

LETTER

Porous titanosilicate nanorods in the structure of yuksporite,  $(\text{Sr,Ba})_2\text{K}_4(\text{Ca,Na})_{14}(\square,\text{Mn,Fe})\{(\text{Ti,Nb})_4(\text{O,OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}(\text{H}_2\text{O,OH})_n$ , resolved using synchrotron radiation

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ABSTRACT

The crystal structure of yuksporite,  $(\text{Sr,Ba})_2\text{K}_4(\text{Ca,Na})_{14}(\square,\text{Mn,Fe})\{(\text{Ti,Nb})_4(\text{O,OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}(\text{H}_2\text{O,OH})_n$ , where  $n \sim 3$  [monoclinic,  $P2_1/m$ ,  $a = 7.126(3)$ ,  $b = 24.913(6)$ ,  $c = 17.075(7)$  Å,  $\beta = 101.89(3)^\circ$ ,  $V = 2966.4(17)$  Å<sup>3</sup>] has been solved using X-ray synchrotron radiation data collected from a needle-like crystal with dimensions of  $6 \times 6 \times 50$  μm<sup>3</sup> at the Swiss-Norwegian beamline BM01 of the European Synchrotron Research Facility (ESRF, Grenoble, France). The structure was refined to  $R_1 = 0.101$  on the basis of 2359 unique observed reflections with  $|F_o| \geq 4\sigma_f$ . The structure of yuksporite is based upon titanosilicate nanorods elongated along **a** and with an elliptical cross-section of ca.  $16 \times 19$  Å =  $1.6 \times 1.9$  nm. Silicate tetrahedra form double xonotlite-like chains  $^1_\infty[\text{Si}_6\text{O}_{17}]$  oriented parallel to (001). Two  $^1_\infty[\text{Si}_6\text{O}_{17}]$  chains are linked into a rod via TiO<sub>6</sub> octahedra and Si<sub>2</sub>O<sub>7</sub> double tetrahedra. The  $\{(\text{Ti,Nb})_4(\text{O,OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}$  nanorods are porous. The internal pores are defined by eight-membered rings (8MR) with open diameters of 3.2 Å. The interior of the titanosilicate nanorods is occupied by Sr, Ba, K, and Na cations and H<sub>2</sub>O molecules. The nanorods are separated by walls of Ca coordination polyhedra that are parallel to (010) and link the rods into a three-dimensional structure.

INTRODUCTION

Titanosilicates represent a new and rapidly expanding class of porous materials with important applications in catalysis, gas separation (Kuznicki 1989; Kuznicki et al. 2001), optoelectronics (Lamberti 1999), ion-exchange (Attar and Dyer 2001), etc. Before being synthesized under laboratory conditions, many of these materials were known in nature, usually from alkaline low-temperature hydrothermal assemblages (Khomyakov 1995). Here we report the occurrence and structure of porous titanosilicate nanorods in the structure of yuksporite, a mineral from the Kola peninsula in Russia. We show that these nanorods are constructed from octahedra (Ti) and tetrahedra (Si) and are structurally related to other titanosilicates such as ETS-4 (Philippou and Anderson 1996; Braunbarth et al. 2000; Nair et al. 2001), a synthetic counterpart of zorite (Mer'kov et al. 1973; Sandomirskii and Belov 1979), another mineral from the Kola peninsula, which is now used in industry on a multiton scale. The structure solution of yuksporite was performed using high-energy synchrotron X-ray radiation (Brown and Sturchio 2002). The occurrence of the titanosilicate nanometer-scale rods are of interest to nanoscience, in either applied (Patzke et al. 2002) or natural aspects (Banfield

and Navrotsky 2002; Hochella 2002).

Yuksporite, a complex titanosilicate of calcium, potassium, and sodium, was first described by Fersman (1923) from the Hackmann Valley, in Yuksporlak Pass, and on the upper Vuonnemiok River, all near Mt. Yukspor in the Khibiny massif. Subsequently, it was found in another part of Russia, in the Murun massif, southwest of Olekminsk, Yakutia (Konev et al. 1985). Yuksporite crystallizes at the late stage of hydrothermal activity and is found in association with microcline, aegirine, titanite, pectolite, biotite, and astrophyllite. Pale pink needles of yuksporite, up to 2–3 mm long and up to 0.01 mm across, usually form radial aggregates in cavities between microcline crystals. Konev et al. (1985) reported for yuksporite an orthorhombic unit cell with  $a = 24.869(8)$ ,  $b = 16.756(6)$ ,  $c = 7.057(3)$  Å. Recently, Men'shikov et al. (2003) re-investigated the crystallographic parameters of yuksporite on the basis of electron microscopy data and reported the mineral to be triclinic,  $a = 16.50(5)$ ,  $b = 25.21(4)$ ,  $c = 21.11(3)$  Å,  $\alpha = 100.4(3)$ ,  $\beta = 110.0(4)$ ,  $\gamma = 90.4(1)^\circ$ .

