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THE STRUCTURE OF FEDORITE: A RE-APPRAISAL

ROGER H. MITCHELL[§]

Department of Geology, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada

PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame,
156 Fitzpatrick Hall, Notre Dame, Indiana 46556-0767, U.S.A.

ABSTRACT

The crystal structures of fedorite from the type locality, the Turiy complex (Kola Peninsula, Russia) and the Little Murun complex (Sakha, Russia), have been refined from single crystals by CCD X-ray diffractometry. Both samples are triclinic, space group *P*1; fedorite from Turiy has *a* 9.6300(7), *b* 9.6392(7), *c* 12.6118(9) Å, α 102.422(1), β 96.227(1), γ 119.888(1)° [*R*1 = 4.87%], whereas that from Little Murun has *a* 9.6450(7), *b* 9.6498(7), *c* 12.6165(9) Å, α 102.427(1), β 96.247(1), γ 119.894(1)° [*R*1 = 3.94%]. The structure is described as a modular centrosymmetric structure (stacking sequence OS_2S_2O) consisting of sheets of edge-sharing $M\phi_6$ (M = Ca, Na; ϕ = O, F, Cl) polyhedra (O-sheet) linked to sheets of $(Si,Al)O_4$ tetrahedra (S_2 and S_2 sheets), with Na, K and H_2O groups occurring as interlayer cations in partially occupied sites. Four distinct $M\phi_6$ polyhedra characterized by different Na and Ca occupancies are recognized in the sheet of octahedra. The sheet of tetrahedra consists of two types of six-member rings of corner-sharing $(Si,Al)O_4$ units: a slightly distorted hexagonal ring of six upwardly pointing (relative to the center of symmetry) tetrahedra, and a strongly distorted hexagonal ring consisting of four upwardly and two downwardly pointing tetrahedra. The latter provide the link between the centrosymmetrically related S_2 and S_2 sheets. This study provides significant improvements in the accuracy and precision of cell dimensions, bond lengths and pattern of cation order relative to previous studies. The ideal structural formula of fedorite is $A_{2-3}M_7T_{16}O_{38}X_2 \bullet nH_2O$, where A = Na, K, Ba, Ca; M = Ca, Na, Mn^{2+}, Fe^{2+}; T = Si, Al, Ti; X = F, Cl or OH, and $n \approx 3.5$.

Keywords: fedorite, structure refinement, modular structure, electron-microprobe data.

SOMMAIRE

Nous avons affiné la structure cristalline de la fédorite provenant de la localité-type, le complexe de Turiy, péninsule de Kola, en Russie, et le complexe du Petit Murun, territoire de Sakha, aussi en Russie, à partir de cristaux uniques par diffraction X et prélèvements par détecteur CCD. Les deux cristaux sont tricliniques, groupe spatial *P*1; pour la fédorite de Turiy, les paramètres réticulaires sont *a* 9.6300(7), *b* 9.6392(7), *c* 12.6118(9) Å, α 102.422(1), β 96.227(1), γ 119.888(1)° [*R*1 = 4.87%], tandis que pour celle du Petit Murun, ils sont *a* 9.6450(7), *b* 9.6498(7), *c* 12.6165(9) Å, α 102.427(1), β 96.247(1), γ 119.894(1)° [*R*1 = 3.94%]. Nous décrivons la fédorite en termes de structure centrosymétrique modulaire, avec une séquence d'empilement OS_2S_2O contenant des feuillets O de polyèdres $M\phi_6$ (M = Ca, Na; ϕ = O, F, Cl) à arêtes partagées liés à des feuillets (S_2 et S_2) de tétraèdres $(Si,Al)O_4$, le Na, le K et les groupes H_2O étant logés entre les feuillets dans des sites partiellement occupés. On distingue quatre polyèdres $M\phi_6$ ayant des populations de cations Na et Ca différentes dans les feuillets O. Le feuillet de tétraèdres est fait de deux types d'anneaux à six tétraèdres $(Si,Al)O_4$ à coins partagés: un anneau légèrement difforme de six tétraèdres orientés vers le haut (par rapport au centre de symétrie), et un autre, fortement difforme, contenant quatre tétraèdres orientés vers le haut et deux autres orientés vers le bas. Le second assure la liaison entre les feuillets S_2 et S_2, dont la relation est centrosymétrique. Nos résultats fournissent des améliorations importantes en justesse et en précision des paramètres réticulaires, des longueurs de liaison, et du schéma de mise en ordre des cations par rapport aux résultats antérieurs. La formule structurale idéale de la fédorite est $A_{2-3}M_7T_{16}O_{38}X_2 \bullet nH_2O$, dans laquelle A = Na, K, Ba, Ca; M = Ca, Na, Mn^{2+}, Fe^{2+}; T = Si, Al, Ti; X = F, Cl ou OH, et $n \approx 3.5$.

(Traduit par la Rédaction)

Mots-clés: fédorite, affinement de la structure, structure modulaire, données de microsonde électronique.

[§] *E-mail address*: rmitchel@gale.lakeheadu.ca

INTRODUCTION

Fedorite, a rare complex hydrous K–Na–Ca-silicate, was initially recognized in fenitized rocks adjacent to the Turiy alkaline complex, Kola Peninsula, Russia (Khukarenko *et al.* 1965). A second occurrence was subsequently reported from metasomatic–hydrothermal charoite-carbonatite rocks of the Little Murun potassic complex, Siberia (Konyev *et al.* 1993). Fedorite is considered to have a modular structure (Ferraris 1997) and is a member of a group of silicates that consist of stacked modules of sheets of tetrahedra and octahedra. Other members of this group include reyerite (Merlino 1988*a*), gyrolite, truscottite, and synthetic K and Z-hydrated calcium silicates (Merlino 1988*b*), and tungusite (Ferraris *et al.* 1995). Fedorite is the only fluorine-bearing member of this group.

