

## THE CRYSTAL CHEMISTRY OF FERSMANITE, $\text{Ca}_4(\text{Na,Ca})_4(\text{Ti,Nb})_4(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$

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### ABSTRACT

Fersmanite,  $\text{Ca}_4(\text{Na,Ca})_4(\text{Ti}^{4+},\text{Nb})_4(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$ , is the only mineral with an isolated layer of corner-sharing ( $\{\text{Ti}^{4+},\text{Nb}\}\text{O}_6$ ) octahedra. The crystal structure of fersmanite from the Khibina alkaline massif, Kola Peninsula, Russia, monoclinic,  $a$  10.183(2),  $b$  10.183(2),  $c$  20.396(4) Å,  $\beta$  97.19(3)°,  $V$  2098.2(2) Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 4$ ,  $D(\text{calc.}) = 3.159 \text{ g}\cdot\text{cm}^{-3}$ , was refined to an  $R$  index of 4.1% based on 2119 observed [ $F_o > 4\sigma F$ ] unique reflections measured with MoK $\alpha$  X-radiation on an automated four-circle diffractometer equipped with a CCD detector. There are two  $Si$  sites occupied solely by Si and tetrahedrally coordinated by four O atoms, and two octahedrally coordinated  $M$  sites containing  $\text{Ti}^{4+}$  and Nb. There are four  $A$  sites occupied by Ca and Na: the  $A(1)$  and  $A(2)$  sites are [6]-coordinated and contain Ca and very minor  $\text{Fe}^{2+} + \text{Mn}^{2+}$ ; the  $A(3)$  and  $A(4)$  sites are [8]-coordinated and contain dominant Na, major Ca and very minor Sr. Each ( $MO_6$ ) octahedron shares two *trans* vertices with two other octahedra to form a 7 Å [ $MO_5$ ] chain. These chains extend along [110] and [ $\bar{1}\bar{1}0$ ], and intermesh to form a layer parallel to (001); where the chains intersect, an [ $M_4O_{18}$ ] cluster occurs; it is the fundamental building block of the layer. In this cluster, each ( $MO_6$ ) octahedron shares three corners with other ( $MO_6$ ) octahedra, forming a vacant octahedron inside the cluster. The [8]-coordinated  $A$  cations fill cages within the layer. The [ $M_4O_{16}$ ] layers decorated with ( $\text{Si}_2\text{O}_7$ ) groups alternate with sheets of ( $AO_6$ ) octahedra along the  $c$  direction. The structures of fersmanite and pyrochlore,  $(\text{CaNa})\text{Nb}_2\text{O}_6(\text{OH,F})$ , are based on the same type of [ $M_4O_{18}$ ] cluster.

**Keywords:** Ti silicate, fersmanite, crystal-structure refinement, pyrochlore, Khibina–Lovozero complex, Kola Peninsula, Russia.

### SOMMAIRE

La fersmanite,  $\text{Ca}_4(\text{Na,Ca})_4(\text{Ti}^{4+},\text{Nb})_4(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$ , est le seul minéral à contenir une couche isolée d'octaèdres ( $\{\text{Ti}^{4+},\text{Nb}\}\text{O}_6$ ) à coins partagés. Nous en avons affiné la structure cristalline avec un échantillon provenant du complexe alcalin de Khibina, péninsule de Kola, en Russie, monoclinique,  $a$  10.183(2),  $b$  10.183(2),  $c$  20.396(4) Å,  $\beta$  97.19(3)°,  $V$  2098.2(2) Å<sup>3</sup>, groupe spatial  $C2/c$ ,  $Z = 4$ ,  $D(\text{calc.}) = 3.159 \text{ g}\cdot\text{cm}^{-3}$ , jusqu'à un résidu  $R$  de 4.1% en utilisant 2119 réflexions uniques observées [ $F_o > 4\sigma F$ ], mesurées avec rayonnement MoK $\alpha$  et un diffractomètre à quatre cercles muni d'un détecteur CCD. Il y a deux sites  $Si$  où logent des atomes de Si à coordinence tétraédrique avec des atomes d'oxygène. Deux sites  $M$  à coordinence octaédrique contiennent les atomes  $\text{Ti}^{4+}$  et Nb. Il y a quatre sites  $A$  contenant Ca et Na: les sites  $A(1)$  et  $A(2)$  ont une coordinence [6] et contiennent Ca et de très petites quantités de  $\text{Fe}^{2+} + \text{Mn}^{2+}$ ; les sites  $A(3)$  et  $A(4)$  ont une coordinence [8] et contiennent surtout des atomes Na, avec Ca important, et de très petites quantités de Sr. Chaque octaèdre ( $MO_6$ ) partage de coins *trans* avec deux autres octaèdres pour former une chaîne [ $MO_5$ ] à 7 Å. Ces chaînes sont disposées le long de [110] et [ $\bar{1}\bar{1}0$ ], et s'entrecroisent pour former une couche parallèle à (001); là où ces chaînes se croisent, il en résulte un groupement [ $M_4O_{18}$ ], qui est en fait le bloc structural fondamental de cette couche. Dans ce groupement, chaque octaèdre ( $MO_6$ ) partage trois coins avec d'autres octaèdres ( $MO_6$ ), pour former un octaèdre intérieur vide. Les cations  $A$  à coordinence [8] occupent des cages dans cette couche. Les couches [ $M_4O_{16}$ ] sont décorées avec des groupes ( $\text{Si}_2\text{O}_7$ ) en alternance avec des couches d'octaèdres ( $AO_6$ ) le long de la direction  $c$ . Les structures de la fersmanite et du pyrochlore,  $(\text{CaNa})\text{Nb}_2\text{O}_6(\text{OH,F})$ , sont fondées sur la même sorte de groupement [ $M_4O_{18}$ ].

(Traduit par la Rédaction)

**Mots-clés:** silicate de Ti, fersmanite, affinement de la structure cristalline, pyrochlore, complexe de Khibina–Lovozero, péninsule de Kola, Russie.