Though yuksporite has been known for at least 80 years, its structure resisted characterization because of the small dimensions and poor diffraction of its crystals. The recent introduction of third-generation X-ray synchrotron sources provided a unique opportunity to structurally characterize many minerals previously inaccessible using in-house X-ray sources (Pluth et al. 1997; Burns et al. 2000; Cahill et al. 2001).

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## EXPERIMENTAL METHODS

X-ray diffraction experiments were performed under ambient conditions at the Swiss-Norwegian beamline BM01 of the European Synchrotron Research Facility (ESRF) with an imaging plate area detector (Mar345; 2300 × 2300 pixels) with a crystal-to-detector distance of 160 mm. Some tens of needle-like crystals of yuksporite were mounted on tapered glass fibers. Most of them yielded very poor diffraction patterns. However, we were able to find two crystals whose diffraction patterns could be indexed. Data were collected from both crystals. However, the data were better for the crystal with dimensions of 6 × 6 × 50 μm<sup>3</sup>. Diffraction data were measured using monochromatized radiation (λ = 0.80000 Å) in an oscillation mode by rotating the crystal in φ by 2° in 2 min per frame; 100 frames were measured. The unit-cell parameters were refined using 387 reflections. We determined that yuksporite is monoclinic,  $P2_1/m$ ,  $a = 7.126(3)$ ,  $b = 24.913(6)$ ,  $c = 17.075(7)$  Å,  $\beta = 101.89(3)^\circ$ ,  $V = 2966.4(17)$  Å<sup>3</sup>. These data are in general agreement with the unit-cell parameters reported by Konev et al. (1985), taking into account weaknesses of spots in the diffraction photographs taken by these authors (A.N. Sapozhnikov, personal communication). However, our unit-cell parameters are in disagreement with those reported by Men'shikov et al. (2003). The intensities were integrated and merged with the program CrysAlis. Lorentz and polarization corrections were applied and absorption effects were corrected using SADABS ( $R_{int} = 0.057$ ). The structure was solved using the SHELXS program. A pseudomerohedral twinning model was introduced by means of a transformation matrix  $[100/010/\bar{1}0\bar{1}]$  which significantly improved the refinement quality (the  $R_1$  index changed from ~15 to 10%). In this model (001) is the twin composition plane. The occupancies of the atom positions were refined using scattering factors for Ti, K, Ca, Na, Sr, and Mn, and were subsequently fixed at the values given in Table 1 so as to be in agreement with the results of chemical analysis (see below). The agreement factor for the final model is  $R_1 = 0.101$  for 2359 unique observed reflections with  $|F_o| \geq 4\sigma_F$ . The refinement results include atomic positional and isotropic displacement parameters (Table 1). Selected bond lengths are given in Table 2. Because of the poor quality of crystals and twinning effects, the bond lengths are somewhat in error. For example, some of the Si-O distances are in the range of 1.49–1.57 Å, which is relatively short. However, the data were good enough to reveal the general topological and geometrical features of the structure.

Because of the errors in the observed bond lengths, bond-valence analysis of the structure does not provide reliable information for the assignment of the OH and H<sub>2</sub>O groups. Therefore, the following measures were undertaken: (1) all anions bonded to Si and Ti are considered to be O atoms; (2) anions not bonded to Si and Ti and bonded to three Ca, Na, or Sr positions each with cation-anion distances of 2.3–2.5 Å are considered to be OH groups; (3) other anions are considered to be H<sub>2</sub>O groups.

The chemical composition of yuksporite 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: lozenite (Na and Ti), diopside (Ca, Si), wadeite (K), MnCO<sub>3</sub> syn. (Mn), hematite (Fe), celestine (Sr), Nb metal (Nb), and synthetic BaSO<sub>4</sub> (Ba). The chemical composition is (in wt%): Na<sub>2</sub>O 5.58, SiO<sub>2</sub> 40.30, K<sub>2</sub>O 7.01, CaO 17.60, TiO<sub>2</sub> 9.31, MnO 0.44, Fe<sub>2</sub>O<sub>3</sub> 0.31, SrO 5.36, Nb<sub>2</sub>O<sub>5</sub> 3.29, BaO 3.75, H<sub>2</sub>O(calc) 7.05, sum 100.00. The empirical chemical formula calculated on the basis of Si = 18 is (Na<sub>4.83</sub>K<sub>4.00</sub>Ba<sub>0.66</sub>)<sub>2–9.49</sub>(Ca<sub>8.42</sub>Sr<sub>1.39</sub>)<sub>2–9.81</sub>(Ti<sub>3.13</sub>Nb<sub>0.66</sub>Mn<sub>0.17</sub>Fe<sub>0.10</sub>)<sub>2–3.89</sub>S<sub>18</sub>O<sub>59/7</sub>H<sub>2</sub>O, where  $n = 3$ , which is in general agreement with the results of the crystal-structure study.

