

HYDROTERSKITE: A NEW MINERAL SPECIES FROM THE SAINT-AMABLE SILL, QUEBEC, AND A COMPARISON WITH TERSKITE AND ELPIDITE

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ABSTRACT

Hydroterskite, ideally $\text{Na}_2\text{ZrSi}_6\text{O}_{12}(\text{OH})_6$, is a new mineral species from the Saint-Amable sill at the Demix-Varennes quarry, near Varennes, Québec, Canada. Hydroterskite crystals are short prismatic in habit, up to 3 mm in width, and bounded by the {100}, {010}, and {001} prisms. The crystals are translucent, pale gray in color, with a white streak and vitreous luster. Hydroterskite is brittle and splintery, with good cleavages on the prismatic planes. It is biaxial negative, $\alpha = 1.562 \pm 0.002$, $\beta = 1.567 \pm 0.002$, $\gamma = 1.571 \pm 0.002$, $2V_{\text{meas.}} = 86(3)^\circ$, $2V_{\text{calc.}} = 83^\circ$. Dispersion could not be observed, and there is no pleochroism. The optical orientation is $X = \mathbf{c}$, $Y = \mathbf{b}$, and $Z = \mathbf{a}$. The average result of three analyses of a single grain (oxide wt.%) gave Na_2O 7.82, K_2O 0.07, CaO 0.62, FeO 0.89, MnO 0.71, Al_2O_3 0.08, La_2O_3 0.12, Ce_2O_3 0.24, SiO_2 59.82, HfO_2 0.11, ThO_2 1.15, ZrO_2 15.00, TiO_2 1.15, Nb_2O_5 1.12, F 0.11, H_2O (by stoichiometry) 8.79, for a total (-0.05 O=F) of 96.84. Magnesium, Y, Sr, and Cl were sought but not detected. The empirical formula on the basis of 18 anions with 6 OH^- is $(\text{Na}_{1.543}\text{K}_{0.009}\text{Ca}_{0.068}\text{La}_{0.005}\text{Ce}_{0.009})\Sigma_{1.634}(\text{Zr}_{0.744}\text{Ti}_{0.088}\text{Nb}_{0.052}\text{Th}_{0.005}\text{Hf}_{0.003}\text{Fe}_{0.076}\text{Mg}_{0.002}\text{Mn}_{0.061}\text{Al}_{0.010})\Sigma_{1.041}\text{Si}_{6.087}\text{O}_{12}(\text{OH}_{5.963}\text{F}_{0.035}\text{Cl}_{0.002})\Sigma_6$. The structure of hydroterskite is orthorhombic in the centric space group *Pnca*, with a 13.956(6), b 14.894(7), c 7.441(4) Å, V 1546.8(2.0) Å³, and $Z = 4$. It has been refined to an R index of 0.036 on the basis of 1080 observed reflections. There are two crystallographically distinct Na sites, both with eight-fold co-ordination: $[\text{Na}/\text{O}_6(\text{OH})_2]$ is a hexagonal dipyrmaid polyhedron, whereas $[\text{Na}_2\text{O}_6(\text{OH})_2]$ is a bifurcated pentagonal dipyrmaid. The Zr atom is in a regular octahedral coordination. Silicon, in tetrahedral coordination with oxygen, forms spiral chains parallel to the \mathbf{c} axis. These chains are cross-linked by edge-sharing $[\text{ZrO}_6]$ octahedra and $[\text{NaO}_8]$ polyhedra. All three H atoms were located. The crystal-structure determination of terskite in the literature was most likely incorrectly assigned to an acentric space-group. The hydroterskite crystal structure is compared to the structures of terskite, elpidite, and yusupovite.

Keywords: hydroterskite, terskite, new mineral species, crystal-structure analysis, centric structure, hydrogen atoms, Saint-Amable sill, Varennes, Québec, Canada.

INTRODUCTION

Terskite was first described from two type localities in Russia, Mt. Alluaiv and Mt. Karnasurt, Lovozero massif, Kola Peninsula, Russia (Khomyakov *et al.* 1983). The chemical formula given in their description is $\text{Na}_4\text{ZrSi}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$. Shortly afterward, terskite was found at the Poudrette quarry, Mont Saint Hilaire, Rouville County, Québec (Mandarin & Anderson 1989). These authors reported PXRD data, but no other data were collected. The chemical formula and optical data they gave are those of Khomyakov *et al.* (1983). The present study was started on the basis of our own PXRD data, which shows considerable differences from the Russian material. Our chemical data also differ from the Russian material, with only half the amount of Na, making it a new mineral species, hydroterskite. The mineral and the name were approved by the Commission of New

Minerals, Nomenclature and Classification (IMA 2015-042).

The crystal structure of terskite was solved in acentric space-group *Pnc2* (# 30) (Pudovkina & Chernitsova 1991). The original chemical formula of Khomyakov *et al.* (1983), $\text{Na}_4\text{ZrSi}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$, was changed to reflect the findings of the crystal-structure determination, to $\text{Na}_4\text{ZrSi}_6\text{O}_{14}(\text{OH})_4$. No H positions were found in this structure determination, but the number of H atoms could be determined with bond-valence calculations. The crystal structure of hydroterskite is in centrosymmetric space-group *Pnca* (# 30).

GEOLOGICAL SETTING AND OCCURRENCE

The hydroterskite crystals used in the present study are part of a recent find by L. Horváth in the Saint-Amable sill at the Demix-Varennes quarry near Varennes, Québec,

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Canada. The amount of material collected was limited to four rock specimens containing one to three crystals of hydroterskite each.

The sill is located between the towns of Varennes and Saint-Amable in Verchères County, Québec, approximately 20 km east-northeast of Montréal, and 7 km east of the St. Lawrence River (latitude: 45°39' N; longitude: 73°17' W). The sill is genetically related to the Cretaceous alkaline Monteregian Hills Petrographic Province, which forms an east–west-trending belt from Mont Megantic (190 km east of Montréal) to Oka (35 km west of Montréal). Along with the Saint-Amable sill, a number of other major sills have been exposed around the Montréal area by quarrying and building excavations. The Saint-Amable sill is the most extensive and thickest (3–24 m) yet exposed. It is likely coeval with the two closest Monteregian Hills, Mont Saint-Bruno and Mont Saint-Hilaire, dated at 90 and 135 ± 10 Ma, respectively (Gold 1979, Eby 1984, Horváth *et al.* 1998). The sill itself is comprised of multiple injections of phonolite 0.6 to 1.2 m thick. The phonolite is fine grained (average grain-size 40 μm), dark gray in color, comprised predominantly of phenocrysts of nepheline in a trachytic matrix of K-feldspar, aegirine, and natrolite. The Saint-Amable phonolite contains numerous mineralized cavities and seams, which are the source of rare and well-formed postmagmatic and hydrothermal minerals. A full description of the mineralogy of the Saint Amable sill can be found in Horváth *et al.* (1998).

MATERIAL STUDIED

The crystal fragments used for the chemical analysis and the crystal-structure determination are from a single, sharp, cloudy gray, glassy crystal, 0.1 mm across, located in the middle of a euhedral face of a larger, brown manganoneptunite crystal. Other crystals from the same occurrence were found to have the same PXRD pattern. According to L. Horváth (*pers. commun.*), the initial discovery of terskite or hydroterskite from Saint-Amable looked more like rough pseudomorphs. Newly found hydroterskite is associated with aegirine, analcime, an astrophyllite-group mineral, catapleiite, a eudialyte-group mineral, fluorite, monazite, natrolite, and a rinkite-group species.

