structure viewed down $[100]$; linkage of titanite $(\text{Ti}_2\text{O}_{10})^{12-}$ chains and $[\text{Si}_4\text{O}_{12}]^{8-}$ rings. Legend as in Figure 2; D-octahedra are shown in blue.

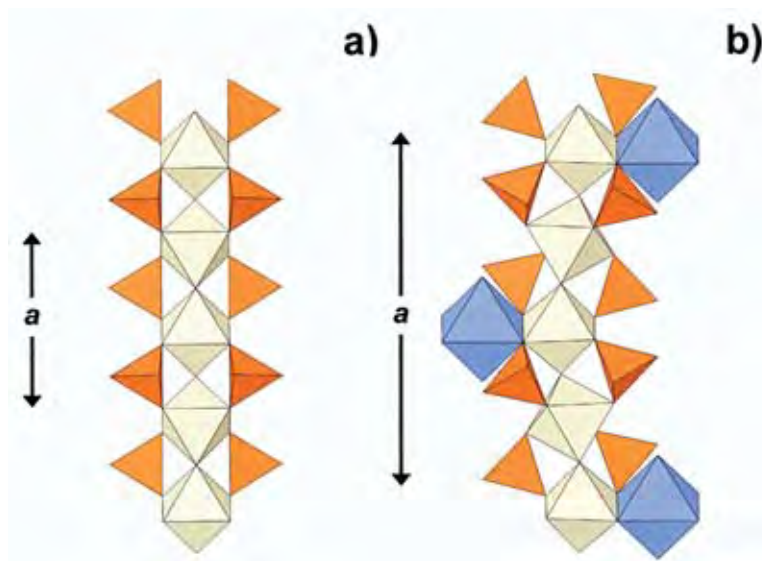


FIG. 14. Linkage of titanite-like $[\text{Ti}_2\text{O}_{10}]^{4-}$ chains with (SiO_4) tetrahedra in the crystal structures of (a) korobitsynite and (b) lemmleinite-Ba. Legend as in Figure 13.

pied (Sandomirskii & Belov 1979). We will consider this structure neglecting its OD character.

In the crystal structure of zorite, Ti occurs in [5]- and [6]-coordination, with a ratio of octahedra to square pyramids of 4:1. There are two principal building units in the crystal structure of zorite: $[\text{M}_2\text{O}_{10}]$ titanite chains of (MO_6) octahedra, where $M = \text{Ti}^{4+}$, Nb, and $[\text{Si}_6\text{O}_{17}]^{10-}$ chains constructed of orthogonal $[\text{Si}_2\text{O}_7]^{6-}$ groups. Titanite chains extend along [010], and $[\text{Si}_6\text{O}_{17}]^{10-}$ chains extend along [001] (Figs. 15a, b). Both chains link through common vertices of (TiO_6) octahedra and (SiO_4) tetrahedra to form a mixed octahedron-tetrahedron framework. Every two $[\text{Si}_6\text{O}_{17}]^{10-}$ chains share two vertices each with a [5]-coordinated (MO_5) polyhedron (Fig. 15a). Na atoms are randomly distributed in large cages of the framework. Recently, the crystal structure of zorite served as a model for the synthesis of titanosilicate molecular sieves (Kuznicki *et al.* 2001).

LAYERS OF (TiO_6) OCTAHEDRA

There are only four known crystal structures of Ti silicate minerals with layers of (TiO_6) octahedra (Table 1). Fersmanite, ideally $\text{Ca}_4(\text{Na,Ca})_4(\text{Ti}^{4+},\text{Nb})_4(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$, contains a layer based on corner-sharing chains of (TiO_6) octahedra. Chevkinite-(Ce) and perrierite-(Ce) contain layers based on rutile chains of edge-sharing octahedra. The crystal structure of lorenzenite, ideally $\text{Na}_2\text{Ti}^{4+}_2(\text{Si}_2\text{O}_6)\text{O}_3$, contains a layer with both corner- and edge-sharing of (TiO_6) octahedra.