## RESULTS

The structure of yuksporite (Fig. 1) is based upon complex rods consisting of corner-sharing TiO<sub>6</sub> octahedra and SiO<sub>4</sub> tetrahedra (Fig. 2). The rods are parallel to **a** and have an elliptical cross-section measuring ca. 16 × 19 Å = 1.6 × 1.9 nm. The structure of titanosilicate rods in yuksporite is remarkable and is unique among both synthetic and natural silicates. Silicate tetrahedra consist of nine symmetry-independent types. Si1O<sub>4</sub>, Si4O<sub>4</sub> and Si5O<sub>4</sub> tetrahedra are linked via common O atoms to form xonotlite-like double *dreier* chains <sup>1</sup><sub>∞</sub>[Si<sub>6</sub>O<sub>17</sub>] according to the Liebau's nomenclature (Liebau 1985; i.e., double chains with three tetrahedra within their identity periods) (Fig. 2c). These chains are parallel to **a** and are oriented perpendicular to **c**. Similar <sup>1</sup><sub>∞</sub>[Si<sub>6</sub>O<sub>17</sub>] chains are made up of Si2O<sub>4</sub>, Si6O<sub>4</sub>, and Si8O<sub>4</sub> tetrahedra (Fig. 2d). Two <sup>1</sup><sub>∞</sub>[Si<sub>6</sub>O<sub>17</sub>] chains are linked into

TABLE 1. Atomic coordinates, occupancies, and displacement parameters (Å<sup>2</sup>) for yuksporite