PHYSICAL AND OPTICAL PROPERTIES

Hydroterskite belongs to the orthorhombic system in the dipyrnidal class, $2/m\ 2/m\ 2/m$. The crystals are short prismatic in habit and bounded by the {100}, {010}, and {001} prisms, up to 3 mm in width. The crystals are translucent, pale gray in color, with a white streak and vitreous luster. The mineral is brittle and splintery, with good cleavages on the prismatic planes.

Hydroterskite is biaxial negative, $\alpha = 1.562 \pm 0.002$, $\beta = 1.567 \pm 0.002$, $\gamma = 1.571 \pm 0.002$, $2V_{\text{meas.}} = 86(3)^\circ$, $2V_{\text{calc.}} = 83^\circ$. Dispersion could not be observed, and there is no pleochroism. The optical orientation is $X = \mathbf{c}$, $Y = \mathbf{b}$, and $Z = \mathbf{a}$. Optical parameters were difficult to measure owing to inclusions and a dark coloration parallel to X. The optical parameters were measured with a spindle stage.

CHEMICAL COMPOSITION

Electron-microprobe analysis

The chemical analyses were performed with a JEOL 8230 electron microprobe in wavelength-dispersion (WD) mode. Data reduction was done with a PAP routine (Pouchou & Pichoir 1984). The operating voltage was 20 kV, the beam current was 5 nA, and the beam diameter was 20 μm . Although there may be some loss of Na content, a larger size of beam could not be used owing to the small size of the sample. Counting times were 20 s peak and 10 s background for all

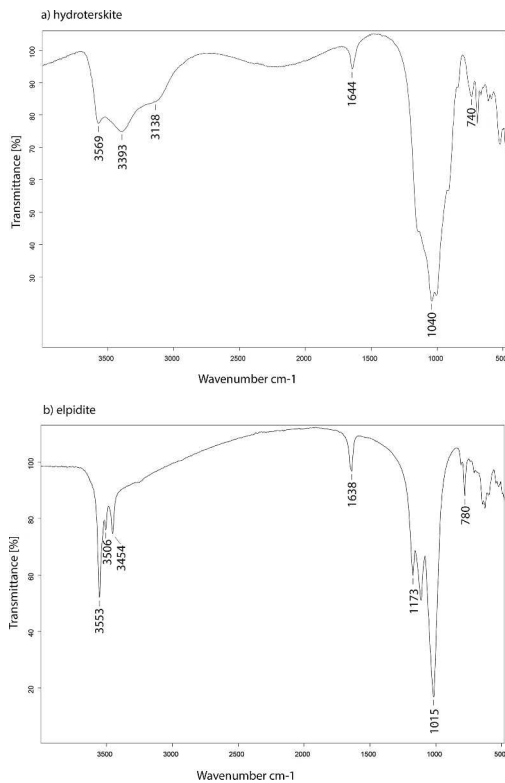


FIG. 1. Infrared absorption spectra for (a) hydroterskite from Varennes, Quebec, and (b) elpidite from Mont Saint Hilaire, Quebec.

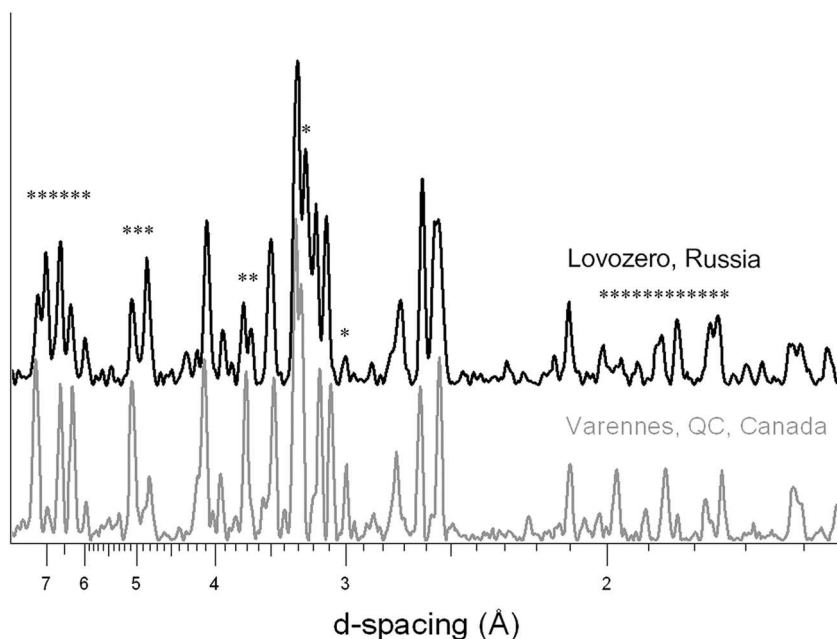


Fig. 2. X-ray powder-diffraction patterns for hydroterskite from Varennes, Québec, and terskite from Lovozero, Russia. Notably different 2 θ ranges are marked with asterisks (*****)

elements The following standards were used: sanidine ($\text{SiK}\alpha$, $\text{AlK}\alpha$, $\text{KK}\alpha$), diopside ($\text{CaK}\alpha$, $\text{MgK}\alpha$), zircon ($\text{ZrL}\alpha$, $\text{HfM}\alpha$), ThO_2 ($\text{ThM}\alpha$), fluorite ($\text{FK}\alpha$), columbite-(Mn) ($\text{MnK}\alpha$, $\text{NbL}\alpha$), rutile ($\text{TiK}\alpha$), hematite ($\text{FeK}\alpha$), LaPO_4 ($\text{LaL}\alpha$), CePO_4 ($\text{CeL}\alpha$), albite ($\text{NaK}\alpha$), and tugtupite ($\text{ClK}\alpha$). The average result of three analyses of a single grain (oxide wt.%) was Na_2O 7.82, K_2O 0.07, CaO 0.62, FeO 0.89, MgO 0.01, MnO 0.71, Al_2O_3 0.08, La_2O_3 0.12, Ce_2O_3 0.24, SiO_2 59.82, HfO_2 0.11, ThO_2 0.22, ZrO_2 15.00, TiO_2 1.15, Nb_2O_5 1.12, F 0.11, Cl 0.01, H_2O (by stoichiometry) 8.79, Total ($-0.05 \text{ O}=\text{F}$) 96.84. Magnesium, Y, Sr, and Cl were sought, but not detected. The low total will be explained below. The empirical formula on the basis of 18 anions including 6 OH^- is: $(\text{Na}_{1.543}\text{K}_{0.009}\text{Ca}_{0.068}\text{La}_{0.005}\text{Ce}_{0.009})_{\Sigma 1.634}(\text{Zr}_{0.744}\text{Ti}_{0.088}\text{Nb}_{0.052}\text{Th}_{0.005}\text{Hf}_{0.003}\text{Fe}_{0.076}\text{Mg}_{0.002}\text{Mn}_{0.061}\text{Al}_{0.010})_{\Sigma 1.041}\text{Si}_{6.087}\text{O}_{12}(\text{OH})_{5.963}\text{F}_{0.035}\text{Cl}_{0.002})_{\Sigma 6}$. The simplified formula is $\text{Na}_2\text{ZrSi}_6\text{O}_{12}(\text{OH})_6$.

