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KOLSKYITE, $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$, A GROUP-IV Ti-DISILICATE MINERAL FROM THE KHIBINY ALKALINE MASSIF, KOLA PENINSULA, RUSSIA: DESCRIPTION AND CRYSTAL STRUCTURE

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Abstract

Kolskyite, $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$, is a Group-IV TS-block mineral from the Kirovskii mine, Mount Kukisvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia. The mineral occurs as single, platy crystals 2–40 μm thick and up to 500 μm across. It is pinkish yellow, with a white streak and a vitreous luster. The mineral formed in a pegmatite as a result of hydrothermal activity. Associated minerals are natrolite, nechelyustovite, kazanskyite, barytolamprophyllite, hydroxylapatite, belovite-(La), belovite-(Ce), gaidonnayite, nenadkevichite, epididymite, apophyllite-(KF), and sphalerite. Kolskyite has perfect cleavage on {001}, splintery fracture, and a Mohs hardness of 3. Its calculated density is 2.509 g/cm^3. Kolskyite is biaxial negative with α 1.669, β 1.701, γ 1.720 (λ 590 nm), $2V_{meas.}$ = 73.6(5)°, $2V_{calc.}$ = 74.0°, with no discernible dispersion. It is nonpleochroic. Kolskyite is triclinic, space group $P\bar{1}$, a 5.387(1), b 7.091(1), c 15.473(3) Å, α 96.580(4), β 93.948(4), γ 89.818(3)°, V 585.8(3) Å^3. The strongest lines in the X-ray powder-diffraction pattern [d(Å)(I)(hkl)] are: 15.161(100)(001), 2.810(19)(121, $1\bar{2}2$), 3.069(12) (005), 2.938(10)($\bar{1}\bar{2}1$,120,$1\bar{2}1$), 2.680(9)($\bar{1}\bar{2}3$,200,114, $\bar{2}01$), 1.771(9) ($0\bar{4}1$,040), 2.618(8)($1\bar{2}3$,122), 2.062(7)(221,$2\bar{2}2$,$\bar{2}\bar{2}3$,$\bar{2}22$), and 1.600(7)($\bar{3}\bar{2}1$,$\bar{3}20$,320). Chemical analysis by electron microprobe gave Nb_2O_5 6.96, ZrO_2 0.12, TiO_2 26.38, SiO_2 27.08, FeO 0.83, MnO 2.95, MgO 0.76, BaO 3.20, SrO 5.21, CaO 4.41, K_2O 0.79, Na_2O 6.75, H_2O 13.81, F 0.70, O = F –0.29, sum 99.66 wt.%; H_2O was determined from structure solution and refinement. The empirical formula was calculated on 25 (O + F) *apfu*: $(Na_{1.93}Mn_{0.04}Ca_{0.03})_{\Sigma 2}(Ca_{0.67}Sr_{0.45}Ba_{0.19}K_{0.15})_{\Sigma 1.46}(Ti_{2.93}Nb_{0.46}Mn_{0.33}Mg_{0.17}Fe^{2+}{}_{0.10}Zr_{0.01})_{\Sigma 4}Si_{4.00}O_{24.67}H_{13.60}F_{0.33}$, Z = 1. Simplified and ideal formulae are as follows: $(Ca,\square)_2Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$ and $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$. The FTIR spectrum of the mineral contains the following bands: ~3300 cm^{-1} (very broad) and ~1600 cm^{-1} (sharp). The crystal structure was solved by direct methods and refined to an R_1 index of 8.8%. The crystal structure of kolskyite is a combination of a TS (titanium-silicate) block and an **I** (intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The TS block exhibits linkage and stereochemistry typical for Group IV [Ti (+ Mg + Mn) = 4 *apfu*] of Ti-disilicate minerals. In the H sheet in kolskyite, Si_2O_7 groups link to [6]-coordinated Ti octahedra. In the O sheet, Ti-dominant and Na octahedra each form brookite-like chains. There is one peripheral A^P site occupied mainly by Ca (less Sr, Ba, and K) at 68%. The **I** block consists of H_2O groups and A^P atoms. The **I** block is topologically identical to those in the kazanskyite and nechelyustovite structures. The mineral is named after the Kola Peninsula (*Kolskyi Poluostrov* in Russian). The chemical formula and structure of kolskyite were predicted by Sokolova & Cámara (2010); this is the first correct prediction of a TS-block mineral.

Keywords: kolskyite, new mineral, Khibiny alkaline massif, Kola Peninsula, Russia, crystal structure, Group IV, Ti-disilicate, TS block

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INTRODUCTION

Kolskyite, ideally $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$, is a new representative of the Ti-disilicate minerals with the TS (titanium-silicate) block (Sokolova 2006). In the crystal structure of kolskyite, the TS block has the stereochemistry and topology of Group IV where Ti (+ Mg + Mn) = 4 *apfu* (atoms per formula unit). In Group IV, the TS block exhibits linkage 3 of H and O sheets: the Si_2O_7 groups of two H sheets link to the two Ti (+ Mg + Mn) octahedra of the O sheet adjacent along $\mathbf{t_1}$ [in kolskyite, $t_1 = a = 5.387(1)$ Å]**.** The crystal structure of kolskyite is a new structure type and does not have any analogues.

The name is after the Kola Peninsula (*Kolskyi Poluostrov* in Russian) and to commemorate the outstanding achievements of Alexander Petrovich Khomyakov, a prominent mineralogist who described more than 100 new minerals (primarily from Kola) and who passed away (October 12, 2012) during work on this new mineral from his sample 2757. Professor Khomyakov worked in the Kola Peninsula for 46 years, focusing on the rocks of the Khibiny and Lovozero alkaline massifs. The new mineral species and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2013-005). The holotype specimen of kolskyite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Pr. 18/2, 119071 Moscow, Russia, catalogue No. 4383/1.

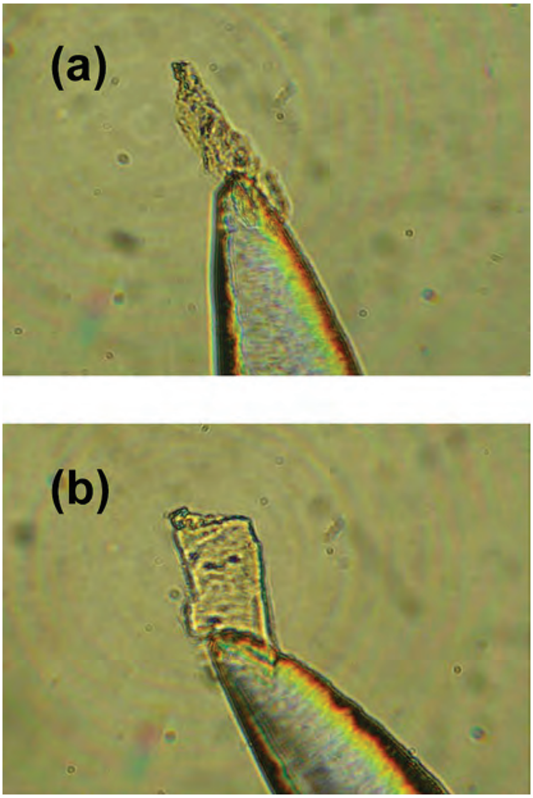

FIG. 1. The crystal of kolskyite used for measuring optics (0.010 × 0.035 × 0.080 mm) on a glass fiber in oil, note the platy nature (a) and irregular surface of the crystal (b).

OCCURRENCE AND ASSOCIATED MINERALS

Kolskyite was discovered in sample 2757 of A.P. Khomyakov from the underground Kirovskii mine (+252 m level), Mount Kukisvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia. At that particular level, two other Ti-disilicate minerals, kazanskyite (Cámara *et al.* 2012) and nechelyustovite (Nèmeth *et al.* 2009, Cámara & Sokolova 2009), have been found (Table 1). Following Nèmeth *et al.* (2009), nechelyustovite is found in one hydrothermally altered pegmatite body emplaced in nepheline syenites near their contact with ijolite–urtites. The pegmatite is a branching vein 0.1–0.5 m wide with a symmetrical zoned structure: a natrolite core, a microcline zone, and a marginal aegirine-dominated external zone with subordinate amounts of microcline, nepheline, lamprophyllite, and eudialyte. Nechelyustovite (and kazanskyite and kolskyite) is confined to the natrolite core. Other associated minerals are barytolamprophyllite, hydroxylapatite, belovite-(La), belovite-(Ce), gaidonnayite, nenadkevichite, epididymite, apophyllite-(KF), and sphalerite.

PHYSICAL AND OPTICAL PROPERTIES

The main properties of kolskyite are presented in Table 1, where they are compared to those of Group-III minerals kazanskyite and nechelyustovite. Kolskyite forms single, platy crystals 2–40 μm thick and up to 500 μm across (Fig. 1). Kolskyite is pinkish yellow, with a white streak and a vitreous luster. The mineral is transparent in thin flakes. The flakes have a perfect {001} cleavage, splintery fracture, and Mohs hardness of 3, and are non-fluorescent under 240–400 nm ultraviolet radiation. The density of the mineral could not be measured owing to the very small thickness of the flakes. Its calculated density (using the empirical formula) is 2.509 g/cm^3. The mineral is biaxial negative with α 1.669(2), β 1.701(2), γ 1.720(3) (λ 590 nm), $2V_{meas.} = 73.6(5)°$, $2V_{calc.} = 74°$, with no discernible dispersion. It is nonpleochroic. Optical orientation is given in Table 2. A Gladstone-Dale calculation gives a compatibility index of 0.027, which is rated as excellent.

