FERSMANITE, $(Ca,Na)_4(Ti,Nb)_2Si_2O_{11}(F,OH)_2$: A RESTUDY

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ABSTRACT

Fersmanite, $(Ca,Na)_4(Ti,Nb)_2Si_2O_{11}(F,OH)_2$, has been shown by X-ray study to be triclinic with a 7.210(1), b 7.213(2), c 20.451(3)Å, α 95.15(3), β 95.60(2), γ 89.04(5)°, V=1054.15Å³, Z=4. Fourteen electron microprobe analyses of four grains lead to the above formula. Fersmanite is not closely related to any other mineral.

SOMMAIRE

Aux rayons X la fersmanite, $(Ca,Na)_4(Ti,Nb)_2$ $Si_2O_{11}(F,OH)_2$, s'avère triclinique: a 7.210(1), b 7.213(2), c 20.451(3)Å, α 95.15(3), β 95.60(2), γ 89.04(5)°, V=1054.15Å³, Z=4. Quatorze analyses à la micro-sonde électronique effectuées sur quatre grains conduisent à la formule ci-dessus. La fersmanite n'est analogue à aucun autre minéral.
(Traduit par la Rédaction)

INTRODUCTION

Fersmanite, a very rare silicate-fluoride of Na, Ca, Ti and Nb was initially described by Labuntsov (1929) after its discovery on the Kola Peninsula where it occurs as brown pseudo-tetragonal crystals associated with aegirine and lamprophyllite in nepheline feldspathoid pegmatites. It has not been found elsewhere.

Crystals of fersmanite display a markedly pseudotetragonal habit, interpreted as monoclinic by Labuntsov (1937) with the morphological axial elements $a:b:c$=0.99113:1:0.99618, β 97°16'. In hand specimen the mineral is dark brown but small pieces as seen under the binocular microscope are golden yellow and when fresh are completely transparent. Clouded areas in some grains may be due to alteration. The hardness is 5-5.5 and the specific gravity is 3.44-3.46 (Labuntsov 1929). Fersmanite is optically biaxial negative, $2V$ 0-7° with $n\alpha$ 1.873, $n\gamma$ 1.914 (according to Yu. S. Slepnev) and $n\alpha$ 1.886, $n\beta$ 1.930, $n\gamma$ 1.939 (Labuntsov 1937).

An unindexed powder pattern of fersmanite by Slepnev appears in Vlasov (1964). A more complete listing of unindexed d-values is given in the P.D.F. The unit cell, not previously determined, is the subject of the present paper.

X-RAY STUDY

Specimens containing fersmanite were obtained from the mineral collection of the University of Göttingen through the courtesy of Mr. G. Schnorrer. Though most of the material available was massive, some parts displayed crystal faces up to 5 mm in greatest dimension. Examination under a hand lens revealed sprays of dark green aegirine needles commonly intimately intergrown with the brown fersmanite. Further examination under a binocular microscope (×40) showed a dark brown platy mineral resembling biotite and having a hardness of 2-3 and a perfect cleavage which passed through the fersmanite. Single-crystal studies of a cleavage fragment of this mineral identified it as lamprophyllite. Fersmanite for X-ray studies was secured by breaking from the dark brown hand specimen pieces which showed crystal faces. The fersmanite was crushed in an agate mortar to less than 0.5 mm; the only impurities found were inclusions of bright emerald-green prisms of aegirine and white to pale pink fibrous aggregates of pectolite which were interstitial to the fersmanite grains.

Hand picking of only the flawless, transparent, fersmanite grains yielded sufficient material for a powder pattern (Table 1) on a diffrac-

TABLE 1. INDEXED POWDER PATTERN OF FERSMANITE

I	d_{obs}(Å)	d_{calc}(Å)	hkl	I	d_{obs}(Å)	d_{calc}(Å)	hkl
10	10.10	10.14	002			2.580	124
17	5.618	5.631	012	16	2.576	2.578	025, 02̄6
		5.607	102			2.575	214
						2.571	2̄21, 2̄15
7	3.586	3.593	2̄01	34	2.530	2.534	008
		3.592	020, 02̄1			2.528	22̄0
		3.590	1̄14				
		3.588	2̄00	7	1.985	1.986	035
3	3.477	3.484	021, 02̄2			1.984	230
		3.476	201			1.983	320
16	3.294	3.304	2̄03	24	1.913	1.915	232
		3.295	022, 02̄3			1.914	23̄3, 322
		3.284	202			1.803	04̄1, 21̄9
10	3.166	3.172	1̄15	51	1.801	1.802	401
		3.168	016			1.800	227, 1̄38
100	3.058	3.061	023, 024̄, 2̄1̄3	45	1.687	+	
		3.058	1̄23	9	1.625	+	
62	2.815	2.817	1̄16	40	1.552	+	
		2.815	024, 02̄5	55	1.518	+	
				24	1.478	+	

+ Numerous possible indices.

