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VARENNESITE, A NEW SPECIES OF HYDRATED Na–Mn SILICATE WITH A UNIQUE MONOPHYLLOSILICATE STRUCTURE

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ABSTRACT

Varennesite, a silicate of Na and Mn, is a new mineral species from the Demix–Varennes quarry, Verchères County, Quebec. It occurs as pale brownish yellow to orange, tabular crystals up to 4 mm in length. Associated minerals commonly include eudialyte, aegirine, natrolite, serandite, mangan-neptunite, microcline, albite and zakharovite, and rarely astrophyllite, villiaumite, makatite and vuonnemite. It is brittle, with a good {010} cleavage and conchoidal fracture. Varennesite is biaxial positive, with indices of refraction α 1.532(2), β 1.540(2), γ 1.550(2), $2V_{\text{meas.}} = 89(1)°$ and $2V_{\text{calc.}} = 84.1°$. It is orthorhombic, space group *Cmcm*, with *a* 13.447(3), *b* 15.022(5), *c* 17.601(4) Å and $Z = 4$. The strongest X-ray powder-diffraction lines [*d* in Å(*I*)(*hkl*)] are: 10.049(100)(110), 8.823(50)(002), 5.025(20)(113), 4.138(10)(132), 3.806(20)(223), 3.659(10)(204), 3.148(10)(402), and 2.718(50)(423). Crystals are platy on {010}, with forms {100}, {010} and {101}. Electron-microprobe analyses gave Na_2O 19.25, CaO 0.11, K_2O 0.21, SrO 0.15, MnO 6.50, FeO 3.25, TiO_2 2.56, MgO 0.03, SiO_2 48.26, Al_2O_3 0.48, SO_3 1.02, Cl 2.20, and H_2O 18.47 (calculated by stoichiometry from the crystal-structure analysis), O=Cl –0.50, total 102.00 wt.%, yielding the empirical formula $(Na_{7.64}Ca_{0.02}K_{0.06}Sr_{0.02})_{\Sigma 7.74}(Mn_{1.13}Fe_{0.56}Ti_{0.39}Mg_{0.01})_{\Sigma 2.09}(Si_{9.88}Al_{0.12})_{\Sigma 10.00}O_{25.31}[Cl_{0.76}(OH)_{1.24}]_{\Sigma 2.00}\cdot 12H_2O(SO_3)_{0.16}$, ideally $Na_8Mn_2Si_{10}O_{25}(OH,Cl)_2\cdot 12H_2O$; $D_{\text{calc.}} = 2.32$ g/cm^3, $D_{\text{meas.}} = 2.31$ g/cm^3. The structure has been refined to $R = 7.9$ and $R_w = 6.3\%$. It consists of alternating, undulating layers of silicate tetrahedra and Na and Mn octahedra. The structure has similarities to the monophyllosilicate structures of manganpyrosmalite, bementite and apophyllite, but is unique in topology. Varennesite crystallized late in the formation of the Saint-Amable sill and appears to be the most Na-rich member of similar phases in peralkaline rocks.

Keywords: varennesite, sodium–manganese silicate, peralkaline, structure determination, layered silicate, Saint-Amable sill, Varennes, Québec.