Transmission FTIR spectra were collected using a Bruker Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled MCT detector. The sample was prepared as a thin film using a diamond micro compression cell. Data over the range (4000–650 cm^{-1}) were

TABLE 1. COMPARATIVE TABLE FOR KOLSKYITE, KAZANSKYITE, AND NECHELYUSTOVITE

	kolskyite	kazanskyite	nechelyustovite	
Reference	(1)	(2)	(3)	(4)
Formula	$(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$	$Ba\square Na_3Ti_2Nb(Si_2O_7)_2O_2(OH)_2(H_2O)_4$	(4): $Na_4Ba_2Mn_{1.5}\square_{2.5}Ti_5Nb(Si_2O_7)_4O_4(OH)_3F(H_2O)_6$	
System	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$A2/m$	$P\bar{1}$
a (Å)	5.387(1)	5.4260	5.38	5.447
b	7.091(1)	7.135	7.04	7.157
c	15.473(3)	25.514	48.10	47.259
α (°)	96.580(4)	98.172	90	95.759
β	93.948(4)	90.916	91.1	92.136
γ	89.818(4)	89.964	90	89.978
V (*Å*^{3})	585.8(3)	977.61	1821	1831.7
Z	1	2	4	2
$D_{meas.}$ (g/cm^3)			3.32–3.42	
$D_{calc.}$ (g/cm^3)	2.509	2.927	3.20	3.041
Strongest lines in the powder pattern: $d_{meas}(I)$	15.161(100), 2.810(19), 3.069(12), 2.938(10), 2.680(9), 1.771(9), 2.618(8)	2.813(100), 2.149(82), 3.938(70), 4.288(44), 2.128(44), 3.127(39), 3.690(36)	24.06(100), 7.05(9), 5.95(97), 3.95(6), 2.828(16), 2.712(19), 2.155(13)	
Optical character	biaxial (–)	biaxial (+)	biaxial (+)	
α	1.669(2)	1.695(2)	1.700(3)	
β	1.701(2)	1.703(3)	1.710(3)	
γ	1.720(3)	1.733(3)	1.734(3)	
$2V_{meas.}$ (°)	73.6(5)	64.8		
$2V_{calc.}$ (°)	74.0	55.4	66.0	
Color	pinkish yellow	colorless to very very pale tan	creamy with grayish, bluish or yellowish shades	
Pleochroism	none observed	none observed	not discernible	
Hardness (Mohs)	3	3	3	

References: (1) This work; (2) Cámara *et al.* (2012); (3) Németh *et al.* (2009); (4) Cámara & Sokolova (2009).

TABLE 2. OPTICAL ORIENTATION (°) FOR KOLSKYITE

	a	**b**	**c**
X	97.8	118.9	22.8
Y	61.6	42.6	68.7
Z	150.4	61.6	82.2

obtained by averaging 100 scans with a resolution of 4 cm^{-1}. Raman spectra in the range 100–1200 cm^{-1} were collected in back-scattered mode with a HORIBA Jobin Yvon-LabRAM ARAMIS integrated confocal micro-Raman system equipped with a 460 mm focal-length spectrograph and a multichannel air-cooled (–70 °C) CCD detector. A magnification of 100× was used with an estimated spot size of ~1 μm, a 1800 gr/mm grating, and a 532 nm excitation laser. The wavenumber was calibrated using the 520.7 cm^{-1} line of elemental Si.

In the FTIR spectrum (Fig. 2a), there is a very broad band centered at ~3300 cm^{-1} and a peak at ~1600 cm^{-1} that are associated with H_2O stretches and H–O–H bends, respectively, indicating the presence of a considerable amount of H_2O in kolskyite. The absorption bands in the 1100–650 cm^{-1} region, dominated by an intense band at ~945 cm^{-1} and a sharp peak at 1038 cm^{-1}, are assigned to Si–O stretching vibrations of the Si_2O_7 groups in the structure of kolskyite. The Si–O stretches in the corresponding Raman spectrum (Fig. 2b) give rise to Raman peaks at 925 (s), 800 (w), and 685 (s) cm^{-1}, the latter may be assigned to stretching vibrations of Si–O–Si bridges. Peaks at 586, 435, and 420 cm^{-1} are assigned to bending vibrations of Si_2O_7 groups and peaks below ~400 cm^{-1} are mainly due to lattice modes. There is an envelope centered at ~1430 cm^{-1} (Fig. 2a) consisting of three distinct components. This may be a set of combination bands involving metal-oxygen deformations, or it may result from intergrown alteration phase(s).

CHEMICAL COMPOSITION

For the chemical analysis, we used a large platy crystal of kolskyite with dimensions 0.01 × 0.17 × 0.20 mm (Fig. 3). The chemical composition of kolskyite was determined with a Cameca SX-100 electron-microprobe in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, a beam size of 10 μm, and count times on peak and background of 20 and 10 s, respectively. The following standards were used: $Ba_2NaNb_5O_{15}$ (Ba, Nb), $SrTiO_3$ (Sr), titanite (Ti,Si), zircon (Zr), diopside (Ca), andalusite (Al), fayalite (Fe), spessartine (Mn), forsterite (Mg), orthoclase (K), albite (Na), and F-bearing riebeckite (F). Tantalum, Zn, Ag, Sn, P, and Cs were sought but not detected. Data were reduced using the 'PAP' procedure of Pouchou & Pichoir (1985). All grains of kolskyite have a very uneven and heterogeneous-looking surface, probably due to alteration. The polished grain used for microprobe analysis showed extreme range in several oxides, especially SiO_2: 22.13–32.60 wt.% (Table 3). The chemical composition of kolskyite was determined using analyses from points 2, 5, 8, and 9 (Fig. 3). We think that variation in content of several oxides is due to the intergrowth of other TS-block minerals, which is common for layered Ti-disilicates (*cf.* TEM of cámaraite, Sokolova *et al.* 2009). We did not have material sufficient for direct determination of H_2O, but the presence of H_2O was confirmed by IR and Raman spectroscopy (see above). H_2O was calculated from the results of the crystal-structure refinement on the basis of OH = 0.40 *pfu* and H_2O = 6.60 *pfu* (per formula unit). The chemical composition of kolskyite is given in Table 3. The empirical formula based on 25 (O + F) atoms *pfu* is $(Na_{1.93}Mn_{0.04}Ca_{0.03})_{\Sigma 2}$ $(Ca_{0.67}Sr_{0.45}Ba_{0.19}K_{0.15})_{\Sigma 1.46}$ $(Ti_{2.93}Nb_{0.46}Mn_{0.33}Mg_{0.17}Fe^{2+}_{0.10}Zr_{0.01})_{\Sigma 4}Si_{4.00}O_{24.67}H_{13.60}F_{0.33}$, $Z = 1$. Simplified and ideal formulae are as follows: $(Ca,\square)_2Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$ and $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$.

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern for kolskyite was recorded using a Bruker D8 Discover SuperSpeed micro-powder diffractometer with a Hi-Star multiwire 2D detector at 15 cm from sample and a modified Gandolfi attachment. Table 4 shows the X-ray powder-diffraction data (for Cu*K*α, λ = 1.54178 Å; 50 kV / 60 mA, two 10-h frames merged, no internal standard used) together with the refined unit-cell dimensions; the latter are in close agreement with corresponding values determined by single-crystal diffraction (Table 5).

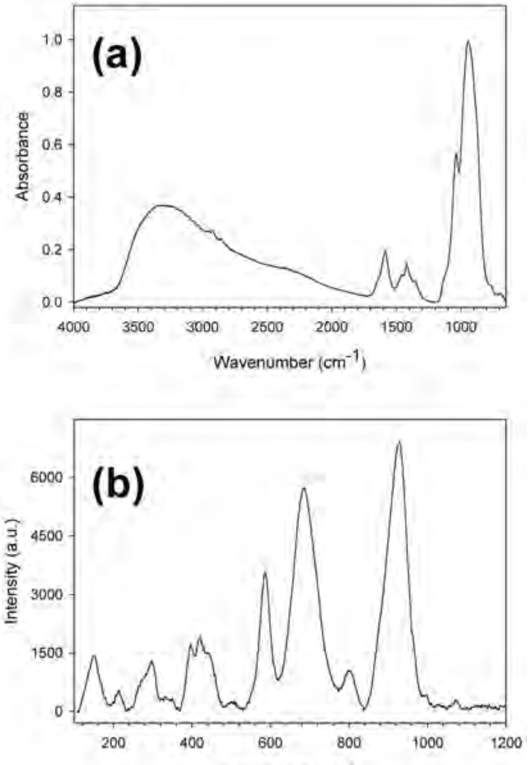

FIG. 2. FTIR (a) and Raman (b) spectra of kolskyite.

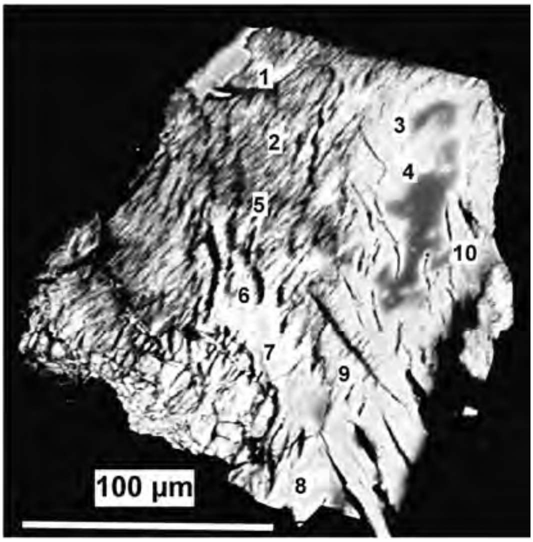

FIG. 3. BSE image of the polished crystal of kolskyite used for the microprobe analysis. Numbers indicate positions of points 1–10 on the surface of the crystal.

CRYSTAL STRUCTURE

X-ray data collection and structure refinement

Single-crystal X-ray diffraction data for kolskyite were collected with a Bruker AXS SMART APEX diffractometer with a CCD detector (Mo$K\alpha$ radiation). The intensities of 8298 reflections with $-6 < h < 6$, $-9 < k < 8$, $-20 < l < 20$ were collected to 60.17° 2θ using 0.2° frame and an integration time of 10 s. The refined unit-cell parameters were obtained from 3802 reflections with $I > 10\sigma I$ (Tables 1, 5), and an empirical absorption correction (SADABS, Sheldrick 2008) was applied. The crystal structure of kolskyite was solved and refined using data up to 54.99° 2θ to an R_1 value of 8.80%, with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 2008). Site-scattering values were refined for the $M^{\mathrm{O}}(1)$ and M^{H} sites with the scattering curve of Nb, $M^{\mathrm{O}}(2)$ site (scattering curve of Na) and A^P site (scattering curve of Sr). For the refinement of the site-scattering at the B^P site partly occupied by cations and H_2O groups, scattering curves of O and Ca were used for two atoms, BW and BCa, respectively, with their coordinates and displacement parameters constrained to be equal. For the last stages of the refinement, site occupancies for BW and BCa were fixed. At the last stages of the refinement, six peaks with magnitudes from 0.84 to 3.8 e/Å^3 were found in the difference-Fourier map, most of these peaks occurring in the space occupied by H_2O groups. Occupancies for peaks $\mathrm{M^H(A)}$ and 1–5 were refined with the scattering curve of Nb and Ba, respectively (the heaviest scatterers, according to Table 3) with U_{iso} fixed at 0.02 Å^2. Refined occupancies of these subsidiary peaks vary from 2 to 7%. Scattering curves for neutral atoms were taken from International Tables for Crystallography (Wilson 1992). Details of data collection and structure refinement are given in Table 5, final atom parameters are given in Table 6, selected interatomic distances in Table 7, refined site-scattering values and assigned populations for selected cation sites are given in Table 8, and bond-valence values in Table 9. A table of structure-factors and a cif file may be obtained from The Depository of Unpublished Data on the MAC website [document Kolskyite CM_921].