TABLE 2. UNIT-CELL DATA FOR FERSMANITE[a]

Triclinic, space group $P1$ or $P\bar{1}$		Reciprocal cell	
a	7.210(1)Å	a^* 0.139372(21)Å^{-1}	α^* 84.92°
b	7.213(2)Å	b^* 0.139210(43)Å^{-1}	β^* 84.46°
c	20.451(3)Å	c^* 0.049326(8)Å^{-1}	γ^* 90.46°
V	1054.15(54)Å^3	V^* 0.0009486(5)Å^{-3}	
Z	4		

Formula: $(Ca,Na)_4(Ti,Nb)_2Si_2O_{11}(F,OH)_2$

[a] This setting of the unit cell was chosen to show the pseudo-tetragonal symmetry and to allow comparison with other compounds.

TABLE 3. FORMULAE FOR FERSMANITE PROPOSED BY DIFFERENT AUTHORS

Formula	Reference
$2Na_2(O,F_2)\cdot4CaO\cdot4TiO_2\cdot3SiO_2$	Labuntsov (1929)
$8(Ca,Na)(O,F_2)\cdot4TiO_2\cdot3SiO_2$	Larsen & Berman (1934)
$(Ca,Na)_2(Ti,Nb)Si(O,F)_6$	Borneman-Starynkevich (1936)
$(Ca,Na)_2(Ti,Nb)SiO_5(F,OH)$	Vlasov (1964)
$(Ca,Na)_2(Ti,Nb)(SiO_4)(OH,F)$	Kostov (1968)
$Na_4Ca_4Ti_4[(O,OH,F)_3(SiO_4)]_3*$	Strunz (1970)
$NaCaTi(SiO_4)OF$	Povarennykh (1972)
$(Ca,Na)_4(Ti,Nb)_2Si_2O_{11}(F,OH)_2**$	Machin (1976, present work)

* This formula does not balance

**The doubled formula $(Ca,Na)_8(Ti,Nb)_4Si_4O_{22}(F,OH)_4$ may be compared with formulae obtained in Tables 4b and 7.

tometer using NaCl as an internal standard. Indexing is based on the calculated d-values from the refined cell dimensions determined on single crystals. Fersmanite grains from the same material as that used for powder work were mounted on goniometers for single-crystal study. Oscillation, rotation, and zero level Weissenberg photographs using Ni-filtered Cu radiation and $hk0$ and $h0l$ precession photographs using Zr-filtered Mo radiation were made, using a NaCl standard. Three least-squares cycles applied to 369 hkl reflections from a combination of precession and Weissenberg films yielded the triclinic reduced cell in Table 2. This cell is incompatible with the monoclinic one found by morphological study. The two cells are probably related in the following way: the diagonal of ab(X-ray) is $\sim\sqrt{2}a$(X-ray)$=10.2$Å and c(X-ray)/2$=10.23$Å. Such a pseudotetragonal cell approximates the morphological cell in axial ratios but a more exact relationship could not be found.

CHEMICAL COMPOSITION

Fersmanite was originally described by Labuntsov (1929) as a silicate-fluoride of Ca, Na and Ti. Later analyses (Borneman-Starynkevich 1936) showed that considerable Nb_2O_5 had been

overlooked in the first analyses. This oxide had been determined as TiO_2. Table 3 provides a listing of the various formulae proposed for fersmanite by different authors. All published chemical analyses of fersmanite are given in Table 4a. Half unit-cell contents (Table 4b)