Infrared analysis

The infrared spectra (Fig. 1) of hydroterskite and elpidite were obtained using a Bomen Michelson MB-120 Fourier-transform infrared spectrometer with a diamond-anvil cell microsampling device. Two samples of hydroterskite gave very similar results and two samples of elpidite, one from Mont Saint-Hilaire, Québec and one from Narssârssuk, Greenland, also

gave very similar results. The frequencies are well resolved. The spectrum of hydroterskite has a moderate, broad peak in the high-frequency range, 3600–3000 cm^{-1} , consisting of three discernible peaks at 3569, 3393, and 3138 cm^{-1} , due to $[\text{OH}]$ stretching. There is a broad, low peak in the 2500–2000 cm^{-1} range due to $[\text{OH}]$ stretching. There is a small, sharp peak at 1644 cm^{-1} due to $[\text{H}_2\text{O}]$ bending. Comparing the remaining part of the spectrum to spectra given in Farmer (1974), the following frequency regions are assigned modes: a series of strong sharp peaks in the 1200–900 cm^{-1} range is the stretching mode of $[\text{SiO}_4]$; the moderate intensity, sharp peaks in the 800–500 cm^{-1} range correspond to the bending mode of $[\text{SiO}_4]$. For comparison, the elpidite spectrum is given. There is a series of moderately strong, sharp peaks in the high frequency range, 3600–3000 cm^{-1} consisting of three discernible peaks at 3533, 3506, and 3454 cm^{-1} , due to $[\text{OH}]$ stretching. There is a small, sharp peak at 1638 cm^{-1} due to $[\text{H}_2\text{O}]$ bending. There is a series of strong sharp peaks in the 1200–1000 cm^{-1} range, which correspond to the stretching mode of $[\text{SiO}_4]$; the moderate-intensity, sharp peaks in the 800–500 cm^{-1} range correspond to the bending mode of $[\text{SiO}_4]$.

The important finding in these spectra is that both minerals have an $[\text{H}_2\text{O}]$ bending frequency at 1640 cm^{-1} . This is expected in elpidite but not in hydroterskite. An explanation follows.

TABLE 1. HYDROTERTSKITE FROM VARENNES AND TERSKITE FROM LOVOZERO: X-RAY POWDER-DIFFRACTION DATA

VARENNES (this study)							LOVOZERO (Pudovkina & Chernitsova 1991)								
<i>I</i> obs.	<i>I</i> calc.*	<i>d</i> obs.*	<i>d</i> calc.**	<i>hkl</i>	<i>I</i> calc.*	<i>d</i> calc.*	<i>hkl</i>	<i>I</i> obs.	<i>I</i> calc.*	<i>d</i> obs.*	<i>d</i> calc.**	<i>hkl</i>	<i>I</i> calc.*	<i>d</i> calc.*	<i>hkl</i>
56	61	7.427	7.422	0 2 0	22	7.375	0 2 0						12	2.021	4 6 0
10	20	7.048	6.979	2 0 0	65	7.098	2 0 0						2	2.020	2 7 0
48	62	6.638	6.640	0 1 1	68	6.693	0 1 1						3	2.018	3 3 3
47	54	6.327	6.316	2 1 0	23	6.396	2 1 0						5	2.002	6 0 2
13	14	6.001	5.996	1 1 1	14	6.054	1 1 1	3		1.9987		3 3 3	3	1.9912	6 4 0
49	65	5.093	5.084	2 2 0	32	5.114	2 2 0	3		1.9748		2 4 3	2	1.9884	2 4 3
9	15	4.916	4.913	1 2 1	13	4.934	1 2 1	22	17	1.9741	1.9745	2 6 2	12	1.9756	2 6 2
20	33	4.813	4.811	2 1 1	60	4.869	2 1 1	6		1.9712		6 0 2	5	1.9713	4 2 3
20	14	4.194	4.195	2 2 1	19	4.227	2 2 1						4	1.9418	4 5 2
55	66	4.123	4.117	0 3 1	73	4.114	0 3 1						3	1.9407	7 1 1
					5	4.042	2 3 0						11	1.9319	6 2 2
21	20	3.952	3.949	1 3 1	23	3.951	1 3 1						4	1.9298	5 4 2
8	4	3.803	3.810	3 1 1	5	3.864	3 1 1	2		1.9097		7 1 1	11	1.9089	0 5 3
53	24	3.716	3.712	0 0 2	11	3.756	0 0 2	11	6	1.9043	1.9052	6 2 2	8	1.8922	7 2 1
	15		3.711	0 4 0	8	3.688	0 4 0	6		1.9009		0 5 3	2	1.8918	1 5 3
15	15	3.569	3.546	2 3 1	6	3.559	2 3 1	11		1.8691		4 3 3	13	1.8888	4 3 3
	11		3.489	4 0 0	7	3.549	4 0 0						27	1.8778	0 0 4
51	46	3.482	3.482	3 2 1	56	3.518	3 2 1	21	4	1.8586	1.8640	2 7 1	2	1.8646	3 7 1
9	14	3.401	3.397	4 1 0	7	3.450	4 1 0	16		1.8561		0 0 4	3	1.8615	1 0 4
100	100	3.322	3.32	0 2 2	76	3.347	0 2 2	14		1.8554		0 8 0	4	1.8540	6 3 2
80	37	3.283	3.277	2 0 2	100	3.319	2 0 2	2		1.8399		1 0 4	3	1.8456	6 5 0
	54		3.276	2 4 0	92	3.272	2 4 0	5		1.8341		2 5 3	29	1.8438	0 8 0
	3		3.229	1 4 1	26	3.238	2 1 2	8	6	1.8335	1.8311	6 5 0	13	1.8434	2 5 3
15	13	3.202	3.200	2 1 2	4	3.224	1 4 1						2	1.8224	1 7 2
54	57	3.158	3.158	4 2 0	57	3.198	4 2 0						4	1.8153	2 0 4
50	53	3.091	3.089	4 1 1	67	3.135	4 1 1						2	1.7923	6 5 1
	2		3.083	3 3 1	5	3.104	3 3 1	12	18	1.7745	1.7731	4 6 2	19	1.7796	4 6 2
25	23	3.000	2.998	2 2 2	9	3.027	2 2 2						17	1.7744	8 0 0
	2		2.998	2 4 1	6	3.000	2 4 1						5	1.7627	2 2 4
					2	2.942	4 2 1						8	1.7617	8 1 0
8	4	2.847	2.852	4 3 0	10	2.878	4 3 0	6	12	1.7608	1.7605	4 7 1	12	1.7613	4 7 1
	12		2.756	0 5 1	7	2.751	2 3 2						21	1.7593	6 4 2
	7		2.732	2 3 2	24	2.746	0 5 1						3	1.7542	5 3 3
27	17	2.736	2.732	2 5 0	4	2.732	3 2 2	22	13	1.7421	1.7448	8 0 0	2	1.7453	3 0 4
					22	2.724	2 5 0			7	1.7436	2 2 4	2	1.7409	1 3 4
					6	2.696	1 5 1			12	1.7409	6 4 2	4	1.7252	8 2 0
48	53	2.625	2.624	0 4 2	81	2.631	0 4 2	2		1.7344		5 3 3			
9	6	2.577	2.579	1 4 2	7	2.614	5 1 1	3		1.7328		8 1 0			
	6		2.573	5 1 1	12	2.587	1 4 2	2		1.6984		8 2 0	6	1.7080	6 1 3
	2		2.564	2 5 1				3		1.6947		6 6 0	4	1.7047	6 6 0
57	32	2.544	2.543	4 0 2	50	2.579	4 0 2	3		1.6841		6 1 3	5	1.6811	4 5 3
					6	2.561	2 5 1	3		1.6693		4 5 3	8	1.6746	6 2 3
	32		2.542	4 4 0	45	2.557	4 4 0	4		1.6525		6 2 3	3	1.6624	6 6 1
					16	2.541	4 1 2						3	1.6618	1 4 4
5	4	2.503	2.506	4 1 2	3	2.499	5 2 1						4	1.6564	6 5 2
7	4	2.490	2.474	0 6 0	5	2.467	2 4 2	2		1.6382		4 8 0	3	1.6361	4 8 0
	2		2.405	4 2 2	3	2.336	6 1 0						10	1.6293	8 3 1
	2		2.304	2 1 3	2	2.305	1 6 1						25	1.6286	2 4 4
					4	2.253	6 2 0						2	1.6232	6 3 3
					5	2.238	5 1 2						12	1.6192	4 2 4
					2	2.231	6 1 1	16	12	1.6134	1.6150	2 4 4	6	1.6122	0 7 3