SOMMAIRE

La varennesite, silicate de sodium et de manganèse, est une nouvelle espèce minérale découverte dans la carrière de Demix–Varennes, comté de Verchères, Québec. Les cristaux se présentent en plaquettes jaune brunâtre pâle ou orange, atteignant 4 mm en longueur. Lui sont associés eudialyte, aegirine, natrolite, sérandite, mangan-neptunite, microcline, albite, zakharovite et, plus rarement, astrophyllite, villiaumite, makatite et vuonnemite. Il s'agit d'un minéral cassant, avec un bon clivage {010} et une cassure conchoïdale. La varennesite est biaxe positive; ses indices de réfraction sont: α 1.532(2), β 1.540(2), γ 1.550(2); $2V_{\text{mes.}} = 89(1)°$ et $2V_{\text{calc.}} = 84.1°$. Elle est orthorhombique, groupe spatial *Cmcm*, avec *a* 13.447(3), *b* 15.022(5), *c* 17.601(4) Å et $Z = 4$. Les raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont 10.049(100)(110), 8.823(50)(002), 5.025(20)(113), 4.138(10)(132), 3.806(20)(223), 3.659(10)(204), 3.148(10)(402), et 2.718(50)(423). Les cristaux sont applatis sur {010}, et montrent les formes {100}, {010} et {101}. Les analyses à la microsonde électronique ont donné Na_2O 19.25, CaO 0.11, K_2O 0.21, SrO 0.15, MnO 6.50, FeO 3.25, TiO_2 2.56, MgO 0.03, SiO_2 48.26, Al_2O_3 0.48, SO_3 1.02, Cl 2.20, et H_2O 18.47 (calculé d'après la stoechiométrie déduite de l'analyse de la structure cristalline), O=Cl –0.50, total 102.00% (poids), ce qui mène à la formule empirique $(Na_{7.64}Ca_{0.02}K_{0.06}Sr_{0.02})_{\Sigma 7.74}(Mn_{1.13}Fe_{0.56}Ti_{0.39}Mg_{0.01})_{\Sigma 2.09}(Si_{9.88}Al_{0.12})_{\Sigma 10.00}O_{25.31}[Cl_{0.76}(OH)_{1.24}]_{\Sigma 2.00}\cdot 12H_2O(SO_3)_{0.16}$, ou, de façon idéale, $Na_8Mn_2Si_{10}O_{25}(OH,Cl)_2\cdot 12H_2O$; $D_{\text{calc.}} = 2.32$, $D_{\text{mes.}} = 2.31$. Nous en avons affiné la structure jusqu'à un résidu *R* de 7.9 ($R_w = 6.3\%$). La varennesite contient des couches ondulées de tétraèdres silicatés en alternance avec des couches d'octaèdres de Na et Mn. La structure ressemble à celle de trois autres monophyllosilicates, manganpyrosmalite, bementite et apophyllite, mais elle s'en distingue par une topologie unique. La varennesite a cristallisé tardivement au cours de la formation du filon-couche de Saint-Amable, et semble être le membre le plus fortement enrichi en Na des phases semblables rencontrées dans un milieu hyperalcalin.

(Traduit par la Rédaction)

Mots-clés: varennesite, silicate de sodium et manganèse, hyperalcalin, détermination de la structure, silicate en couches, filon-couche de Saint-Amable, Varennes, Québec.

INTRODUCTION

Varennesite occurs in the Demix–Varennes quarry, which exposes alkaline rocks of the Saint-Amable sill. The quarry lies between the villages of Varennes and Saint-Amable, approximately 20 km east of Montreal, in Verchères County, Québec. Whereas the quarry itself has been in continuous operation for over 20 years, only recently has the mineralogy been investigated, resulting in over 90 species being identified. The cotype specimens were collected in 1993 by Dr. P. Tarassoff of Beaconsfield, Québec. Varennesite (pronounced VARENAIT) is named for the locality; it is the first new species to be described from there. The new mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the collection of the Canadian Museum of Nature, Ottawa under catalogue number 81521. In this paper, we provide the physical and chemical data that establish varennesite as a new species, and describe its novel structure.