TABLE 4a. CHEMICAL ANALYSES OF FERSMANITE FROM THE KHIBINY MASSIF

Wt.%	Basin of Vuonnemiok River				Valley of Vorkeuai River
	1	2	3a	3b	4a
Na_2O	8.10	9.88	7.62	7.62	7.39
K_2O	0.37	-	0.62	0.62	0.43
CaO	25.15	26.16	25.88	25.88	26.23
SrO	-	-	0.32	0.32	-
MgO	-	0.08	0.12	0.12	-
MnO	-	0.25	0.26	0.26	0.13
FeO	1.36	0.30	-	-	0.88
Fe_2O_3	0.34	0.45	0.52	0.52	-
Ce_2O_3	-	-	Traces		-
SiO_2	23.42	22.30	23.36	21.93	21.87
TiO_2	37.95	37.34	21.72	23.15	21.42
Nb_2O_5	undetermined		15.00	15.00	17.95
Ta_2O_5	"		0.36	0.36	
H_2O^+	0.84	1.26	1.80	1.80	1.38
H_2O^-	-	-	-	-	0.14
F	3.09	3.61	4.56	4.56	4.65
Subtotal	100.62	101.63	102.14	102.14	102.47
$-O=F$	1.30	1.52	1.92	1.92	1.96
Total	99.32	100.11	100.22	100.22	100.51
Analyst(s)	Vrevs-kaya	Vloda-vets	Vladimirova & Bykova		Kazakova
Reference	Labuntsov (1929)	Labuntsov (1933)	Slepneva, IMGRE		

TABLE 4b. HALF UNIT-CELL CONTENTS OF ANALYSES 3 AND 4 IN TABLE 4a

	3a	3b	4a	4b
Ca	5.06	5.06	5.12	5.14
Na	2.70	2.70	2.61	2.62
K	0.14	0.14	0.10	0.10
Sr	0.03	0.03	-	-
Mn	0.04	0.04	0.02	0.02
Mg	0.03	0.03	-	-
Fe^{2+}	-	-	0.13	0.13
Σ	8.00	8.00	7.98	8.01
Si	4.26	4.00	3.98	4.00
Ti	2.98	3.18	2.93	2.95
Nb	1.24	1.24	1.48	1.48
Fe^{3+}	0.07	0.07	-	-
Ta	0.02	0.02	-	-
Σ	4.31	4.51	4.41	4.43
O	21.91	21.79	21.97	22.07
F	2.63	2.63	2.68	2.69
OH	2.19	2.19	1.68	1.68
Σ	26.73	26.61	26.33	26.44

3a. From analysis 3a using specific gravity 3.46 and cell volume 1054.15Å^3.

3b. From analysis 3b (same as 3a except for corrected values for SiO_2 and TiO_2).

4a. From analysis 4a using specific gravity 3.46 and cell volume 1054.15Å^3.

4b. As for 4a on basis of 4 Si. Calculated specific gravity is 3.475.

have been calculated only for the later analyses 3 and 4 using the triclinic cell constants of Table 2 and a specific gravity of 3.46.

In analysis 3a, Si exceeds its probable value of 8 atoms per cell whereas (Ti,Nb) is between 8 and 9. Analysis 4a, on the other hand, shows good agreement with the unit-cell formula $Na_6Ca_{10}Ti_8$ $Nb_3Si_8O_{44}(F,OH)_9$ with F:OH near 5.5:3.5. The high Si in analysis 3a may be due to incomplete removal of TiO_2 from the analytical SiO_2 precipitate. If we assume exactly 8 Si per unit cell, analysis 3a would require 21.93% SiO_2 instead of the 23.36% recorded. Transfer of the excess 'silica' to the TiO_2 (analysis 3b Table 4a) gives a new TiO_2 of 23.15% and a total of 9.02(Ti,Nb,Fe, Ta). However the unit-cell content of Na_8Ca_{10} $Ti_8Nb_3Si_8O_{44}(F,OH)_9$ cannot be simplified into a simpler formula. The empirical formula (Ca, Na)$_4$(Ti,Nb)$_2$Si$_2$O$_{11}$(F,OH)$_2$, which has been confirmed by the microprobe analyses described below, is somewhat close but requires different contents of TiO_2 and Nb_2O_5. In order to estab-

lish the formula of fersmanite more precisely, microprobe analyses by the author were made with an ARL-EMX electron microprobe. Corrections for absorption, fluorescence, dead time and drift were made by the computer program EMPADR VII (Rucklidge & Gasparrini 1969). Table 5 summarizes the analytical conditions

TABLE 5. MICROPROBE ANALYTICAL CONDITIONS

Analyzed material: Fersmanite from Kola Peninsula, U.S.S.R.