Fersmanite: $\text{Ca}_4(\text{Na,Ca})_4(\text{Ti}^{4+},\text{Nb})_4(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$

Fersmanite is the only silicate mineral with a layer of corner-sharing (TiO_6) octahedra. In this sense, it has no structural analogues. Safy'anov *et al.* (1984) described fersmanite as a Ti-silicate with perovskite-like chains of corner-sharing $(\{\text{Ti,Nb}\}\text{O}_6)$ octahedra. In perovskite, there are extended chains of (TiO_6) octahedra with $\angle\text{Ti-O-Ti} \approx 180^\circ$; in fersmanite, there are zig-zag chains of (TiO_6) octahedra with $\angle\text{Ti-O-Ti} \approx 130^\circ$ and 144° . In fersmanite, $[\text{TiO}_5]^{6-}$ chains polymerize to form a layer parallel to (001) (Fig. 16a) (Sokolova *et al.* 2002). The $[\text{Ti}_4\text{O}_{16}]^{16-}$ layer is decorated by $[\text{Si}_2\text{O}_7]$ groups (Fig. 16b). Where two $[\text{TiO}_5]^{6-}$ chains intersect, four octahedra share corners to form a $[\text{Ti}_4\text{O}_{18}]^{20-}$ cluster. In this cluster, each (TiO_6) octahedron shares three corners with other octahedra, forming a vacant octahedron at the center of the cluster. Four faces of this vacant octahedron are shared with faces of four (TiO_6) octahedra. Figure 16c shows a fragment of the layer containing four clusters; the $[\text{Ti}_4\text{O}_{18}]^{20-}$ cluster may be regarded as the *FBB* (Fundamental Building Block) of the layer, rather than the $[\text{TiO}_5]^{6-}$ chain. In the $[\text{TiO}_5]^{6-}$ chain, an octahedron shares vertices with two adjacent octahedra, whereas in a layer, each octahedron shares corners with four adjacent octahedra. According to the approach of Hawthorne (1983), the FBB should be defined as the most strongly connected fragment of the structure, which in this case is the $[\text{Ti}_4\text{O}_{18}]^{20-}$ cluster.

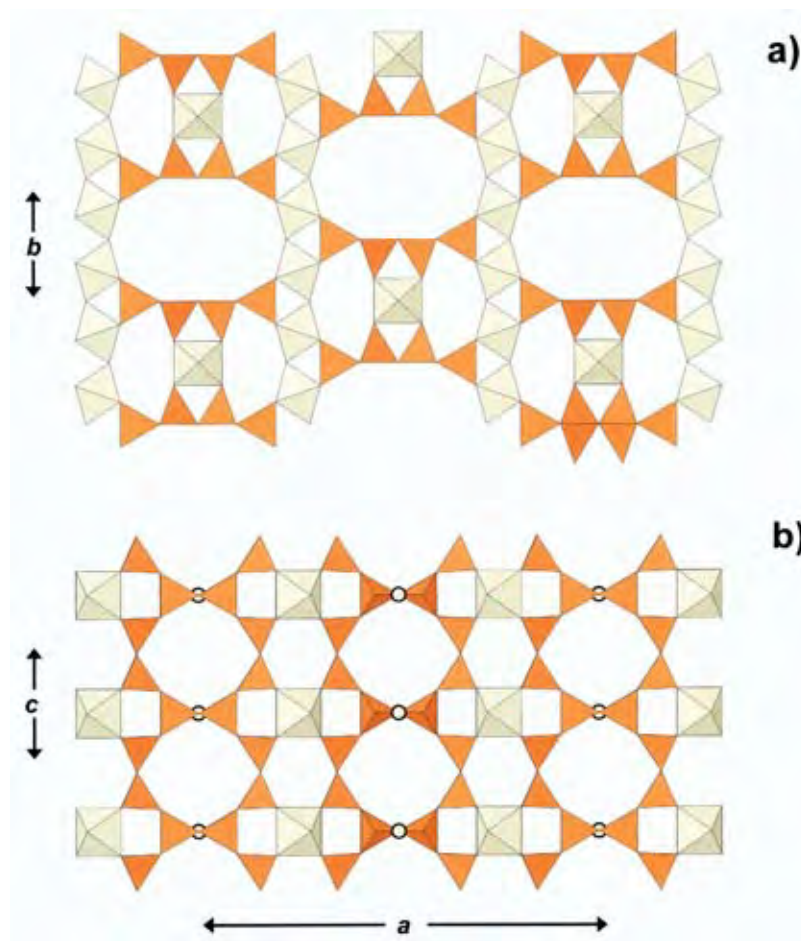


FIG. 15. Fragments of the crystal structure of zorite: (a) linkage of titanite-like $[\text{Ti}_2\text{O}_{10}]^{4-}$ chains and $[\text{Si}_6\text{O}_{17}]^{10-}$ chains; (b) mixed framework of (TiO_6) octahedra, (TiO_5) polyhedra and (SiO_4) tetrahedra. In (b), the (TiO_5) polyhedra are shown as yellow circles. Legend as in Figure 2.

rather than the $[\text{TiO}_5]^{6-}$ chain (as in Safy'anov *et al.* 1984).