OCCURRENCE

The Saint-Amable sill has been variously described as tinguaite (Clark 1955, Hodgson 1969), phonolite (Hanes 1962) and nepheline syenite (Currie 1976, Globensky 1985). The sill, which is Cretaceous in age, is related to the Monteregian plutonism and lies just north of Mont Bruno and Mont Saint-Hilaire, the latter being well known for its large suite of rare peralkaline minerals. The sill forms at least part of a slightly elevated plateau, approximately 20 m in height and approximately 100 km^2 in area. The plateau is covered for the most part by glacial overburden and dense bush and shows little sill outcrop. The sill is best exposed by the Demix–Varennes quarry, several adjacent quarries, associated test drill sites and stripping, which in total covers an area 3 km × 3 km. The sill intrudes shale and limestone of the Lorraine Group and truncates several small dykes in the quarry. The sill averages 13 m in thickness, with some areas of multiple injections reaching 20 m. It is fine-grained in texture, with slightly larger grain-size toward the central portion. The average grain-size is approximately 40 µm. On a microscopic scale, the rock is quite porous, with many small cavities hosting a complex suite of rare minerals. Well-defined border zones visible in the quarry walls average 1 m in thickness and are the result of contamination of the sill magma by the host sedimentary rocks. There is also a narrow hornfels zone of only a few millimeters in thickness at the contact of the sill with the sedimentary rocks. Besides the large number of rare species, the most significant mineralogical feature of the sill is the abundance of apparent primary natrolite (Hodgson 1969). Examination of a single thin section from the central part of the sill shows the composition by volume to be alkali feldspar 45%, natrolite 40%, nepheline 5% and aegirine 5%, with accessory minerals such as albite, analcime, eudialyte and mosandrite making up the difference. This roughly confirms the composition reported in Hodgson (1969); however, no thorough petrological examination of the sill has ever been reported.

Varennesite must be considered a rare species, as approximately 10 specimens, each containing only a few milligrams of material, have been found to date. It appears to be a primary, late-stage mineral of the sill and is most commonly associated with eudialyte, aegirine, natrolite, serandite, mangan-neptunite, microcline, albite and zakharovite. Other associated species include astrophyllite, villiaumite, makatite and vuonnemite.

PHYSICAL AND OPTICAL PROPERTIES

Varennesite occurs as tabular crystals up to 4 mm in length, showing the pinacoids {100} and {010} and a set of {101} prism faces (Fig. 1). The basal pinacoid {001} also has been observed (L. Horváth, pers. comm.). The crystals commonly contain numerous inclusions of aegirine. Some crystals of varennesite seem to alter to a powdery material that retains the X-ray powder pattern of varennesite. The crystals are translucent to transparent in small areas. Varennesite is pale, brownish yellow to orange, with a white streak and vitreous luster. It shows no fluorescence with either short-wave or long-wave ultraviolet light. It has an approximate hardness of 4 (Mohs hardness scale),

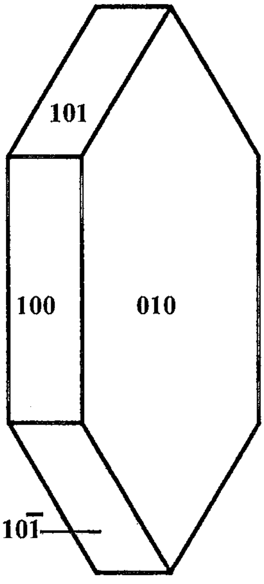


FIG. 1. Idealized crystal drawing of varennesite.

is brittle, has good cleavage {010} and conchoidal fracture. A density of 2.31 g/cm^3 measured by suspension in bromoform agrees well with the calculated density of 2.32 g/cm^3.

Varennesite is biaxial positive, with indices of refraction α 1.532(2), β 1.540(2) and γ 1.550(2) (for λ = 590 nm); $2V_{\text{meas.}}$ = 89(1)°, $2V_{\text{calc.}}$ = 84.1°; dispersion is weak, with $r > v$. Varennesite shows yellow-green (Z) to very pale yellow (X) pleochroism; absorption is $Z > Y > X$. The optical orientation is $X \parallel c$, $Y \parallel a$, $Z \parallel b$.