The structure of fedorite was determined by Sokolova *et al.* (1983) and refined by Joswig *et al.* (1988). However, there remain uncertainties in the positions of the interlayer atoms and in the pattern of order of the cations occupying the octahedral and tetrahedral positions.

The structural formula of fedorite requires revision, as it has been variously given as: $(K_{1.65}Na_{0.83})(Ca_{4.52}Na_{2.48})Si_{16}O_{38}(OH,F){\bullet}H_2O$ (Sokolova *et al.* 1983), $(K_{0.82}Na_{1.95})(Ca_{4.35}Na_{2.34}Al_{0.31})(Si_{15.35}Al_{0.65})O_{38}(OH,F){\bullet}H_2O$ (Joswig *et al.* 1988), $K_2(Ca_5Na_2)Si_{16}O_{38}(OH,F)_2{\bullet}H_2O$ (Merlino 1988*b*), and $KNa_4Ca_4(Si,Al)_{16}O_{36}(OH)_4{\bullet}6H_2O$ (Blackburn & Dennen (1997).

Given the lower precision of previous studies and the uncertainty in the structural formula, coupled with the fact the structure of fedorite from the Little Murun potassic complex has not been determined, we considered that a re-appraisal of the structure of fedorite using modern techniques was desirable.

PREVIOUS WORK

The structure of fedorite from the type locality was initially determined by single-crystal X-ray diffraction by Sokolova *et al.* (1983). Their study established that the framework consists of sheets of $(Na,Ca)O_6$ octahedra attached to double sheets of SiO_4 tetrahedra with H_2O groups or hydroxyl anions (or both) plus potassium and sodium cations occurring in the interlayer regions (see below). Sokolova *et al.* (1983) reported the structure in the unconventional *C* triclinic setting. The high R-value (9.5%) and the imprecision in locating the interlayer atoms prompted a subsequent combined X-ray- and neutron-diffraction study by Joswig *et al.* (1988). That work improved the R-value for the X-ray-structure determination to 4.0% using 3149 unique reflections with $|F_o| \geq 3\sigma_F$, and included anisotropic displacement parameters for all atoms. In that study, the atomic coordinates determined by Sokolova *et al.* (1983) were used as a starting point for the structural model. Joswig *et al.* (1988) did not report any change in these data subsequent to their new refinement, as they considered that the positional differences were negligible. Thus, the coordinates and errors quoted for the atoms comprising the sheets of octahedra and tetrahedra remain the same in both studies (see ICSD Collection Codes 20853 and 65342). The neutron-diffraction study gave an R-value of 6.9% for a model including isotropic displacements of the atoms and was used primarily to locate interlayer atoms. Significant differences in cell dimensions, interaxial angles, and positions of the interlayer atoms were reported by Joswig *et al.* (1988).

Sokolova *et al.* (1983) and Joswig *et al.* (1988) refined the positions of atoms in the sheet of octahedra with a statistically uniform distribution of Na, Ca and Al in the polyhedron as $(Ca_{0.62}Na_{0.33}Al_{0.04})$. We consider that this site occupancy, and especially the assignment of Al to the octahedra, is improbable. Positions of atoms in the silicon–oxygen tetrahedra were also refined assuming an occupancy of $(Si_{0.96}Al_{0.04})O_4$.

EXPERIMENTAL

Crystals investigated

The compositions of fedorite, determined by standard methods of wavelength-dispersion electron-microprobe analysis (Cameca SX–50; University of Manitoba) on material from the type locality at Turiy (Smithsonian Institution catalog # NMHM 169443) and the Little Murun complex (this work) are given in Table 1. These differ with respect to their Al, Ca, K, Cl and F contents. In particular, it should be noted that the Murun material is essentially devoid of Al. The crystals

TABLE 1. THE COMPOSITION OF FEDORITE

	Turiy	Murun		Turiy	Murun
SiO_2 wt.%	67.02(0.63)	66.60(0.28)	Si *apfu*	16.011	15.956
TiO_2	0.02(0.04)	0.01(0.02)	Al	0.090	0.028
Al_2O_3	0.32(0.06)	0.10(0.02)			
FeO^*	0.11(0.04)	0.02(0.02)	Layer of octahedra (7 cations)		
MnO	0.32(0.03)	0.19(0.02)			
MgO	0.01(0.01)	n.d.	Ti	0.004	0.002
CaO	15.85(0.21)	17.19(0.07)	Fe	0.022	0.004
Na_2O	8.91(0.22)	9.08(0.17)	Mn	0.065	0.039
K_2O	3.01(0.05)	1.58(0.08)	Mg	0.004	-
BaO	0.27(0.09)	n.d	^{VI}Ca	4.057	4.413
F	2.69(0.15)	3.19(0.16)	^{VI}Na	2.848	2.542
Cl	0.61(0.01)	0.14(0.01)			
			Interlayer		
total	99.28	98.10			
			Na	1.271	1.676
-F≡O	1.13	1.34	K	0.917	0.483
-Cl≡O	0.13	0.03	Ba	0.025	-
Total	98.02	96.73			

The structural formulae, expressed in atoms per formula unit, *apfu*, are based on 40 (O,F,Cl). * Total Fe expressed as FeO; n.d. = not detected. Errors are 1σ standard deviation of the compositions of 10 different grains.

selected for single-crystal X-ray diffractometry measured approximately 0.2 × 0.2 × 0.2 mm.

X-ray diffraction

Crystals were fixed with epoxy on thin glass rods and mounted on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. Burns (1998) has discussed the application of CCD detectors to the analysis of crystal structures.

The diffraction data were collected using monochromatic Mo*K*α radiation and frame widths of 0.3° in ω, with 30 seconds used to acquire each frame. A sphere of three-dimensional data was collected, and these data were analyzed to locate peaks for the determination of unit-cell dimensions (Table 2). Data were collected over the interval $3° \leq 2\theta \leq 56.6°$. The three-dimensional data were reduced and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. Empirical absorption corrections were applied to all data on the basis of the intensities of equivalent reflections, with the crystal shapes modeled as ellipsoids. The total number of observations and unique reflections used in the crystal-structure determinations is listed in Table 2.