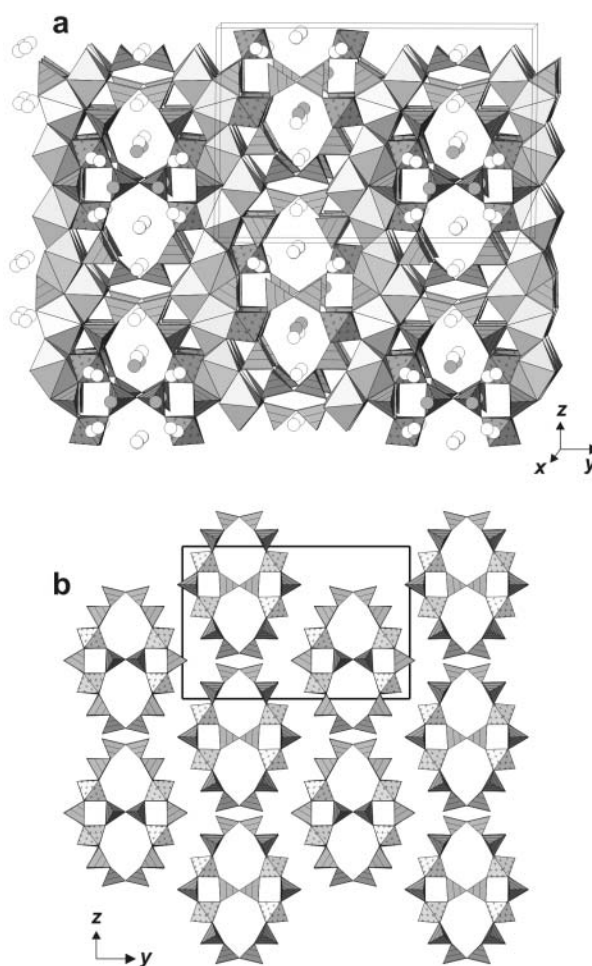
Atom	Occupation	x	y	z	U <sub>iso</sub>
Ti1	Ti <sub>0.80</sub> Nb <sub>0.20</sub>	0.1754(5)	0.59949(13)	0.0992(2)	0.008(2)
Ti2	Ti <sub>0.75</sub> Nb <sub>0.25</sub>	-0.6751(6)	0.59968(13)	0.4004(2)	0.020*
Si1	Si	-0.1835(10)	0.6319(2)	-0.0579(4)	0.014(2)
Si2	Si	-0.8749(11)	0.6333(2)	0.5566(4)	0.020(2)
Si3	Si	-0.0272(9)	0.5414(3)	0.2471(4)	0.020(2)
Si4	Si	-0.6302(10)	0.6324(2)	-0.0584(4)	0.016(2)
Si5	Si	0.0419(10)	0.6874(3)	-0.1648(4)	0.022(2)
Si6	Si	-0.5417(9)	0.6891(2)	0.6629(4)	0.016(2)
Si7	Si	0.5259(7)	0.5442(2)	0.2476(3)	0.007(2)
Si8	Si	-0.3152(10)	0.6335(2)	0.5563(4)	0.015(2)
Si9	Si	-0.6591(9)	0.6881(2)	0.2500(4)	0.016(2)
Sr1	Sr <sub>0.35</sub> Ba <sub>0.15</sub>	-0.3119(7)	0.6337(3)	0.1271(3)	0.012(3)
Sr2	Sr <sub>0.35</sub> Ba <sub>0.15</sub>	-0.1863(6)	0.6332(3)	0.3752(2)	0.008(2)
K1	K <sub>0.90</sub>	-0.0560(12)	3/4	-0.3617(5)	0.021(5)
K2	K <sub>0.95</sub> Ba <sub>0.05</sub>	-0.4425(12)	3/4	-0.1352(5)	0.038(5)
K3	K <sub>0.60</sub>	0.1902(44)	3/4	0.0472(10)	0.036(9)
K4	K <sub>0.90</sub>	-0.6430(21)	3/4	0.4511(9)	0.070(8)
K5	K <sub>0.40</sub>	0.0889(64)	3/4	0.0476(14)	0.031(13)
Na1	Na <sub>0.50</sub>	-0.1885(35)	0.6082(17)	0.3830(13)	0.005(13)
Na2	Na <sub>0.50</sub>	-0.3189(28)	0.6097(11)	0.1054(13)	0.030(9)
Na3	Ca <sub>0.25</sub> Na <sub>0.75</sub>	-0.9222(14)	0.4848(3)	0.4125(4)	0.013(4)
Ca1	Ca	0.2479(8)	0.5873(1)	-0.2500(3)	0.0146(11)
Ca2	Ca <sub>0.70</sub> Na <sub>0.30</sub>	0.0767(11)	0.5177(2)	-0.0915(3)	0.010(3)
Ca3	Ca	-0.2491(8)	0.5851(2)	-0.2499(3)	0.015(2)
Ca4	Ca <sub>0.50</sub> Na <sub>0.50</sub>	-0.4213(13)	0.5163(3)	-0.0831(4)	0.020(3)
Ca5	Ca <sub>0.80</sub> Na <sub>0.20</sub>	-0.4237(12)	0.4826(3)	0.4110(3)	0.030(3)
M	Mn <sub>0.15</sub> Fe <sub>0.10</sub>	-0.2532(23)	3/4	0.2424(10)	0.054(7)
O1		0.4922(20)	0.5223(9)	-0.2541(9)	0.032(5)
O2		-0.6784(29)	0.4232(6)	0.3872(8)	0.012(3)
O3		0.0050(21)	0.6483(8)	-0.2381(10)	0.034(5)
O4		-0.5099(18)	0.6449(6)	0.7320(9)	0.010*
O5		-0.0116(19)	0.4794(8)	0.2479(9)	0.026(5)
O6		-0.6730(34)	0.5801(7)	-0.1130(10)	0.032(5)
O7		-0.6206(22)	0.5344(6)	0.4595(8)	0.010*
O8		0.1427(25)	0.5373(6)	0.0446(8)	0.010*
OH9		-0.6310(22)	0.4644(6)	-0.0463(8)	0.010*
OH10		-0.1454(22)	0.5359(5)	0.4488(7)	0.010*
O11		-0.1951(27)	0.5804(6)	-0.1031(8)	0.010*
O12		-0.8177(24)	0.5794(5)	0.0465(7)	0.010*
O13		-0.7554(41)	3/4	0.2536(18)	0.038(6)
O14		-0.5332(35)	3/4	0.6948(15)	0.034(6)
O15		-0.6560(22)	0.6297(6)	0.0333(9)	0.018(4)
O16		-0.4460(22)	0.6325(6)	0.4665(9)	0.016(4)
O17		-0.1207(23)	0.6880(6)	-0.1051(9)	0.023(4)
O18		-0.5105(22)	0.5697(6)	0.3312(9)	0.016(4)
O19		-0.0716(29)	0.6329(8)	0.0291(11)	0.046(6)
O20		-0.3925(27)	0.6514(8)	-0.0434(11)	0.042(5)
O21		-0.8293(20)	0.6331(5)	0.4682(8)	0.011(4)
O22		-0.1003(18)	0.6491(5)	0.5519(7)	0.010*
O23		-0.7397(28)	0.6862(7)	-0.1083(11)	0.039(5)
O24		0.0144(23)	0.5659(6)	0.1678(9)	0.024(4)
O25		-0.3915(18)	0.6801(5)	0.6046(7)	0.010*
O26		0.4059(23)	0.5637(6)	0.1673(9)	0.022(4)
O27		-0.2740(18)	0.5594(4)	0.2416(8)	0.005(3)
O28		0.0890(23)	0.5693(6)	0.3301(9)	0.025(4)
O29		0.0303(26)	3/4	-0.2011(10)	0.002(4)
O30		-0.7571(20)	0.6820(5)	0.6058(7)	0.004(3)
O31		-0.1671(35)	3/4	0.4211(11)	0.010*
O32		0.2116(24)	0.6637(7)	0.1684(10)	0.027(4)
O33		-0.7124(23)	0.6635(7)	0.3297(9)	0.024(4)
O34		-0.4310(29)	0.6918(16)	0.2469(23)	0.119(10)
H <sub>2</sub> O35	(H <sub>2</sub> O) <sub>0.59</sub>	-0.0783(76)	0.6870(22)	0.2321(33)	0.100*
H <sub>2</sub> O36	(H <sub>2</sub> O) <sub>0.56</sub>	-0.349(12)	3/4	0.0981(49)	0.100*