TABLE 1. (CONTINUED)

VARENNES (this study)						LOVOZERO (Pudovkina & Chernitsova 1991)									
<i>l obs.</i>	<i>l calc.*</i>	<i>d obs.*</i>	<i>d calc.**</i>	<i>hkl</i>	<i>l calc.*</i>	<i>d calc.*</i>	<i>hkl</i>	<i>l obs.</i>	<i>l calc.*</i>	<i>d obs.*</i>	<i>d calc.**</i>	<i>hkl</i>	<i>l calc.*</i>	<i>d calc.*</i>	<i>hkl</i>
7	7	2.221	2.220	6 2 0	6	2.188	3 1 3	11		1.6146	2 8 2	24	1.6118	2 8 2	
	3		2.163	4 5 1	6	2.172	4 5 1	4		1.6102	0 7 3				
	3		2.162	3 1 3	4	2.158	6 2 1	7		1.6065	8 3 1				
	3		2.136	5 4 1	6	2.155	5 4 1	2		1.6051	2 9 0				
	5		2.127	6 2 1	6	2.132	6 3 0	12	2	1.6014	1.6035	6 3 3	5	1.6019	1 7 3
	3		2.110	2 3 3	7	2.128	2 3 3	11		1.6002	4 2 4	3	1.6012	0 9 1	
23	25	2.098	2.097	4 4 2	58	2.114	4 4 2	3		1.5996	1 7 3	3	1.5969	2 9 0	
	3		2.096	3 6 1	4	2.095	3 6 1	4	3	1.5682	1.5690	2 7 3	23	1.5677	8 2 2
8	4	2.057	2.059	0 6 2	2	2.057	0 6 2						3	1.5620	2 9 1
9	9	2.017	2.018	4 6 0	5	2.026	4 1 3	11	12	1.5441	1.5445	8 2 2	4	1.5401	6 7 1

* Calculated from single-crystal structure determination.

** Calculated from PXRD cell refinement with *a* 13.958(3), *b* 14.843(5), *c* 7.424(3) Å. Bold-face type indicates the strongest 12 lines.

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction

X-ray powder-diffraction data (PXRD) for the mineral hydroterskite found at the Demix-Varennès quarry were obtained using a Bruker AXS Discover 8 microdiffractometer equipped with a Hi-Star 2-D area detector, using CuK α radiation, and calibrated using the method of Rowe (2009). Unit-cell parameters refined from the powder data for space group *Pnca* are: *a* 13.958(3), *b* 14.843(5), *c* 7.424(3) Å, *V* 1538.2(5) Å³. Further research was instigated because of notable

differences between the PXRD pattern for the Varennès material and the Lovozero material (CMN collection), which can easily be identified by comparing the patterns in Figure 2 and Table 1. There are differences both in the *d* values and the intensities of certain peaks. During our research, we noted that the material from Mont Saint-Hilaire has a PXRD pattern very similar to the material from Varennès.

Crystal-structure determination

The single crystal of hydroterskite used for the collection of X-ray intensity data was a sliver measuring

TABLE 2. HYDROTERSKITE: INFORMATION ON DATA COLLECTION AND STRUCTURE REFINEMENT

Space group	<i>Pnca</i> (# 60)	Measured reflections	55853
<i>a</i> (Å)	13.956(6)	Unique reflections	1358
<i>b</i> (Å)	14.894(7)	Observed reflections	1080
<i>c</i> (Å)	7.441(4)	[> 4s(<i>F</i>)]	
<i>V</i> (Å ³)	1546.8(12)	<i>R</i> (int)	0.0509
Range of reflections, <i>hkl</i>	± 16/ ± 17/ ± 8	Goodness of fit on <i>F</i> ²	0.98
<i>R</i> index (%) for all data	5.19		
Number least-squares parameters	136		
<i>R</i> index (%) for observed data	3.65		
<i>F</i> (000)	1184		
<i>wR</i> ² (%) for all data	10.67		
Ideal unit-cell contents:	$\mu = 1.33 \text{ mm}^{-1}$		
Na ₈ Zr ₄ Si ₂₄ O ₄₈ (OH) ₂₄			
Refinement by full-matrix least squares on <i>F</i> ²			

TABLE 3. HYDROTERSKITE: ATOM COORDINATES, ANISOTROPIC DISPLACEMENT FACTORS (\AA^3) AND BOND-VALENCE SUMS

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso}	BVS*
Zr	0	0	0	0.0163(4)	0.0173(4)	0.0125(4)	-0.0027(3)	0.0011(2)	-0.0010(3)	0.0154(2)	4.24(2)
Si1	0.3357(1)	0.1289(1)	0.7649(2)	0.0220(8)	0.0257(8)	0.0224(8)	0.0044(6)	0.0013(6)	0.0043(6)	0.0234(4)	4.05(5)
Si2	0.1324(1)	0.1404(1)	0.2974(2)	0.0203(7)	0.0128(7)	0.0113(7)	-0.0003(5)	-0.0006(5)	-0.0016(5)	0.0148(3)	4.17(2)
Si3	0.1152(1)	0.1558(1)	0.7188(2)	0.0164(7)	0.0137(7)	0.0116(6)	-0.0006(5)	-0.0017(5)	0.0003(5)	0.0139(3)	4.21(2)
Na1	1/2	0	1/2	0.024(2)	0.024(2)	0.039(2)	-0.010(1)	0.009(1)	-0.005(1)	0.0291(7)	0.971(5)
Na2	3/4	0	-0.0714(4)	0.027(2)	0.030(2)	0.028(2)	0	0	0.001(1)	0.028(1)	0.986(5)
O1	0.2476(3)	0.1291(3)	0.2682(6)	0.028(2)	0.031(2)	0.041(2)	-0.006(2)	0.008(2)	0.002(2)	0.034(1)	1.82(2)
O2	0.2208(2)	0.1352(3)	0.7965(5)	0.018(2)	0.036(2)	0.028(2)	0.006(2)	-0.003(2)	-0.001(2)	0.0275(8)	2.15(1)
O3	0.6105(3)	0.1302(3)	0.4917(4)	0.045(2)	0.030(2)	0.011(2)	0.004(1)	-0.002(2)	0.000(2)	0.0289(9)	2.24(1)
O4	0.0950(3)	0.2378(2)	0.2319(5)	0.0371(2)	0.018(2)	0.036(2)	0.006(2)	-0.011(2)	-0.005(2)	0.0304(9)	2.17(2)
O5	-0.1292(3)	0.2659(3)	0.7364(7)	0.0296(2)	0.030(2)	0.078(3)	0.004(2)	-0.010(2)	0.002(2)	0.046(1)	1.86(4)
O6	0.0353(2)	0.0990(2)	0.8181(5)	0.020(2)	0.030(2)	0.028(2)	0.008(2)	0.001(2)	-0.005(2)	0.0264(8)	1.94(1)
O7	0.0803(2)	0.0606(2)	0.1975(4)	0.038(2)	0.017(2)	0.021(2)	-0.002(1)	-0.010(2)	-0.007(2)	0.0254(8)	2.15(2)
O8	0.3806(2)	0.0701(3)	0.9234(4)	0.023(2)	0.036(2)	0.024(2)	0.003(2)	-0.006(2)	0.008(2)	0.0277(9)	2.13(2)
O9	0.3626(2)	0.0833(2)	0.5737(5)	0.041(2)	0.053(3)	0.023(2)	-0.002(2)	-0.002(2)	0.018(2)	0.039(1)	1.89(3)
H1	0.235(4)	0.143(4)	0.142(3)	0.05							1.03(2)
H5	-0.082(3)	0.232(4)	0.807(7)	0.05							0.89(3)
H9	0.391(4)	0.141(2)	0.601(9)	0.05							1.02(3)