CHEMISTRY

Chemical analyses were performed on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. The wavelength-dispersion mode was used. Data reduction were done with a conventional ZAF routine in the Tracor Northern TASK series of programs. The operating voltage was 15 kV, and the beam current was 0.20 µA. Sample degradation under the electron beam was severe. To minimize this effect, the beam was defocused to 40 µm, and three spots were used for each analysis after first checking the sample for chemical homogeneity using the BSE detector. To further reduce volatilization and migration of Na, a count time of 10 s was used. Data for all other elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100-s energy-dispersion scan indicated no elements with $Z > 8$ other than those reported here. P, Ce, Nb, F, Zr and Ba were sought but not detected. Standards used were: vlasovite (Na$K\alpha$, Si$K\alpha$), tephroite (Mn$K\alpha$), almandine (Fe$K\alpha$, Al$K\alpha$), rutile (Ti$K\alpha$), celestine (Sr$L\alpha$, S$K\alpha$), diopside (Ca$K\alpha$, Mg$K\alpha$), scapolite (Cl$K\alpha$) and sanidine (K$K\alpha$). Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. An average result of three analyses on three separate grains gave Na_2O 19.25(18.50–19.85), CaO 0.11(0.06–0.19), K_2O 0.21(0.08–0.39), SrO 0.15(0.15–0.16), MnO 6.50(5.45–8.40), FeO 3.25(2.96–3.71), TiO_2 2.56(1.55–3.28), MgO 0.03(0.00–0.08), SiO_2 48.26(47.55–49.22), Al_2O_3 0.48(0.22–0.78), SO_3 1.02(0.98–1.07), Cl 2.20(2.05–2.39), and H_2O 18.47(18.37–18.68) (calculated by stoichiometry from results of the crystal-structure analysis), O=Cl –0.50, total 102.00 wt. %. The empirical formula based on 10 (Si + Al) is $(Na_{7.64}Ca_{0.02}K_{0.06}Sr_{0.02})_{\Sigma 7.74}(Mn_{1.13}Fe_{0.56}Ti_{0.39}Mg_{0.01})_{\Sigma 2.09}(Si_{9.88}Al_{0.12})_{\Sigma 10.00}O_{25.31}\ [Cl_{0.76}(OH)_{1.24}]_{\Sigma 2.00}\cdot 12H_2O\ (SO_3)_{0.16}$, ideally $Na_8Mn_2Si_{10}O_{25}(OH,Cl)_2\cdot 12H_2O$.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray precession photographs show varennesite to be orthorhombic with possible space-groups $Cmc2_1$ (space group #36) or $Cmcm$ (space group #63). X-ray powder-diffraction (XRPD) data collected with a Debye–Scherrer camera, 114.6 mm in diameter, with Cu$K\alpha$ (Ni-filtered) radiation, are given in Table 1. Whether or not an *hkl* plane contributed to a reflection was determined from a powder pattern calculated using the atomic parameters determined in the structure analysis.

TABLE 1. VARENNESITE: X-RAY POWDER DIFFRACTION DATA

I/I_o	d_{obs}(Å)	d_{calc}(Å)	hkl	I/I_o	d_{obs}(Å)	d_{calc}(Å)	hkl
100	10.049	10.013	110	7	2.844	2.846	044
50	8.823	8.753	002	50	2.718	2.717	423
2	7.468	7.491	020	7	2.654	2.668	404
5	6.733	6.730	200			2.654	334
20	5.025	5.042	113			2.650	510
10	4.138	4.128	132	7	2.557	2.558	045
2	3.995	4.010	114	8	2.512	2.513	424
20	3.806	3.800	223	10	2.405	2.407	442
10	3.659	3.669	204	5	2.307	2.302	046
5	3.443	3.443	042	10	2.171	2.173	444
5	3.311	3.305	115	2	1.521	1.521	$42\underline{10}$
10	3.148	3.141	402	2	1.408	1.408	$53\underline{10}$
2	3.074	3.065	242	2	1.355	1.355	$1\underline{11}0$
		2.924	150	2	1.323	1.323	952
		2.918	006	2	1.286	1.286	936
5	2.917	2.915	403				

114.6 mm Debye-Scherrer camera, Cu$K\alpha$ radiation, visually estimated intensities, indexing based on a cell having a = 13.461(2), b = 14.981(1), c = 17.506(2) Å.

