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Synchrotron X-ray diffraction study of the structure of shafranovskite, $K_2Na_3(Mn,Fe,Na)_4[Si_9(O,OH)_{27}](OH)_2 \cdot nH_2O$, a rare manganese phyllosilicate from the Kola peninsula, Russia

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ABSTRACT

The structure of shafranovskite, ideally $K_2Na_3(Mn,Fe,Na)_4[Si_9(O,OH)_{27}](OH)_2 \cdot nH_2O$ (n ~ 2.33), a K-Na-manganese hydrous silicate from Kola peninsula, Russia, was studied using synchrotron X-ray radiation and a MAR345 image-plate detector at the Swiss-Norwegian beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The structure [trigonal, space group *P*31c, a = 14.519(3), c = 21.062(6) Å, V = 3844.9(14) Å^3] was solved by direct methods and partially refined to $R_1 = 0.085$ ($wR_2 = 0.238$) on the basis of 2243 unique observed reflections ($|F_o| \geq 4\sigma_F$). Shafranovskite is a 2:1 hydrous phyllosilicate. Sheets of Mn and Na octahedra (***O*** sheets) are sandwiched between two silicate tetrahedral sheets ($\boldsymbol{T}_1$ and $\boldsymbol{T}_2$). The 2:1 layers are parallel to (001). The upper tetrahedral sheet $\boldsymbol{T}_1$ consists of isolated $[Si_{13}(O,OH)_{37}]$ islands composed of three six-membered rings. The octahedral sheet ***O*** consists of $Mn\varphi_6$, $Na1\varphi_6$, and $Na2\varphi_6$ octahedra (φ = O, OH, H_2O). This unit can be considered as a trioctahedral sheet with each 20th octahedron vacant. The lower tetrahedral sheet $\boldsymbol{T}_2$ consists of $[Si_{13}(O,OH)_{37}]$ islands linked into a sheet through an additional SiO_3OH tetrahedron. The Na3, K1, K2 atoms, and H_2O32 groups are between the 2:1 layers and provide their linkage along **c**.

INTRODUCTION

Hydrous manganese silicates represent an interesting class of phyllosilicate minerals (Liebau 1985; Guggenheim and Eggleton 1987, 1988; Hughes et al. 2003). One of their most distinguishing structural features is the existence of various complex types of silicate anions that result from inversion and tilting of silicate tetrahedra. Very often, hydrous manganese silicates are difficult objects for a single-crystal X-ray diffraction study owing to the absence of crystals sufficiently large for radiation produced by sealed X-ray tubes. Recently introduced third-generation synchrotron X-ray sources make it possible to study much smaller crystals than those accessible for in-house structure determination with sealed X-ray tubes (Pluth et al. 1997; Burns et al. 2000; Cahill et al. 2001; Pluth and Smith 2002). In this paper, we report our determination of the crystal structure of shafranovskite, a rare hydrous manganese silicate from the Kola peninsula, Russia, performed using intensity data collected from a microcrystal at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

PREVIOUS STUDIES

Shafranovskite was first described by Khomyakov et al. (1982a, 1983a) from pegmatites in the Khibiny and Lovozero alkaline complexes, Kola peninsula, Russia. The type specimen comes from a pegmatite vein at Mt. Rasvumchorr (Khibiny). Here shafranovskite was found as a secondary mineral in association with villiaumite, natrophosphate, olympite, sidorenkite, phosinaite, and aegirine. The empirical chemical formula determined by wet chemical analysis and calculated on the basis of O = 24 was given as $(Na_{3.63}K_{1.82}Ca_{0.12}Mn^{2+}_{0.29})_{5.86}(Mn^{2+}_{1.95}Fe^{2+}_{0.93}Mg_{0.09}Ti_{0.02}Fe^{3+}_{0.01})_{3.00}(Si_{8.68}Fe^{3+}_{0.24}Al_{0.01})_{9.00}O_{24} \cdot 5.96H_2O$ (Khomyakov et al. 1982a, 1983a). The simplified formula corresponds to $(Na,K)_6(Mn^{2+},Fe^{2+})_3Si_9O_{24} \cdot 6H_2O$. Shafranovskite was found as fine-grained aggregates of green or yellowish-green crystals with a perfect cleavage on (001). After exposure to air, the crystals become yellow. Owing to the absence of crystals suitable for conventional single-crystal X-ray diffraction study, the unit-cell parameters of shafranovskite were determined by electron diffraction (Khomyakov et al. 1982a). The mineral was described as trigonal, with possible space groups *P*31*m* or *P*3*m*1; a = 14.58, c = 21.01 Å, V = 3867.8 Å^3, Z = 6. As noted by Khomyakov et al. (1982a, 1983a), A. Kato (in 1982, Chairman of Commission on New Minerals and Mineral Names of the International Mineral-

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ogical Association) suggested that the structure of shafranovskite probably contains nine-membered Si_9O_{27} silicate rings similar to those observed in the structure of eudialyte.