TABLE 3. CHEMICAL COMPOSITION AND UNIT FORMULA* FOR KOLSKYITE

Oxide	wt.%	Range	ESD	Formula unit	*apfu*
Nb_2O_5	6.96	6.49 – 7.81	0.51	Si	4.00
ZrO_2	0.12	0.06 – 0.18	0.04		
TiO_2	26.38	23.95 – 28.84	2.15	Na	1.93
SiO_2	27.08	22.13 – 32.60	4.79	Mn^{2+}	0.04
FeO	0.83	0.60 – 1.04	0.19	Ca	0.03
MnO	2.95	2.42 – 3.44	0.41	$\Sigma 2\mathrm{M^O}(2)$	2.00
MgO	0.76	0.60 – 1.10	0.20		
BaO	3.20	2.51 – 3.78	0.45	Ti	2.93
SrO	5.21	4.06 – 6.16	0.95	Nb	0.46
CaO	4.41	3.37 – 5.00	0.64	Mn	0.33
K_2O	0.79	0.48 – 1.29	0.32	Mg	0.17
Na_2O	6.75	6.23 – 7.40	0.42	Fe^{2+}	0.10
H_2O**	13.81			Zr	0.01
F	0.70	0.54 – 0.82	0.10	$\Sigma 2\mathrm{M^H}+2\mathrm{M^O}(1)$	4.00
O = F	–0.29				
Total	99.66			Ca	0.67
				Sr	0.34
				Ba	0.19
				K	0.15
				$\Sigma 2A^P$	1.35
				H_2O	1.80
				Sr	0.11
				ΣB^P+W(3)	1.91
				F	0.33
				OH	0.40
				H_2O	4.80
				O	24.67

*calculated on 25 (O + F) anions
**calculated from structure-refinement results.

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR KOLSKYITE*

$I_{est.}$	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	*h k l*	$I_{est.}$	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	*h k l*
100	15.161	15.343	0 0 1	8	2.595	2.594	$\bar{2}$ 0 2
5	7.625	7.672	0 0 2	4 B	2.493	2.510 **	1 $\bar{1}$ 5
4	6.702	6.694	0 $\bar{1}$ 1			2.499 **	$\bar{1}$ $\bar{2}$ 4
3 Sh	5.505	5.511	0 $\bar{1}$ 2			2.496	$\bar{1}$ 2 3
4	5.382	5.372	1 0 0	1 B	2.318	2.319	0 1 6
6	4.272	4.286	$\bar{1}$ 1 0	1 B	2.278	2.278	$\bar{2}$ 0 4
4	4.124	4.114	$\bar{1}$ 1 1	2 B	2.190	2.191 **	1 2 4
5	3.920	3.937	$\bar{1}$ $\bar{1}$ 2			2.192	1 $\bar{2}$ 5
4	3.845	3.845 **	$\bar{1}$ 0 3			2.192 **	0 0 7
		3.836	0 0 4			2.192 **	0 $\bar{2}$ 6
6 B	3.516	3.518 **	0 $\bar{2}$ 1	5 B	2.144	2.144	$\bar{2}$ $\bar{2}$ 1
		3.517 **	0 2 0			2.143	$\bar{2}$ 2 0
		3.495 **	$\bar{1}$ $\bar{1}$ 3	7 B	2.062	2.071 **	2 2 1
4 B	3.287	3.306 **	1 $\bar{1}$ 3			2.071 **	2 $\bar{2}$ 2
		3.264 **	$\bar{1}$ 1 3			2.058	$\bar{2}$ $\bar{2}$ 3
		3.215 **	0 1 4			2.057 **	$\bar{2}$ 2 2
12	3.069	3.067	0 0 5	2 B	1.982	1.977 **	0 $\bar{3}$ 5
10	2.938	2.955 **	$\bar{1}$ $\bar{2}$ 1	2 B	1.929	1.944 **	1 $\bar{3}$ 4
		2.932 **	1 2 0	9	1.771	1.771	0 $\bar{4}$ 1
		2.932	1 $\bar{2}$ 1			1.759 **	0 4 0
19	2.810	2.811	1 2 1	3B	1.653	1.652	1 2 7
		2.811	1 $\bar{2}$ 2			1.652 **	1 $\bar{2}$ 8
9	2.680	2.707 **	$\bar{1}$ $\bar{2}$ 3			1.640 **	3 $\bar{1}$ 4
		2.686 **	2 0 0	7	1.600	1.601	$\bar{3}$ $\bar{2}$ 1
		2.684 **	1 1 4			1.601	$\bar{3}$ 2 0
		2.679	$\bar{2}$ 0 1			1.591 **	3 2 0
8	2.618	2.624 **	1 $\bar{2}$ 3				
		2.623	1 2 2				

* Indexed on a = 5.386(4), b = 7.082(5), c = 15.486(14) Å, α = 96.61(8), β = 94.10(10), γ = 89.97(6)°, V = 585.2(6)Å^3; B = broad reflection; Sh = shoulder;

** = not used in the refinement; $d_{meas.}$ values are the observed powder lines; $d_{calc.}$ and *h k l* values are from the powder pattern calculated from single-crystal data.

Site-population assignment

Here we divide the cation sites (Table 6) into 3 groups: M^O sites of the O sheet, M^H and Si sites of the H sheet, and peripheral A^P and B^P sites; site labeling is in accord with Sokolova (2006). Consider first the Ti-dominant sites. We assign cations to these sites based on our knowledge from previous work on Ti-disilicate minerals: (1) Ti-dominant sites are always fully occupied; (2) Ti-dominant sites in the O sheet can have a significant content of Mn as in another Group-IV mineral sobolevite, $Na_{12}Ca(NaCaMn)Ti_2(TiMn)(Si_2O_7)_2(PO_4)_4O_3F_3$ (Sokolova *et al.* 2005). Table 3 shows that the Ti-dominant M^H and $M^O(1)$ sites are occupied by (2.93 Ti + 0.46 Nb + 0.33 Mn + 0.17 Mg + 0.10 Fe^{2+} + 0.01 Zr) *apfu*, with an aggregate scattering of 96.61 *epfu* (electrons per formula unit), and the total refined scattering at these sites (100.6 *epfu*, Table 8) is in reasonable accord with this composition. The refined site-scattering value at the M^H site is slightly higher, 51.5 *epfu*, than that at $M^O(1)$ site, 49.1 *epfu*, indicating that more of the heavier atoms, specifically Nb, must be assigned to the M^H site. The mean bond-length for the $M^O(1)$ site is larger than that for the M^H site, 2.043 > 1.955 Å (Tables 7, 8), and we assign more Mn (r = 0.83 Å, Shannon 1976) and all Fe^{2+} (r = 0.78 Å) to the $M^O(1)$ site: 1.56 Ti + 0.23 Mn + 0.10 Nb + 0.10 Fe^{2+} + 0.01 Zr [*cf.* $M^O(3)$: 0.80 Ti + 0.49 Mn + 0.42 Mg + 0.20 Nb + 0.09 Zr and $M^O(4)$: 0.94 Ti + 0.45 Mn + 0.32 Mg + 0.29 Nb in sobolevite]. There is a good match between the observed and calculated site-scattering values for the M^H and $M^O(1)$ sites (Table 8).

The refined scattering for the alkali-cation $M^O(2)$ site in the O sheet is 23.8 *epfu*, and this tells us that Na is the dominant cation species at this site. Hence to the $M^O(2)$ site, we assign 1.93 Na + 0.04 Mn + 0.03 Ca = 2 *apfu*, with a total scattering of 22.83 *epfu*. The occurrence of both Na and Mn^{2+} at one site is fairly common in Ti-disilicate minerals; it has been previously described for the other Group-IV minerals quadruphite, $Na_{14}Ca_2Ti_4(Si_2O_7)_2(PO_4)_4O_4F_2$ (Sokolova & Hawthorne

2001), and polyphite, $Na_{10}(Na_4Ca_2)_2Ti_4(Si_2O_7)_2(PO_4)_6O_4F_4$ (Sokolova *et al*. 2005).

Consider last the peripheral A^P and B^P sites, with refined site-scattering values of 40.4 and 12.8 *epfu*, respectively, summing to 53.20 *epfu* (Table 8). The cations to be assigned to these sites are 0.67 Ca + 0.45 Sr + 0.19 Ba + 0.15 K (Table 3), with a total scattering 43.99 *epfu*. We suggest that the excess of the refined site-scattering of 9.21 *epfu* is due to the presence of H_2O groups at the B^P site and assign 1.10 H_2O *pfu* to the B^P site (Table 8). This assignment of H_2O groups is in accord with the occurrence of the B^P site fully occupied by H_2O groups in the crystal structures of nechelyustovite, $Na_4Ba_2Mn_{1.5}\square_{2.5}Ti_5Nb(Si_2O_7)_4O_4(OH)_3F(H_2O)_6$ (Cámara & Sokolova 2009) and kazanskyite, $Ba\square Na_3Ti_2Nb(Si_2O_7)_2O_2(OH)_2(H_2O)_4$ (Cámara *et al*. 2012) (see comparison of kolskyite, kazanskyite, and nechelyustovite below). We add 0.11 Sr *apfu* to the B^P site to achieve an exact match between refined and calculated site-scattering values, 12.80 *epfu* (Table 8). We chose not to assign 0.21 Ca instead of 0.11 Sr *apfu* to the B^P site, as it would agree less with the short-range-order arrangements of H_2O groups around the A^P site (see below). We assigned the rest of the cations, 0.67 Ca + 0.34 Sr + 0.19 Ba + 0.15 K, with total of 1.35 *apfu*, to the A^P site. Therefore at the A^P and B^P sites, Ca and H_2O are dominant species, respectively (Table 8).