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## INTRODUCTION

Fersmanite from the Khibina alkaline massif, in the Kola Peninsula, Russia, was described as a new mineral species by Labuntsov (1929), and Machin (1977) reported the following information: (1) fersmanite,  $(\text{Ca},\text{Na})_4(\text{Ti},\text{Nb})_2\text{Si}_2\text{O}_{11}(\text{F},\text{OH})_2$ , is triclinic,  $a$  7.210(1),  $b$  7.213(2),  $c$  20.451(3) Å,  $\alpha$  95.15(3),  $\beta$  95.60(2),  $\gamma$  89.04(5)°,  $V$  1054.15 Å<sup>3</sup>; (2) fersmanite is not closely related to any other mineral; (3) fersmanite has not been found elsewhere. At present, fersmanite is also known from the Poços de Caldas massif, Minas Gerais, Brazil (Atencio *et al.* 1999), and Üdersdorf, western Eifel region, Rheinland-Pfalz, Germany (Hentschel 1993). Saf'yanov *et al.* (1984) determined the crystal structure of fersmanite with the following cell:  $a$  10.212(6),  $b$  20.450(20),  $c$  10.198(9) Å,  $\gamma$  97.22(5)°,  $B2/b$ ,  $Z = 4$ . They reported the chemical formula as  $\text{Ca}_{4.72}\text{Na}_{3.28}\text{Ti}_{3.20}\text{Nb}_{0.80}[\text{Si}_2\text{O}_7]_2\text{O}_8\text{F}_3$ , and quoted two possible structural formulae:  $(\text{Ca}_{0.76}\text{Na}_{0.24})_4(\text{Na}_{0.58}\text{Ca}_{0.42})_4(\text{Ti}_{0.80}\text{Nb}_{0.20})_4[\text{Si}_2\text{O}_7]_2\text{O}_8\text{F}_3$  and  $\text{Ca}_{4.72}\text{Na}_{3.28}\text{Ti}_{3.20}\text{Nb}_{0.80}[\text{Si}_2\text{O}_7]_2\text{O}_8\text{F}_3$ . This ambivalence has led to the use of an erroneous formula:  $(\text{Ca},\text{Na})_4(\text{Ti},\text{Nb})_2\text{Si}_2\text{O}_{11}(\text{F},\text{OH})_2$  (*e.g.*, Mandarino 1999).

The Ti-silicate minerals are, for the most part, rare accessory minerals. However, they may be of increasing importance in the future as models for industrial materials. Recently, a new Ti-silicate molecular sieve was reported (Kuznicki *et al.* 2001) with a structure closely related to that of zorite,  $\text{Na}_2\text{Ti}^{4+}(\text{Si},\text{Al})_3\text{O}_9(\text{H}_2\text{O})_n$  (Sandomirskii & Belov 1979). Our continuing interest in Ti silicates led us to examine fersmanite from the type locality, Khibina, Kola, particularly with regard to (1) the anomalies in the currently accepted chemical and structural formulae of fersmanite, and (2) the statement of Machin (1977) that fersmanite is not closely related to any other mineral.

## EXPERIMENTAL

*Crystal-structure refinement (SREF)*

A single crystal of fersmanite (Table 1) was mounted on a Bruker P4 automated four-circle diffractometer equipped with graphite-filtered  $\text{MoK}\alpha$  X-radiation and a Smart 1K CCD detector. The intensities of 9001 reflections with  $13 < h < 13$ ,  $13 < k < 13$ ,  $13 < l < 26$  were collected to  $55.6^\circ 2\theta$  using 60 s per frame. An empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters were obtained from 6621 reflections with  $I > 10\sigma I$ .

The SHELXTL 5.1 system of programs was used for refinement of the structure. The atom coordinates of Saf'yanov *et al.* (1984) were used as the initial model. We used the standard space-group  $C2/c$  with  $b$  unique (instead of  $B2/b$  with  $c$  unique as in Saf'yanov *et al.* 1984). Details concerning collection of the X-ray data and crystal-structure refinement are given in Table 1.

Structure refinement converged to an  $R$ -index of 4.1% for 2119 independent observed reflections (196 refined parameters, including extinction). The site populations of the  $A(1)$  and  $A(2)$  sites refined to 2.00(1) Ca and 1.97(1) Ca *apfu* [40.0(2) at 39.5(2) *epfu*], respectively, indicating that these two sites are completely occupied by Ca; hence in the final cycles of refinement, the sites were fixed at complete occupancy by Ca. Final atom coordinates and anisotropic-displacement parameters are given in Table 2, selected interatomic distances are listed in Table 3, and refined site-scattering values (in *epfu*: electrons per formula unit) are given in Table 4. Table 5 gives the bond-valence summations for fersmanite. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

*Electron-microprobe analysis (EMPA)*

Subsequent to collection of the X-ray intensity data, the crystal used for this purpose was embedded in epoxy, ground, polished, carbon-coated and analyzed with a Cameca SX-50 electron-microprobe operating in wavelength-dispersion mode. Ten points were analyzed, using the following standards (for  $K\alpha$  X-ray lines): F: F-bearing riebeckite; Na: jadeite; Mg: forsterite; Al: andalusite; Si, Ca: diopside; K: sanidine; Ti: titanite; Mn, Nb:  $\text{MnNb}_2\text{O}_6$ ; Fe: fayalite; Sr:  $\text{SrTiO}_3$ ; Ta: manganotantalite. The chemical composition is given in Table 6. The unit formula was calculated on the basis of 25 anions with  $F = 3$  *apfu* (atoms per formula unit):  $(\text{Ca}_{5.29}\text{Na}_{2.56}\text{Sr}_{0.09}\text{Fe}^{2+}_{0.02}\text{Mn}^{2+}_{0.03})_{\Sigma 7.99}(\text{Ti}_{2.32}\text{Nb}_{1.64}\text{Ta}_{0.02})_{\Sigma 3.98}\text{Si}_{4.00}\text{O}_{22}\text{F}_3$ .