For the intensity-data measurements, a platy crystal fragment of varennesite from the cotype material (CMN #81521) was mounted on a fully automated Nicolet $R3m$ four-circle diffractometer. Data relevant to the structure determination are given in Table 2. There was no appreciable deterioration of the crystal due to radiation damage during the experiment.

The structure was solved using direct methods, and the refinement was done with the SHELXTL PC (Sheldrick 1990) package of computer programs. The assignment of a phase to a set of normalized structure-factors gave a mean value $|E^2-1|$ of 0.94, indicative of the centrosymmetric space-group $Cmcm$. The E-map coordinates were assigned, with appropriate scattering curves, to one Mn, three Si, two Na and thirteen O atomic sites. This initial model refined to R = 16%. Difference-Fourier maps showed additional peaks, which were added as additional atomic sites in subsequent refinements.

TABLE 2. VARENNESITE: STRUCTURE-DETERMINATION DATA

Ideal formula:	$Na_8Mn_2Si_{10}O_{25}(OH,Cl)_2\bullet 12{+}xH_2O$	a = 13.447(3) Å
Space group:	*Cmcm*	b = 15.022(5) Å
Crystal size:	0.10 x 0.17 x 0.20 mm	c = 17.601(4) Å
		V = 3555(2) Å^3
Rad./Mon.:	Mo/graphite	Z = 4
µ	1.34 mm^{-1}	Total no. of I's 2895
ψ merge, before/after	0.021/0.020	F unique 2797
Min. transmission	0.66	$Fo > 6\delta$ 2093
Max. transmission	0.72	Final R = 7.9%
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$,	$w = [\delta^2(F_o)]^{-1}$	Final R_w = 6.3%

TABLE 3. VARENNESITE: ATOMIC COORDINATES (X 10^4), ISOTROPIC DISPLACEMENT FACTOR (X 10^4, Å^2) AND BOND-VALENCE SUM (v.u.)

ATOM	*x*	*y*	*z*	*U*	BVS*
Na1	1/2	480(2)	3372(2)	12(1)	1.21
Na2	7419(2)	438(2)	3385(1)	20(1)	1.01
Na3	8689(3)	0	1/2	31(1)	1.09
Mn	6216(1)	0	1/2	10(1)	2.70
Si1	3861(2)	1223(1)	3/4	7(1)	4.06
Si2	2819(1)	1637(1)	5943(1)	7(1)	4.02
Si3	1135(1)	2924(1)	5522(1)	6(1)	4.02
O1	1/2	1596(5)	3/4	13(2)	1.96
O2	3788(4)	174(3)	3/4	14(2)	1.85
O3	3326(3)	1715(3)	8220(2)	14(1)	1.97
O4	1793(3)	2222(3)	6021(2)	15(1)	1.93
O5	1459(3)	2792(2)	4633(2)	9(1)	1.91
O6	2676(3)	650(2)	5655(2)	12(1)	1.97
O7	1/2	2459(3)	4408(3)	10(1)	1.94
O8	1262(3)	3927(2)	5788(2)	11(1)	1.93
OH	1/2	524(4)	5605(3)	21(2)	1.21
OW1	2679(7)	1729(5)	1/4	42(3)	0.31
OW2	1/2	1758(9)	1/4	59(5)	0.34
OW3	8878(4)	1143(3)	3985(32)	41(2)	0.32
OW4	0	665(4)	5766(4)	30(2)	0.36
OW5	9057(6)	-322(4)	1/4	9(2)	0.09
OW6	0	1518(7)	1/4	62(5)	0.00

* constants from Brese & O'Keeffe (1991)

In the final least-squares refinement, the sites of all atoms were refined with anisotropic displacement factors, to the final residuals $R = 8.4$ and $R_w = 6.9\%$. At this point in the refinement the ΔF-map was found to have a peak of 2.5 $e^-/\text{Å}^3$, 0.7 Å distant from OW5, which became atom site OW51. Including OW51 [with a refined site-occupancy of 31(3) %] in the refinement gave the final residuals listed in Table 2. With this as the final model, the ΔF-map was found to have several peaks of 1 $e^-/\text{Å}^3$ along channels in the structure.