\* Fixed during refinement.

a rod via Ti1O<sub>6</sub> and Ti2O<sub>6</sub> octahedra and Si<sub>2</sub>O<sub>7</sub> double tetrahedra formed by Si3 and Si7 atoms (Fig. 2e). Another Si<sub>2</sub>O<sub>7</sub> group composed of two corner-sharing Si9O<sub>4</sub> tetrahedra is located within the rod and is oriented parallel to **b**. This group provides linkage of two opposite walls of the rod along the **b** axis (Fig. 2b). There are two different TiO<sub>6</sub> octahedra and both of them show

**TABLE 2.** Selected bond lengths (Å) in the structure of yuksporite

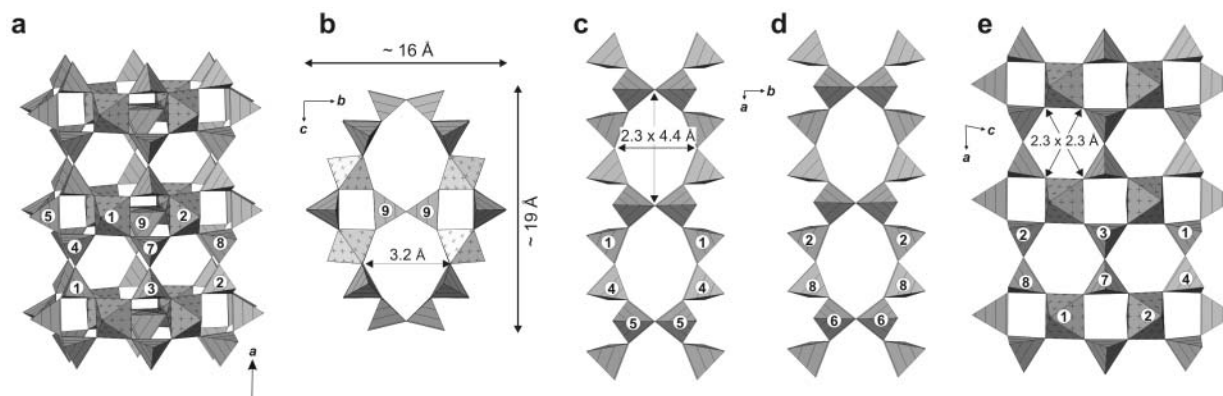
Ti1-O8	1.80(1)	Sr1-H <sub>2</sub> O35	2.55(6)	Na3-OH10	2.22(2)
Ti1-O15	1.96(2)	Sr1-O19	2.63(2)	Na3-OH10	2.37(1)
Ti1-O32	1.97(2)	Sr1-O15	2.64(2)	Na3-O12	2.42(2)
Ti1-O24	1.99(2)	Sr1-O27	2.67(1)	Na3-O2	2.42(2)
Ti1-O26	2.02(2)	Sr1-O34	2.78(4)	Na3-O7	2.47(2)
Ti1-O19	2.09(2)	Sr1-OH9	2.80(2)	Na3-O28	2.54(2)
<Ti1-O>	1.97	Sr1-O24	2.84(2)	Na3-O5	2.76(2)
		Sr1-O26	2.85(2)	<Na3-φ>	2.46
		Sr1-O20	2.88(2)		
Ti2-O7	1.91(2)	Sr1-H <sub>2</sub> O36	2.94(2)	Ca1-O6	2.30(2)
Ti2-O21	1.94(1)	<Sr1-φ>	2.76	Ca1-O4	2.31(2)
Ti2-O16	1.96(2)			Ca1-O3	2.34(2)
Ti2-O18	1.98(2)	Sr2-O16	2.65(2)	Ca1-O5	2.37(2)
Ti2-O33	1.98(2)	Sr2-O21	2.71(1)	Ca1-O1	2.39(2)
Ti2-O28	2.00(2)	Sr2-OH10	2.72(2)	Ca1-O12	2.44(1)
<Ti2-O>	1.96	Sr2-O28	2.76(2)	<Ca1-O>	2.36
		Sr2-O18	2.77(2)		
Si1-O11	1.49(2)	Sr2-O27	2.90(1)	Ca2-O8	2.33(2)
Si1-O19	1.54(2)	Sr2-O34	2.90(4)	Ca2-O8	2.34(2)
Si1-O20	1.63(2)	Sr2-O22	2.98(1)	Ca2-O6	2.45(2)
Si1-O17	1.72(2)	Sr2-O31	3.01(1)	Ca2-OH9	2.46(2)
<Si1-O>	1.60	Sr2-H <sub>2</sub> O35	3.02(6)	Ca2-O11	2.46(2)
		<Sr2-φ>	2.84	Ca2-O24	2.47(2)
Si2-O12	1.58(2)			Ca2-O5	2.61(2)
Si2-O21	1.61(2)	K1-O29	2.68(2)	<Ca2-φ>	2.45
Si2-O30	1.61(2)	K1-O30	2.86(2) ×2		