Description of the structure

Site nomenclature. As stated above, the cation sites are divided into 3 groups: M^O sites of the O sheet, M^H and *Si* sites of the H sheet, and peripheral A^P and B^P sites. Also in accord with Sokolova (2006), we label the X anions as follows: X^O_M = anion at the common vertex of four polyhedra, 3 M^O and M^H; X^O_A = anion at the common vertex of four polyhedra, 3 M^O and A^P,

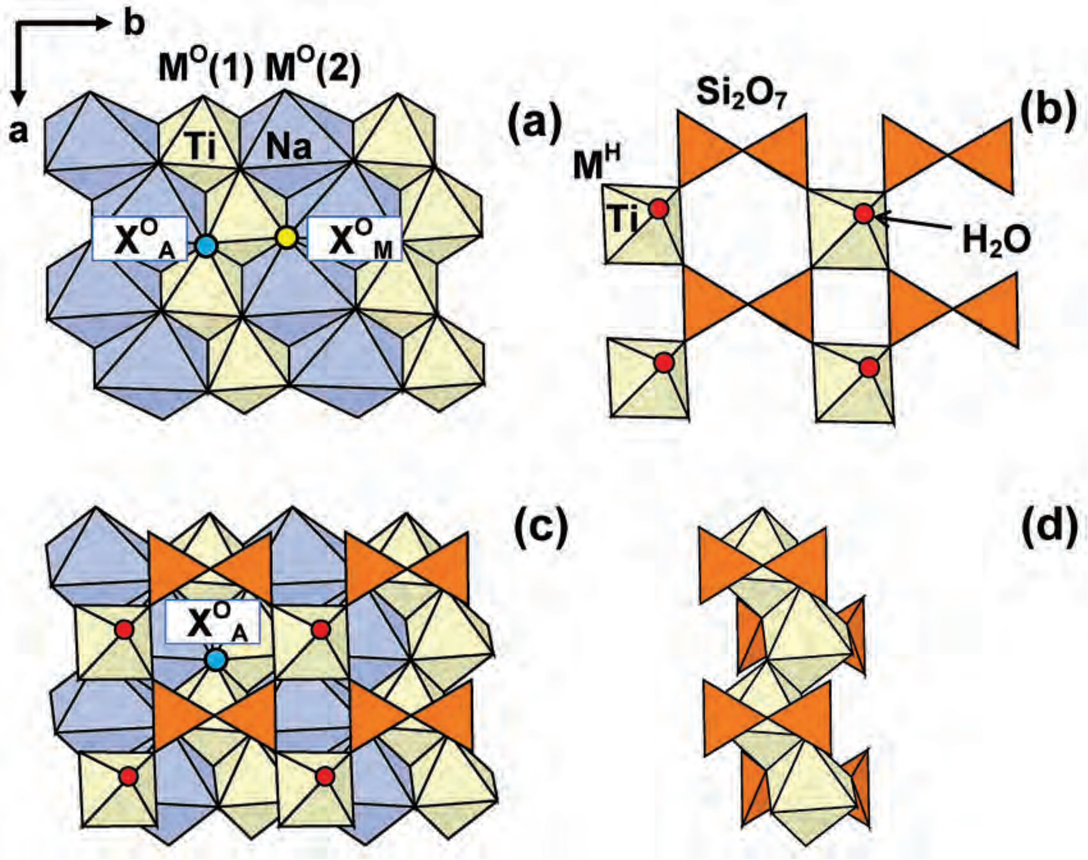

FIG. 4. The details of the TS block in the crystal structure of kolskyite: the close-packed octahedral (O) sheet (a); the heteropolyhedral (H) sheet (b); linkage of H and O sheets in the TS block (c); linkage 3 (Group IV): Si_2O_7 groups of two H sheets link to Ti octahedra adjacent along **a** (d); SiO_4 tetrahedra are orange, Ti-dominant and Na-dominant octahedra are yellow and navy blue, respectively; O atoms at the X^O_M and X^O_A sites are shown as pale-blue and yellow spheres.

where A^{P}–$\mathrm{X^{O}_{A}} \leq 3$ Å, or at the common vertex of three $\mathrm{M^{O}}$ octahedra where A^{P}–$\mathrm{X^{O}_{A}} > 3$ Å, and hence the $\mathrm{X^{O}_{A}}$ anion does not coordinate the A^{P} atom; $\mathrm{X}^{P} = \mathrm{X}^{P}_{\mathrm{M}}$, $\mathrm{X}^{P}_{\mathrm{A}}$, and $\mathrm{X}^{P}_{\mathrm{B}}$ = apical anions of $\mathrm{M^{H}}$, A^{P}, and B^{P} cations at the periphery of the TS block.

Cation sites. In the crystal structure of kolskyite, there is one TS block composed of HOH sheets. We will describe the cation sites of the O sheet, H sheets, and peripheral A^{P} and B^{P} sites.

In the O sheet, there are two [6]-coordinated cation sites: the Ti-dominant $M^{\mathrm{O}}(1)$ site and the Na-dominant $M^{\mathrm{O}}(2)$ site (Fig. 4a). The $M^{\mathrm{O}}(1)$ site is occupied by 1.56 Ti + 0.23 Mn + 0.10 Nb + 0.10 Fe^{2+} + 0.01 Zr *apfu*, and is coordinated by five O atoms and the $\mathrm{X^{O}_{A}}$ anion [$\mathrm{X^{O}_{A}} = \mathrm{O_{0.835}F_{0.165}}$, see section *Anion considerations* below] with a $\langle\mathrm{M^{O}}(1)$–$\phi\rangle$ distance of 2.043 Å (ϕ = unspecified anion) (Tables 7, 8). The $M^{\mathrm{O}}(2)$ site is occupied mainly by Na (Table 8) and is coordinated by six O atoms, with a $\langle\mathrm{M^{O}}(2)$–$\mathrm{O}\rangle$ distance of 2.431 Å. For the O sheet, the total of the $4\mathrm{M^{O}}$ cations is $[(\mathrm{Na_{1.93}Mn_{0.04}Ca_{0.03}})(\mathrm{Ti_{1.56}Mn_{0.23}Nb_{0.10}Fe^{2+}_{0.10}Zr_{0.01}})]_{\Sigma 4}$, with an ideal composition of $\mathrm{Na_2Ti_2}$ *apfu*.

In the H sheet, there are two tetrahedrally coordinated sites occupied by Si with a $\langle\mathrm{Si}$–$\mathrm{O}\rangle$ distance of 1.614 Å (Table 7, Fig. 4b). The [6]-coordinated M^{H} site is occupied by 1.37 Ti + 0.36 Nb + 0.17 Mg + 0.10 Mn *apfu* (Table 8) and is coordinated by five O atoms and an $\mathrm{H_2O}$ group at the $\mathrm{X}^{P}_{\mathrm{M}}$ site, with $\langle\mathrm{M^{H}}$–$\phi\rangle = 1.955$ Å, a short $\mathrm{M^{H}}$–$\mathrm{X^{O}_{M}}$ distance of 1.839, and a long $\mathrm{M^{H}}$–$\mathrm{X}^{P}_{\mathrm{M}}$ distance of 2.143 Å (Table 7), in accord with the structure topology of Group-IV minerals (Sokolova 2006, her Fig. 31). For the H sheet, the total of $2\mathrm{M^{H}}$ cations is ideally $\mathrm{Ti_2}$ *apfu*.

TABLE 5. MISCELLANEOUS REFINEMENT DATA FOR KOLSKYITE

a (Å)	5.387(1)
b	7.091(1)
c	15.473(3)
α (°)	96.580(4)
β	93.948(4)
γ	89.818(4)
V (Å^3)	585.8(3)
Space group	$P\bar{1}$
Z	1
Absorption coefficient (mm^{-1})	3.30
F(000)	433.4
$D_{\mathrm{calc.}}$ (g/cm^3)	2.509
Crystal size (mm)	0.30 × 0.14 × 0.02
Radiation/filter	Mo$K\alpha$/graphite
2θ-range for structure refinement (°)	3.22 – 55.00
R(int) (%)	3.96
Reflections collected	8298
Independent reflections	2667
$F_o > 4\sigma F$	2424
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to 1/σF_o^2
No. of refined parameters	226
Final $R_{\mathrm{(obs)}}$ (%) [$F_o > 4\sigma F$]	8.80
R_1	9.52
wR_2	20.83
Highest peak, deepest hole (e Å^{-3})	+1.32 –1.38
Goodness of fit on F^2	1.284

In kolskyite, there are two peripheral A^{P} and B^{P} sites. The A^{P} site is occupied by $\mathrm{Ca_{0.67}Sr_{0.34}Ba_{0.19}K_{0.15}\square_{0.65}}$ *pfu*, *i.e.*, at 68%. It is coordinated by six O atoms and four $X^{P}_{\mathrm{A}}(1$–$4)$ sites, each occupied by $\mathrm{H_2O}$ groups at 16% (Tables 6, 7), hence taking into account four A^{P}–X^{P}_{A} distances weighted by their occupancies [68%-occupancy of the A^{P} site : 16%-occupancy of the X^{P}_{A} sites ≈ 4 : 1], the A^{P} site is [7]-coordinated by six O atoms and one aggregate $\mathrm{H_2O}$ group (4 × ¼), with $\langle\mathrm{A}^{P}$–$\phi\rangle = 2.79$ Å. Cations at the A^{P} site sum to 1.35 *apfu*, Ca is the dominant cation species, and we write simplified and ideal compositions of the A^{P} site as $(\mathrm{Ca},\square)$ and $(\mathrm{Ca}\square)$, respectively. The B^{P} site is occupied by $(\mathrm{H_2O})_{1.10}\mathrm{Sr_{0.11}}\square_{0.79}$ *pfu* (Table 8). Where the B^{P} site is occupied by Sr, it is [9]-coordinated by four O atoms, mainly $\mathrm{H_2O}$ groups at the X^{P}_{M}, $X^{P}_{\mathrm{A}}(1,4)$, and X^{P}_{B} sites, with $\langle\mathrm{B}^{P}$–$\phi\rangle = 2.73$ Å. The ideal composition of the B^{P} site is $[(\mathrm{H_2O})\square]$ *pfu*.