Table 3 contains the final positional and isotropic displacement parameters for the varennesite structure, and Table 4 lists selected interatomic distances and angles. The observed and calculated structure-factors, as well as the anisotropic displacement-factors, have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION OF THE STRUCTURE

Varennesite has a layered structure consisting of alternating layers of tetrahedra and octahedra (Fig. 2). The layer of tetrahedra, of composition $(Si_2O_5)^{2-}$,

TABLE 4. VARENNESITE: SELECTED BOND LENGTHS (Å) AND ANGLES(°)

		Na1 octahedron				Mn octahedron	
Na1-O2	2.445(5) x 2	O2-Na1-O2'	83.7(3)	Mn-O6	2.122(4) x 2	O6-Mn-O6'	90.8(2)
Na1-O8	2.422(4) x 2	O2-Na1-O8'	93.6(1) x 2	Mn-O8	2.127(4) x 2	O6-Mn-O8	88.5(1) x 2
Na1-OH	2.349(7)	O2-Na1-OH	102.9(2) x 2	Mn-OH	2.104(4) x 2	O6'-Mn-O8	89.1(1) x 2
Na1-OW2	2.457(11)	O2-Na1-OW2	85.5(2) x 2			O6-Mn-OH	95.6(2) x 2
		O8-Na1-O8'	89.0(2)	<Mn-O>	2.118	O8-Mn-OH	94.0(2) x 2
< Na1-O >	2.423	O8-Na1-OH	76.6(2) x 2			OH-Mn-OH'	78.0(3)
Na1-Na1	3.068(6)	O8-Na1-OW2	95.4(2) x 2				
						Si1 tetrahedron	
		Na2 octahedron					
				Si1-O1	1.631(4)	O1-Si1-O2	113.7(4)
Na2-O2	2.429(5)	O2-Na2-O6	99.3(2)	Si1-O2	1.579(6)	O1-Si1-O3	105.0(2) x 2
Na2-O6	2.355(5)	O2-Na2-O8	96.3(2)	Si1-O3	1.633(4) x 2	O2-Si1-O3	115.0(2) x 2
Na2-O8	2.335(5)	O2-Na2-OW1	81.9(2)	<Si1-O>	1.619	O3-Si1-O3'	101.8(3)
Na2-OW1	2.490(6)	O2-Na2-OW5	90.8(2)				
Na2-OW3	2.468(6)	O6-Na2-O8	78.5(2)			Si2 tetrahedron	
Na2-OW5	2.929(7)	O6-Na2-OW3	91.9(2)				
		O6-Na2-OW5	98.7(2)	Si2-O3	1.628(4)	O3-Si2-O4	103.9(2)
< Na2-O >	2.501	O8-Na2-OW1	92.1(2)	Si2-O4	1.640(4)	O3-Si2-O5	105.8(2)
		O8-Na2-OW5	95.0(2)	Si2-O5	1.645(4)	O3-Si2-O6	114.1(2)
Na2-Na2	3.114(5)	OW1-Na2-OW3	88.6(2)	Si2-O6	1.579(4)	O4-Si2-O5	105.6(2)
		OW1-Na2-OW5	90.6(2)			O4-Si2-O6	115.3(2)
		OW3-Na2-OW5	78.3(2)	<Si2-O>	1.623	O5-Si2-O6	111.4(2)
		Na3 octahedron				Si3 tetrahedron	
Na3-O6	2.378(5) x 2	O6-Na3-O6'	79.0(2)	Si3-O4	1.633(4)	O4-Si3-O5	106.9(2)
Na3-OW3	2.489(5) x 2	O6-Na3-OW3	90.8(2) x 2	Si3-O5	1.637(4)	O4-Si3-O7	103.7(2)
Na3-OW4	2.434(5) x 2	O6-Na3-OW3'	98.3(2) x 2	Si3-O7	1.636(4)	O4-Si3-O8	113.3(2)
		O6-Na3-OW4	97.0(1) x 2	Si3-O8	1.586(4)	O5-Si3-O7	106.1(2)
< Na-O >	2.434	OW3-Na3-OW4	79.1(2) x 2			O5-Si3-O8	111.7(2)
		OW3-Na2-OW4'	92.3(2) x 2	<Si3-O>	1.623	O7-Si3-O8	114.4(2)
		OW4-Na3-OW4'	87.1(3)				