STRUCTURE SOLUTION AND REFINEMENT

Scattering factors for neutral atoms together with anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structures.

The structures of the fedorite crystals were refined by direct methods in the triclinic space-group *P*1. The initial refinement, including isotropic displacement of the cations, was used to establish the positions of the atoms comprising the sheets of octahedra and tetrahedra. Subsequently, displacement parameters were converted to an anisotropic form. The positions of fluorine and the interlayer atoms (designated *A*1, *A*2 and *W*; see below) were initially refined isotropically and subsequently anisotropically for those sites for which displacement parameters remained acceptable.

TABLE 2. CELL DIMENSIONS AND OTHER DATA FOR THE FEDORITE CRYSTALS STUDIED BY CCD DIFFRACTOMETRY

Sample	Turiy	Murun		Turiy	Murun
a(Å)	9.6300(7)	9.6450(7)	Count time/frame	30 s	30 s
b(Å)	9.6392(7)	9.6498(7)	Collection time	18 hr	18 hr
c(Å)	12.6118(9)	12.6165(9)	Total reflections	11652	10262
α	102.422(1)	102.427(1)	Unique reflections	4575	4535
β	96.227(1)	96.247(1)	$F_o > 4\sigma_F$	2584	2883
γ	119.888(1)	119.894(1)	Final *R*1(%) obs. rfl.	4.87	3.94
V(Å^3)	958.54	961.24	Final *R*1(%) all data	10.76	7.80
Space Group	*P*1	*P*1	GooF = S	0.927	1.035
D_{calc}(g/cm^3)	4.22	4.21			

The octahedral sites were constrained to be fully occupied by Na and Ca, although their proportions were refined. In the case of the interlayer cations, sites were generally refined as partially occupied, that is, the occupancies of these sites were not constrained.

We investigated split-site models involving the interlayer sites owing to the presence of strong anisotropy of the *A*1 and *A*2 sites. In the case of the crystal from Murun, *R*1 prior to introducing split sites was 4.30%. The electron density of the *A*1 site was significantly elongate approximately in the [001] direction, and was replaced by sites designated *A*1 and *A*1*a*. The separation of these sites refined to 0.72(2) Å, with the coordination polyhedron about *A*1 involving considerably shorter bonds than that about *A*1*a*. We therefore assumed that *A*1 and *A*1*a* are occupied mainly by Na and K, respectively, and refined their occupancies with the appropriate scattering-factors, resulting in occupancies of 0.64(3) and 0.16(2) for *A*1 and *A*1*a*, respectively. The incorporation of the split-site model for the *A*1 site lowered *R*1 to 4.03%. The *A*2 site showed elongation in the [100] direction, and was replaced by sites designated *A*2 and *A*2*a*, which subsequently refined to a separation of 1.32(2) Å. The polyhedron geometries about each of these sites are consistent with occupancy mainly by K; the refined occupancies using the scattering factor for K are 0.047(3) and 0.183(5) for *A*2 and *A*2*a*, respectively. Introduction of the split-site model for *A*2 further lowered *R*1 to 3.94%.

The *R*1 for the crystal from Turiy was 5.21% prior to the introduction of split sites. The *A*1 site showed significant elongation along [001], and was replaced by sites designated *A*1 and *A*1*a*. The sites refined to a separation of 0.92(2) Å, and as was the case for the crystal from Murun, the polyhedron geometries about *A*1 and *A*1*a* suggested they are mainly occupied by Na and K, respectively. Refinement with the appropriate scattering-factors gave occupancies of 0.77(1) and 0.149(8) for *A*1 and *A*1*a*, respectively. Incorporation of the split-site model for the *A*1 site lowered *R*1 to 4.87%. We also attempted to refine a split-site model for the *A*2 site, but the refinement did not converge.

The structure models were refined on the basis of F^2 for all unique reflections. In the final cycles of refinement, the mean parameter shift/esd was 0.000. The final *R*1 values are given in Table 2. The maximum and minimum peaks in the final difference-Fourier maps for the Turiy and Murun samples were –0.83 to 0.84 and –0.78 to 1.08 e/Å^3. The final atomic positional parameters are given in Tables 3 and 4, with occupancies in the sheet of octahedra and of the interlayer sites as shown in in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

RESULTS OF THE STRUCTURE REFINEMENT

Cell dimensions

Transformation of the unit-cell data given by Joswig *et al.* (1988) from $C1$ to $P1$ gives a 9.646(2), b 9.646(3), c 12.616(2)Å, α 102.52(1), β 96.26(1), γ 119.98(1)°. Table 1 shows that fedorite from Turiy and that from Murun differ slightly in their cell dimensions as a consequence of their differences in composition.

Crystal structure

The crystal structure of fedorite consists of a sheet of octahedrally coordinated cations bonded to a double sheet of Si–O tetrahedra (Fig. 1). Interlayer species include H_2O molecules, K, and Na. The structure is described below using the modular concepts advocated by Merlino (1988a, b) and Ferraris (1997). In this model, the frameworks of hydrous Na–Ca-silicates are constructed by stacking sheets of octahedra (O,O) and tetrahedra (S_1, S_2, S_2) in various combinations. In this