We write the cation part of the ideal structural formula as the sum of (1) the peripheral A^{P} and B^{P} sites + (2) two H sheets + (3) the O sheet: (1) $[(\mathrm{Ca}\square)(\mathrm{H_2O})\square]$ + (2) $\mathrm{Ti_2}$ + (3) $\mathrm{Na_2Ti_2} = (\mathrm{Ca}\square)[(\mathrm{H_2O})\square]\mathrm{Ti_2Na_2Ti_2}$, with a total charge of 20^{+}.

Anion considerations. There are 7 anion sites, O(1–7), occupied by O atoms which form the tetrahedral coordination of the Si atoms and have bond-valence sums of 2.12–1.84 *vu* (valence units) (Tables 6, 7, 9). An anion common to the $\mathrm{M^{H}}$ octahedron and three octahedra of the O sheet occurs at the $X^{\mathrm{O}}_{\mathrm{M}}$ site (Table 7, Figs. 4a, 4c), it receives bond valences of 1.90 *vu* (Table 9) and hence is an O atom (Table 6). The anion at the $X^{\mathrm{O}}_{\mathrm{A}}$ site is coordinated by three $\mathrm{M^{O}}$ cations of the O sheet, 2 $\mathrm{M^{O}}(1)$ and $\mathrm{M^{O}}(2)$ (Figs. 4a, 4c). The $\mathrm{X^{O}_{A}}$ anion receives bond valence of 1.43 *vu* (Table 9) and we assign $\mathrm{O_{1.67}F_{0.33}}$ *apfu* to the $X^{\mathrm{O}}_{\mathrm{A}}$ site, with an aggregate charge of 1.835^{-} per 1 *apfu*. Occurrence of F at this site is quite common in Group-IV minerals and correlates with the content of divalent cations at the $M^{\mathrm{O}}(1)$ site; *cf*. sobolevite (Sokolova *et al*. 2005) and lomonosovite, $\mathrm{Na_{10}Ti_4(Si_2O_7)_2(PO_4)_2O_4}$ (Cámara *et al*. 2008). In kolskyite, 0.33 F *apfu* correlates with (0.23 Mn + 0.10 Fe^{2+}) *apfu* at the $M^{\mathrm{O}}(1)$ site (Table 8). There is a difference of 0.405^{-} between the aggregate charge of this anion and the incident bond-valence sum (Table 9). The latter difference is probably due to the difference of 0.47^{+} between the aggregate charge of this anion and the incident bond-valence sum for the $\mathrm{M^{O}}(1)$ cation (Table 9). Low incident bond-valence sums for the $M^O(1)$ cation have been observed in several TS-block minerals, and we suggest that it results from the adjacent positions of a small Ti atom and a large Na atom in the O sheet; as a result, Ti *rattles* in its octahedron (too large for Ti), which shares edges with the neighboring Na octahedron (Figs. 4a, 4c). Ideally, the X^O_A site gives O_2 *apfu*. There are six X^P anions. The X^P_M is an apical anion for the M^H cation (Tables 6, 7); it receives bond valence of 0.41 *vu* from the M^H cation and 0.02 *vu* from two B^P cations, where the B^P site is occupied by Sr at ~6% (Table 9), and is mainly an H_2O group. However, an OH group occurs at X^P_M site associated with the short-range-ordered arrangement of the B^P sites fully occupied by Sr plus hydrogen bonding from the H_2O groups at the *W*(1) and *W*(3) sites (Table 10). Hence we assign $(H_2O)_{1.60}(OH)_{0.40}$ *pfu* to the X^P_M site, ideally $(H_2O)_2$ *pfu*. There are five $X^P_{(A+B)}$ anions occupied by H_2O groups at 16% (Tables 6, 9). The occupancies of the four $X^P_A(1–4)$ anions sum to 16 × 4 = 64% ≈ 68%-occupancy of the A^P site, and it is possible that the four $X^P_A(1–4)$ anions alternatively coordinate the A^P cation. The X^P_B anion coordinates the B^P cation (Table 7). The five $X^P_{(A+B)}$ anions give $(H_2O)_{1.60}$ *pfu*, ideally $(H_2O)_2$ *pfu*. The three *W*(1–3) sites are partly occupied by H_2O groups which are not bonded to any cation (Table 6). The *W*(1–3) sites give $(H_2O)_{1.60}$ *pfu*, ideally $(H_2O)_2$ *pfu*. Note that the *W*(3) and B^P sites (see above) are very close, 0.64 Å, and we write their aggregate composition as $[(H_2O)_{0.70}\square_{1.30}]$ [W(3)] + $[(H_2O)_{1.10}Sr_{0.11}\square_{0.79}]$ $[B^P]$ = $[(H_2O)_{1.80}Sr_{0.11}]$ *pfu* $[B^P$ + W(3)] (Table 3). The anions and H_2O groups at the two X^P_M, five $X^P_{(A+B)}$ and three *W*(1–3) sites ideally sum to $(H_2O)_2 + (H_2O)_2 + (H_2O)_2 = (H_2O)_6$ *pfu*.

TABLE 6. ATOM COORDINATES AND EQUIVALENT* DISPLACEMENT PARAMETERS FOR KOLSKYITE

Atom	Anion specification	Site occ.(%)	*x*	*y*	*z*	U_{eq} (Å^2)
$M^O(1)$		100	0.2267(3)	0.38225(19)	0.49412(10)	0.0188(5)
$M^O(2)$		100	0.2412(7)	0.8823(5)	0.4941(3)	0.0240(14)
M^H		100	0.0568(2)	0.09422(18)	0.29925(15)	0.0143(6)
Si(1)		100	0.5703(4)	0.8111(3)	0.33161(16)	0.0113(6)
Si(2)		100	0.5537(4)	0.3788(3)	0.32064(16)	0.0100(5)
A^P		68	0.0384(4)	0.5778(3)	0.2204(2)	0.0347(10)
B^P	0.55 H_2O + 0.055 Sr + 0.395 □	61	0.5321(14)	0.0508(12)	0.1609(6)	0.0202(16)
O(1)	O	100	0.6028(14)	0.8164(10)	0.4354(5)	0.0249(16)
O(2)	O	100	0.5558(13)	0.5904(9)	0.2885(5)	0.0209(15)
O(3)	O	100	0.3130(14)	0.9019(11)	0.2994(5)	0.0301(18)
O(4)	O	100	0.2996(12)	0.2830(9)	0.2760(5)	0.0208(15)
O(5)	O	100	0.8100(14)	0.8977(11)	0.2937(5)	0.0292(17)
O(6)	O	100	0.5547(12)	0.3991(9)	0.4261(4)	0.0152(13)
O(7)	O	100	0.7949(13)	0.2764(10)	0.2810(5)	0.0225(15)
X^O_M	O	100	0.0840(13)	0.1614(11)	0.4179(4)	0.0240(16)
X^O_A	0.835 O + 0.165 F	100	0.0542(12)	0.5825(8)	0.4329(4)	0.0147(13)
X^P_M	0.80 H_2O + 0.20 OH	100	0.0323(17)	0.0338(12)	0.1601(6)	0.037(2)
$X^P_A(1)$	0.16 H_2O + 0.84 □	16	0.832(11)	0.336(8)	0.091(4)	0.042(13)
$X^P_A(2)$	0.16 H_2O + 0.84 □	16	0.250(12)	0.692(9)	0.088(4)	0.048(15)
$X^P_A(3)$	0.16 H_2O + 0.84 □	16	0.754(13)	0.711(9)	0.093(4)	0.049(15)
$X^P_A(4)$	0.16 H_2O + 0.84 □	16	0.236(12)	0.340(9)	0.086(4)	0.050(15)
X^P_B	0.16 H_2O + 0.84 □	16	0.568(15)	0.717(11)	0.094(5)	0.063(18)
W(1)	0.30 H_2O + 0.70 □	30	0.153(6)	0.993(5)	0.001(2)	0.047(8)
W(2)	0.50 H_2O + 0.50 □	50	0.714(3)	0.500(3)	–0.0023(12)	0.039(4)
W(3)	0.35 H_2O + 0.65 □	35	0.528(4)	0.042(3)	0.1190(17)	0.022(5)
Subsidiary peaks**						
			0.031(9)	0.081(7)	0.254(5)	0.02
$M^H(A)$						
1			0.817(5)	0.114(3)	0.0964(16)	0.02
2			0.220(5)	0.116(4)	0.0961(17)	0.02
3			0.222(5)	0.940(3)	0.0951(16)	0.02
4			0.815(4)	0.942(3)	0.0978(14)	0.02
5			0.0495(17)	0.5882(13)	0.2747(8)	0.02

*U_{iso} for $X^P_A(1–4)$, W(1–3)

** for subsidiary peaks, U_{iso} = 0.02 Å^2 (fixed)

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR KOLSKYITE*

M^{O}(1)–(X$^{O}_{A}$)a	1.948(6)	M^{O}(2)–O(1)	2.232(8)	M^{H}–X$^{O}_{M}$	1.839(7)
M^{O}(1)–X$^{O}_{M}$	1.974(8)	M^{O}(2)–(X$^{O}_{M}$)a	2.334(8)	M^{H}–O(5)e	1.920(7)
M^{O}(1)–X$^{O}_{A}$	1.989(6)	M^{O}(2)–O(1)c	2.410(8)	M^{H}–O(3)f	1.937(7)
M^{O}(1)–O(1)b	2.055(8)	M^{O}(2)–X$^{O}_{A}$	2.419(7)	M^{H}(2)–O(7)g	1.938(7)
M^{O}(1)–O(6)	2.128(7)	M^{O}(2)–(X$^{O}_{M}$)d	2.532(8)	M^{H}–O(4)	1.954(7)
M^{O}(1)–O(6)b	2.165(6)	M^{O}(2)–O(6)b	2.660(7)	M^{H}–X$^{P}_{M}$	2.143(9)
<M^{O}(1)–ϕ>	2.043	<M^{O}(2)–ϕ>	2.431	<M^{H}–ϕ>	1.955
		Si(1)–O(3)	1.599(7)	Si(2)–O(4)	1.606(7)
		Si(1)–O(1)	1.600(7)	Si(2)–O(7)	1.610(7)
		Si(1)–O(5)	1.606(7)	Si(2)–O(6)	1.622(5)
		Si(1)–O(2)	1.629(7)	Si(2)–O(2)	1.635(7)
		<Si(1)–O>	1.609	<Si(2)–O>	1.618
Si(1)–O(2)–Si(2)	138.5(5)				
A^{P}–X$^{P}_{A}$(2)	2.62(6)	B^{P}–(X$^{P}_{B}$)f	2.49(8)		
A^{P}–X$^{P}_{A}$(1)g	2.66(6)	B^{P}–O(7)	2.64(1)		
A^{P}–X$^{P}_{A}$(3)g	2.67(7)	B^{P}–O(4)	2.66(1)		
A^{P}–O(4)	2.706(7)	B^{P}–X$^{P}_{M}$	2.69(1)		
A^{P}–O(5)g	2.744(8)	B^{P}–(X$^{P}_{M}$)h	2.70(1)		
A^{P}–X$^{P}_{A}$(4)	2.79(6)	B^{P}–O(5)f	2.78(1)		
A^{P}–O(7)g	2.796(8)	B^{P}–O(3)f	2.82(1)		
A^{P}–O(3)	2.844(8)	B^{P}–X$^{P}_{A}$(4)	2.89(7)		
A^{P}–O(2)g	2.869(8)	B^{P}–X$^{P}_{A}$(1)	2.94(6)		
A^{P}–O(2)	2.909(7)	<B^{P}–ϕ>	2.73		
<A^{P}–ϕ>	2.79				