Si2-O22	1.64(2)	K1-O22	2.90(1) ×2	Ca3-O2	2.31(2)
<Si2-O>	1.61	K1-O25	2.92(1) ×2	Ca3-O4	2.35(2)
		K1-O3	3.27(2) ×2	Ca3-O3	2.38(2)
Si3-O5	1.55(2)	<K1-O>	2.95	Ca3-O1	2.41(2)
Si3-O24	1.57(2)			Ca3-O5	2.45(2)
Si3-O28	1.64(2)	K2-O17	2.73(2) ×2	Ca3-O11	2.46(2)
Si3-O27	1.80(1)	K2-O23	2.76(2) ×2	<Ca3-O>	2.39
<Si3-O>	1.64	K2-O14	2.84(3)		
		K2-O20	2.90(2) ×2	Ca4-OH9	2.17(2)
Si4-O6	1.60(2)	<K2-O>	2.80	Ca4-OH9	2.22(2)
Si4-O15	1.62(2)			Ca4-O11	2.34(2)
Si4-O23	1.69(2)	K3-O32	2.97(2) ×2	Ca4-O6	2.37(2)
Si4-O20	1.73(2)	K3-O15	3.22(2) ×2	Ca4-O8	2.37(2)
<Si4-O>	1.66	K3-H <sub>2</sub> O36	3.22(9)	Ca4-O26	2.47(2)
		K3-O23	3.22(3) ×2	Ca4-O1	2.86(2)
Si5-O3	1.57(2)	<K3-φ>	3.15	<Ca4-φ>	2.40
Si5-O23	1.65(2)				
Si5-O29	1.67(1)	K4-O33	2.96(2) ×2	Ca5-O7	2.19(2)
Si5-O17	1.69(2)	K4-O16	3.23(2) ×2	Ca5-O7	2.21(2)
<Si5-O>	1.65	K4-O21	3.24(2) ×2	Ca5-O2	2.31(2)
		K4-O13	3.30(3)	Ca5-OH10	2.36(2)
Si6-O4	1.60(2)	K4-O25	3.34(2) ×2	Ca5-O12	2.37(2)
Si6-O14	1.61(1)	K4-O30	3.38(2) ×2	Ca5-O18	2.57(2)
Si6-O25	1.62(1)	<K4-O>	3.24	Ca5-O1	2.63(2)
Si6-O30	1.65(2)			<Ca5-φ>	2.38
<Si6-O>	1.62				
		K5-O32	2.98(2) ×2		
Si7-O27	1.50(1)	K5-O19	3.13(3) ×2		
Si7-O26	1.54(2)	K5-O17	3.13(3) ×2		
Si7-O18	1.63(2)	<K5-O>	3.08		
Si7-O1	1.67(2)				
<Si7-O>	1.59	Na1-OH10	2.11(4)		
		Na1-O18	2.48(3)		
Si8-O25	1.58(1)	Na1-O28	2.53(3)		
Si8-O22	1.60(2)	Na1-O16	2.62(3)		
Si8-O16	1.62(2)	Na1-O27	2.66(3)		
Si8-O2	1.72(2)	Na1-O21	2.74(3)		
<Si8-O>	1.63	Na1-O22	3.00(2)		
		<Na1-φ>	2.59		
Si9-O33	1.61(2)				
Si9-O32	1.62(2)	Na2-OH9	2.10(3)		
Si9-O34	1.64(2)	Na2-O19	2.47(3)		
Si9-O13	1.70(1)	Na2-O15	2.51(3)		
<Si9-O>	1.64	Na2-O27	2.60(2)		
		Na2-O24	2.63(3)		
M-O34	1.94(3) ×2	Na2-O26	2.67(3)		
M-H <sub>2</sub> O35	2.03(5) ×2	Na2-O20	2.70(3)		
M-H <sub>2</sub> O36	2.42(8)	<Na2-φ>	2.53		
<M-φ>	2.07				