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR FEDORITE FROM TURIY

	x	y	z	U_{eq}
M1	0.0	0.0	-0.5	0.0151(11)
M2	0.4219(2)	0.2842(2)	-0.4907(1)	0.0145(5)
M3	0.7114(1)	0.1477(1)	-0.4993(1)	0.0125(4)
M4	0.1489(1)	-0.5667(2)	-0.4845(1)	0.0131(5)
Si1	0.2840(2)	-0.3975(2)	-0.1307(1)	0.0114(3)
Si2	0.1393(2)	-0.2573(2)	-0.2708(1)	0.0116(3)
Si3	0.7679(2)	0.4967(2)	-0.2736(1)	0.0117(3)
Si4	0.2640(2)	0.1092(2)	-0.2718(1)	0.0126(3)
Si5	1.0205(2)	0.2422(2)	-0.2685(1)	0.0118(3)
Si6	0.3902(2)	-0.2634(2)	-0.8626(1)	0.0112(3)
Si7	0.6519(2)	-0.0040(2)	-0.2710(1)	0.0117(3)
Si8	0.5278(2)	-0.3731(2)	-0.2681(1)	0.0123(3)
O1	0.7043(4)	0.3862(4)	-0.4010(3)	0.0204(9)
O2	0.1323(4)	-0.3290(4)	-0.3972(3)	0.0197(9)
O3	0.2794(4)	0.0832(5)	-0.3966(3)	0.0227(9)
O4	0.4207(5)	-0.4726(5)	-0.3931(3)	0.0301(10)
O5	-0.0149(4)	-0.7512(5)	-0.3918(3)	0.0253(9)
O6	0.5713(4)	-0.0427(5)	-0.3976(3)	0.0220(9)
O7	0.8524(4)	0.1211(4)	-0.2342(3)	0.0183(9)
O8	0.6759(4)	0.5950(4)	-0.2380(3)	0.0178(9)
O9	0.1939(4)	-0.0614(4)	-0.2350(3)	0.0167(8)
O10	0.6242(4)	-0.1704(4)	-0.2416(3)	0.0203(9)
O11	0.4381(4)	0.2504(4)	-0.1784(3)	0.0154(8)
O12	0.5843(4)	0.0800(4)	-0.1827(3)	0.0169(8)
O13	0.4262(4)	-0.4182(5)	-0.1735(3)	0.0217(9)
O14	0.2651(4)	-0.2655(4)	-0.1811(3)	0.0192(9)
O15	-0.0388(4)	-0.3513(4)	-0.2412(3)	0.0191(9)
O16	1.1114(4)	0.4226(4)	-0.1718(3)	0.0197(9)
O17	0.1324(4)	0.1633(4)	-0.2500(3)	0.0214(9)
O18	0.7525(4)	0.3924(4)	-0.1854(3)	0.0191(9)
O19	0.3339(5)	-0.3276(5)	0.0035(3)	0.0264(10)
F1	-0.1592(4)	-0.2046(4)	-0.4171(3)	0.0281(8)
A1	-0.0820(4)	-0.1033(4)	-0.2128(5)	0.0302(17)
A1A	-0.0555(21)	-0.0718(22)	-0.1359(23)	0.0853(72)
A2	0.6705(11)	-0.0182(9)	0.0002(6)	0.0727(35)
W1	0.9826(7)	0.3181(9)	0.0038(5)	0.0485(28)
W2	0.7009(11)	-0.3274(11)	0.0015(6)	0.0736(40)
W3	0	0	0	0.1317(45)

M1-M4 sites are occupied by Ca and Na; interlayer A-sites by Na and K; interlayer W1,W2 and W3 sites are occupied by H_2O.

TABLE 4. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR FEDORITE FROM MURUN

	x	y	z	U_{eq}
M1	0.0	0.0	-0.5	0.0150(7)
M2	0.4220(1)	0.2843(1)	-0.4904(1)	0.0130(4)
M3	0.7114(1)	0.1478(1)	-0.4996(1)	0.0117(3)
M4	0.1490(1)	-0.5665(1)	-0.4841(1)	0.0126(4)
Si1	0.2847(1)	-0.3971(1)	-0.1305(1)	0.0102(3)
Si2	0.1390(1)	-0.2573(1)	-0.2704(1)	0.0101(3)
Si3	0.7681(1)	0.4969(1)	-0.2733(1)	0.0107(3)
Si4	0.2633(1)	0.1090(1)	-0.2711(1)	0.0114(3)
Si5	1.0202(1)	0.2418(1)	-0.2678(1)	0.0106(3)
Si6	0.3907(1)	-0.2629(1)	-0.8628(1)	0.0097(3)
Si7	0.6520(1)	-0.0040(1)	-0.2710(1)	0.0104(3)
Si8	0.5285(1)	-0.3724(1)	-0.2677(1)	0.0109(3)
O1	0.7026(4)	0.3856(4)	-0.4011(2)	0.0193(7)
O2	0.1310(4)	-0.3295(4)	-0.3984(2)	0.0182(7)
O3	0.2788(4)	0.0829(4)	-0.3961(2)	0.0219(7)
O4	0.4209(4)	-0.4724(4)	-0.3924(3)	0.0287(8)
O5	-0.0149(4)	-0.7527(4)	-0.3917(3)	0.0252(8)
O6	0.5712(4)	-0.0434(4)	-0.3986(2)	0.0191(7)
O7	0.8523(3)	0.1215(3)	-0.2337(2)	0.0156(7)
O8	0.6763(3)	0.5957(4)	-0.2379(3)	0.0179(7)
O9	0.1932(3)	-0.0620(3)	-0.2349(2)	0.0149(7)
O10	0.6240(4)	-0.1704(4)	-0.2418(3)	0.0186(7)
O11	0.4374(3)	0.2503(3)	-0.1779(2)	0.0153(7)
O12	0.5825(3)	0.0796(3)	-0.1832(2)	0.0146(7)
O13	0.4269(4)	-0.4176(4)	-0.1729(3)	0.0202(7)
O14	0.2662(3)	-0.2666(3)	-0.1817(2)	0.0156(7)
O15	-0.0392(3)	-0.3527(4)	-0.2414(2)	0.0159(7)
O16	1.1120(3)	0.4240(3)	-0.1713(3)	0.0166(7)
O17	0.1318(3)	0.1629(4)	-0.2490(3)	0.0210(8)
O18	0.7510(3)	0.3919(4)	-0.1851(2)	0.0162(7)
O19	0.3340(4)	-0.3269(4)	0.0029(3)	0.0260(8)
F1	-0.1599(3)	-0.2060(3)	-0.4190(2)	0.0263(7)
A1	-0.0814(8)	-0.1022(10)	-0.2083(16)	0.0291(31)
A1A	-0.0576(19)	-0.0745(17)	-0.1481(32)	0.0340(39)
A2	0.8243(32)	0.0324(30)	-0.0017(20)	0.0300(0)
A2A	0.6701(15)	-0.0179(11)	-0.0061(7)	0.0863(52)
W1	0.9845(6)	0.3304(10)	0.0037(4)	0.0689(33)
W2	0.7124(12)	-0.3203(12)	0.0015(8)	0.1138(50)
W3	0	0	0	0.3321(96)