*ϕ = O, OH, F, H_2O; B^{P} = Sr; A^{P}–X$^{P}_{A}$(1–4) distances are weighted by 1/4 [68%-occupancy of the *A*^{P} site : 16%-occupancy of the *X*$^{P}_{A}$ sites ≈ 4 : 1].

a: –*x*, –*y*+1, –*z*+1; b: –*x*+1, –*y*+1, –*z*+1; c: –*x*+1, –*y*+2, –*z*+1; d: *x*, *y*+1, *z*; e: *x*–1, *y*–1, *z*; f: *x*, *y*–1, *z*; g: *x*–1, *y*, *z*; h: *x*+1, *y*, *z*.

TABLE 8. REFINED SITE-SCATTERING AND ASSIGNED SITE-POPULATIONS FOR KOLSKYITE

Site*	Refined site-scattering (*epfu*)	Assigned site-population (*apfu*)	Calculated site-scattering (*epfu*)	<X–ϕ>$_{\mathrm{obs.}}$ (Å)
M^{H}	51.5(2)	1.37 Ti + 0.36 Nb + 0.17 Mg + 0.10 Mn	49.44	1.955
M^{O}(1)	49.1(5)	1.56 Ti + 0.23 Mn + 0.10 Nb + 0.10 Fe^{2+} + 0.01 Zr	47.17	2.043
M^{O}(2)	23.8(4)	1.93 Na + 0.04 Mn + 0.03 Ca	22.83	2.431
$^{[7]}$A^{P}**	40.4(6)	0.67 Ca + 0.34 Sr + 0.19 Ba + 0.15 K + 0.65 □	39.98	2.79
$^{[9]}$B^{P} ***	12.8	1.10 H_2O + 0.11 Sr + 0.79 □	12.80	2.73

* Coordination number is given only for non-[6]-coordinated sites

** Calculated by summing constituent ionic radii; values from Shannon (1976); X = cation; ϕ = O, OH, F, H_2O

*** Site scattering was refined, adjusted in accord with chemical analysis (Table 2), and then fixed at the last stages of the refinement (see discussion in text).

We write the anion part of the ideal structural formula as the sum of the anion sites: O_{14} (O atoms of Si_2 tetrahedra) + O_2 [X^{O}_{M}] + O_2 [X^{O}_{A}] + $(H_2O)_6$ [$(X^{P}_{M})_2$ + $(X^{P}_{[A+B]})_5$ + *W*(1–3)]. We consider an Si_2O_7 group as a complex oxyanion and write the anion part of the ideal structural formula as $(Si_2O_7)_2O_4(H_2O)_6$ with a total charge of 20^{-}.

Ideal formula of kolskyite

Based on the SREF results and bond-valence calculations, we write the ideal structural formula of kolskyite as the sum of the cation and anion components: $(\mathrm{Ca}\square)\mathrm{Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7}$, space group $P\bar{1}$, $Z = 1$. The validity of the ideal formula is supported by the good agreement between the total charges for cations in the ideal and empirical formulae: 4^+ $[(\mathrm{Ca}\square)\mathrm{Na_2}]$ $+16^+$ $[\mathrm{Ti_4}]$ $= 20^+$ *versus* 4.84^+ $[(\mathrm{Ca_{0.67}Sr_{0.45}Ba_{0.19}K_{0.15}}\square_{0.65})$ + $(\mathrm{Na_{1.93}Mn_{0.04}Ca_{0.03}})]$ + 15.26^+ $[\mathrm{Ti_{2.93}Nb_{0.46}Mn_{0.33}Mg_{0.17}Fe^{2+}_{0.10}Zr_{0.01}}]$ = 20.10^+.

Structure topology

The TS block. In the Ti-disilicate minerals (Sokolova 2006), the TS block consists of HOH sheets where H is a heteropolyhedral sheet including $\mathrm{Si_2O_7}$ groups, and O is a trioctahedral close-packed sheet. In kolskyite, there is one unique TS block which consists of HOH sheets (Fig. 4). The O sheet comprises $\mathrm{M^O}(1)$ and $\mathrm{M^O}(2)$ octahedra, each of which forms a brookite-like chain along **a** (Fig. 4a). In the H sheet, $\mathrm{Si_2O_7}$ groups and Ti-dominant $\mathrm{M^H}$ octahedra share common vertices to form the sheet (Fig. 4b). The peripheral A^P and B^P sites are shifted from the plane of the H sheet into the intermediate space between two TS blocks and will be considered as part of the **I** block (see below). The H and O sheets link *via* common vertices of $\mathrm{M^H}$, Si, and $\mathrm{M^O}$ polyhedra (Fig. 4c). In kolskyite, the TS block exhibits linkage 3 and a stereochemistry typical of Group IV where Ti (+ Mg + Mn) = 4 *apfu*: $\mathrm{Si_2O_7}$ groups of two H sheets link to two Ti-dominant $\mathrm{M^O}(1)$ octahedra adjacent along **a** (Fig. 4d).

*The **I** block.* In kolskyite, the TS blocks alternate with intermediate (**I**) blocks. The **I** block is composed mainly of $\mathrm{H_2O}$ groups and two **I** layers ($m = 2$) of cations (mainly Ca) at the 68% occupied A^P sites (Fig. 4b). The two **I** layers of A^P atoms are parallel to (001) and are related by an inversion center. There are two types of $\mathrm{H_2O}$ groups in the **I** block, bonded and nonbonded to cations. $\mathrm{H_2O}$ groups at the X^P_M, X^P_A, and X^P_B sites are ligands of $\mathrm{M^H}$, A^P, and B^P cations (Table 7). The X^P_M and $X^P_{\mathrm{A}(1\text{–}4)}$ + X^P_B sites are occupied at 100 and 16%, respectively, ideally giving $\mathrm{(H_2O)_4}$ *pfu* (see above). The 65%-vacant $W(3)$ and 39%-vacant B^P sites

TABLE 9. BOND-VALENCE* VALUES FOR KOLSKYITE

Atom	Si(1)	Si(2)	$\mathrm{M^O}(1)$	$\mathrm{M^O}(2)$	$\mathrm{M^H}$	A^P	B^P(Sr)	Σ
O(1)	1.06		0.51	0.25 0.18				2.00
O(2)	0.98	0.97				0.09 0.08		2.12
O(3)	1.06				0.69	0.09	0.01	1.85
O(4)		1.04			0.66	0.13	0.01	1.84
O(5)	1.04				0.73	0.12	0.01	1.90
O(6)		1.00	0.43 0.39	0.12				1.94
O(7)		1.03			0.69	0.10	0.01	1.84
$\mathrm{X^O_M}$			0.63	0.21 0.15	0.91			1.90
$^{[3]}\mathrm{X^O_A}$			0.68 0.61	0.18				1.47
$^{[1]}\mathrm{X}^P_\mathrm{M}$					0.41		0.01 0.01	0.43
$^{[1]}\mathrm{X}^P_\mathrm{A}$ (1)						$0.22\downarrow^{1/4}$	<0.01	0.22
$^{[1]}\mathrm{X}^P_\mathrm{A}$ (2)						$0.24\downarrow^{1/4}$		0.24
$^{[1]}\mathrm{X}^P_\mathrm{A}$ (3)						$0.21\downarrow^{1/4}$		0.21
$^{[1]}\mathrm{X}^P_\mathrm{A}$ (4)						$0.16\downarrow^{1/4}$	<0.01	0.16
$^{[1]}\mathrm{X}^P_\mathrm{B}$							0.02	0.02
Total	4.14	4.04	3.25	1.09	4.09	0.82	0.08	
Aggregate charge	4.00	4.00	3.72	1.04	3.91	1.28	0.11	

*Bond-valence parameters (*vu*) are from Brown (1981); coordination numbers are shown for non-[4]-coordinated anions; $\mathrm{H_2O}$ groups at the X^P sites are bonded each to one cation; the X^P_M site is occupied by $\mathrm{H_2O}$ groups (80%) and OH groups (20%); where the X^P_M site is occupied by OH groups, the OH group is bonded to three cations (see text).