\* φ = O, OH, H<sub>2</sub>O

**FIGURE 1.** The crystal structure of yuksporite (a) and arrangement of titanosilicate nanorods along a (b). Legend: TiO<sub>6</sub> octahedra = crosshatched; SiO<sub>4</sub> tetrahedra = lined; Caφ polyhedra = shaded; K, Sr, and Na cations are shown as white circles; H<sub>2</sub>O groups are shown as gray circles.

an out-of-center distortion of octahedral geometry typical for the *d*<sup>0</sup> transitional metal cations (Kunz and Brown 1995). These octahedra are predominantly occupied by Ti, however, some admixture of Nb into this site should also be taken into account. Of the six O atoms coordinating the Ti<sup>4+</sup> cations, five are shared with silicate tetrahedra, and one is not. The O atoms of this type form a shortened Ti-O bond. The total composition of a rod is {(Ti,Nb)<sub>4</sub>(O,OH)<sub>4</sub>[Si<sub>6</sub>O<sub>17</sub>]<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>]<sub>3</sub>}. Note that the titanosilicate rod is negatively charged; thus the structure contains additional cations for charge balance.

The {(Ti,Nb)<sub>4</sub>(O,OH)<sub>4</sub>[Si<sub>6</sub>O<sub>17</sub>]<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>]<sub>3</sub>} nanorods are porous. The internal pores are defined by eight-membered rings (8MR) oriented perpendicular to (100). Their free diameter estimated as the distance between O atoms across the ring minus 2.7 Å (two oxygen radii taken as 1.35 Å) is 3.2 Å. These 8MRs consist of two octahedra and six tetrahedra each (Fig. 2b). Within the rod, the 8MRs are arranged in two parallel internal channels separated by the Si<sub>2</sub>O<sub>7</sub> groups formed by SiO<sub>4</sub> tetrahedra. From the



**FIGURE 2.** Structure of titanosilicate nanorods in yuksporite: view from the side (a) and from the top (b); two xonotlite-like  $[\text{Si}_6\text{O}_{17}]$  chains (c, d) form walls of nanorods perpendicular to c;  $\text{TiO}_6$  octahedra,  $\text{Si}_2\text{O}_7$  groups and halves of the xonotlite chains form walls of nanorods perpendicular to b (e). Legend:  $\text{TiO}_6$  octahedra = crosshatched;  $\text{SiO}_4$  tetrahedra = lined. The numbers in circles correspond to the numbers of Ti and Si atoms in Table 1.

outside, the rods are bounded by 8MRs formed solely by silicate tetrahedra (Fig. 2c). The plane of these rings is parallel to (001); their apertures have an elliptical section with free diameters of  $2.3 \times 4.4 \text{ \AA}$ . Other outside rings are 6MRs as shown in Figure 2e. These rings consist of two octahedra and four tetrahedra and have a free diameter of ca.  $2.3 \text{ \AA}$ .

The interior of the titanosilicate nanorods is occupied by alkali metal cations ( $\text{Na}_1$ ,  $\text{Na}_2$ ,  $\text{K}_1$ - $\text{K}_5$ ) and  $\text{H}_2\text{O}$  molecules. In addition, there is a low-occupancy M site located within the rod between two  $\text{Si}_2\text{O}_7$  groups formed by Si9 atoms. This position has a square pyramidal coordination and provides additional blockage between the two internal channels parallel to a. In the structure, the  $\{(\text{Ti},\text{Nb})_4(\text{O},\text{OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}$  rods are separated by walls composed of Ca coordination polyhedra. The walls are parallel to (010) and provide linkage of the rods into a three-dimensional structure.