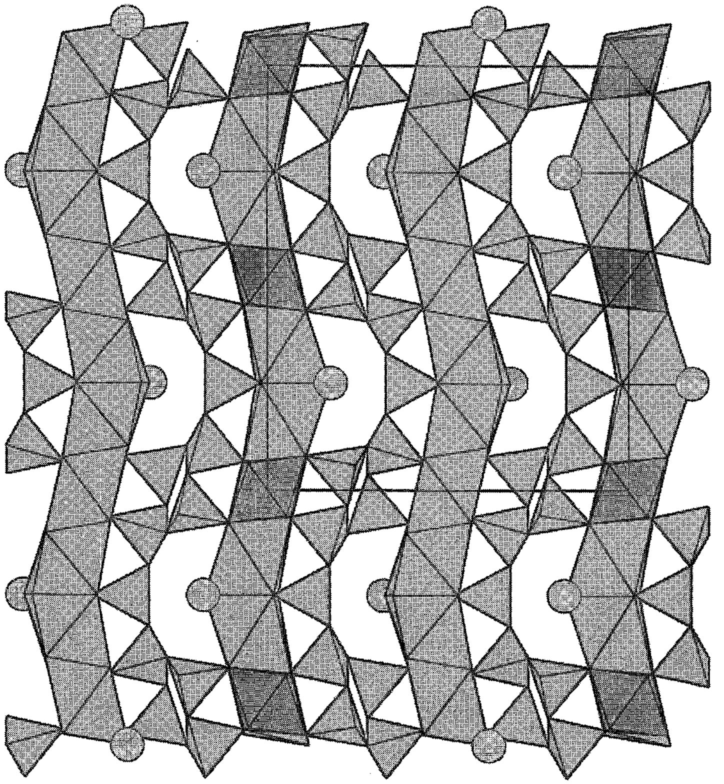
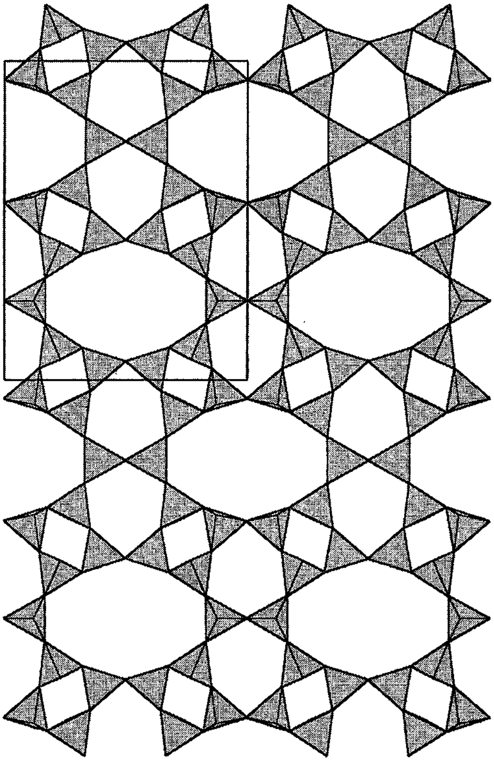


FIG. 2. Varennesite, (100) plane showing undulating layers of silicate tetrahedra and Na (lighter shading) and Mn (darker shading) octahedra. Water molecule OW6 is shown as a filled circle, and the unit cell is outlined ($b < c$).