Elements*	Ca	F	Si	Na	Nb	Ti
Line	$K\alpha_{1,2}$	$K\alpha$	$K\alpha_{1,2}$	$K\alpha_{1,2}$	$L\alpha_1$	$K\alpha_{1,2}$
(Å)	3.360	18.32	7.126	11.91	5.724	2.750
Crystal	ADP	RAP	ADP	RAP	ADP	LiF
Sequence	1	2	3	4	5	6
Standard	Pyroxene	Apatite	Pyroxene	Jadeite	Glass	BaTiO$_3$
Sample current (μA)	0.05	0.15	0.10	0.10	0.05	0.05
Voltage (kV)	15	15	15	15	15	15
Time (secs)	10	20	10	10	10	10

* The elements K, Sr, Mg, Mn, Fe and Ta which have been reported in chemical analyses, were looked for but not found.

TABLE 6. MICROPROBE ANALYSES OF FERSMANITE

Anal.	1.12	1.3	1.45	2.12	2.3	2.45	3.12	3.3	3.45	4.1	4.2	4.3	4.4	4.5
Na$_2$O	7.11	7.04	7.03	7.12	7.04	7.02	6.78	6.73	6.78	6.94	6.96	6.99	7.00	6.92
CaO	29.57	29.57	29.33	29.89	30.20	28.65	29.43	30.36	30.40	28.76	28.77	28.99	28.65	28.80
SiO$_2$	22.11	22.20	22.30	22.22	22.36	22.48	22.32	22.12	22.28	22.09	22.05	22.38	22.65	22.46
TiO$_2$	17.39	17.96	17.61	17.29	17.04	17.57	17.97	18.04	18.08	17.10	17.13	17.19	17.10	17.08
Nb$_2$O$_5$	21.71	20.66	21.38	21.33	21.55	21.05	20.06	20.21	20.57	21.97	21.83	21.55	21.57	21.79
F	3.84	3.97	3.83	3.99	4.04	4.04	4.04	4.03	3.99	4.15	4.15	4.27	4.16	4.23
Total	101.73	101.40	101.48	101.84	102.23	100.82	100.60	101.49	102.10	101.01	100.89	101.37	101.13	101.28
-O=F	1.62	1.67	1.61	1.68	1.70	1.70	1.70	1.70	1.68	1.75	1.75	1.80	1.75	1.78
Total	100.11	99.73	99.87	100.16	100.53	99.11	98.90	99.79	100.42	99.26	99.14	99.57	99.38	99.50

TABLE 7. MICROPROBE ANALYSES OF FERSMANITE CALCULATED ON BASIS OF 4Si AND 26(O,F,OH) PER HALF CELL

	Grain 1			Grain 2			Grain 3			Grain 4					
Anal.	1.12	1.3	1.45	2.12	2.3	2.45	3.12	3.3	3.45	4.1	4.2	4.3	4.4	4.5	Av.
Ca	5.73	5.71	5.64	5.77	5.79	5.46	5.65	5.88	5.85	5.58	5.59	5.55	5.42	5.50	5.65
Na	2.49	2.46	2.45	2.48	2.44	2.42	2.36	2.36	2.36	2.44	2.45	2.42	2.40	2.39	2.42
Σ	8.22	8.17	8.09	8.25	8.23	7.88	8.01	8.24	8.21	8.02	8.04	7.97	7.82	7.89	8.07
Si	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Ti	2.37	2.43	2.38	2.34	2.29	2.35	2.42	2.45	2.44	2.33	2.34	2.31	2.27	2.29	2.36
Nb	1.78	1.68	1.73	1.74	1.74	1.69	1.63	1.65	1.67	1.80	1.79	1.74	1.72	1.75	1.72
Σ	4.15	4.11	4.11	4.08	4.03	4.04	4.05	4.10	4.11	4.13	4.13	4.05	3.99	4.04	4.08
O	22.33	22.00	21.90	22.08	21.88	21.19	21.49	22.17	22.17	21.92	21.94	21.46	20.92	21.30	21.77
F	2.20	2.26	2.17	2.27	2.29	2.27	2.29	2.30	2.27	2.38	2.38	2.41	2.32	2.38	2.30
OH	1.47	1.74	1.93	1.65	1.83	2.54	2.22	1.53	1.56	1.70	1.68	2.13	2.76	2.32	1.93
Σ	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00
†	1.20	1.43	1.59	1.35	1.50	2.12	1.84	1.26	1.28	1.40	1.38	1.76	2.30	1.92	1.60
††	3.472	3.448	3.446	3.461	3.454	3.407	3.419	3.457	3.457	3.452	3.452	3.427	3.399	3.419	3.440
†††	3.430	3.399	3.391	3.414	3.402	3.335	3.356	3.413	3.413	3.403	3.404	3.367	3.321	3.353	3.386

† Calculated weight percent H$_2$O in above formulae so that for 4Si total (O,F,OH) is 26.