M1-M4 sites are occupied by Ca and Na; interlayer A-sites by Na and K; interlayer W1,W2 and W3 sites are occupied by H_2O.

scheme, identical sheets related by a center of symmetry are given a "bar" symbol. For example, neglecting interlayer atoms, the structure of reyerite may considered as repetitions of the module $S_1OS_2S_2OS_1$ (Merlino 1988a). Fedorite is one of simplest of these modular structures, as it consists only of O and S_2 structural units (Fig. 1) in the stacking sequence OS_2S_2O (Merlino 1988b).

Sheets of octahedra (*O*)

Figure 2 illustrates the structure of the sheet of octahedra and shows that it consists of edge-sharing $(M)\phi_6$ polyhedra, where *M* stands for Na and Ca, and ϕ represents O or F. The structural refinements demonstrate the existence of four crystallographically distinct polyhedra, denoted *M*1 to *M*4 in Tables 3 and 4. Bond lengths and polyhedron-distortion parameters (Δ), calculated by the method of Shannon (1976), are given in Table 5, which shows that polyhedra cross-linked by F atoms exhibit the highest degrees of distortion from a perfect octahedron. The *M*1 polyhedron containing two atoms of fluorine exhibits the greatest distortion, whereas the *M*3 polyhedron, which does not contain F atoms, is only slightly distorted. Occupancy refinement (Table 6) shows that the *M*1 polyhedron is occupied predominantly by Na, the *M*2 polyhedron has near-equal Na and Ca occupancy, and the *M*3 and *M*4 polyhedra are dominated by Ca. The dominance of Na in the *M*1 site reflects the presence of F atoms in a *trans* position such that *M*1 polyhedron has the composition $(Na,Ca)(O_4F_2)$. Our occupancy scheme is considered an improvement over the random model proposed by Joswig *et al.* (1988). In addition, Joswig *et al.* (1988) located F and OH (designated as O21 in their work) as occupying the same sites in the *M*1 polyhedra. Our occupancy refinement does not permit the recognition of OH in the same site as F.

Sheets of tetrahedra (S_2 *and* $\overline{S}_2$)

Our data and those of Joswig *et al.* (1988) show that the tetrahedral-sheet module is of the S_2 type of Merlino (1988a, b). Figure 3 shows a plan view of the S_2 layer, which consists of two types of six-member rings. One distortion-free hexagonal ring consists of six upward-pointing tetrahedra (Si2, Si3, Si4, Si5, Si7, Si8). The apices of these are joined to atoms of oxygen at the corners of the O-sheet polyhedra (Fig. 1). The other ring is a distorted hexagonal ring consisting of four upward-pointing tetrahedra (Si2, Si3, Si5, Si7) and two downward-pointing tetrahedra (Si1, Si6). The latter link the regular hexagonal rings in the *a*–*b* plane (Fig. 1). The S_2 layer is related to the S_2 layer by the center of symmetry *via* the bridging oxygen O19, linking Si1 and Si6 tetrahedra (Fig. 1).

Table 7 lists Si–O bond lengths and polyhedron-distortion parameters for the tetrahedra of the S_2 sheet. The bond lengths of the Turiy sample are significantly smaller those of the Murun material. In addition, maximum and minimum bond-lengths of the basal oxygen atoms differ in the two samples. Bond lengths between Si and apical shared oxygen atoms in the regular hexagonal rings linked to the O-sheets are reduced relative to those in $S_2 - S_2$ bridging tetrahedra (Si1, Si6). This greater distortion results from the geometrical requirements of the O–S_2 sheet linkage and results in the regular hexagonal ring being distorted so that it is arched in a convex manner toward the O-layer (Fig. 1). Note that the F atom in the O-sheet polyhedra is located directly over the center of this ring.

Our data for the sheet of tetrahedra are in general agreement with those given by Joswig *et al.* (1988), although our precision is better, and we did not find (Si,Al)–O bonds as short as 1.547Å. Because of the low Al contents of fedorite, and in common with Joswig *et al.* (1988), we find no evidence for ordering of Si and Al.

TABLE 5. OCTAHEDRON BOND-LENGTHS (Å) AND POLYHEDRON DISTORTION-PARAMETERS (Δ) IN FEDORITE

	Turiy	Murun		Turiy	Murun
M1-F1	2.357(3) × 2	2.353(3) × 2	M3-O3	2.378(4)	2.382(3)
-O3	2.494(4) × 2	2.496(3) × 2	-O6	2.399(4)	2.399(3)
-O5	2.571(4) × 2	2.563(3) × 2	-O1	2.403(4)	2.409(3)
Δ	1.280	1.257	-O2	2.411(4)	2.406(3)
			-O5	2.415(4)	2.423(3)
M2-F1	2.320(3)	2.316(3)	-O6	2.459(4)	2.457(3)
-O3	2.396(4)	2.404(3)	Δ	0.104	0.093
-O4	2.408(4)	2.412(4)			
-O1	2.415(4)	2.403(3)	M4-F1	2.341(3)	2.329(3)
-O6	2.484(4)	2.478(3)	-O5	2.348(4)	2.358(3)
-O4	2.574(5)	2.584(4)	-O4	2.352(4)	2.357(3)
Δ	1.058	1.169	-O2	2.410(4)	2.409(3)
			-O1	2.488(4)	2.498(3)
			-O2	2.517(4)	2.507(3)
			Δ	0.847	0.839