## DESCRIPTION OF THE STRUCTURE

*Cation polyhedra*

There are two  $\text{Si}$  sites, each occupied only by Si and coordinated by a tetrahedral array of O atoms with a  $\langle\text{Si}-\text{O}\rangle$  distance of 1.626 Å. Two tetrahedra share a

TABLE 1. MISCELLANEOUS INFORMATION FOR FERSMANITE

$a$ (Å)	10.183(2)	crystal size (mm)	0.16, sphere
$b$	10.183(2)	radiation	$\text{MoK}\alpha$
$c$	20.356(4)	maximum $2\theta$ (°)	55.6
$\beta$ (°)	97.19(3)	$R(\text{int})$ (%)	4.3
$V$ (Å <sup>3</sup> )	2068.2(2)	Reflections collected	5001
Sp Gr	$C2/c$	$F_o > 4\sigma F$	4327
$Z$	4	Unique reflections	2418
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	3.159	$F_o > 4\sigma F$	2119
Absorption coefficient (mm <sup>-1</sup> )	3.31	Refinement method	Least-squares on $F^2$ , fixed weights $\sim 1/\sigma(F)$
$F(000)$	1823.9	Goodness of fit on $F^2$	1.202
		Final $R$ index (%) [ $F_o > 4\sigma F$ ]	4.0
		$R$ index (%) (all data)	4.7
		$wR_2$ (%)	10.9

TABLE 2. ATOM POSITIONS AND DISPLACEMENT FACTORS FOR FERSMANITE

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
M(1)	0.10817(4)	0.56293(5)	0.18725(2)	0.0141(3)	0.0146(3)	0.0160(3)	-0.00018(17)	0.00143(19)	-0.00003(16)	0.0149(2)
M(2)	0.14013(4)	0.81125(5)	0.31258(2)	0.0133(3)	0.0147(3)	0.0152(3)	-0.00040(18)	0.00043(19)	-0.00001(13)	0.0145(2)
A(1)	0.33102(7)	1.06505(8)	0.06387(4)	0.0199(4)	0.0210(4)	0.0166(4)	0.0002(3)	0.0011(3)	-0.0062(3)	0.0192(2)
A(2)	0.07673(8)	0.81020(8)	0.06675(4)	0.0199(4)	0.0207(4)	0.0171(4)	-0.0003(3)	0.0009(3)	-0.0067(3)	0.0194(2)
A(3)	0.38457(10)	0.55893(12)	0.30528(6)	0.0240(8)	0.0236(8)	0.0243(8)	0.0021(4)	0.0045(5)	-0.0025(4)	0.0239(6)
A(4)	0.35750(10)	0.81652(12)	0.19449(5)	0.0212(8)	0.0232(8)	0.0236(8)	0.0023(4)	-0.0006(5)	0.0027(4)	0.0230(6)
Si(1)	-0.06952(10)	0.70163(10)	-0.08346(5)	0.0132(5)	0.0146(5)	0.0139(5)	-0.0022(4)	-0.0008(4)	0.0000(4)	0.0141(2)
Si(2)	0.15357(10)	0.92428(10)	-0.08300(5)	0.0143(5)	0.0148(5)	0.0147(5)	0.0022(4)	0.0026(4)	0.0003(4)	0.0145(2)
O(1)	-0.2105(3)	0.7588(3)	-0.11832(14)	0.0195(13)	0.0256(14)	0.0235(14)	-0.0042(12)	-0.0020(11)	0.0064(11)	0.0233(6)
O(2)	-0.0213(3)	0.5686(3)	-0.11832(14)	0.0251(14)	0.0205(14)	0.0223(14)	-0.0056(11)	-0.0021(12)	0.0051(11)	0.0231(6)
O(3)	-0.0622(3)	0.6891(3)	-0.00553(13)	0.0294(15)	0.0277(15)	0.0161(13)	-0.0004(12)	0.0013(11)	-0.0078(12)	0.0245(6)
O(4)	0.0366(3)	0.8130(3)	-0.10396(15)	0.0275(15)	0.0258(16)	0.0327(16)	0.0020(13)	0.0030(12)	-0.0140(12)	0.0287(7)
O(5)	0.0878(3)	1.0567(3)	-0.11826(14)	0.0289(15)	0.0209(14)	0.0230(14)	0.0049(11)	0.0092(12)	0.0074(11)	0.0238(6)
O(6)	0.1849(3)	0.9365(3)	-0.00537(14)	0.0321(16)	0.0364(17)	0.0160(14)	-0.0003(12)	0.0009(12)	-0.0100(13)	0.0283(7)
O(7)	0.2773(3)	0.8675(3)	-0.11807(14)	0.0222(14)	0.0280(15)	0.0224(14)	0.0090(12)	0.0066(11)	0.0059(11)	0.0242(6)
O(8)	0.2586(3)	0.9371(3)	0.28388(13)	0.0168(13)	0.0167(13)	0.0192(13)	0.0011(11)	0.0017(10)	-0.0030(10)	0.0190(6)
O(9)	0.1915(3)	0.6872(3)	0.24989(13)	0.0198(13)	0.0196(13)	0.0169(12)	-0.0042(11)	0.0021(10)	-0.0022(10)	0.0188(6)
O(10)	0.0264(2)	0.6869(3)	0.35313(13)	0.0159(12)	0.0147(12)	0.0193(13)	-0.0014(10)	0.0022(10)	-0.0003(10)	0.0168(5)
O(11)	0	0.4963(4)	1/4	0.0185(18)	0.0206(19)	0.0160(18)	0	0.0026(14)	0	0.0184(8)
O(12)	0	0.8787(4)	1/4	0.0215(18)	0.0175(18)	0.0210(19)	0	-0.0022(15)	0	0.0204(8)
F(1)	0.2213(2)	0.9385(2)	0.13101(11)	0.0225(11)	0.0238(12)	0.0184(11)	-0.0008(9)	0.0018(9)	-0.0032(9)	0.0217(5)
F(2)	1/2	0.6876(3)	1/4	0.0260(17)	0.0233(17)	0.0300(18)	0	0.0019(14)	0	0.0268(7)