EXPERIMENTAL METHODS

Single-crystal X-ray diffraction

The crystals used in this study are from a pegmatite vein at Rasvumchorr Mountain, which is the type locality for this mineral. The sample consists of aggregates of small greenish plates to 0.1 mm in width and to 0.01 mm thick. Several small crystals of shafranovskite obtained after splitting the larger crystals were mounted on glass fibers and placed on a Bruker SMART CCD diffractometer (with a sealed X-ray tube), but none yielded an indexable and tractable diffraction pattern. Subsequently, some of the plates were split into smaller fragments and mounted for synchrotron X-ray diffraction study.

A plate of shafranovskite was mounted on a tapered glass fiber. X-ray diffraction data collection was performed under ambient conditions at the Swiss-Norwegian beamline BM01 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with an imaging plate area detector (MAR345; 2300 × 2300 pixels) and a crystal-to-detector distance of 160 mm. Diffraction data were measured using monochromatized radiation (λ = 0.80000 Å) in an oscillation mode by rotating the crystal in ϕ by 2° for 2 min per frame; 100 frames were measured. The diffraction maxima show essential streaking. Reciprocal space reconstruction performed by means of the CrysAlis RED program (Oxford Diffraction 2002) demonstrated that the reflections are diffuse along the **c*** direction (see reconstructed *hk*0 and *h*0*l* reciprocal lattice layers in Fig. 1). The observed character of diffuse reflections indicates that the structure reveals substantial stacking faults parallel to **c**. The unit-cell parameters (Table 1) were refined using 674 reflections. The intensities were integrated and merged with the CrysAlis program (Oxford Diffraction 2002). Lorentz and polarization corrections were applied and absorption effects were corrected using SADABS (R_{int} = 0.058). The structure was solved and refined using the SHELXS-93 and SHELXL-93 programs. A model for merohedral twinning with the inversion center as the twin law was introduced, which improved the refinement quality. The Si11-OH15 bond length was constrained to be within the usual range of Si-O bond lengths in silicates (1.60–1.67 Å). The H positions were not determined. The agreement factor for the final model is R_1 = 0.085 (wR_2 = 0.238) for 2443 unique observed reflections with $|F_o| \geq 4\sigma_F$. The refinement was not perfect, probably because of the non-perfect quality of the shafranovskite crystal (Fig. 1). Final atomic positional and displacement parameters and selected bond lengths are given in Tables 2 and 3, respectively.

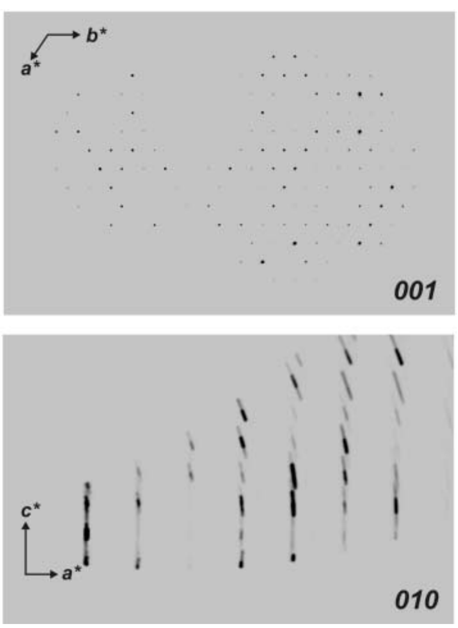

FIGURE 1. The *hk*0 (above) and *h*0*l* (below) layers of reciprocal space of shafranovskite reconstructed from diffraction images of shafranovskite collected using a MAR345 image plate and synchrotron X-ray radiation. Note streaking of reflections along the **c*** axis. The streaks at higher *l*- and *h*-indices are slightly bent, probably due to the slight curvature of flexible shafranovskite plates.