TABLE 6. SITE OCCUPANCIES (%) OF OCTAHEDRON SHEET AND INTERLAYER POSITION IN FEDORITE

		Turiy	Murun			Turiy	Murun
	Octahedron Sheet				Interlayer cations and anions		
*M*1	Ca	5.0(1.4)	22.6(1.0)	*A*1	Na	77.1(1.3)	64.3(3.5)
	Na	95.0(1.4)	77.3(1.0)	*A*1*a*	K	14.9(0.9)	16.3(2.1)
*M*2	Ca	51.0(1.1)	56.7(0.8)	*A*2	K	25.3(0.6)	4.7(2.7)
	Na	49.0(1.1)	43.3(0.8)	*A*2*a*	K	-	18.3(4.8)
*M*3	Ca	79.2(1.1)	82.1(0.8)	*W*1	(H_2O)	68.6(1.2)	63.1(1.0)
	Na	20.8(1.1)	17.9(0.8)	*W*2	(H_2O)	65.9(1.3)	60.4(1.3)
*M*4	Ca	68.9(1.1)	74.0(0.8)	*W*3	(H_2O)	100	100
	Na	31.1(1.1)	26.0(0.8)				

The *M*1 and *W*3 sites are located on centers of symmetry. The occupancy of *W*3 was fixed at 100%.

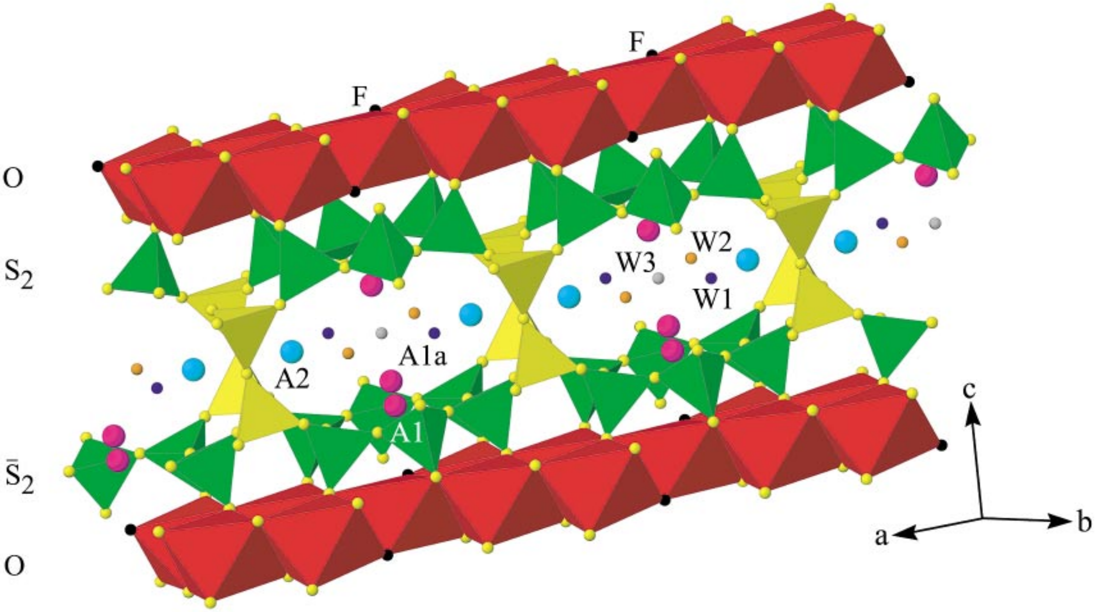

FIG. 1. Polyhedral model of the structure of fedorite illustrating the sheets of octahedra (red) and tetrahedra (green and yellow), together with the locations of the interlayer cations (*A*1 and *A*2) and H_2O groups (*W*1 – *W*3).

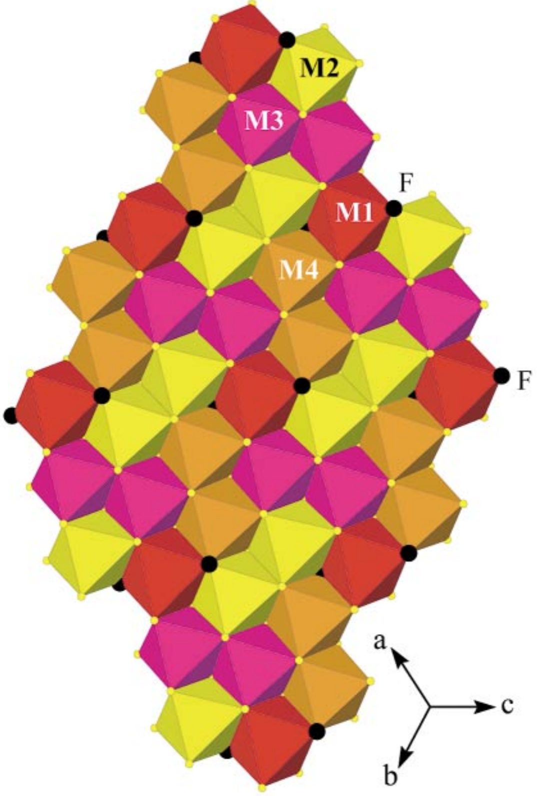

FIG. 2. Plan view of the sheet of $M\phi_6$ octahedra. See Table 6 for individual occupancies of the octahedral sites.

Interlayer atoms

The structure of fedorite contains large cavities between the sheets of tetrahedra that are occupied by large low-valence cations and H_2O molecules. Initially, we identified five sites in the interlayer, two of which have relatively high electron-densities, indicating occupancy by cations, and three of relatively low electron-density, and thus presumably occupied by H_2O molecules. Each of these sites is partially occupied, with large displacement-parameters, indicating that the positions correspond to averages, with local variations in the structure presumably due to cation substitution.