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR FERSMANITE

M(1)—O(2)	2.060(3)	M(2)—O(1)	2.067(3)
M(1)—O(7)	2.065(3)	M(2)—O(5)	2.066(3)
M(1)—O(8)	1.905(3)	M(2)—O(8)	1.902(3)
M(1)—O(9)	1.918(3)	M(2)—O(9)	1.916(3)
M(1)—O(10)	1.966(3)	M(2)—O(10)	1.967(3)
M(1)—O(11)	<u>1.914(1)</u>	M(2)—O(12)	<u>1.918(1)</u>
<M(1)—O>	1.972	<M(2)—O>	1.973
A(1)—O(1)	2.509(3)	A(2)—O(3)	2.274(3)
A(1)—O(2)	2.510(3)	A(2)—O(5)	2.488(3)
A(1)—O(3)	2.273(3)	A(2)—O(6)	2.332(3)
A(1)—O(6)	2.323(3)	A(2)—O(7)	2.487(3)
A(1)—O(10)	2.429(3)	A(2)—O(10)	2.404(3)
A(1)—F(1)	<u>2.273(2)</u>	A(2)—F(1)	<u>2.260(2)</u>
<A(1)—O,F>	2.386	<A(2)—O,F>	2.374
A(3)—O(1)	2.681(3)	A(4)—O(2)	2.686(3)
A(3)—O(4)	2.609(3)	A(4)—O(4)	2.610(3)
A(1)—O(5)	2.701(3)	A(4)—O(7)	2.700(3)
A(3)—O(8)	2.511(3)	A(4)—O(8)	2.511(3)
A(3)—O(9)	2.508(3)	A(4)—O(9)	2.519(3)
A(3)—O(12)	2.521(3)	A(4)—O(11)	2.515(3)
A(3)—F(1)	2.169(3)	A(4)—F(1)	2.166(3)
A(3)—F(2)	<u>2.168(2)</u>	A(4)—F(2)	<u>2.168(2)</u>
<A(3)—O,F>	2.484	<A(4)—O,F>	2.484
Si(1)—O(1)	1.628(3)	Si(2)—O(4)	1.661(3)
Si(1)—O(2)	1.634(3)	Si(2)—O(5)	1.632(3)
Si(1)—O(3)	1.587(3)	Si(2)—O(6)	1.580(3)
Si(1)—O(4)	<u>1.656(3)</u>	Si(2)—O(7)	<u>1.631(3)</u>
<Si(1)—O>	1.626	<Si(2)—O>	1.626
Si(1)—O(4)—Si(2)	150.7(2)		

common vertex, O(4), to form an  $[\text{Si}_2\text{O}_7]$  group with an  $\text{Si}(1)\text{—O}(4)\text{—Si}(2)$  angle of  $150.7(2)^\circ$  (Table 3).

There are two *M* sites, each occupied by  $\text{Ti}^{4+} + \text{Nb}$  and coordinated by a distorted octahedral array of O atoms with a  $\langle M\text{—O} \rangle$  distance of 1.973 Å (Table 3). For each octahedron, four distances are in the range 1.902–1.967 Å, and two distances [ $M(1)\text{—O}(2,7)$  and  $M(2)\text{—O}(1,5)$ ] are in the range 2.060–2.067 Å (Table 3) and subtend a common edge. The total refined scattering at the *M* sites is 117.6(8) *epfu*, and the analogous scattering calculated from the unit formula (EMPA, Table 6) is 119.4 *epfu*; the difference is 2.2  $\sigma$ , ignoring any uncertainty in the unit formula, and hence these two values are not significantly different. Site populations (Table 4) were assigned according to the refined scattering adjusted such that the total assigned scattering is the average of the SREF and EMPA values: 118.6 *epfu*.

The *A*(1) and *A*(2) sites (Table 3) are each coordinated by an octahedral arrangement of five O and one F atoms, and are occupied solely by Ca (possibly with very minor  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ). The two [8]-coordinated *A*(3) and *A*(4) sites (Table 3) are occupied by dominant Na, major Ca and minor Sr. Each *A*(3,4) site is coordinated by six O and two F atoms, with long *A*—O bonds (2.508–2.701 Å) and short *A*—F bonds (2.166–2.169 Å). The total refined scattering at the *A*(1) to *A*(4) sites is 141.5(1.2) *epfu*, and the analogous scattering calculated from the unit formula (Table 4) is 138.7 *epfu*; the difference is 2.3  $\sigma$  ignoring any uncertainty in the unit formula, and hence these two values are not significantly

TABLE 4. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR FERSMANITE

	Scattering species	Refined site-scattering	Assigned site-population	Predicted site-scattering	( $X-\phi$ ) <sub>obs</sub>	( $X-\phi$ ) <sub>calc</sub> *
<i>M</i> (1)	Nb, Ti	58.9(6)	1.19 Ti + 0.81 Nb	59.4	1.972	1.999
<i>M</i> (2)	Nb, Ti	58.7(6)	1.20 Ti + 0.80 Nb	59.2	1.973	1.999
<sup>16</sup> <i>A</i> (1)	Ca	40**	1.97 Ca + 0.03 (Fe <sup>2+</sup> , Mn <sup>2+</sup> )	40.2	2.386	2.375
<sup>16</sup> <i>A</i> (2)	Ca	40**	1.97 Ca + 0.03 (Fe <sup>2+</sup> , Mn <sup>2+</sup> )	40.2	2.374	2.375
<sup>18</sup> <i>A</i> (3)	Ca, Na	31.0(7)	1.16 Na + 0.80 Ca + 0.04 Sr	30.3	2.484	2.535
<sup>18</sup> <i>A</i> (4)	Ca, Na	30.5(7)	1.21 Na + 0.75 Ca + 0.04 Sr	29.8	2.484	2.535

\* sum of constituent ionic radii (Shannon 1976);  $X$  = unspecified cation,  $\phi$  = unspecified anion.

\*\* refined to 40.0(2) and 39.5(2) *apfu*, respectively, and hence set equal to 40 *epfu* (complete occupancy by Ca) for the final cycles of refinement.