Chemical analysis

The composition of shafranovskite was determined by wavelength-dispersion spectrometry using a Cameca MS-46 electron microprobe operating at 20 kV and 20 nA. The following standards were used: lorenzenite (Na), diopside (Ca, Si), wadeite (K), synthetic $MnCO_3$ (Mn), hematite (Fe), diopside (Mg), and Al_2O_3 (Al). The crystals of shafranovskite were unstable under the electron beam and a precise chemical analysis using the electron microprobe is difficult. The average chemical composition of shafranovskite used for the single-crystal study is (wt%): Na_2O 7.40, SiO_2 51.58, K_2O 7.98, CaO 0.20, MnO 17.06, Fe_2O_3 4.79, MgO 0.15, Al_2O_3 0.08, subtotal 89.24, H_2O_{calc} 10.76 (calculated by difference), total 100.00. The empirical chemical formula calculated on the basis of Si = 9 is $(Na_{2.50}K_{1.78})_{\Sigma=4.28}(Mn_{2.52}Fe_{0.63}Ca_{0.04}Mg_{0.04}Al_{0.02})_{\Sigma=3.25}Si_9O_{23.71}\cdot 6.27H_2O$. This formula is in general agreement with that given by Khomyakov et al. (1982a) on the basis of wet chemical analyses. However, the Na content was determined as 2.50 per formula unit (pfu) instead of the 3.63 given by Khomyakov et al. (1982a). We believe that this difference is caused by loss of Na owing to the electron beam. Results of our structural studies (see below) are more consistent with the higher value than the lower value.

RESULTS

Cation positions and bond-valence analysis

The structure of shafranovskite contains four Mn positions octahedrally coordinated by O atoms and OH groups. The Mn1 and Mn2 sites are fully occupied by Mn (and probably by Fe) and have average <Mn-O> bond lengths of 2.17 and 2.13 Å, respectively. In contrast, refinement of the occupancy of the octahedrally coordinated Mn3 and Mn4 sites results in values of 0.80(2) and 0.82(2), respectively. The <Mn-O> bond lengths for these sites are 2.28 and 2.26 Å, respectively, i.e., ~0.1 Å longer than those for the Mn1 and Mn2 sites. As a possible explanation, we suggest that the Mn3 and Mn4 positions have mixed occupations of Mn and Na; the calculated occupancies are $Mn_{0.64}Na_{0.36}$ and $Mn_{0.61}Na_{0.39}$, respectively.

There are three symmetry independent Na sites; all are in octahedral coordination with individual Na-O bond lengths in the range of 2.31–2.77 Å. Na1 and Na2 are part of the octahedral sheet whereas Na3 represents an interlayer cation site. Two symmetry independent interlayer K positions, K1 and K2, are coordinated by nine and eight anions, respectively. The K2-OH19 bond is rather short (2.48 Å) for a K-O bond and this value suggests partial incorporation of Na at the K2 site. Additional evidence for this interpretation comes from the site-occupancy factor of 0.90 for this position.

There are eleven Si sites in the structure. All are tetrahedrally

TABLE 1. Crystallographic data and refinement parameters for shafranovskite

a (Å)	14.519(3)	Total Ref.	11152
c (Å)	21.062(6)	Unique Ref.	2443
V (Å^3)	3844.9(14)	Unique $\|F_o\| \geq 4\sigma_F$	2243
Space group	*P*31*c*	R_1	0.085
F_{000}	3091	wR_2	0.238
D_{calc} (g/cm^3)	2.83	*S*	1.087
Crystal size (μm)	80 × 80 × 10		

Notes: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$;
$s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters.

coordinated by either O atoms or OH groups. The Si-O bond lengths are within the range of 1.53–1.67 Å.

Bond-valence sums (BVS) for atomic positions calculated using bond-valence parameters for Mn^{2+}-O, Si^{4+}-O, Na^{+}-O, and K^{+}-O taken from Brown and Altermatt (1985) are given in Table 2. The BVSs for the Mn1 and Mn2 sites are 2.19 and 2.45 valence units (v.u.) and this is probably an indication that these sites may accommodate both Mn^{2+} and Mn^{3+} cations. Anion positions with BVS < 0.40 v.u., <1.50 v.u., and >1.70 v.u. were assigned to H_2O molecules, OH groups, and O atoms, respectively. However, note that the contributions of H bonds were not included into the calculation. Thus, the assignment of some anions to OH positions are tentative. In particular, the BVSs for the OH10, OH14, OH19, and OH20 sites are in the range of 1.34–1.49 v.u. To achieve a charge-balanced chemical formula (see below), partial occupation of these sites by OH and O is required. Thus, occupations of the OH10 and OH19 sites (BVS = 1.46 and 1.49 v.u., respectively) were chosen as $(OH)_{0.600}O_{0.400}$, whereas occupations of the OH14 and OH20 sites (BVS = 1.36 and 1.34 v.u., respectively) were chosen to be $(OH)_{0.798}O_{0.202}$.