The refinement of split-site models for the interlayer *A* sites is described above. The separations between the *A*1 and *A*1*a* sites are only 0.72(2) and 0.92(2)Å for crystals from Murun and Turiy, respectively, which prohibits occupancy of both sites locally. The sum of the refined site-occupancies for these two sites totals 0.80 and 0.92 for the crystals from Murun and Turiy, respectively, which is consistent with only one of the sites being occupied locally. The coordination polyhedra about the *A*1 sites in the two crystals contain eight ligands (six atoms of oxygen, one H_2O molecule and

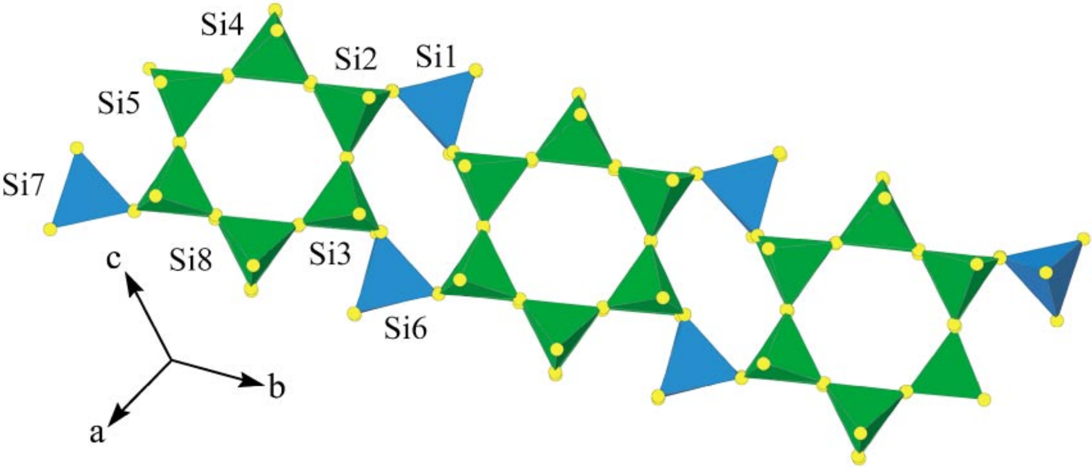

FIG. 3. The structure of the S_2 sheet of $(Si,Al)O_4$ tetrahedra.

one atom fluorine), with mean bond-lengths of 2.55 and 2.54 Å for the crystals from Murun and Turiy, respectively. The *A*1*a* site has a larger coordination polyhedron, with six atoms of oxygen at a mean distance of 2.77 and 2.83 Å for the crystals from Murun and Turiy, respectively, and a fluorine atom at 3.22 and 3.35 Å, respectively. The *A*1*a* site involves a short distance of about 1.6 to 1.7 Å to the H_2O molecule *W*3 in both crystals studied. The isotropic displacement parameters are large for *W*3, which is located on a center of symmetry.

TABLE 7. TETRAHEDAL SHEET BOND LENGTHS (Å) AND POLYHEDRON DISTORTION PARAMETERS (Δ)

	Turiy	Murun		Turiy	Murun
Si1-O19*	1.600#	1.591#	Si5-O5	1.578	1.581
-O13	1.610	1.609	-O16	1.617	1.628
-O16	1.610	1.607	-O17	1.623	1.623
-O14	1.615	1.609	-O7	1.630	1.627
Δ	0.012	0.022		0.156	0.147
Si2-O2	1.575	1.592	Si6-O19*	1.596	1.601
-O14	1.609	1.618	-O11	1.612	1.617
-O15	1.624	1.625	-O18	1.613	1.609
-O9	1.625	1.622	-O12	1.616	1.613
Δ	0.158	0.060		0.023	0.014
Si3-O1	1.579	1.585	Si7-O6	1.573	1.585
-O8	1.621	1.623	-O12	1.617	1.625
-O18	1.623	1.628	-O10	1.622	1.621
-O15	1.625	1.619	-O7	1.625	1.627
Δ	0.141	0.110		0.172	0.113
Si4-O3	1.575	1.578	Si8-O4	1.575	1.574
-O17	1.620	1.622	-O13	1.619	1.624
-O11	1.630	1.631	-O10	1.624	1.621
-O9	1.633	1.634	-O8	1.626	1.624
Δ	0.208	0.194		0.169	0.174

* Bridging oxygen: # standard deviation for all bond lengths is 0.004Å and 0.003Å for Turiy and Murun samples, respectively.

Refinement of the site-occupancy factor for *W*3 is difficult owing to correlation with the displacement factor; thus we fixed it at full occupancy during the refinement. Given the short distance between *W*3 and *A*1*a*, it is likely that the *W*3 site is vacant locally if the *A*1*a* site is occupied.

The *A*2 and *A*2*a* sites (*A*2 only for the crystal from Turiy) occur in large coordination polyhedra that are consistent with occupancy of these sites mainly by K. For the crystal from Murun, the *A*2 and *A*2*a* sites are separated by 1.32(2) Å, indicating that only one of these sites may be locally occupied. The *A*2 site is coordinated by five atoms of oxygen and one H_2O molecule, with a mean bond-length of 3.01 Å, whereas the *A*2*a* site is coordinated by as many as eleven ligands with bond lengths less than 3.4 Å, with a mean polyhedron bond-length of 3.12 Å. Site occupancy refinement showed that the *A*2*a* site contains more K [0.183(5)] than the *A*2 [0.047(3)]. In the case of the crystal from Turiy, the coordination polyhedra about the *A*2 site contains eleven ligands that are less than 3.4 Å from *A*2, with a mean polyhedron bond-distance of 3.11 Å. The refined site-occupancy, obtained using the scattering factor for K, is 0.256(6). The *A*2*a* site in the crystal from Murun is very similar to the *A*2 site in the Turiy crystal, and both contain nine atoms of oxygen and two H_2O molecules.

The distance between the *A*1*a* and the *A*2 sites in the crystal from Murun is 2.56(3) Å, which is inconsistent with both of these sites being occupied locally in the structure. The refined occupancy of the *A*2 site is only 0.047(3), thus it is possible for this site to be vacant locally where the *A*1*a* site is occupied. It is also possible that where occupied locally, the *A*2 site contains H_2O.