TABLE 5. BOND-VALENCE TABLE FOR FERSMANITE

	<i>M</i> (1)	<i>M</i> (2)	<i>A</i> (1)	<i>A</i> (2)	<i>A</i> (3)	<i>A</i> (4)	Si(1)	Si(2)	$\Sigma$
O(1)		0.56	0.23		0.15		1.00		1.94
O(2)	0.58		0.23			0.14	0.99		1.94
O(3)			0.39	0.39			1.12		1.90
O(4)					0.17	0.17	0.94	0.92	2.20
O(5)		0.56		0.24	0.14			0.99	1.93
O(6)			0.35	0.34				1.14	1.83
O(7)	0.56			0.25		0.17		1.00	1.98
O(8)	0.85	0.87			0.21	0.20			2.13
O(9)	0.82	0.82			0.20	0.20			2.04
O(10)	0.72	0.72	0.27	0.29					2.00
O(11)	0.83 <sup>±2</sup> -					0.20 <sup>±2</sup> -			2.06
O(12)		0.83 <sup>±2</sup> -			0.20 <sup>±2</sup> -				2.06
F(1)			0.33	0.34	0.34	0.34			1.35
F(2)					0.34 <sup>±2</sup> -	0.34 <sup>±2</sup> -			1.36
$\Sigma$	4.36	4.36	1.80	1.85	1.75	1.76	4.05	4.05	

\* bond-valence curves (*vu*) from Brown (1981)

different. Site populations (Table 4) were assigned as for the *M* sites, with the small amount of Fe<sup>2+</sup> and Mn<sup>2+</sup> assigned to *A*(1) + *A*(2) and Sr assigned to *A*(3) + *A*(4) in accord with the observed mean bond-lengths.

### Structure topology

The {*M*(1)O<sub>6</sub>} and {*M*(2)O<sub>6</sub>} octahedra share *trans* vertices [O(8) and O(10)] to form [*MO*<sub>5</sub>] chains that extend in the [110] and [1 $\bar{1}$ 0] directions and meld by sharing corners to form a layer parallel to (001) (Fig. 1a). The [8]-coordinated *A*(3) and *A*(4) sites are located within the layer (Fig. 1a). Where two [*MO*<sub>5</sub>] chains intersect, four octahedra share corners to form an [*M*<sub>4</sub>O<sub>18</sub>] cluster. In this cluster, each (*MO*<sub>6</sub>) 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 (*MO*<sub>6</sub>) octahedra. Figure 1b shows a fragment of the layer containing four clusters; the [*M*<sub>4</sub>O<sub>18</sub>] cluster may be regarded as the *FBB* (Fundamental Building

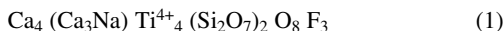
Block) of the layer, rather than the [*MO*<sub>5</sub>] chain. In the [*MO*<sub>5</sub>] chain, an octahedron shares vertices with two adjacent octahedra, whereas in a layer, each octahedron shares corners with four adjacent octahedra. According to the approach of Hawthorne (1983), the *FBB* should be defined as the most strongly connected fragment of the structure, which in this case is the [*M*<sub>4</sub>O<sub>18</sub>] cluster rather than the [*MO*<sub>5</sub>] chain. The [*M*<sub>4</sub>O<sub>18</sub>] clusters are arranged at the vertices of a 4<sup>+</sup> net and link by sharing octahedron corners to form a sheet of the form [*M*<sub>4</sub>O<sub>16</sub>] (*i.e.*, it is a *metastructure* in the terminology of Schindler *et al.* 1999).

The [*M*<sub>4</sub>O<sub>16</sub>] layer is decorated by [Si<sub>2</sub>O<sub>7</sub>] groups; each tetrahedron of an [Si<sub>2</sub>O<sub>7</sub>] group shares two vertices with two octahedra of one [*MO*<sub>5</sub>] chain, and [Si<sub>2</sub>O<sub>7</sub>] groups superimpose when viewed along [001] (Fig. 1c). Figures 1a and 1c reveal the pseudotetragonal symmetry described for the habit of fersmanite (Labuntsov 1929). Ribbons of *A*(1,2) octahedra extend in the [1 $\bar{1}$ 0] direction at  $z \approx \pm 0.08$  and are linked by [Si<sub>2</sub>O<sub>7</sub>] groups to form a layer (Fig. 1d). In this [AO<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)] layer, each *A*(1,2) octahedron shares two *trans* corners with [Si<sub>2</sub>O<sub>7</sub>] groups. These two layers (one of them shown in Fig. 1d) form a slab *via* the inversion centers at  $z = 0$ . In the crystal structure of fersmanite, there are two *M*-*A*(3,4) layers and two [AO<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)] layers per repeat distance along the *c* axis (Fig. 2).

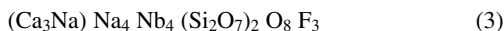
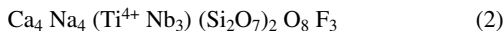
### THE CHEMICAL COMPOSITION OF FERSMANITE

As noted above, the chemical formulae previously written for fersmanite are either not electronically neutral or are written in a structurally inappropriate fashion. There is no argument as to the anionic part of the formulae; our work supports the previously established (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> O<sub>8</sub> F<sub>3</sub>, with a formal charge of 31<sup>-</sup>. The cationic part of the formula must balance this charge, whereas the formula of Saf'yanov *et al.* (1984) for fersmanite from Khibina has a net cation charge of 29.52<sup>+</sup>. As indicated in Table 5, there is no significant order between the *M*(1) and *M*(2) sites, between the *A*(1) and *A*(2) sites, or between the *A*(3) and *A*(4) sites. Hence we can write a structural formula as A<sub>4</sub> A'<sub>4</sub> M<sub>4</sub> (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

$O_8 F_3$ , where  $A = A(1) + A(2)$ ,  $A' = A(3) + A(4)$ ,  $M = M(1) + M(2)$ . It is useful to examine the (neutral) formula derived here (Table 6) and write the possible end-members according to the criteria of Hawthorne (2002). From Tables 4 and 6, Ti is dominant at  $M$ , Ca almost fills  $A$ , and Ca is dominant at  $A'$  (but with significant Na present); thus the closest end-member to this composition is as follows:



This formula satisfies the criteria of Hawthorne (2002) for an end member: it is neutral, it is compatible with the crystal structure, its composition is fixed, and one site contains two species (each of the other sites contains only one species). There are two other possible end-member compositions:



There are no other chemical components of major significance in the composition of Table 2, and hence we should be able to describe the chemical formula of fersmanite adequately with these end-members. As there is no Na at the  $A$  site, end-member (3) is not a constituent of the formula of Table 6. Taking end-members (1) and (2) in the ratio 0.46:0.54 gives the following chemical composition:  $Ca_4 (Na_{2.60} Ca_{1.38}) (Ti_{2.38} Nb_{1.62}) (Si_2O_7)_2 O_8 F_3$ , in close agreement with the composition given in Table 6. This leads to the rather interesting conclusion that the primary end-member composition of the fersmanite analysis in Table 2 is composition (2):  $Ca_4 Na_4 (Ti^{4+} Nb_3) (Si_2O_7)_2 O_8 F_3$ . At first sight, this might seem counterintuitive as the composition listed in Table 6 has  $Ti^{4+}$  dominant at  $M$ , whereas the end-member has Nb dominant at  $M$ . However, this apparent anomaly is illusory. The  $M$  site has compositions  $Ti^{4+}_4$  and  $Ti^{4+}Nb_3$  in end-members (1) and (2). A 50:50 mixture of these two compositions gives  $M_4 = (Ti^{4+}_{2.50} Nb_{1.50})$ , and hence the composition  $(Ti^{4+}_{2.32} Nb_{1.66})$  lies closer to composition (2), with  $M_4 = Ti^{4+}Nb_3$ , than it does to composition (1), with  $M_4 = Ti^{4+}_4$ .

Examination of the small amount of chemical-compositional data available for fersmanite (Labuntsov 1933, Machin 1977, Saf'yanov *et al.* 1984, this work) shows that they tend to concentrate around the 50:50 ratio of end-members (1) and (2);  $Ca_4 (Na_{2.5} Ca_{1.5}) (Ti^{4+}_{2.5} Nb_{1.5}) (Si_2O_7)_2 O_8 F_3$ . The one exception is the formula listed by Saf'yanov *et al.* (1984):  $Ca_4 (Na_{3.28} Ca_{0.72}) (Ti_{3.20} Nb_{0.80}) (Si_2O_7)_2 O_8 F_3$ . The Ti:Nb ratio lies nearer end-member composition (1), whereas the Ca:Na ratio lies nearer end-member composition (2); in accord with this anomaly, the formula bears a charge of  $1.5^-$ , and cannot be considered reliable. The original analytical data of Labuntsov (1929) did not include  $Nb_2O_5$ , although later work (Labuntsov 1933) did pro-

vide this information. The resulting  $A$ -group cations are  $Ti^{4+}_{2.93} Nb_{1.48}$ ; the sum of the  $A$  cations is 4.41 *apfu*, far in excess of the required sum of 4 *apfu*. As a result of this anomalously large sum, and the constituent values of  $Ti^{4+}$  and Nb, it is not possible to say on which side of the composition  $(Ti^{4+}_{2.5} Nb_{1.5})$  [that divides the compositional fields corresponding to end-members (1) and (2)] the original composition lies; hence we cannot be sure of the end-member corresponding to the composition of holotype fersmanite. From the small amount of data currently available, the optimal way to write the general chemical formula of fersmanite is  $Ca_4 (Na,Ca)_4 (Ti^{4+},Nb)_4 (Si_2O_7)_2 O_8 F_3$ , recognizing that all compositions (except those with obvious major errors) lie close to the 50:50 boundary between the end members  $Ca_4 (Ca_3Na) Ti^{4+}_4 (Si_2O_7)_2 O_8 F_3$  and  $Ca_4 Na_4 (Ti^{4+}Nb_3) (Si_2O_7)_2 O_8 F_3$ .

## RELATED STRUCTURES

Fersmanite is the only mineral with a layer of corner-sharing  $(\{Ti^{4+},Nb\}O_6)$  octahedra. In this sense, it has no structural analogues. Saf'yanov *et al.* (1984) described fersmanite as a Ti-silicate with chains of corner-sharing  $(\{Ti,Nb\}O_6)$  octahedra. Two types of chains of corner-sharing octahedra are known in Ti silicates: extended chains and kinked chains (note that these chains are topologically the same but geometrically different). For example, batisite,  $Ba (K,Na)_2 Ti_2 Si_4 O_{14}$ , contains extended chains of  $(TiO_6)$  octahedra (Nikitin & Belov 1962). Figure 3a shows the chains viewed "end-on" and their linkage to  $(NaO_n)$  polyhedra and  $(SiO_4)$  tetrahedra. The linkage of  $[TiO_5]$  chains and  $[Si_4O_{12}]$  chains is shown in Figure 3b: each  $[Si_2O_7]$  group is linked to two  $(TiO_6)$  octahedra, and the anion separations match exactly. Thus two structural fragments,  $(TiO_6)$  octahedra and  $(SiO_4)$  tetrahedra, link together quite easily in the structure. The second type of chain occurs in titanite,  $Ca Ti Si O_5$ . The linkage of kinked  $[TiO_5]$  chains and  $(SiO_4)$  tetrahedra is shown in Figure 4. The  $[TiO_5]$  chains extend along  $[100]$ , and  $(SiO_4)$  tetrahedra share vertices with four  $(TiO_6)$  octahedra of three different chains.

In fersmanite,  $[MO_5]$  chains polymerize to form a layer (Fig. 1a); in pyrochlore,  $[MO_5]$  chains polymerize to form a framework. The crystal structure of pyrochlore, ideally  $(CaNa) Nb_2 O_6 (OH)$ , consists of two frameworks. The first framework consists of  $(\{Ca,Na\}O_8)$  polyhedra, and the second framework is formed from  $(NbO_6)$  octahedra. In the framework of  $(NbO_6)$  octahedra, chains intersect to form tetrameric  $[Nb_4O_{18}]$  clusters (Fig. 5a). These clusters are arranged in the same way as the  $[M_4O_{18}]$  clusters in the structure of fersmanite (Fig. 1a), but with two fersmanite-type layers per repeat distance in pyrochlore. Figure 5b shows the framework of octahedra in pyrochlore that contains large cages which are occupied by  $[8]$ -coordinated  $(Na,Ca)$  atoms.