†† Calculated specific gravities with water included in the composition.

††† Calculated specific gravities with water omitted from the composition.

employed and Table 6 presents 14 microprobe analyses made on 4 grains. Water, which is reported in chemical analyses of fersmanite (Table 4) could not be measured by the microprobe technique and has been calculated so that for a half unit cell the total of (O,F,OH) is 26 when Si is 4 (Table 1). The microprobe analyses in Table 6 are probably on an anhydrous basis as a result of water evaporating under the beam and consequently are slightly high. It is clear from Table 7 that including water into the formula (as hydroxyl) gives a better agreement between observed and calculated specific gravities. Comparison of the microprobe analyses in Table 6 with the chemical analyses in Table 4a shows that the main differences are in the content of TiO_2 and Nb_2O_5, and that CaO determined by microprobe is higher than in the chemical analyses. However, the similarity of the sum of TiO_2 and Nb_2O_5 for both types of analyses suggests that complete separation of these oxides was not attained by the wet-chemical method. The crystallochemical formulae obtained by grouping elements of similar size and chemistry together in Table 7 confirm that fersmanite is $(Ca,Na)_4(Ti,Nb)_2Si_2O_{11}(F,OH)_2$.

DISCUSSION

In the new formula proposed for fersmanite, the main substitution is of the type $CaTi \rightleftharpoons NaNb$, but the analyses show that this is not the only replacement since Na always exceeds Nb. If a certain amount of sodium which replaces calcium is also balanced by the replacement of some oxygen by hydroxyl, the formula could be be modified to $(Ca,Na)_4(Ti,Nb)_2Si_2(O,OH)_{11}$ (F, OH)$_2$.

Fersmanite has no mineral or synthetic analogues, though some features of its cell and chemistry are found in other phases, both natural and synthetic. Wöhlerite, låvenite, niocalite, götzenite and other titanium, zirconium or niobium silicates have one crystallographic axis about 7Å which agrees with the a and b axes of fersmanite, and some of these minerals have another axis in the region of 10Å or c/2 of fersmanite. The synthetic compound $Na_2TiO(SiO_4)$ (Nikitin et al. 1964) which has recently been discovered as a mineral and named natisite after its composition (Men'shikov et al. 1975) may be remotely related to fersmanite. Natisite is tetragonal, space group P4/nmm with a 6.47 and c 5.08Å, Z=2; its a axis is slightly shorter whereas c is c/4 of fersmanite. If fersmanite is a derivative of natisite its quadrupled c axis could be related to ordering of Ti and Nb atoms along the c-axis or to the inclusion of interstitial

atoms into its structure. In natisite the Ti atoms are surrounded by five oxygens which describe a square pyramid in which the apical Ti-O bond is shorter than the other four. Deriving fersmanite from this structure would necessitate transforming the square pyramids into octahedra by the addition of oxygen atoms at the opposite verticles and moving the (Ti,Nb) atoms to the centre of the octahedron to equalize bond lengths and strengths. Distortion of the tetragonal to a triclinic structure could be the result of stuffing extra oxygens and fluorines (hydroxyls) into the $Na_2TiO(SiO_4)$ model as well as coordination changes around the calcium and sodium atoms. Dividing our new formula of fersmanite by two we get $(Ca,Na)_2(Ti,Nb)O$ $(SiO_4)O_{0.5}(F,OH)$. In this formula $O_{0.5}$ and (F,OH) would be the interstitial atoms needed to form the triclinic fersmanite structure from the tetragonal one of $Na_2TiO(SiO_4)$. Placing interstitial oxygen atoms into a structure may be questioned, but the coordination changes described above are comparable with the related structural pair melilite–fresnoite (Moore & Louisnathan 1967).

The new formula of fersmanite $(Ca,Na)_4$ $(Ti,Nb)_2Si_2O_{11}$ $(F,OH)_2$ could be also written as: (1) an orthosilicate, $(Ca,Na)_4(Ti,Nb)_2O_3(SiO_4)_2$ $(F,OH)_2$, or as (2) a diorthosilicate of formula $(Ca,Na)_4(Ti,Nb)_2O_4(Si_2O_7)(F,OH)_2$; the final formula must await structural analysis.

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