TABLE 2. Atomic coordinates, isotropic displacement parameters (Å^2), and bond-valence sums* (BVS, valence units) for shafranovskite

Atom	Occupancy	*x*	*y*	*z*	U_{eq}	BVS
Na1	1	0.0681(6)	0.5602(5)	0.7052(4)	0.043(4)	1.06
Na2	1	0.2252(5)	0.8230(5)	0.7248(3)	0.043(4)	1.16
Na3	1	0.9206(9)	0.4395(9)	0.4498(5)	0.096(7)	0.93
K1	1	0.1909(5)	0.7494(4)	0.4561(3)	0.081(4)	0.82
K2	0.90	0.1464(5)	0.9166(5)	0.9865(2)	0.068(3)	1.32
Mn1	1	0.9629(2)	0.7169(2)	0.71758(11)	0.033(2)	2.19
Mn2	1	0.9150(2)	0.2978(2)	0.71055(11)	0.030(2)	2.45
Mn3	0.82(2)	0.8563(3)	0.8767(3)	0.7376(2)	0.041(2)	1.59
Mn4	0.80(2)	0.8092(2)	0.4569(2)	0.69027(13)	0.028(2)	1.72
Si1	1	0.9527(4)	0.6271(4)	0.5734(2)	0.0353(14)	4.17
Si2	1	0	0	0.6080(4)	0.033(2)	4.11
Si3	1	0.9511(5)	0.8083(5)	0.8625(3)	0.051(2)	4.10
Si4	1	0.0546(4)	0.6703(4)	0.8464(2)	0.0411(15)	4.33
Si5	1	0.0996(4)	0.8621(4)	0.5978(2)	0.0353(14)	3.89
Si6	1	0.7082(4)	0.5229(4)	0.5676(2)	0.0353(13)	4.33
Si7	1	0.9916(4)	0.2923(4)	0.8547(2)	0.043(2)	4.08
Si8	1	0.8978(4)	0.4320(4)	0.8288(2)	0.0393(15)	4.15
Si9	1	0.0563(4)	0.3964(4)	0.5849(2)	0.0343(13)	4.09
Si10	1	2/3	1/3	0.8197(4)	0.038(2)	4.18
Si11	0.72(5)	2/3	1/3	0.4923(6)	0.035(6)	4.45
O1	1	0.0964(10)	0.8446(9)	0.6737(6)	0.041(3)	1.97
O2	1	0.9496(10)	0.6004(10)	0.6452(6)	0.043(3)	1.96
O3	1	0.0464(10)	0.3989(10)	0.6572(6)	0.044(3)	2.13
OH4	1	0.8408(11)	0.7411(11)	0.6739(6)	0.051(3)	1.08
O5	1	0.8824(10)	0.9240(9)	0.5775(5)	0.033(3)	2.07
O6	1	0.6627(11)	0.6002(10)	0.5506(6)	0.050(3)	2.19
OH7	1	0.8156(10)	0.5869(10)	0.7518(6)	0.043(3)	1.11
OH8	1	0.1314(12)	0.5110(13)	0.5521(6)	0.060(4)	1.08
O9	1	0.2125(9)	0.8924(9)	0.5651(5)	0.037(3)	2.05
OH10	1	0.0893(14)	0.3668(13)	0.8974(8)	0.075(4)	1.46
O11	1	0.0655(10)	0.6929(10)	0.7722(5)	0.039(3)	2.02
O12	1	0.7980(13)	0.3095(12)	0.6395(8)	0.067(4)	1.91
O13	1	0.8262(13)	0.7504(12)	0.8825(6)	0.060(4)	2.20
OH14	1	0.1570(12)	0.7087(12)	0.8844(7)	0.065(4)	1.36
OH15	0.72(5)	2/3	1/3	0.4164(9)	0.055(11)	1.07
O16	1	0.9745(14)	0.8456(14)	0.7891(8)	0.068(4)	1.75
O17	1	0.7149(9)	0.7277(11)	0.7802(5)	0.044(3)	1.92
O18	1	0	0	0.6826(9)	0.041(5)	1.97
OH19	1	0.0100(13)	0.9045(14)	0.9110(7)	0.069(4)	1.49
OH20	1	0.0076(10)	0.5850(11)	0.5232(5)	0.045(3)	1.34
O21	1	0.0892(11)	0.4307(11)	0.3646(6)	0.046(3)	2.05
O22	1	0.6471(10)	0.4233(12)	0.5196(6)	0.048(3)	2.37
O23	1	0.9856(11)	0.7203(11)	0.8785(7)	0.059(4)	2.05
O24	1	0.7546(11)	0.1695(11)	0.5481(6)	0.046(3)	2.17
H_2O25	1	0.4569(15)	0.7811(14)	0.6385(9)	0.086(5)	0.25
O26	1	0.0096(10)	0.7536(10)	0.5616(5)	0.040(3)	2.11
O27	1	2/3	1/3	0.7425(9)	0.044(6)	1.88
O28	1	0.9087(10)	0.4267(9)	0.7557(6)	0.040(3)	2.15
O29	1	0.9853(10)	0.5450(11)	0.8638(5)	0.045(3)	2.15
H_2O30	1	0.3500(15)	0.7967(14)	0.7853(9)	0.080(5)	0.31
O31	1	0.7811(11)	0.4129(12)	0.8491(6)	0.049(3)	2.15
H_2O32	1	1/3	2/3	0.4932(30)	0.174(51)	0.10