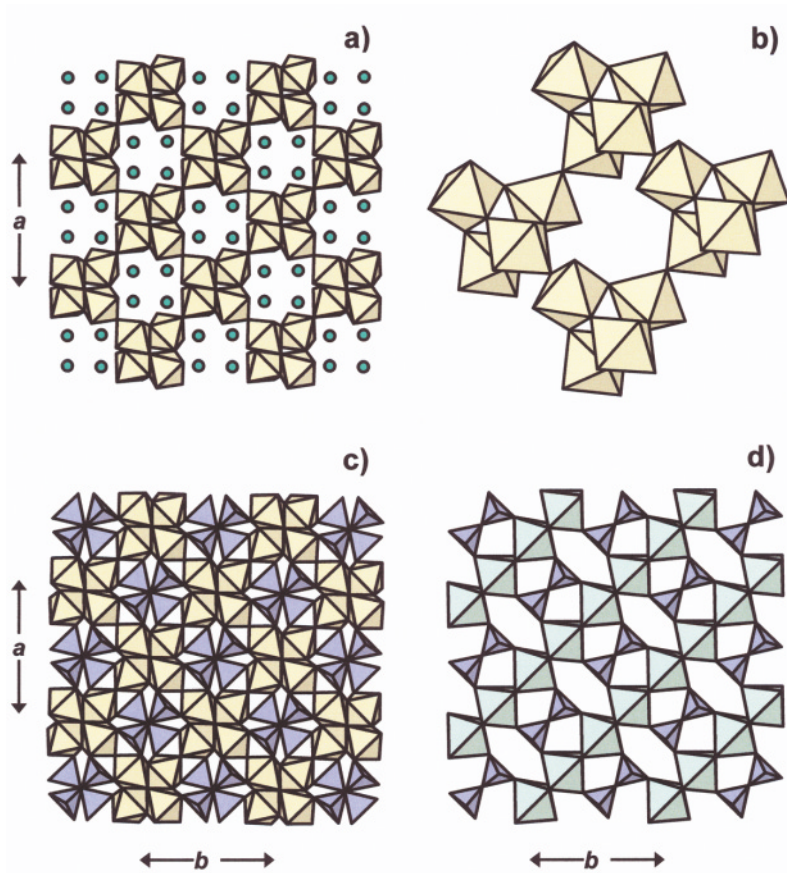


FIG. 1. Fersmanite: (a) the layer formed by the intersection of chains of corner-sharing ( $MO_6$ ) octahedra projected onto (001); (b) linkage of four  $[M_4O_{18}]$  clusters; (c) the layer of corner-sharing ( $MO_6$ ) octahedra decorated with  $[Si_2O_7]$  groups; (d) linkage of  $\{A(3,4)O_6\}$  octahedra and  $[Si_2O_7]$  groups. ( $MO_6$ ) octahedra are honey-yellow,  $A(1)$  and  $A(2)$  atoms are shown as bright green circles,  $\{A(3)O_6\}$  and  $\{A(4)O_6\}$  octahedra are pale green;  $(SiO_4)$  tetrahedra are purple.

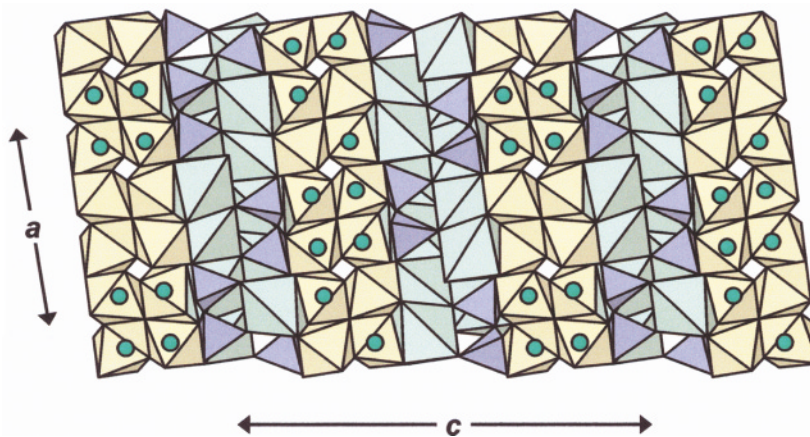


FIG. 2. The crystal structure of fersmanite projected onto (010); legend as in Figure 1.



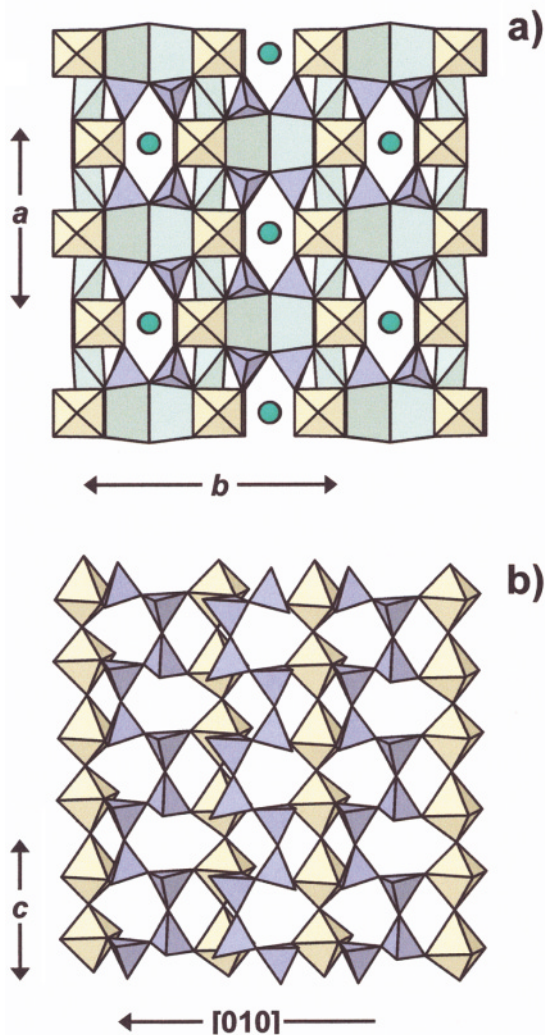


FIG. 3. Batisite: (a) crystal structure projected onto (001); (b) linkage of linear chains of corner-sharing  $(\text{TiO}_6)$  octahedra and  $[\text{Si}_4\text{O}_{12}]$  chains.  $(\text{TiO}_6)$  octahedra are honey-yellow, Ba atoms are shown as bright green circles,  $(\text{NaO}_6)$  octahedra are pale green;  $(\text{SiO}_4)$  tetrahedra are purple.