** the X^P_M site is [1]-coordinated at 80%.

TABLE 10. THE O–O DISTANCES (Å) FOR H_2O GROUPS IN THE **I** BLOCK IN KOLSKYITE*

	X^P_M	$X^P_A(1)$	$X^P_A(2)$	$X^P_A(3)$	$X^P_A(4)$	X^P_B	$B^P(H_2O)$	W(1)	W(2)	W(3)
X^P_M					2.82(7)		2.69(1)			2.79(2)
X^P_M a			2.84(6)					2.58(3)		
X^P_M c		2.69(6)					2.70(1)			2.75(3)
X^P_M g								2.60(3)		
$X^P_A(1)$				2.69(9)	3.21(9)	3.04(10)	2.94(6)		$\underline{2.02(6)}$	2.75(6)
$X^P_A(2)$				2.71(9)	2.50(9)	$\underline{1.71(10)}$		2.69(7)	3.17(7)	
$X^P_A(2)$b							3.03(6)			2.88(7)
$X^P_A(2)$e		2.76(9)							$\underline{1.81(7)}$	
$X^P_A(3)$			2.71(9)			$\underline{1.00(9)}$			$\underline{1.98(7)}$	
$X^P_A(3)$d		2.69(9)	2.69(9)							
$X^P_A(3)$b							2.81(7)			2.65(7)
$X^P_A(3)$f	2.80(7)									
$X^P_A(4)$			2.50(9)			3.20(10)	2.89(7)			
$X^P_A(4)$c		$\underline{2.18(9)}$								2.70(7)
$X^P_A(4)$e				2.76(9)		3.04(10)			$\underline{1.86(7)}$	
X^P_B b							2.49(8)			$\underline{2.31(8)}$
W(1)b	2.58(3)				2.68(7)		3.09(2)			2.63(4)
W(1)e		2.59(7)					3.11(3)			2.61(4)
W(1)j				2.75(7)		3.11(8)				
W(1)i								$\underline{1.65(7)}$		
W(2)		$\underline{2.02(6)}$	3.17(7)	$\underline{1.98(7)}$		$\underline{2.20(8)}$				
W(2)h		3.17(6)							3.08(4)	
W(2)e			$\underline{1.81(7)}$	3.10(7)	$\underline{1.86(7)}$	2.43(8)			$\underline{2.31(4)}$	
W(3)	2.79(2)	2.75(6)			2.70(7)		$\underline{0.64(2)}$			
W(3)a			2.88(7)	2.65(7)		$\underline{2.31(7)}$		2.63(4)		

a: *x*, *y*+1, *z*; b: *x*, *y*–1, *z*; c: *x*+1, *y*, *z*; d: *x*–1, *y*, *z*; e: –*x*+1, –*y*+1, –*z*; f: *x*–1, *y*–1, *z*; g: –*x*, –*y*+1, –*z*; h: –*x*+2, –*y*+1, –*z*; i: –*x*, –*y*+2, –*z*; j: –*x*+1, –*y*+2, –*z*;

*The X^P_M. X^P_A(1–4), X^P_B and *W*(1–3) sites are 16–50% occupied by H_2O groups (Table 5) and short O–O distances (underlined) must not be taken into account.

are 0.64 Å apart (Fig. 5). The ideal composition of the B^P site is $[(H_2O)\square]$ *pfu*. The *W*(1–3) sites ideally give $(H_2O)_2$ *pfu*. H_2O groups at the *W*(1–3) sites (Table 6, Fig. 5) are not bonded to any cation; they occur in the intermediate space between two TS blocks and ideally give $(H_2O)_2$ *pfu*. We write the composition of the **I** block as the sum of two A^P, two B^P, five $X^P_{(A+B)}$, and *W*(1–3) sites: $(Ca_{0.67}Sr_{0.34}Ba_{0.19}K_{0.15}\square_{0.65})$ + $[(H_2O)_5Sr_{0.11}]$ = $(Ca_{0.67}Sr_{0.34}Ba_{0.19}K_{0.15}\square_{0.65})[(H_2O)_5Sr_{0.11}]$ *pfu*, with simplified and ideal compositions of $(Ca,\square)(H_2O)_5$ and $(Ca\square)(H_2O)_5$ *pfu*, respectively.

Hydrogen bonding. Table 10 reports O–O distances less than 3.2 Å between O atoms of H_2O groups that occupy X^P_M, $X^P_{(A,B)}$, *W*(1–3), and B^P sites. Only the X^P_M site is 100% occupied, mainly by H_2O groups and less by OH groups. The $X^P_{(A,B)}$, *W*(1–3), and B^P sites are partly occupied at 16–50% (Table 6). Short (less than 2.5 Å) distances between partly occupied sites are underlined in Table 10. However, inspection of Table 10 gives O–O distances from 2.50 to 3.20 Å and these distances are suitable for hydrogen bonds (Fig. 5).

The crystal structure of kolskyite has one type of TS block and one type of the **I** block and they alternate along **c** (Fig. 6a). This is a *basic* TS-block structure in accord with Sokolova and Cámara (2013).

THE IDEAL STRUCTURAL FORMULA OF KOLSKYITE

Above, we wrote the ideal formulae of kolskyite based on the occupancies of the cation and anion sites. Here, we write the ideal structural formula of the TS block kolskyite of the form $A^P_2B^P_2M^H_2M^O_4(Si_2O_7)_2X^O_4(X^P_M)_2(X^P_{A+B})_mW_n$ (in accord with Sokolova 2006) where A^P and B^P are cations at the peripheral (*P*) sites; M^H and M^O are cations of the H and O sheets; X^O are anions of the O sheet; X^P_M and X^P_{A+B} are apical anions of the M^H and $(A+B)^P$ and B^P cations at the periphery of the TS block, W are H_2O groups not bonded to cations, m = n = 2. In kolskyite, $A^P_2 = (Ca\square)$; $B^P_2 = [(H_2O)\square]$; $M^H_2 = Ti_2$; $M^O_4 = Na_2Ti_2$; $X^O_4 = O_4$; $X^P_M + X^P_A = (H_2O)_2 + \square = (H_2O)$; W = H_2O. Hence, we write the ideal composition of the TS block as follows:

$$^{A^P}[(Ca\square)]\ ^{B^P}[(H_2O)\square]\ ^{M^H}[Ti_2]\ ^{M^O}[Na_2Ti_2]\ (Si_2O_7)_2\ ^{X^O}[O_4]\ ^{X^P_M}[(H_2O)_2]\ ^{X^P_{(A+B)}}[(H_2O)_2] = (Ca\square)[(H_2O)\square]Ti_2Na_2Ti_2(Si_2O_7)_2O_4(H_2O)_4,\ Z = 1$$

The **I** block comprises the A^P and B^P atoms and the $X^P_M + X^P_A + X^P_B$ anions, which have been already counted in the formula of the TS block, and (H_2O) groups at the *W*(1–3) sites, ideally $(H_2O)_2$ *pfu*.

We sum the TS block and an H_2O component [W(1–3)] of the **I** block to write the ideal structural formula for kolskyite: $(Ca\square)[(H_2O)\square]Ti_2Na_2Ti_2(Si_2O_7)_2O_4(H_2O)_6$, with Z = 1.

RELATED MINERALS

Group IV

Kolskyite is a Group-IV TS-block mineral. There are six other minerals in this Group which also have basic structures: murmanite, schüllerite, lomonosovite, quadruphite, sobolevite, and polyphite; they are listed in Table 11. In the structures of all seven Ti-disilicate minerals, the TS block exhibits linkage and stereochemistry typical of Group IV where Ti (+ Mg + Mn) = 4 *apfu*: two H sheets connect to the O sheet such that two Si_2O_7 groups link to Ti polyhedra of the O sheet adjacent along $\mathbf{t_1}$ (Fig. 4d).

Group III

Kolskyite, a Group-IV mineral, is closely related to Group-III minerals kazanskyite (Fig. 6b) and nechelyustovite (Fig. 6c): all three structures have an **I** block of the same topology, containing H_2O groups and A^P sites partly occupied by cations. In the **I** block of kolskyite, the A^P site is ~50% occupied by Ca and the **I** block has ideal composition $[(Ca\square)(H_2O)_5]$; in the $\mathbf{I}_2$ blocks of kazanskyite and nechelyustovite, the A^P site is ~25% occupied by Ba and the $\mathbf{I}_2$ blocks have ideal composition $[\square_2(H_2O)_6]$ (Table 1). There are two major differences between the crystal structures of kolskyite and kazanskyite + nechelyustovite: (1) The topology and stereochemistry of the TS blocks are different in Groups III and IV; (2) the *basic* crystal structure of kolskyite has one type of **I** block, and the structures of kazanskyite and nechelyustovite have two different types of **I** blocks: an $\mathbf{I}_1$ block which is a distorted layer of Ba atoms and an $\mathbf{I}_2$ block which contains H_2O groups and A^P sites which are ~25% occupied by Ba, and hence they are *derivative* structures (Sokolova and Cámara 2013).

INVERSE PREDICTION

The discovery of kolskyite is extremely important for us as it has confirmed our prediction of its structure. Sokolova & Cámara (2010) introduced the concept of *basic* and *derivative* structures for TS-block minerals and stated that a *derivative structure* is related to two or more *basic structures* of the same Group. Hence a *derivative structure* can be built by adding *basic structures* via sharing the central O sheet of the TS blocks of adjacent structural fragments. The relation between basic and derivative structures (Sokolova & Cámara 2010, 2013) contains the implicit suggestion that derivative structures are built from basic struc-

TABLE 11. IDEAL STRUCTURAL FORMULAE* AND UNIT-CELL PARAMETERS FOR GROUP-IV TS-BLOCK MINERALS

Mineral Structure type**	Ideal structural formula								a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)	Sp.gr.	Z	Ref.
	TS block							**I** block									
	$2A^P$	$2M^H$	$2M^O(1)$	$2M^O(2)$	$(Si_2O_7)_2$	X^O_4	X^P_{2-4}										
murmanite B1(GIV)	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2$	O_4	$(H_2O)_4$	absent	5.3875	7.0579	12.1764	93.511	107.943	90.093	$P\bar{1}$	1	(1)
kolskyite** B7(GIV)		Ti_2	Ti_2	Na_2	$(Si_2O_7)_2$	O_4	$(H_2O)_2$	$(Ca\square)(H_2O)_5$	5.387	7.091	15.473	96.580	93.948	89.818	$P\bar{1}$	1	(2)
schüllerite** B6(GIV)		Ti_2	Mg_2	Na_2	$(Si_2O_7)_2$	O_2F_2		Ba_2	5.396	7.071	10.226	99.73	99.55	90.09	$P\bar{1}$	1	(3)
lomonosovite B2(GIV)	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2$	O_4		$Na_6(PO_4)_2$	5.4170	7.1190	14.4869	99.957	96.711	90.360	$P\bar{1}$	1	(1)
quadruphite B3(GIV)	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2$	O_4		$Na_8Ca_2(PO_4)_4F_2$	5.4206	7.0846	20.3641	86.89	94.42	89.94	$P1$	1	(4)
sobolevite B4(GIV)	Na_2	Ti_2	(TiMn)	Na_2	$(Si_2O_7)_2$	$O_2(OF)$		$Na_9Ca_2Mn(PO_4)_4F_2$	7.0755	5.4106	40.623		93.156		Pc	2	(5)
polyphite B5(GIV)	Na_2	Ti_2	Ti_2	Na_2	$(Si_2O_7)_2$	O_4		$Na_{14}Ca_4Mn(PO_4)_6F_4$	5.3933	7.0553	26.451	95.216	93.490	90.101	$P\bar{1}$	1	(5)

* The ideal structural formulae are presented as the sum of the titanium-silicate (TS) block, $A^P_2M^H_2M^O_4(Si_2O_7)_2X^O_4X^P_4$, and the intermediate (**I**) block, in accord with Sokolova (2006); A^P = cations at the peripheral (*P*) sites; M^H = cations of the H sheet; M^O = cations of the O sheet; X^O_4 = anions shared between O and H sheets and not bonded to Si atoms; X^P_4 = apical anions of the M^H and A^P cations (where X^P anions are ligands of P^{5+} cations they are considered as part of the **I** block); coordination numbers are given for non-octahedral sites in the TS block; ** in accord with Sokolova & Cámara (2013), Bn(GIV) denotes B for basic structure of group IV, n = 1–7; ***Ba and Ca atoms occur at the A^P site which is shifted from the plane of the H sheet; hence we consider Ba_2 and (Ca) as the **I** block.