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
* Calculated using bond-valence parameters for the Mn^{2+}-O, Si^{4+}-O, Na^{+}-O, and K^{+}-O bonds from Brown and Altermatt (1985).

Structure description

The structure of shafranovskite is shown in Figure 2. The structure is based upon sheets of Mn and Na octahedra sandwiched between two silicate sheets. Thus, shafranovskite is a 2:1 hydrous phyllosilicate. The 2:1 octahedral-tetrahedral layers are parallel to the (001) plane. Projections of the tetrahedral and octahedral sheets along **c** are shown in Figure 3.

The upper tetrahedral sheet $\boldsymbol{T}_1$ (Fig. 3a) consists of isolated $[Si_{13}O_{28}(OH)_9]^{13-}$ groups (Fig. 4a). The $[Si_{13}O_{28}(OH)_9]^{13-}$ group consists of three six-membered rings with point symmetry 3. The $Si10O_4$ tetrahedron is at the center of the group, the $Si8O_4$ tetrahedra are shared between two adjacent rings, and the $Si3O_3OH$, $Si4O_3OH$, and $Si7O_3OH$ tetrahedra are on the periphery of the rings. The $[Si_{13}O_{28}(OH)_9]^{13-}$ groups are islands of the ideal Si_2O_5 tetrahedral sheets as observed in micas. The octahedral sheet $\boldsymbol{O}$ (Fig. 3b) consists of $Mn\varphi_6$, $Na1\varphi_6$, and $Na2\varphi_6$ octahedra (φ = O, OH, H_2O). This sheet is a trioctahedral sheet with each 20th octahedron vacant. The ratio of Mn- to Na-centered octahedra is 13:6. The lower tetrahedral sheet $\boldsymbol{T}_2$ (Fig. 3c) consists of $[Si_{13}O_{31}(OH)_6]^{16-}$ islands similar to those observed in the $\boldsymbol{T}_1$ sheet (Fig. 4b). The central $Si2O_4$ and $Si5O_4$ tetrahedra are shared between two adjacent rings, whereas $Si9O_3OH$, $Si6O_4$, and $Si1O_3OH$ are peripheral. In contrast to the $\boldsymbol{T}_1$ sheet, the tetrahedral islands are not completely isolated but are linked into the sheet through the additional $Si11O_3OH$ tetrahedron (Fig. 3c). The Si11 atom in this tetrahedron and its non-shared OH15 corner have a site-occupancy factor of 0.72(5). Existence of the $Si11O_3OH$ tetrahedron accounts for the non-centrosymmetricity of the structure of shafranovskite (space group *P*31*c*).

The 2:1 layers in shafranovskite are undulating (Fig. 2). The Na3, K1, K2, and H_2O32 groups are between the 2:1 layers and provide their linkage along **c**.

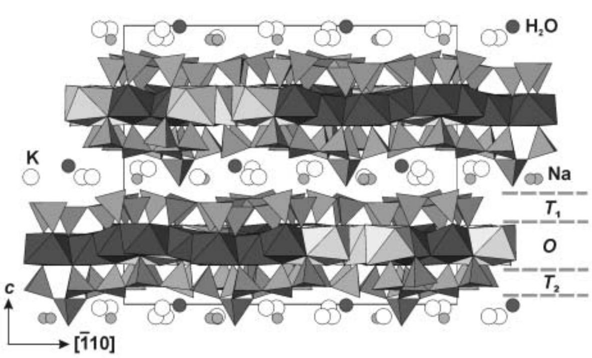

FIGURE 2. The structure of shafranovskite projected along [110]. The structure consists of 2:1 tetrahedral-octahedral layers composed of two tetrahedral ($\boldsymbol{T}_1$ and $\boldsymbol{T}_2$) and one octahedral ($\boldsymbol{O}$) sheets.