Chevkinite-(Ce) and *perrierite-(Ce)*:
 $(\text{REE}, \text{Ca})_4 \text{Fe}^{2+} (\text{Ti}^{4+}, \text{Fe}^{3+}, \text{Nb})_4 \text{Si}_4 \text{O}_{22}$
 and $\text{Ce}_4 \text{Fe}^{2+} (\text{Ti}^{4+}, \text{Fe}^{3+})_4 \text{Si}_4 \text{O}_{22}$

Originally, the crystal structures of chevkinite-(Ce) (Peng & Bun 1964) and perrierite-(Ce) (Gottardi 1960) were described as having layers of chains of (TiO_6) octahedra. Pyatenko *et al.* (1976) showed that the layers in the perrierite-(Ce) structure are built of octahedra with Ti dominant over other M cations. The layer is formed by $[\text{TiO}_4]^{4-}$ rutile chains connected to each other via common vertices (Fig. 17a). Sokolova *et al.* (2004) showed that there are two possibilities for cation assignment at the M sites, resulting in different degrees of

polymerization of (TiO_6) octahedra: a chain or a sheet. The latter possibility results in identical sheets in chevkinite-(Ce) and perrierite-(Ce), but with different linkages between the sheets and the (SiO_4) tetrahedra (Figs. 17a, b).

Lorenzenite: $\text{Na}_2 \text{Ti}^{4+}_2 [\text{Si}_2\text{O}_6] \text{O}_3$

Lorenzenite is another silicate mineral with a (001) layer of corner-sharing and edge-sharing (TiO_6) octahedra (Sundberg *et al.* 1987). The layer is built of brookite chains sharing common vertices (Fig. 18a). In the layer, each (TiO_6) octahedron shares an edge with two adjacent octahedra within one brookite chain and one corner, with an octahedron from a neighboring chain. Within a layer, brookite chains extend along [010] (Figs. 18a, b), and there is a difference of about 0.16 in the z

coordinates of Ti atoms of neighboring chains. Therefore, brookite ribbons occur at two levels, giving rise to pseudotrigonal rings of six octahedra, each three from a different chain. Thus, linkage of $(\text{Ti}_2\text{O}_8)^{8-}$ brookite chains results in a $[\text{Ti}_2\text{O}_7]^{6-}$ layer. Each (TiO_6) octahedron shares three *cis* vertices with three (SiO_4) tetrahedra from two $[\text{Si}_2\text{O}_6]$ chains (Fig. 18b). The repeat distances along the chain of (TiO_6) octahedra and the chain of (SiO_4) tetrahedra (in the *b* direction) are intrinsically similar, and the corresponding *b* dimension is 5.233 Å. The brookite chains and $[\text{Si}_2\text{O}_6]$ chains form a block; stacking of two blocks along the $[001]$ direction results in a *c* parameter of 14.487 Å (Fig. 18c). In the

crystal structure of lorenzenite, [7]-coordinated Na atoms occupy interstices of the mixed tetrahedron–octahedron framework.

GENERAL TOPOLOGICAL RELATIONS

Observations

There are some interesting general observations that may be made concerning these structures based on chains of (TiO_6) octahedra:

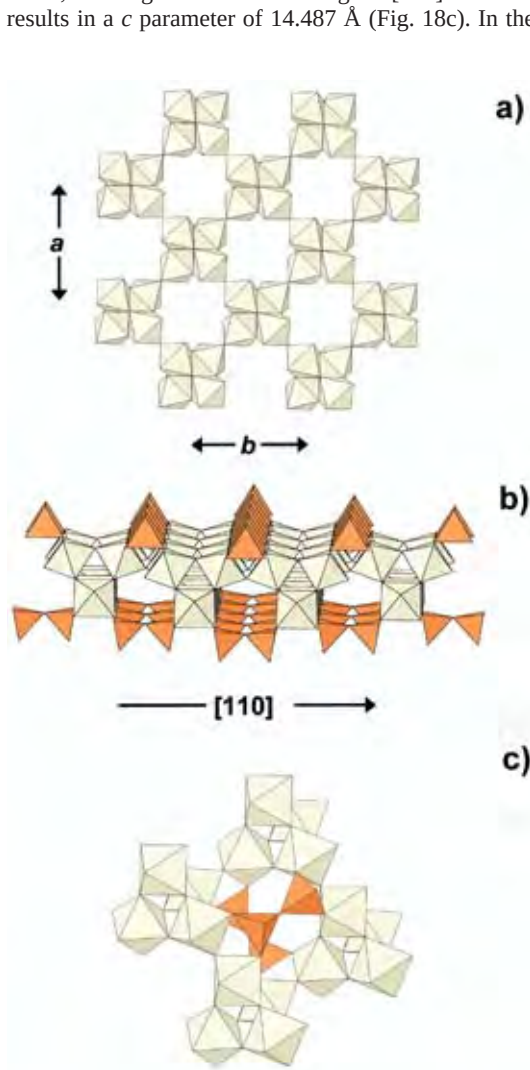


FIG. 16. Fragments of the crystal structure of fersmanite: (a) the layer of corner-sharing (TiO_6) octahedra viewed down $[001]$; (b) the layer of (TiO_6) octahedra decorated with $[\text{Si}_2\text{O}_7]$ groups; (c) linkage of four $(\text{Ti}_4\text{O}_{18})^{20-}$ clusters with two $[\text{Si}_2\text{O}_7]$ groups. Legend as in Figure 2.

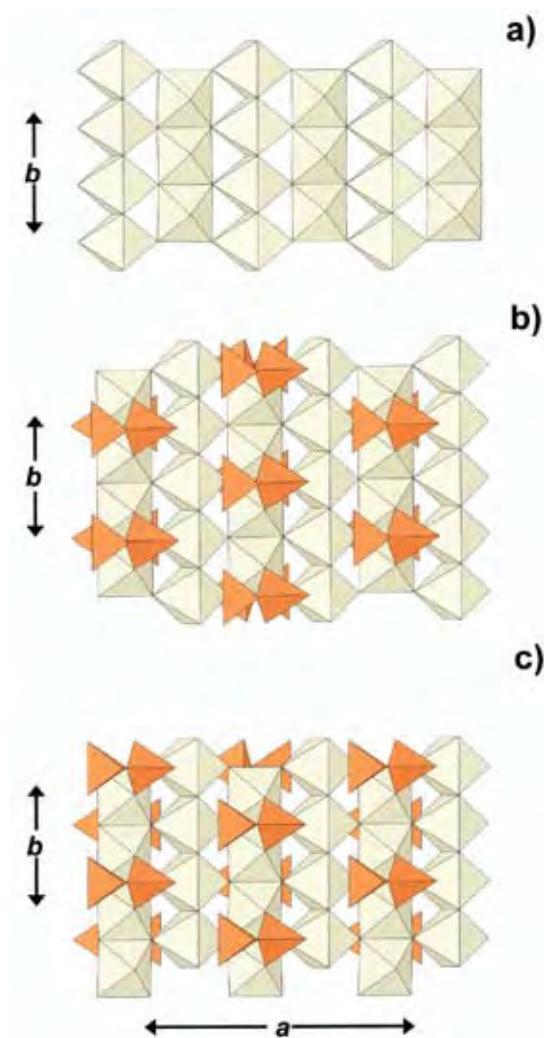


FIG. 17. A layer formed by rutile $(\text{TiO}_4)^{4-}$ chains in the crystal structures of chevkinite-group minerals: (a) general view; (b) linkage of (TiO_6) octahedra and (SiO_4) tetrahedra in the crystal structure of perrierite-(Ce); (c) linkage of (TiO_6) octahedra and (SiO_4) tetrahedra in the crystal structure of chevkinite-(Ce). Legend as in Figure 2..