References (the most recent reference on the structure): (1) Cámara *et al.* (2008); (2) this work; (3) Sokolova *et al*. (2013); (4) Sokolova & Hawthorne (2001); (5) Sokolova *et al.* (2005).

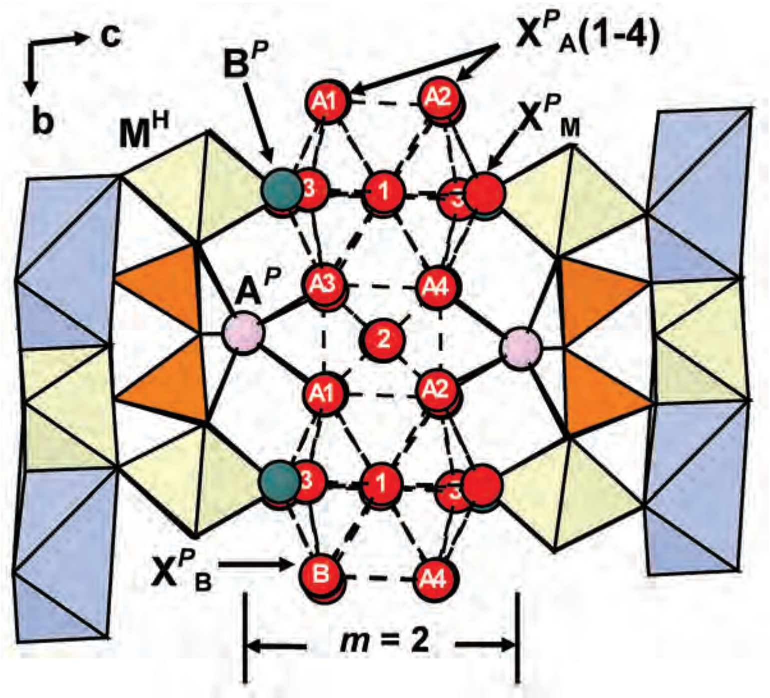

FIG. 5. Details of the intermediate (**I**) block in the crystal structure of kolskyite. Legend as in Figure 3, m = number of cation layers in the **I** block, solid black lines show the positions of the m layers; Ca atoms at the A^P site and Sr atoms at the B^P site are shown as pink and green spheres; bonds from the A^P atom to coordinating anions are shown as black lines; H_2O groups coordinating M^H, A^P, and B^P atoms are labeled $X^P{}_M$, A(1–4) [=$X^P{}_A$(1–4)], and B [=$X^P{}_B$], respectively, and H_2O groups at the *W*(1–3) sites which do not coordinate cations are labeled 1–3, respectively. Distances in the range 2.5–3.2 Å between H_2O groups are shown as black dashed lines and they are possible directions for hydrogen bonds.

tures. This relationship between basic and derivative structures gave them an excellent opportunity to predict possible structural arrangements. Prediction of new derivative structures is a direct prediction; it goes from basic structures to a derivative structure. The recognition of a new component of a derivative structure in turn suggests that a basic structure based on this component should be possible, hence the term "inverse prediction". Occurrence of a new component of the composition $\square_2(H_2O)_8$ in the derivative crystal structures of kazanskyite [D2(GIII)] and nechelyustovite [D3(GIII)] was related to an as yet unknown basic structure of Group III (Sokolova & Cámara 2010, 2013). Hence they used inverse prediction within Group III: they went from a derivative structure of kazanskyite [D2(GIII)] to a hypothetical basic structure [B5(GIII)], $\square_2Nb_2Na_2M^{2+}Ti(Si_2O_7)_2O_2(OH)_2(H_2O)_8$, where $M^{2+} = Mn^{2+}, Ca^{2+}$ (Sokolova & Cámara 2013). Next they considered an interesting relationship between a pair of minerals of Groups III and IV. The Group-III structure of vuonnemite, ideally $Na_6Na_2Nb_2Na_3Ti(Si_2O_7)_2(PO_4)_2O_2(FO)$ (Group III) (Ercit *et al*. 1998), has a counterpart Group-IV structure: lomonosovite, ideally $Na_6Na_2Ti_2Na_2Ti_2(Si_2O_7)_2(PO_4)_2O_4$ (Cámara *et al*. 2008). Vuonnemite and lomonosovite have TS blocks of different topology and chemistry: linkage 1 for vuonnemite and linkage 3 for lomonosovite. However, vuonnemite and lomonosovite have **I** blocks of identical topology and stereochemistry: two layers of [4-7]-coordinated Na polyhedra and (PO_4) tetrahedra. Hence these two minerals have TS blocks of different topology but have identical intermediate blocks. Sokolova & Cámara (2010, 2013) suggested that a mineral of Group-III with a hypothetical basic structure which they had predicted earlier could have a counterpart in Group IV. So they predicted the counterpart structure [B7(GIV)] in Group IV, with the formula $(Ca\square)Na_2Ti_4(Si_2O_7)_2\,O_4(H_2O)_8$. The B5(GIII) and B7(GIV) structures have TS blocks of different topology and identical intermediate blocks. The crystal structure of kolskyite presented here is iden-

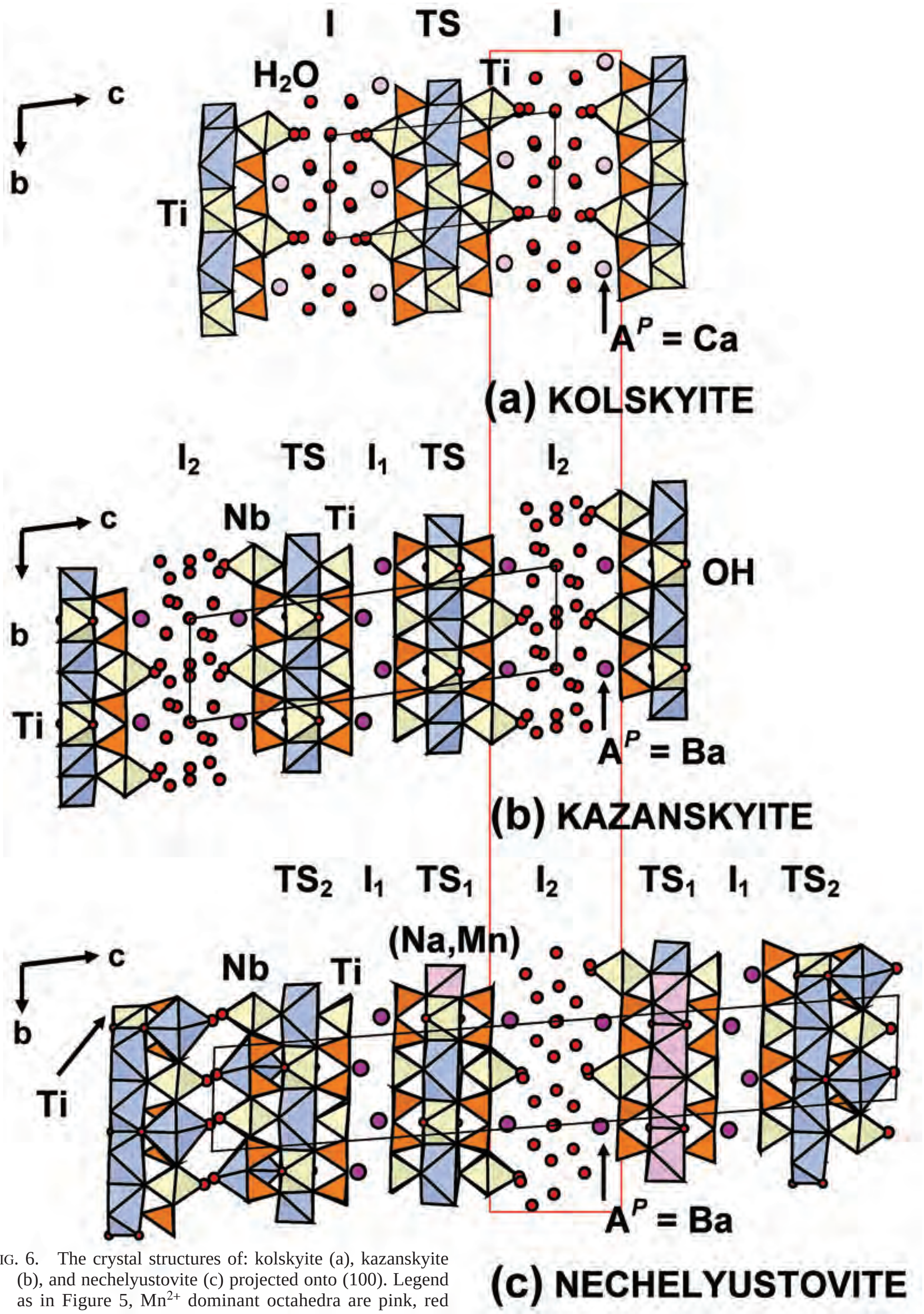

FIG. 6. The crystal structures of: kolskyite (a), kazanskyite (b), and nechelyustovite (c) projected onto (100). Legend as in Figure 5, Mn^{2+} dominant octahedra are pink, red frame shows **I** blocks of the same topology.

tical to that of the predicted B7(GIV) structure, and the chemical formulae of the predicted B7(GIV) structure, $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_8$, and kolskyite, $(Ca\square)Na_2Ti_4(Si_2O_7)_2O_4(H_2O)_7$, differ only in a number of H_2O groups: 8 and 7, respectively. Kolskyite is the first correctly predicted crystal structure of a Ti-disilicate with the TS block.

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