Interrelations of silicate anions

Kato (1980) described the structure of ganophyllite, $(K,Na,Ca)_6(Mg,Fe,Mn)_{24}(Si,Al)_{40}(O,OH)_{120}$, as being based upon layers consisting of a continuous octahedral sheet and opposing triple-wide silicate tetrahedral chains. However, Eggleton and Guggenheim (1986) demonstrated that the opposing chains are linked by additional disordered tetrahedra that were "missed" in the original study. Thus, we took special care to check for the possible presence of "missing" silicate tetrahedra that may provide linkage of opposing silicate anions. We are confident that, in our crystal, no additional tetrahedral sites are present for the following reasons: (1) no such sites were found during inspection of the first hundred strongest peaks in the Fourier difference electron density map; the largest peak in the Fourier map was 0.83 e/Å^3 located 1.27 Å from the Mn3 position; (2) the distance between opposing silicate anions in shafranovskite (measured as a distance between planes of bridging O atoms) is about 4 Å, whereas the corresponding distances in ganophyllite (Eggleton and Guggenheim 1986; Noe and Veblen 1999) are in the range of 5 to 6 Å (Figs. 5a and 5b); (3) the $Si11(O,OH)_4$ tetrahedron of the $\boldsymbol{T}_2$ sheet points into free space in the $\boldsymbol{T}_1$ sheet (Fig. 5c). Thus, the structure of shafranovskite simply possesses no space for additional silicate tetrahedra.

Crystal chemical formula and charge-balance mechanism

Taking all anion positions as they are assigned from the bond-valence analysis, the crystal chemical formula of shafranovskite is written as $K_{5.70}Na_9(Mn_{3.25}Na_{0.75})_3$ $[Si_{13}O_{31.006}(OH)_{5.994}][Si_{13.72}O_{31.604}(OH)_{6.116}](OH)_6{\cdot}7H_2O$. This formula gives 3.75 Na per 9 Si in shafranovskite and is in agreement with the results obtained by wet chemical analysis (Khomyakov et al. 1982a). The formula supports our conclusion that Na loss occurred during electron-microprobe analysis.

Taking into account all structural information, the simplified formula of shafranovskite is $K_2Na_3(Mn,Fe,Na)_4[Si_9(O,OH)_{27}](OH)_2{\cdot}nH_2O$ ($n \sim 2.33$).

Discussion

Khomyakov et al. (1982a, 1983a) and Korovushkin et al. (1987) described an Fe-dominant analogue of shafranovskite which has not been approved as an independent mineral species. Khomyakov et al. (1982a) demonstrated that K^+ and Na^+ cations are easily exchanged in aqueous solutions with the formation of a decationated hydrated and oxidized variety of shafranovskite, with hypothetical formula of $H_6(Na,K)_3(Mn^{2+},Mn^{4+},Fe^{3+})_3Si_9O_{27}{\cdot}nH_2O$. On the basis of these experiments, Khomyakov et al. (1982a) suggested the possible existence of decationated

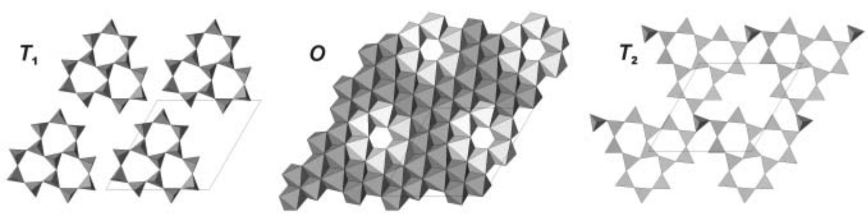

Figure 3. View of the tetrahedral and octahedral sheets down **c**. The unit cell is shown to indicate proper orientation of the sheets. Legend for (**b**): Mn octahedra = dark, Na octahedra = light.

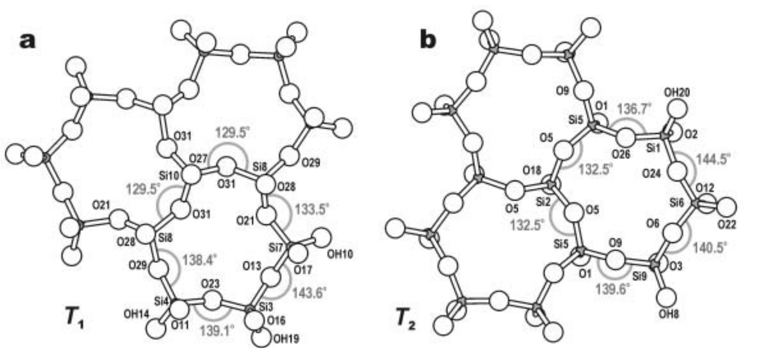

Figure 4. Ball-and-stick models of the tetrahedral islands consisting of 13 SiO_4 tetrahedra. (**a**) and (**b**) are islands from the $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ tetrahedral sheets, respectively. Si-O-Si angles are given for comparison of the structural geometry of the islands.