(1) None of these structures have cubic, hexagonal or trigonal symmetry (Table 1). There is a simple explanation for this. Let us consider first a chain of octahedra that are parallel to a symmetry axis. If the chain lies on the axis of symmetry, the topology of the linkages must correspond to that symmetry. Obviously, the only way that a chain of octahedra can lie on a 3-fold or 6-fold axis is if the octahedra share faces such that the 3-fold axis of the (holosymmetric) octahedra are coincident with the symmetry axis of the general structure. A chain of face-sharing (Ti^{4+}O_6) octahedra is not expected to be stable because of the strong repulsive cat-

ion-cation interaction caused by this arrangement. If the chain lies off the axis of symmetry but is still parallel to that axis, it is possible to construct atom arrangements of chains of octahedra and silicate units, but the resulting structures are very microporous and unlikely to occur as structures without interstitial groups to support the structure. A similar argument applies to arrangements involving chains of octahedra that are not parallel to 3-fold or 6-fold axes in cubic, hexagonal and trigonal symmetry.

(2) In structures based on chains of corner-sharing ($\text{Ti}^{4+}\phi_6$) octahedra, the chains are neither branched nor looped; they are topologically simple $[\text{Ti}\phi_n]$ chains with $n = 5$.

(3) Chains of corner-sharing (Ti^{4+}O_6) octahedra can be extended ($\text{Ti}-\text{O}[\text{bridging}]-\text{Ti} \approx 180^\circ$) or kinked ($\text{Ti}-\text{O}[\text{bridging}]-\text{Ti} < 180^\circ$). Extended chains can link easily to $[\text{Si}_2\text{O}_7]$ groups, as in batisite and narsarsukite, whereas kinked chains can link easily to (SiO_4) groups, as in titanite and the labuntsovite-group minerals.

(4) In structures based on chains of edge-sharing ($\text{Ti}^{4+}\phi_6$) octahedra, the situation is much more complicated than in the case of structures based on chains of corner-sharing ($\text{Ti}^{4+}\phi_6$) octahedra. The Ti-chains are generally not simple, and they can also be branched or looped. In addition, there is commonly at least one other complicating factor in the bond topology. In minerals based on chains of corner-sharing octahedra, the structures consist of a Ti-silicate structural unit and an interstitial complex of alkali or alkaline-earth cations plus (OH) or (H_2O) (or both). Minerals based on chains of edge-sharing octahedra do not usually have such a simple constitution; they usually have a Ti-silicate component, an interstitial complex of alkali or alkaline-earth cations plus (OH) or (H_2O) (or both), and *additional* cation or anion components (or both). Polyakovite-(Ce) has a structural unit consisting of $[\text{Ti}\phi_4]$ chains and $[(\text{Cr}^{3+}, \text{Fe}^{3+})\phi_4]$ chains that share vertices (Fig. 2a) to form a sheet. Vinogradovite (and paravinogradovite) are unusual in that the tetrahedrally coordinated part of the structural unit is an aluminosilicate unit rather than a silicate unit (as is the case in all other structures of this group). The minerals of the lomonosovite group all contain phosphate groups in addition to the silicate groups. Baotite has Cl as a component of the interstitial complex (no other mineral of this group has interstitial Cl). Sitinakite has a looped chain in its structural unit, and this chain has both corner- and edge-sharing between ($\text{Ti}^{4+}\phi_6$) octahedra. Murmanite (Fig. 5) is the only exception; it has a branched Ti-chain, but otherwise has no additional compositional complication.

Why do structures with chains of corner-sharing ($\text{Ti}^{4+}\phi_6$) octahedra have simple structural units with non-branched non-looped $[\text{Ti}\phi_5]$ chains and silicate units, whereas structures with chains of edge-sharing ($\text{Ti}^{4+}\phi_6$) octahedra have complicated structural units with titanate chains that are generally not simple but branched or looped, tetrahedrally coordinated units that