*Bond-valence constants from Brese & O'Keeffe (1991).

TABLE 4. HYDROTERSKITE: SELECTED BOND-LENGTHS (\AA) AND ANGLES ($^\circ$)

Zr-O8	2.050(3) × 2	O8-O8'	180	Si1-O8	1.590(4)	O8-O9	108.9(2)
Zr-O7	2.057(3) × 2	O8-O7	91.0(1)	Si1-O9	1.629(4)	O8-O2	108.3(2)
Zr-O6	2.062(3) × 2	O8-O7'	89.0(1)	Si1-O2	1.624(4)	O8-O5	114.4(2)
<Zr-O>	<2.056>	O8-O6	90.8(1)	Si1-O5	1.642(3)	O9-O2	112.0(2)
		O8-O6'	89.1(1)	<Si1-O>	<1.621>	O9-O5	109.4(2)
						O2-O5	103.9(2)
						<O-O>	<109.5>
Si2-O7	1.579(3)	O7-O3	107.5(2)	Si3-O6	1.582(4)	O6-O4	112.0(2)
Si2-O3	1.607(3)	O7-O4	112.6(2)	Si3-O4	1.613(4)	O6-O2	112.0(2)
Si2-O4	1.617(4)	O7-O1	108.3(2)	Si3-O2	1.613(4)	O6-O3	107.4(2)
Si2-O1	1.630(4)	O3-O4	108.5(2)	Si3-O3	1.613(3)	O4-O2	108.9(2)
<Si2-O>	<1.608>	O3-O1	108.0(2)	<Si3-O>	<1.605>	O4-O3	106.5(2)
		O4-O1	111.7(2)			O2-O3	109.9(2)
		<O-O>	<109.4>			<O-O>	<109.4>
Na1-O9	2.346(4) × 2	O9-O3	96.1(1)	Na2-O8	2.375(4) × 2	O2-O8	82.4(1)
Na1-O3	2.478(4) × 2	O9-O7	88.4(1)	Na2-O1	2.417(5) × 2	O2-O8'	58.2(1)
Na1-O7	2.672(4) × 2	O9-O6	86.4(1)	Na2-O7	2.702(4) × 2	O2-O1	82.7(1)
Na1-O6	2.833(4) × 2			Na2-O2	2.900(4) × 2	O2-O7	83.7(1)
<Na1-O>	<2.582>			<Na2-O>	<2.598>	O2-O2	90.2(2)

TABLE 5. HYDROTERSKITE: HYDROGEN INTER-ATOMIC DISTANCES

D-H	d(D-H) (Å)	d(H...A) (Å)	<DHA (°)	d(D...A) (Å)	A
O1-H1	0.976(10)	2.58(2)	164(5)	3.531(6)	O2
O5-H5	0.979(10)	2.57(6)	116(4)	3.131(6)	O4
O5-H5	0.979(10)	2.58(4)	147(5)	3.438(6)	O6
O9-H9	0.981(10)	1.86(5)	137(5)	2.668(6)	O5

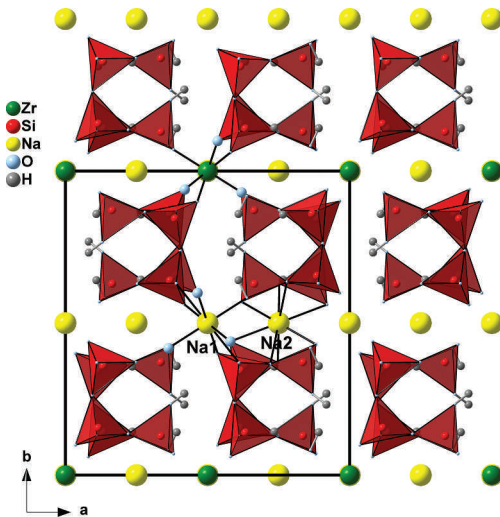


Fig. 3. Hydroterskite, Varennes: crystal structure.

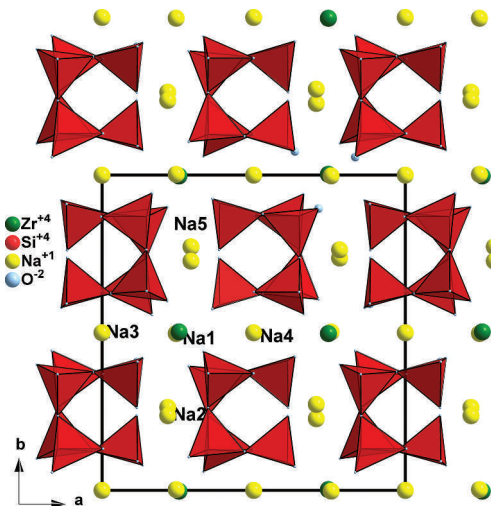


Fig. 4. Terskite, Lovozero: crystal structure.

$20 \times 20 \times 25 \mu\text{m}$. Intensity data were collected with a fully automated Bruker D8 three-circle diffractometer equipped with a rotating anode generator operating at 50 kV and 24 mA, with $\text{MoK}\alpha$ radiation, multilayer optics, and an APEX-II CCD detector. This setup yields a very intense X-ray beam. A full sphere of intensity data was collected up to $2\theta = 50^\circ$ using 50 s frames at frame widths of 0.3° , giving a total of 55,853 reflections (1358 within the Ewald sphere). Information relevant to the data collection and structure determination is given in Table 2. The three-dimensional data were corrected for Lorentz, polarization, and background effects, and an empirical absorption-correction was applied (SADABS, Sheldrick 1998), which reduced the