In their study of fedorite, Joswig *et al*. (1988) identified two cation sites (designated *D*1 and *D*2) and an

H_2O group in the interlayer. Inspection of their structure demonstrates that their *D*1 and *D*2 sites correspond to our *A*1 and *A*2 sites, respectively. Their structural model did not involve splitting of either of the cation sites, although extreme elongation of the displacement ellipsoid of the *D*1 site was observed. Joswig *et al.* (1988) reported that the *D*1 site is dominated by Na, whereas the *D*2 site contains mainly K, in accord with our findings.

The *A*1 site, dominated by Na, is located at the center of the basal plane of the distortion-free hexagonal ring of silicate tetrahedra. The site is coordinated by six atoms of oxygen located at the bases of the silicate tetrahedra, together with the F atom lying above the center of the hexagonal ring of tetrahedra. The *A*1*a* site has a similar coordination but is displaced 0.72Å towards the center of symmetry (Fig. 1). The *A*2 site, dominated by K, is located in the centers of the octagonal tunnels formed by $S_2 – S_2$ layers when viewed along the *a* axis. Pairs of K atoms in the unsplit *A*2 site in the Turiy material are situated 6.18 Å apart and together with the H_2O molecule *W*3 located at the center of symmetry, form the sequence K–H_2O–K–K–H_2O–K along the tunnel axis. The other H_2O molecules designated *W*1 and *W*2 forms rows alternating with the O19 bridging atoms of oxygen (Fig. 1), in the sequence O19–*W*2–*W*1–O19 (3.54–3.013–3.09 Å).

DISCUSSION

We have refined the crystal structures of two samples of fedorite of differing provenance and shown that they are very similar. Small differences in bond lengths and site occupancies are probably related to small differences in composition. Our data agree in general with those of Joswig *et al.* (1988) with respect to the structure of the O and S_2 layers, but not with respect to the site occupancies of the octahedra or the positions and occupancies of interlayer Na, K and OH. Our data confirm that fedorite may be considered a modular structure containing the stacking sequence $O – S_2 – S_2 – O$. Our study provides improved estimates of cell dimensions and bond lengths.

From our crystal-structure refinements, the structural formulae of fedorite are:

(1) $(Na_{1.54}K_{0.80})_{\Sigma 2.34}(Ca_{4.03}Na_{2.97})_{\Sigma 7.0}(Si,Al)_{16}O_{38}F_2 \bullet 3.69H_2O$ for Turiy, and

(2) $(Na_{1.29}K_{0.79})_{\Sigma 2.08}(Ca_{4.48}Na_{2.52})_{\Sigma 7.0}(Si,Al)_{16}O_{38}F_2 \bullet 3.47H_2O$ for Murun.

These formulae are “similar” to that proposed by Joswig *et al.* (1988), but our site occupancies differ, and we do not find any sites, apart from the F-site, which may be considered as occupied by hydroxyl anions. From Table 1, the structural formulae of fedorite from Turiy (1) and Murun (2), calculated on the basis of 40 atoms of (O,F,Cl), are:

(1) $(Na_{1.27}K_{0.92}Ba_{0.03})_{\Sigma 2.22}(Ca_{4.06}Na_{2.85}Mn_{0.07}Fe_{0.02}Ti_{0.004}Mg_{0.004})_{\Sigma 7.0}(Si_{16.01}Al_{0.09})_{\Sigma 16.10}O_{38}(F,Cl)_{2.27}$

(2) $(Na_{1.68}K_{0.48})_{\Sigma 2.16}(Ca_{4.41}Na_{2.54}Mn_{0.04}Fe_{0.04}Ti_{0.002})_{\Sigma 7.0}(Si_{15.96},Al_{0.03})_{\Sigma 15.98}O_{38}(F,Cl)_{2.47}$

These are in reasonable agreement with the structural formula determined from the X-ray study, except for the halides and interlayer cation occupancies, and justify our site occupancies for the cations of the layer of octahedra. Assuming that both crystals contain approximately 3.5 molecules of interlayer H_2O, compositional totals of 102.46 wt.% and 101.27 wt.% for the Turiy and Murun samples, respectively, are reasonable given the uncertainty in determining the site occupancies of the *W* sites. Our data indicate that fedorite does not contain any structural OH^- groups.

Natural fedorite is not an end-member composition and, ignoring interlayer H_2O, may be considered from a crystallochemical viewpoint as a solid solution involving four principal end-members: $K_2(Ca_5Na_2)_7Si_{16}O_{38}F_2$, $Na_2(Ca_5Na_2)_7Si_{16}O_{38}F_2$, $K_3(Ca_4Na_3)_7Si_{16}O_{38}F_2$, and $Na_3(Ca_4Na_3)_7Si_{16}O_{38}F_2$. None of these end-member compositions has been synthesized, although $Na_2(Ca_5Na_2)Si_{16}O_{38}(OH)_2 \bullet H_2O$ has been prepared by hydrothermal corrosion of silica-rich glass (Clauss *et al.* 1995). From the above formulae, it is evident that as the Ca content of the sheet of octahedra decreases, the charge balance of the structure is maintained by entry of monovalent cations to the interlayer sites. The Turiy fedorite has a composition near $(Na,K)_{2+x}(Ca_4Na_3)_7Si_{16}O_{38}F_2$, and thus contains more interlayer Na, K and Ba than the Murun sample, which contains more Ca in the sheet of octahedra.

On the basis of our structure refinement and compositional data, we consider that the ideal general formula for the fedorite group is $A_{2–3}M_7T_{16}O_{38}X_2 \bullet nH_2O$, where *A* = Na, K, Ba, Ca; *M* = Ca, Na, Mn^{2+}, Fe^{2+}; *T* = Si, Al, Ti; *X* = F, Cl or OH, and $n \approx 3.5$, although we recognize that occupancy of the *A* and H_2O sites may vary considerably.

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