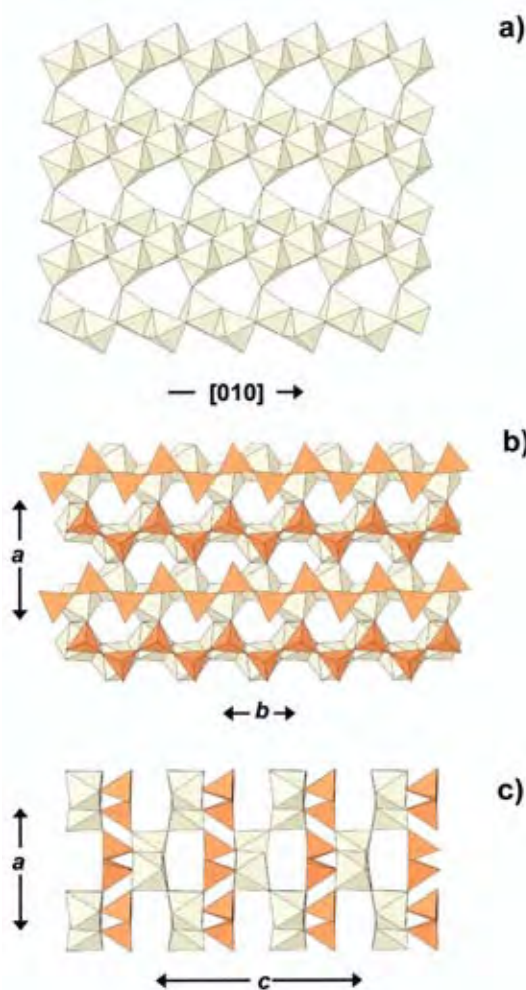


FIG. 18. Fragments of the crystal structure of lorenzenite: (a) the layer of corner-sharing and edge-sharing (TiO_6) octahedra; (b) linkage of $[\text{Si}_2\text{O}_6]^{4-}$ chains and $[\text{Ti}_2\text{O}_8]^{8-}$ chains; (c) xy projection of the mixed octahedron-tetrahedron framework. Legend as in Figure 2.

are not purely silicate in composition, and with additional compositional and topological complications in either the structural unit or the interstitial complex?

(5) In Ti-silicate minerals, chains of (Ti⁴⁺O₆) octahedra are common, sheets of (Ti⁴⁺O₆) octahedra are uncommon, and frameworks of (Ti⁴⁺O₆) octahedra do not occur.

CHAINS OF CORNER-SHARING (Ti⁴⁺Φ₆) OCTAHEDRA

Table 2 indicates the possible linkages that can occur in a Ti-silicate structure, together with the ideal bond-valences incident at the anions and the possible identities of those anions. This table will serve as a guide to the linkages that are possible in a Ti-silicate structure.

We may write the stoichiometry of a simple chain of corner-sharing (TiO₆) octahedra as [TiΦO₄], where Φ is the bridging anion of the chain. Inspection of Table 2 indicates that Φ can be (OH)⁻ or O²⁻. We may write the formula of a general silicate unit as [Si_cO_dO_e], where „*c*“ is the number of bridging (Si–O–Si) anions in the group, and *d* is the number of non-bridging anions in the group. The easiest way to satisfy the incident bond-valence requirements of these non-bridging anions is for them to link to Ti atoms (Table 2). If all of the equatorial bonds of the Ti-chain are used to satisfy all of the non-bridging anions of the silicate group, we may write the formula of the resulting Ti-silicate framework in the following way:

$$[\text{Ti}\Phi]^{b+}_a [\text{Si}_c \text{O}_d \text{O}_e]^{[2(d+e)-4c]-} \quad [1]$$

Note that the requirement that bonds from Ti satisfy the non-bridging bonds of the silicate group means that

$$4a = e \quad (1)$$

Moreover, the connectivity within the silicate unit requires that

$$e = 4c - 2d \quad (2)$$

The charge, *Z*⁻, on the resulting Ti-silicate structure can be written as follows:

$$Z^- = 2(d + e) - 4c - ab \quad (3)$$

Substituting for *a* and *e* from equations (1) and (2) gives

$$Z^- = 4c - 2d - b(c - d/2) \quad (4)$$

As *b* is the charge on [TiΦ] and Φ = (OH)⁻ or O²⁻, *b* can only take the values 3⁺ or 2⁺. Thus we may simplify equation (3) to give the following relations:

$$\Phi = \text{O}^{2-}: \quad Z^- = 2c - d \quad (4a)$$

$$\Phi = (\text{OH}): \quad Z^- = c - d/2 \quad (4b)$$

Note that the variables *c* and *d* in equations (4a) and (4b) involve only the silicate part of the structure. Hence we can systematically examine possible structure-topologies and the charge constraints on the interstitial cations by examining *Z*⁻ as a function of possible values of *c* and *d*. However, there are additional constraints operative on the possible stoichiometries of these structures. Eliminating *e* from equations (1) and (2) gives