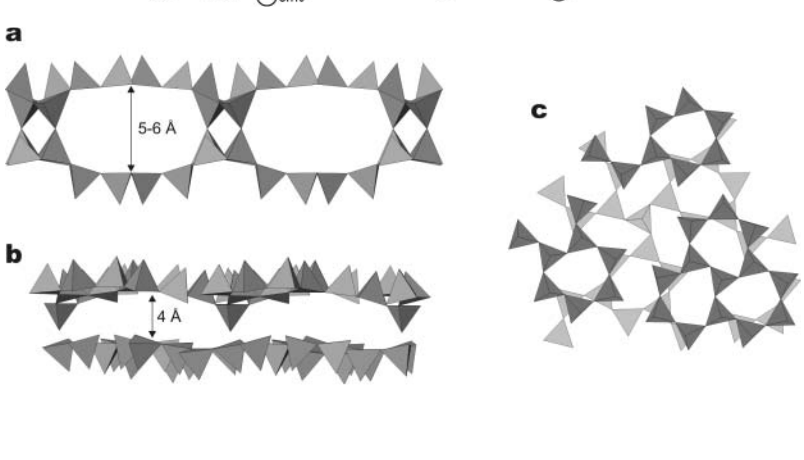

Figure 5. Relationships of opposing silicate anions in ganophyllite (**a**) and shafranovskite (**b**) showing difference in the intersheet distances and the relationships of the $\boldsymbol{T}_1$ (dark) and $\boldsymbol{T}_2$ (light) sheets of silicate tetrahedra in shafranovskite. Note that the $Si11(O,OH)_4$ tetrahedron of the $\boldsymbol{T}_2$ sheet points into free space within the $\boldsymbol{T}_1$ sheet.

TABLE 3. Selected bond lengths (Å) in the structure of shafranovskite

Mn1-O11	2.05(1)	Si8-O28	1.55(1)
Mn1-O1	2.11(1)	Si8-O21	1.61(2)
Mn1-OH7	2.15(1)	Si8-O31	1.63(2)
Mn1-OH4	2.18(1)	Si8-O29	1.66(1)
Mn1-O2	2.21(1)	<Si8-O>	1.61
Mn1-O16	2.34(2)		
<Mn1-φ>	2.17	Si9-O3	1.53(1)
		Si9-OH8	1.62(2)
Mn2-OH4	2.06(1)	Si9-O6	1.66(2)
Mn2-O3	2.06(1)	Si9-O9	1.67(1)
Mn2-OH7	2.09(1)	<Si9-φ>	1.62
Mn2-O17	2.11(1)		
Mn2-O28	2.14(1)	Si10-O31	1.60(1) 3×
Mn2-O12	2.33(2)	Si10-O27	1.63(2)
<Mn2-φ>	2.13	<Si10-O>	1.61
Mn3-O1	2.25(1)	Si11-O22	1.58(2) 3×
Mn3-O16	2.26(2)	Si11-OH15	1.60(2)
Mn3-O18	2.27(1)	<Si11-φ>	1.59
Mn3-O17	2.29(1)		
Mn3-OH4	2.30(1)	Na1-O11	2.40(1)
Mn3-O16	2.33(2)	Na1-O28	2.40(1)
<Mn3-φ>	2.28	Na1-O3	2.42(1)
		Na1-O2	2.43(1)
Mn4-O28	2.19(1)	Na1-H_2O25	2.43(2)
Mn4-O27	2.24(1)	Na1-H_2O30	2.63(2)
Mn4-OH7	2.25(1)	<Na1-φ>	2.45
Mn4-O12	2.26(2)		
Mn4-O2	2.27(1)	Na2-O1	2.31(1)
Mn4-O12	2.32(2)	Na2-O3	2.35(1)
<Mn4-φ>	2.26	Na2-O11	2.36(1)
		Na2-H_2O30	2.40(2)
Si1-O2	1.56(1)	Na2-O17	2.43(1)
Si1-O26	1.61(1)	Na2-H_2O25	2.77(2)
Si1-OH20	1.62(1)	<Na2-φ>	2.44
Si1-O24	1.65(2)		
<Si1-φ>	1.61	Na3-O22	2.35(2)
		Na3-OH20	2.40(2)
Si2-O18	1.57(2)	Na3-O29	2.41(2)
Si2-O5	1.63(1) 3×	Na3-OH10	2.54(2)
<Si2-O>	1.62	Na3-O6	2.67(2)
		Na3-OH14	2.77(2)
Si3-OH19	1.59(2)	<Na3-φ>	2.52
Si3-O16	1.62(2)		
Si3-O23	1.62(2)	K1-OH20	2.90(1)
Si3-O13	1.63(2)	K1-O23	2.96(2)
<Si3-φ>	1.62	K1-O31	2.97(1)
		K1-O21	2.98(2)
Si4-OH14	1.53(2)	K1-H_2O32	2.97(2)
Si4-O11	1.59(1)	K1-O9	3.01(1)
Si4-O29	1.62(2)	K1-O13	3.09(2)
Si4-O23	1.65(2)	K1-OH8	3.14(2)
<Si4-φ>	1.60	K1-O29	3.30(1)
		<K1-φ>	3.04
Si5-O1	1.62(1)		
Si5-O9	1.62(1)	K2-OH19	2.48(2)
Si5-O26	1.65(1)	K2-OH10	2.70(2)
Si5-O5	1.65(1)	K2-O5	2.81(1)
<Si5-O>	1.64	K2-O24	2.85(2)
		K2-O26	2.87(1)
Si6-O12	1.57(2)	K2-O6	2.96(1)
Si6-O24	1.59(2)	K2-O13	2.99(2)
Si6-O6	1.60(2)	K2-O9	3.13(1)
Si6-O22	1.62(2)	<K2-φ>	2.85
<Si6-O>	1.60		
Si7-OH10	1.59(2)		
Si7-O13	1.61(2)		
Si7-O17	1.61(1)		
Si7-O21	1.66(2)		
<Si7-φ>	1.62		