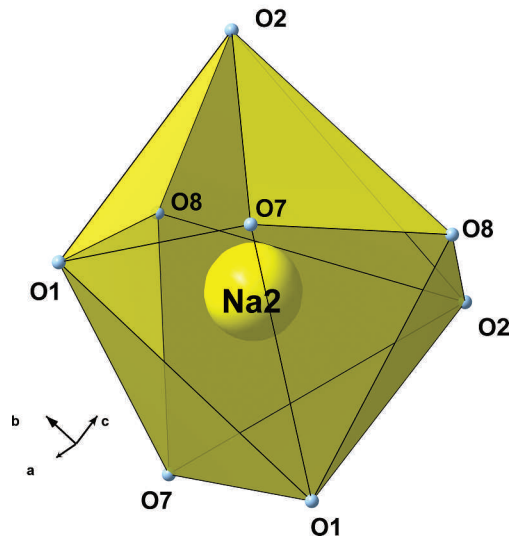
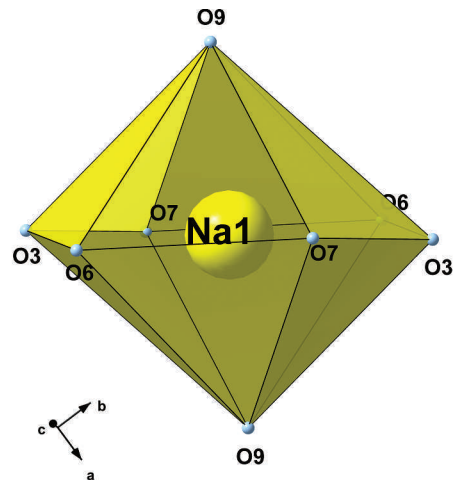


Fig. 5. Na polyhedra in the hydroterskite structure: top: hexagonal dipyramid, and bottom: bifurcated pentagonal dipyramid.

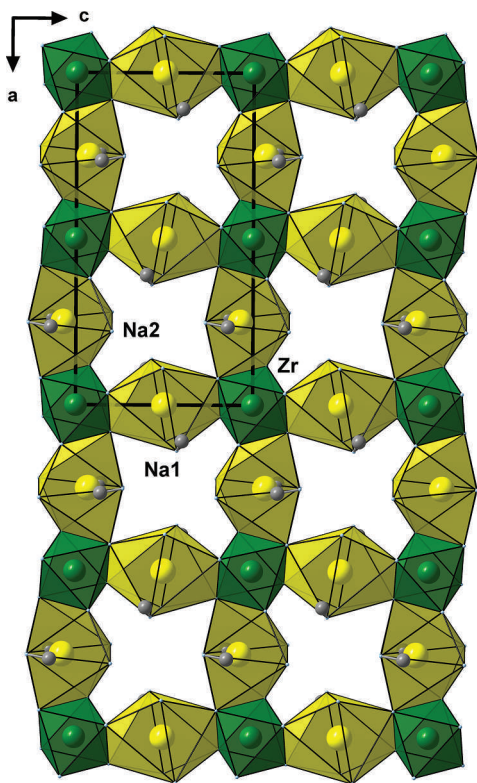


FIG. 6. Hydroterskite, Varennes: the layer of Na-Zr polyhedra.

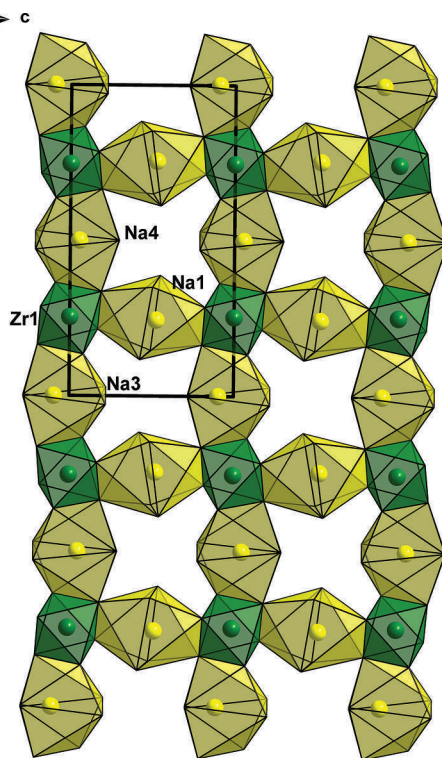


FIG. 7. Terskite, Lovozero: the layer of Na-Zr-Si polyhedra.

internal residual for merging data from 7.83% before the absorption correction to 4.50% after the absorption correction (for certain reflections). All calculations were done with the Siemens SHELXTL 5.1 system of programs (Sheldrick 1997), with scattering factors of neutral atoms taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Assigning phases to a set of normalized structure-factors gave a mean $|E^2 - 1|$ value of 1.02, which suggests a centrosymmetric space-group.

For easy comparison, we kept the site assignments of Pudovkina & Chernitsova (1991) in the starting model for the refinement. In keeping with the original determination, the structure was initially refined in acentric *Pnc2* to $R = 0.051$ for 2881 $F_o > 4\sigma(F_o)$ and 0.0992 for all 4544 data, and not including H positions, as none could be discerned in the final difference-Fourier map. The structure was checked for symmetry aspects with MISSYM (Le Page 1988) and found to be in centrosymmetric space-group *Pnca*. The structure of Pudovkina & Chernitsova (1991) was also checked and found to indicate the same centrosymmetric space-group as our study. We thus believe that these authors used an incorrect space-group.

The atomic parameters given by Pudovkina & Chernitsova (1991) were found to have a center of symmetry at 0.254, -0.003, 0.000 (MISSYM, Le Page 1988). Note that *Pnc2* is a subgroup of *Pnca*; we conclude that the two minerals have the same centric space-group. Without the full dataset for the Russian material, this is not a certainty, but it is considered highly likely.

Refining the structure in *Pnca* starting with a set of centric atomic coordinates taken from Pudovkina & Chernitsova (1991), the H positions were determined from the difference Fourier map and were refined with soft constraints: an O-H distance of 0.98 ± 0.01 Å and a fixed isotropic displacement parameter. The O-H distance of 0.98 ± 0.01 Å is a proton-proton distance, as found in neutron-diffraction experiments, and longer than the O-H distance of 0.85 Å in XRSC experiments. The authors believe the proton-proton distance more accurately represents the atomic structure.

The maximum and minimum electron-densities in the final cycle of refinement were $+0.93$ and -0.58 $e^{-\text{Å}^3}$. With all atoms located and assigning anisotropic displacement factors, the structure refined to $R = 0.0365$ for 1080 $F_o > 4\sigma(F_o)$ and 0.0519 for all 1358 data.

The final positional and anisotropic displacement parameters of atoms are given in Table 3, and selected

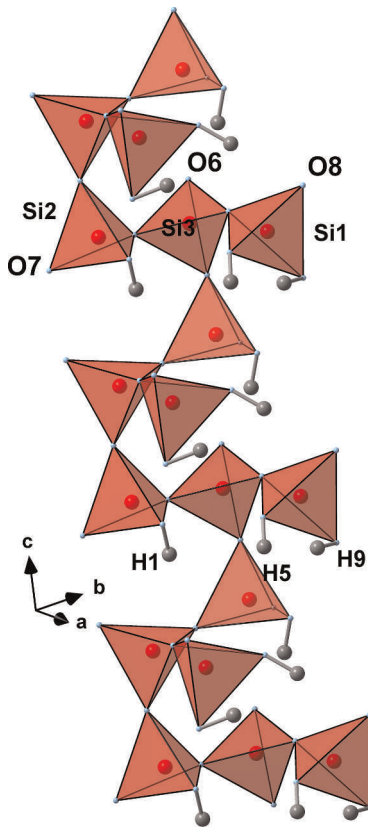


FIG. 8. Open-branched vierer single chain of $[\text{SiO}_4]$, $[\text{HSiO}_4]$, and $[\text{H}_2\text{SiO}_4]$ tetrahedra.

bond-lengths and angles are presented in Table 4. Table 5 contains details about the hydrogen bonding in hydroterskite. Tables listing the observed and calculated structure-factors and a .cif file may be obtained from the Depository of Unpublished Data on the MAC website [Hydroterskite CM53-5_1400105].