$$a = c - d/2 \quad (5)$$

As *a* must be an integer, *d* must be even, i.e.,

$$d = 2n \quad (n = 0, 1, \dots) \quad (6)$$

Also, in order that the silicate unit be continuous,

$$d \neq c \quad (7)$$

Case 1: Φ = O²⁻

Where Φ = O²⁻, *b* = 2 and the charge, *Z*⁻, is given by equation (4a). The general formula of such structures is: Na_{2a}(TiO)_a[Si_cO_{2(a+c)}](H₂O)_n. Table 3 lists the resulting values of *c*, *d*, *a* and *Z*, together with some allowed formulae, the general formula and structural examples. Titanite, batisite, korobitsynite (plus all other labuntsovite-group minerals) and narsarsukite (plus quartz as a Ti-free example) are all generated by this scheme, together with several other predicted stoichiometries.

Case 2: Φ = (OH)⁻

Where Φ = (OH)⁻, *b* = 3, and the charge, *Z*⁻, is given by equation (4b). The general formula of such structures is: Na_a[Ti(OH)]_a[Si_cO_{2(a+c)}](H₂O)_n. Table 4 lists some resulting values of *c*, *a* and *Z*, together with representative mineral structures. Zorite does not quite fit this scheme. For *a* = 4 and *c* = 12, the predicted stoichiometry is Na₄Ti⁴⁺₄Si₁₂O₃₂(OH)₄(H₂O)_n. The difference is that an additional isolated Ti⁴⁺ cation is incorporated into the zorite structure, together with two Na and O atoms required for electroneutrality, and zorite is not

TABLE 2. POSSIBLE ANIONS AND ANION COORDINATIONS IN TI-SILICATE FRAMEWORKS

Anion coordination	Σs (vu)	Anion
O–Ti ₂	1.34	(OH) ⁻ , O ²⁻
O–Ti ₃	2.00	O ²⁻
O–TiSi	1.67	O ²⁻
O–Si ₂	2.00	O ²⁻

solely based on chains of corner-sharing (TiO_6) octahedra.

SUMMARY

(1) Minerals based on chains of (TiO_6) octahedra do not have cubic, hexagonal or trigonal symmetry.

TABLE 3. POSSIBLE STRUCTURES WITH CHAINS OF CORNER-SHARING (TiO_6) OCTAHEDRA LINKED BY SILICATE UNITS

c	d	a	Z	Formula*	Example
1	0*	1	-2	$\text{Ca} (\text{TiO})_1 [\text{SiO}_4]$	Titanite
2	2	1	-2	$\text{Na}_2 (\text{TiO})_1 [\text{Si}_2\text{O}_6]$	
2	4	0	-0	$[\text{Si}_2\text{O}_4] = [\text{SiO}_2]_2$	Quartz
3	4	2	-2	$\text{Na}_2 (\text{TiO})_1 [\text{Si}_3\text{O}_8]$	
4	4	2	-4	$\text{Na}_4 (\text{TiO})_2 [\text{Si}_4\text{O}_{12}]$	Batisite
4	6	1	-2	$\text{Na}_2 (\text{TiO})_1 [\text{Si}_4\text{O}_{12}]$	
5	6	2	-4	$\text{Na}_4 (\text{TiO})_2 [\text{Si}_5\text{O}_{14}]$	
5	8	1	-2	$\text{Na}_2 (\text{TiO})_1 [\text{Si}_6\text{O}_{16}]$	
6	6	3	-6	$\text{Na}_6 (\text{TiO})_3 [\text{Si}_6\text{O}_{18}]$	
6	8	2	-4	$\text{Na}_4 (\text{TiO})_2 [\text{Si}_6\text{O}_{18}]$	
6	10	1	-2	$\text{Na}_2 (\text{TiO})_1 [\text{Si}_6\text{O}_{18}]$	
8	8	4	-8	$\text{Na}_8 (\text{TiO})_4 [\text{Si}_8\text{O}_{24}]$	Korobitsynite**
8	10	3	-6	$\text{Na}_6 (\text{TiO})_3 [\text{Si}_8\text{O}_{22}]$	
8	12	2	-4	$\text{Na}_4 (\text{TiO})_2 [\text{Si}_8\text{O}_{20}]$	Narsarsukite
8	14	1	-2	$\text{Na}_2 (\text{TiO})_1 [\text{Si}_8\text{O}_{18}]$	

General formula: $\text{Na}_{2a} (\text{TiO})_d [\text{Si}_c \text{O}_{2(a+c)}] (\text{H}_2\text{O})_n$

* for definitions of c, d, a and Z, see text;

** plus other OH-free labuntsovite-group minerals;

* the term $(\text{H}_2\text{O})_n$ is omitted for simplicity.