Taking into account all atomic positions, the structural formula of yuksporite should be written as  $\text{Sr}_{1.40}\text{Ba}_{0.65}\text{K}_{3.75}\text{Ca}_{8.50}\text{Na}_{5.50}\text{Mn}_{0.15}\text{Fe}_{0.10}\{(\text{Ti},\text{Nb})_4(\text{O},\text{OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}(\text{H}_2\text{O},\text{OH})_3$ . A simplified formula may be written as  $(\text{Sr},\text{Ba})_2\text{K}_4(\text{Ca},\text{Na})_{14}(\square, \text{Mn},\text{Fe})\{(\text{Ti},\text{Nb})_4(\text{O},\text{OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}(\text{H}_2\text{O},\text{OH})_n$ , where  $n \sim 3$  ( $\square$  = vacancy). This formula is in good agreement with the results of the chemical analysis given above. Moreover, it is in general agreement with the chemical data reported by Konev et al. (1985) for Yakutian yuksporite. On the basis  $\text{Si} + \text{Al} = 18$ , the empirical chemical formula for the sample studied by Konev et al. (1985) can be written as  $(\text{Na}_{3.48}\text{K}_{3.67}\text{Ba}_{1.58})_{\Sigma=8.73}(\text{Ca}_{9.47}\text{Sr}_{1.59})_{\Sigma=11.06}(\text{Ti}_{3.88}\text{Mn}_{0.11}\text{Fe}_{0.26})_{\Sigma=4.25}\text{Si}_{17.96}\text{Al}_{0.04}\text{O}_{60.39}\text{F}_{4.51}\text{Cl}_{0.63}/n\text{H}_2$ . This formula has many similarities with the formula of the Khibiny sample studied in this work: (1) the amount of K is about 4 atoms per formula units (apfu), (2)  $\text{Ca} + \text{Na} \approx 14$ , and (3) the amount of Ti is about 4 apfu. However, there are important differences as well: (1)  $\text{Ba} + \text{Sr} \approx 3$ , instead of 2 in our yuksporite and (2) there is a considerable amount of F in the Yakutian yuksporite. The latter allows us to identify yuksporite from the Murun massif (Yakutia) as an F-bearing variety that can potentially be considered as a different mineral species. However, more detailed investigations of the type material of the Yakutian yuksporite are necessary before making final conclusion.

## DISCUSSION

The discovery of titanosilicate nanorods in the structure of yuksporite provides important new information for understanding the structural diversity of titanosilicates and related materials. The structures of natural and synthetic titanosilicates usually consist of either frameworks or layers of corner-sharing  $\text{TiO}_6$  octahedra (or  $\text{TiO}_5$  square pyramids) and  $\text{SiO}_4$  tetrahedra (Rocha and Anderson 2000; Krivovichev et al. 2003; Krivovichev and Armbruster 2004). Thus, structures of ETS-4 (Philippou and Anderson 1996; Braunbarth et al. 2000; Nair et al. 2001) and ETS-10 (Anderson et al. 1994; Wang and Jacobson 1999) are based upon chains of  $\text{TiO}_6$  octahedra interlinked by silicate anions, whereas structures of a titanosilicate catalyst JDF-L1 (Roberts et al. 1996) and fresnoite  $\text{Ba}_2(\text{TiO})(\text{Si}_2\text{O}_7)$  (Moore and Louisnathan 1967) consist of layers of  $\text{TiO}_5$  square pyramids and  $\text{SiO}_4$  tetrahedra. The structure of jonesite,  $\text{Ba}_2(\text{K},\text{Na})[\text{Ti}_2(\text{Si}_5\text{Al})\text{O}_{18}(\text{H}_2\text{O})](\text{H}_2\text{O})_n$  (Krivovichev and Armbruster 2004) is based upon porous double layers consisting of  $\text{TiO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra. The structure of ohmilite,  $\text{Sr}_3(\text{Ti},\text{Fe}^{3+})(\text{O},\text{OH})(\text{Si}_2\text{O}_6)_2 \cdot 2\text{-}3\text{H}_2\text{O}$  (Mizota et al. 1983) contains complex chains of  $\text{Ti}(\text{O},\text{OH})_6$  octahedra and  $\text{SiO}_4$  tetrahedra. The titanosilicate nanorods in yuksporite demonstrate new and unusual possibilities in the class of titanosilicate materials, especially in the field of synthesis of titanosilicate-based oxide nanorods with potential technological applications (Patzke et al. 2002).

Titanium phyllosilicate minerals have recently attracted attention due to their interesting modular crystal chemistry (Ferraris 1997; Ferraris et al. 2004). Men'shikov et al. (2003) suggested that yuksporite and the related mineral eveslogite belong to the astrophyllite-group minerals and that their structures contain titanosilicate heteropolyhedral layers. This study has demonstrated that, at least for yuksporite, this hypothesis could not be confirmed.

## ACKNOWLEDGMENTS

We are grateful to P. Burns, G. Ferraris, and R. Downs for useful comments on the manuscript. S.V.K. thanks the Alexander von Humboldt Foundation and the Swiss National Science Foundation (grant 20-65084.01 to T.A., Crystal Chemistry of Minerals) for financial support.

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MANUSCRIPT RECEIVED FEBRUARY 6, 2004

MANUSCRIPT ACCEPTED MAY 25, 2004

MANUSCRIPT HANDLED BY KEVIN ROSSO