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Hydroterskite has a layered structure on (010) (Fig. 3). There are two types of layer, one layer of Na and Zr polyhedra in an open net, and a layer of Si tetrahedra in single chains. The (010) layers determined in the terskite structure differ from those presented here. Figure 4 shows the two extra *Na* sites in the terskite structure. These two additional *Na* sites share the layer of chains of $\text{Si}(\text{O},\text{OH})_4$ tetrahedra.

The layer of Na–Zr polyhedra

There are two crystallographically distinct *Na* sites, both with eight-fold coordination: $[\text{Na}1\text{O}_6(\text{OH})_2]$ is a

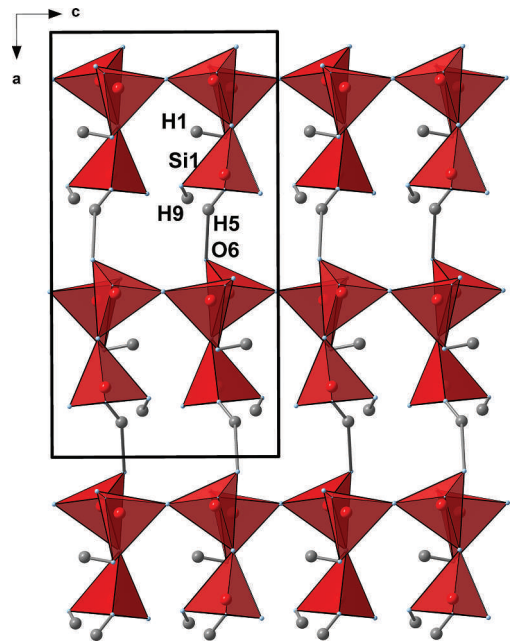


FIG. 9. The layer of (SiO,OH) tetrahedra in the Varennes hydroterskite structure.

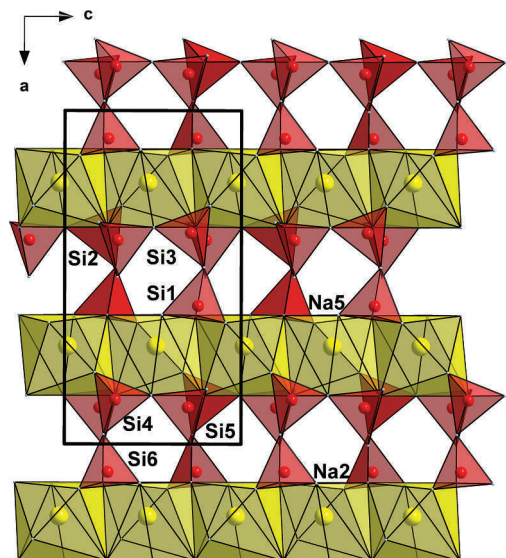


FIG. 10. The layer of Si–Na polyhedra of the Lovozero terskite structure.

hexagonal dipyramid polyhedron (Fig. 5a), whereas $[\text{Na}2\text{O}_6(\text{OH})_2]$ is a bifurcated pentagonal dipyramid (Fig. 5b). The $[\text{ZrO}_6]$ polyhedron is a regular octahedron. The *Na*2 and *Zr* polyhedra share edges, forming

TABLE 6. HYDROTERSKITE, TERSKITE, AND ELPIDITE COMPARED

	HYDROTERSKITE	TERSKITE	ELPIDITE
Location	Varenes, Canada	Kola Peninsula Kola, Russia	Narsârssuk, Greenland
Space group	<i>Pnca</i> (# 60)	<i>Pnc2</i> (# 30)	<i>Pbcm</i> (# 57)
Actual space group	<i>Pnca</i> (# 60)	<i>Pnca</i> (# 60)	<i>Pbcm</i> (# 57)
<i>a</i> (Å)	13.956	14.195	7.14
<i>b</i> (Å)	14.894	14.750	14.68
<i>c</i> (Å)	7.441	7.511	14.65
<i>V</i> (Å ³)	1540	1573	1535
D calc. g/cm ³	2.57	2.74	2.59
α	1.562	1.576	1.560
β	1.567	1.582	1.567
γ	1.571	1.584	1.576
2 <i>V</i> calc. (°)	-83	-60	+83
2 <i>V</i> meas. (°)	-86	-53	+82
Simplified formula	H ₆ Na ₂ ZrSi ₆ O ₁₈	H ₄ Na ₄ ZrSi ₆ O ₁₈	Na ₂ ZrSi ₆ O ₁₅ · 3H ₂ O
Structural formula	Na ₂ Zr [Si ₆ O ₁₂ (OH) ₆]	Na ₄ Zr [Si ₆ O ₁₄ (OH) ₄]	Na ₂ Zr [Si ₆ O ₁₅ · 3H ₂ O]

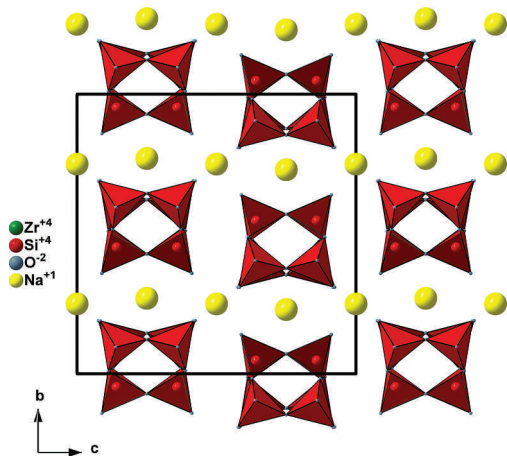


Fig. 11. The crystal structure of elpidite.

linear chains parallel to the *c* axis. These chains are cross-linked by the *Na1* polyhedra. The H atoms associated with the two Na polyhedra are directed perpendicular to the plane, despite the availability of holes within the plane (Fig. 6).

This layer is identical to that in the terskite structure described by Pudovkina & Chernitsova (1991). Figure 7 shows the structure of the Lovozero material. The [ZrO₆] polyhedron is also in this case a regular octahedron, the Na–O polyhedra are the same as in the Varenes

hydroterskite, and the cross-linkage is the same. There is a shift in origin of approximately $x = -0.25$.

The slab of Si(O,OH)₄

There are three Si sites. Each site is crystal-chemically distinct: [SiO₂(OH)₂] is quite rare in minerals, whereas [Si₂O₃(OH)] and [Si₃O₄] are the most common tetrahedra in silicates. The Si in tetrahedral coordination forms spiral chains parallel to the *c* axis. It is an open-branched vierer single chain (Fig. 8). This is the same type of chain as in astrophyllite, but it differs in visual aspect as it is a spiral, whereas that in astrophyllite is linear. These chains are cross-linked by edge-sharing [ZrO₆] octahedra and [NaO₈] polyhedra. Although all chains lie within a single (010) slab (Fig. 2), there is only one weak H-bond between chains, O5–H5 ··· O6 (Fig. 9) (Table 5). In the Lovozero terskite, the chain of Si(O,OH)₄ tetrahedra is similar, but there are no [SiO₂(OH)₂] tetrahedra. The [SiO₃(OH)] and [Si₂O₃(OH)] are related by a center of symmetry to [Si₅O₃(OH)] and [Si₆O₃(OH)], respectively, as are [Si₃O₄] and [Si₄O₄].