TABLE 4. POSSIBLE STRUCTURES WITH CHAINS OF CORNER-SHARING $(\text{TiO}_2(\text{OH}))_2$ OCTAHEDRA LINKED BY SILICATE UNITS

c	a	Z	Formula*	Example
1	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{SiO}_4]$	
1	0	-0	$[\text{SiO}_2]$	Quartz
2	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{Si}_2\text{O}_6]$	
3	2	-2	$\text{Na}_2 [\text{Ti}(\text{OH})]_2 [\text{Si}_2\text{O}_6]$	
3	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{Si}_3\text{O}_8]$	
4	3	-3	$\text{Na}_3 [\text{Ti}(\text{OH})]_3 [\text{Si}_4\text{O}_{14}]$	
4	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{Si}_4\text{O}_{10}]$	
5	4	-4	$\text{Na}_4 [\text{Ti}(\text{OH})]_4 [\text{Si}_4\text{O}_{16}]$	
5	3	-3	$\text{Na}_3 [\text{Ti}(\text{OH})]_3 [\text{Si}_5\text{O}_{16}]$	
5	2	-2	$\text{Na}_2 [\text{Ti}(\text{OH})]_2 [\text{Si}_4\text{O}_{14}]$	
5	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{Si}_5\text{O}_{12}]$	
6	5	-5	$\text{Na}_5 [\text{Ti}(\text{OH})]_5 [\text{Si}_6\text{O}_{22}]$	
6	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{Si}_6\text{O}_{14}]$	
7	6	-6	$\text{Na}_6 [\text{Ti}(\text{OH})]_6 [\text{Si}_6\text{O}_{24}]$	
7	5	-5	$\text{Na}_5 [\text{Ti}(\text{OH})]_5 [\text{Si}_7\text{O}_{24}]$	
7	4	-4	$\text{Na}_4 [\text{Ti}(\text{OH})]_4 [\text{Si}_7\text{O}_{22}]$	
7	3	-3	$\text{Na}_3 [\text{Ti}(\text{OH})]_3 [\text{Si}_7\text{O}_{20}]$	
7	2	-2	$\text{Na}_2 [\text{Ti}(\text{OH})]_2 [\text{Si}_7\text{O}_{18}]$	
7	1	-1	$\text{Na} [\text{Ti}(\text{OH})]_1 [\text{Si}_7\text{O}_{16}]$	
16	8	-4	$\text{Na}_8 [\text{Ti}(\text{OH})]_8 [\text{Si}_{16}\text{O}_{48}]$	Labuntsovite*

General formula: $\text{Na}_a [\text{Ti}(\text{OH})]_d [\text{Si}_c \text{O}_{2(a+c)}] (\text{H}_2\text{O})_n$

* plus other (OH)-bearing labuntsovite-group minerals.

(2) In Ti-silicate structures based on chains of corner-sharing ($\text{Ti}^{4+}\phi_6$) octahedra, the chains are neither branched nor looped; they are topologically simple $[\text{Ti}\phi_5]$ chains.

(3) The chemical formulae of such structures may be written in a very general way as $\text{Na}_{2a} (\text{TiO})_a [\text{Si}_c \text{O}_{2(a+c)}] (\text{H}_2\text{O})_n$ and $\text{Na}_a (\text{Ti}\{\text{OH}\})_a [\text{Si}_c \text{O}_{2(a+c)}] (\text{H}_2\text{O})_n$. These are not arbitrary formulae; the bond topology is such that all anions obey the valence-matching principle.

(4) In structures based on chains of edge-sharing ($\text{Ti}^{4+}\phi_6$) octahedra, the chains are simple, branched and looped. These structures commonly contain other high-bond-valence polyhedra [unlike the structures based on chains of corner-sharing ($\text{Ti}^{4+}\phi_6$) octahedra] and need to be considered from a more general perspective.

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