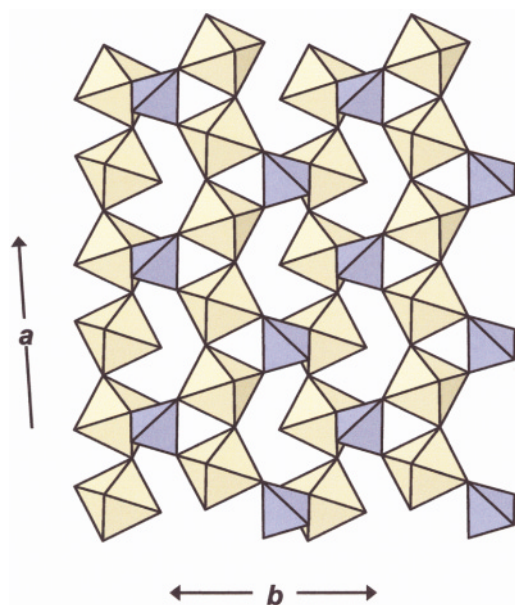


FIG. 4. Titanite: linkage of 7 Å chains of corner-sharing  $(\text{TiO}_6)$  octahedra and  $(\text{SiO}_4)$  tetrahedra.  $(\text{TiO}_6)$  octahedra are honey-yellow,  $(\text{SiO}_4)$  tetrahedra are purple.

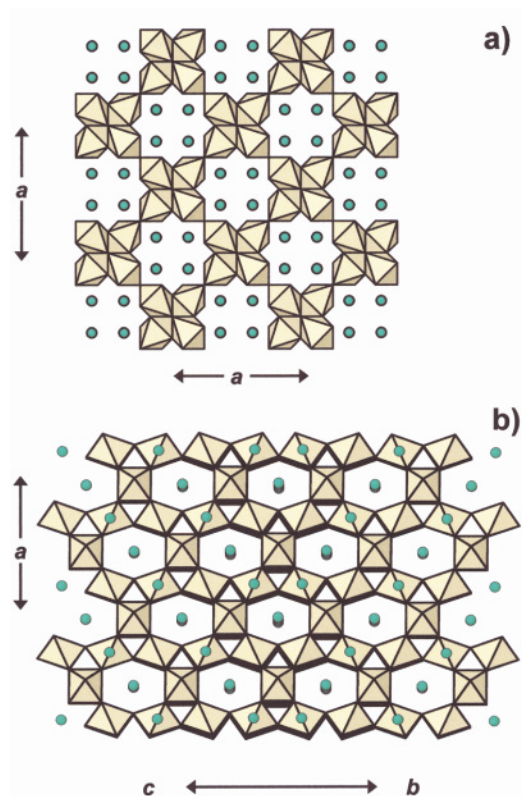


FIG. 5. The crystal structure of pyrochlore: (a) the sheet formed by corner-sharing chains of  $(\text{NbO}_6)$  octahedra projected onto (001); (b) general view of the crystal structure.  $(\text{NbO}_6)$  octahedra are honey-yellow,  $(\text{Ca,Na})$  atoms are shown as bright green circles.

## PSEUDOSYMMETRY IN FERSMANITE

In the crystal structure of fersmanite, all the cation polyhedra of the same sort are associated in pairs: the  $M(1)$  and  $M(2)$ ,  $A(1)$  and  $A(2)$ ,  $A(3)$  and  $A(4)$ ,  $Si(1)$  and  $Si(2)$  polyhedra have the same constituent scattering and similar geometry (Tables 4, 5). This fact strongly suggests a higher symmetry. The values of the  $a$  and  $b$  cell parameters, 10.183(2) Å, with  $\gamma$  90°, induced us to look for evidence of tetragonal symmetry. The  $(\frac{1}{2} \frac{1}{2} 0, -\frac{1}{2} \frac{1}{2} 0, 1 \ 0 \ 4)$  matrix transformation of the  $C$ -centered fersmanite cell gives a tetragonal  $I$ -centered cell:  $a = b = 7.20$ ,  $c$  80.94 Å. In this regard, there was some weak scattering corresponding to a  $c$ -repeat distance of ~40.8 Å, and very weak scattering at ~81 Å. Labuntsov (1929) described a pseudotetragonal habit for holotype crystals of fersmanite, and many fersmanite crystals show pronounced uniaxial optical behavior. Figures 1a and 1d show a pseudotetragonal symmetry for the principal structural fragments of the fersmanite structure. Moreover, every two layers of the same type are related by the  $4_1$  axis. Coupled cation sites can be united into sites with double multiplicity by the mirror planes, (110) or (110) corresponding to the [100] or [010] directions of the tetragonal cell. It is tempting to suggest that fersmanite crystallizes with tetragonal symmetry and inverts to monoclinic symmetry on cooling.

## SUMMARY

(1) The chemical formula of fersmanite should be written as  $Ca_4 (Na,Ca)_4 (Ti,Nb)_4 (Si_2O_7)_2 O_8 F_3$ .

(2) The principal end-members for fersmanite are  $Ca_4 (Ca_3Na) Ti^{4+}_4 (Si_2O_7)_2 O_8 F_3$  and  $Ca_4 Na_4 Ti^{4+} Nb_3 (Si_2O_7)_2 O_8 F_3$ .

(3) The crystal structures of fersmanite,  $Ca_4 (Na,Ca)_4 (Ti,Nb)_4 (Si_2O_7)_2 O_8 F_3$ , and pyrochlore,  $(CaNa) Nb_2 O_6 (OH)$ , have the same fundamental building block, *i.e.*, a tetrameric  $[M_4O_{18}]$  cluster of octahedra ( $M = Ti^{4+}, Nb$ ).

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