In the Varenes material, the hydroterskite structure has extra H atoms (Fig. 9) that replace Na and charge-balance the structure. Allowing the *Na* sites to refine gives site occupancies of *Na1* = 0.516(2) and *Na2* = 0.504(2), *i.e.*, slightly above the ideal full occupancy of 0.5 in these crystallographically special sites. Looking again at the microprobe analysis, we see that the measured

COMPARISON WITH OTHER STRUCTURES

Elpidite, $\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$, is closely related to hydroterskite, $\text{Na}_2\text{ZrSi}_6\text{O}_{12}(\text{OH})_6$, in chemical composition and crystal structure (Table 6). Like hydroterskite, elpidite has a layered structure on (010) (Cannillo *et al.* 1973) (Fig. 11). In both structures, there are two types of layer, the layer of Na and Zr polyhedra in an open net, and the layer of chains of $\text{Si}(\text{O},\text{OH})_4$ tetrahedra. In elpidite, there are H_2O groups in the layer of Na–Zr polyhedra. The chains differ in the two structures, and the two minerals thus cannot be considered polymorphs. Hydroterskite has an open-branched vierer single chain (Fig. 8), whereas elpidite has an unbranched drier double chain (Fig. 12). The recently described new mineral, yusupovite (Agakhanov *et al.* 2015), is a dimorph of elpidite with an elpidite-type superstructure. The a cell dimension of yusupovite is double that of elpidite, and the symmetry is lower, monoclinic. This decrease in symmetry is due to order affecting the large cation sites.

CONCLUSIONS

To date, two chemically different terskite-type minerals have been described; the Lovozero terskite has more Na, $\text{Na}_4\text{ZrSi}_6\text{O}_{12}(\text{OH})_4$, whereas the Varennes hydroterskite has lower Na, $\text{Na}_2\text{ZrSi}_6\text{O}_{14}(\text{OH})_6$. The lower Na content of the Varennes material lowers the indices of refraction considerably. Hydrogen atoms substitute for the Na atoms to maintain charge balance. Part of the Na sites have non-structural molecular water, which explains the low sums in the chemical analyses. The general simplified formula for the series is $\text{H}_{4+x}\text{Na}_{4-x}\text{ZrSi}_6\text{O}_{18}$, with $x \leq 2$. The two minerals are isostructural. In the Lovozero terskite, the Na sites are fully occupied, whereas in the Varennes mineral, only half of the Na sites are occupied by Na^+ , the rest being replaced by H^+ . The changes in chemical composition affect the unit cell. The Varennes hydroterskite has a and c cell dimensions shorter than those of the Lovozero terskite, whereas the b cell dimension is longer. The overall effect is that Varennes terskite has a cell volume that is 2% smaller. In Figure 9, one can see why adding additional Na atoms to the (100) layer increases both the a and c dimensions. The reason for the decrease in the b cell dimension with the addition of the Na atoms is less obvious, but it relates to the $\text{Si}(\text{O},\text{OH})_4$ chains. With Na atoms in the chain layer, as in the Lovozero terskite, the $[\text{NaO}_8]$ polyhedra tighten the spiral diameter, thus decreasing the b cell dimension.

An important observation is that bond-valence considerations preclude any further addition of H^+ atoms, as all other O^{2-} atoms are valence-saturated. Thus the Varennes mineral presented here is endmember

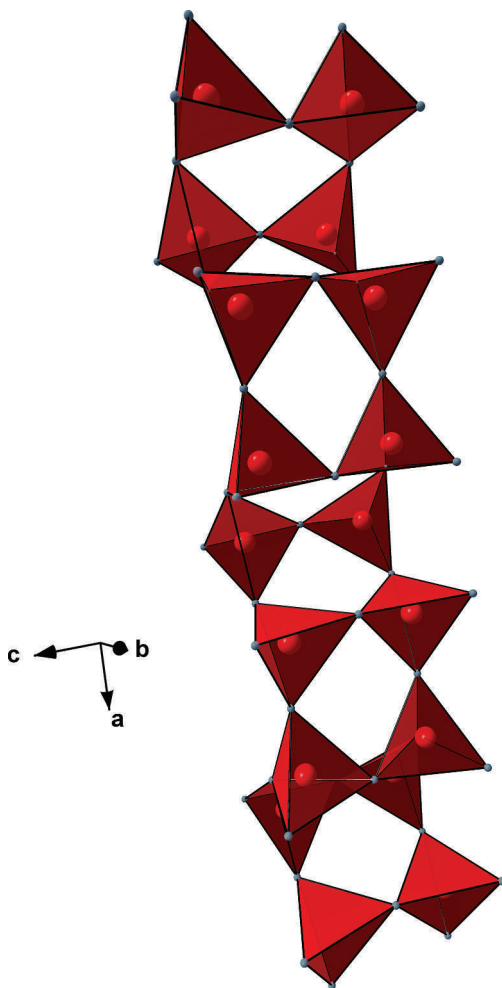


FIG. 12. The chain of (SiO,OH) tetrahedra in the elpidite structure.

result is low in Na, $(\text{Na}_{1.543}\text{K}_{0.009}\text{Ca}_{0.068}\text{La}_{0.005}\text{Ce}_{0.009})_{\Sigma 1.634}$, and also has a low total, 96.84 wt.%. It is likely, although not directly observed, that part of each Na site is occupied by molecular water, which has approximately the same scattering power as Na. If this is assumed to be true, the addition of approximately 0.38 $[\text{H}_2\text{O}]$ groups would increase the H_2O content by 1.38 wt.%, giving a total of 98.31 wt.%. This slab differs in the Russian material; the Russian terskite has two extra Na sites (Fig. 10), Na2 and Na5. These two sites are symmetry-related when placed in the correct, *i.e.*, probably centric, space-group $Pbcn$. It is the H5 site in the Varennes hydroterskite that replaces these Na sites in the Lovozero terskite. The H9 site of the Varennes mineral would still exist in the Lovozero terskite.

hydroterskite, $\text{Na}_2\text{Zr}[\text{Si}_6\text{O}_{12}(\text{OH})_6]$: it is not possible to have $\text{Na}_1\text{Zr}[\text{Si}_6\text{O}_{12}(\text{OH})_7]$ or $\text{Na}_0\text{Zr}[\text{Si}_6\text{O}_{12}(\text{OH})_8]$ with this silicate-chain structure.

ACKNOWLEDGMENTS

I (JDG) dedicate this paper to my former colleague and friend, John Jambor. My first job after graduation was with the Mines Branch (now CANMET) where John worked. In the mid-seventies, this institution and the Geological Survey of Canada next door boasted some Canada's finest mineralogists. My relationship with John in those early years developed from mentor to that of a friend in later years, where we shared many excellent meals finished with a port of John's choice. John's lessons to me were perseverance, no problem is too difficult, the strengths of immaculate lab work, and the necessity of well-honed powers of observation. John was the most gracious individual I have ever met.

The authors gratefully thank Frank C. Hawthorne, University of Manitoba, for the use of his laboratory and Mark Cooper for his technical assistance. Helpful comments from referees Igor Pekov and Nikita Chukanov, Associate Editor Frédéric Hatert, Guest Editor Robert F. Martin, and Editor Lee Groat improved the quality of the manuscript. We are indebted to these individuals for their time and suggestions.

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Received November 7, 2014. Revised manuscript accepted September 14, 2015.