* φ = O, OH, H_2O.

shafranovskite in nature. Based on the structural data reported here, only the interlayer K sites and Na3 site may be replaced by other cations. Na1 and Na2 cations belong to the octahedral sheet and will not exchange. Thus, the formula of shafranovskite may also be written as $M_3\{Na(Mn,Fe,Na)_4[Si_9(O,OH)_{27}](OH)_2(H_2O)_2\}\cdot mH_2O$, where M is an exchangeable cation, and the part in brackets is the composition of the 2:1 layer. The observed streaking of diffraction maxima (Fig. 1) is consistent with the layered character of the structure of shafranovskite and the observed disorder of the Si11 site.

Our study shows that the structure of shafranovskite contains complex islands composed of three hexagonal silicate rings. These islands are either linked to each other or they are isolated. Both types of silicate anions are heretofore unknown in minerals or inorganic compounds. However, the formation of island structures in 2:1 hydrous phyllosilicates was previously discussed by Guggenheim and Eggleton (1987, 1988). Among manganese hydrous phyllosilicates, the structures of greenalite and caryopilite, both 1:1 phyllosilicates, are the most closely related to that of shafranovskite, with islands similar to those observed in shafranovskite (Guggenheim and Eggleton 1998). However, in contrast to shafranovskite, adjacent islands are inverted and are linked by four- or five-membered rings. The arrangement of the islands is not ordered and can only be deciphered using high-resolution transmission electron microscopy (Guggenheim and Eggleton 1998). In contrast, the tetrahedral arrangements in shafranovskite are ordered and can be resolved by single-crystal X-ray diffraction methods.

Khomyakov et al. (1982b, 1983b) described another manganese phyllosilicate, zakharovite, ideally $Na_4Mn^{2+}_5Si_{10}O_{24}(OH)_6\cdot 6H_2O$, from the Lovozero and Khibiny alkaline massifs, Kola peninsula, Russia. Later, Horváth et al. (1998) found zakharovite in the Saint-Amable sill, near Varennes, and at Mont Saint-Hillaire, Québec, Canada. Khomyakov et al. (1982b) determined zakharovite to be trigonal, possible space groups $P31m$ or $P3m1$, a = 14.58, c = 37.71 Å. Note that the a parameters of shafranovskite (14.519 Å) and zakharovite (14.58 Å) are similar, whereas the c parameters are different (21.062 and 37.71 Å, respectively). Both minerals have similar symmetry and perhaps their structures are related. However, the structure of zakharovite awaits detailed structural characterization.

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