is an unbranched fünfer single layer (Liebau 1985) consisting of pairs of 6-membered rings with a common edge (Fig. 3). The orientation of the tetrahedra, with respect to the direction in which the apical oxygen points within the paired rings, alternates along +**b** and –**b** (Fig. 2). The layer of octahedra, of composition $[Na_8Mn_2O_{10}(OH)_2{\cdot}11H_2O]^{10-}$, consists of face-sharing $Na\phi_6$ and edge-sharing $Na\phi_6$ and $Mn\phi_6$, where ϕ is O^{2-}, $(OH)^-$ or H_2O (Fig. 4). The sheet of octahedra has holes occupied by H_2O molecule OW6. The layer of tetrahedra overlies the layer of octahedra in a manner that maximizes the number of tetrahedra along the band of edge-sharing octahedra (Fig. 5), whereas the large holes of the 10-membered ring are located at the sites of the water molecules that are bonded to face-sharing Na polyhedra. The undulation noted in the layers (Fig. 2) is caused by ribbons of face-sharing octahedra alternating with chains of edge-sharing octahedra (Fig. 4). Channels that parallel the **a** axis in the structure are filled by H_2O molecules. Five of these are bonded to Na atoms, whereas the OW6 is H-bonded to O1 (OW6–O1 bond distance is 2.83 Å). Additional disordered molecules, likely of H_2O or perhaps some S- or Cl-bearing species, lie along these channels, as noted by electron-density peaks on the final difference-Fourier map. This residual in electron density explains the rather high final R values.

FIG. 3. Varennesite, (010) silicate layer. The unit cell is outlined ($a < c$).



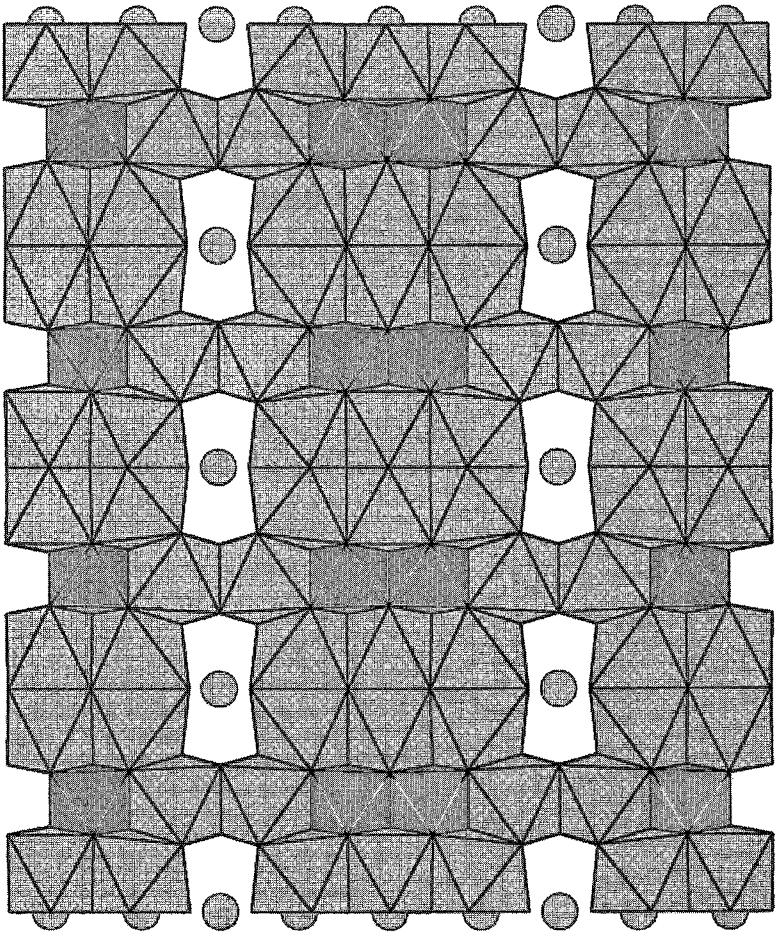


FIG. 4. Varennesite, (010) layer of octahedra with Na octahedra (lighter shading) and Mn octahedra (darker shading). Water molecule OW6 is shown as a filled circle.

DISCUSSION

Although there are many monophyllosilicates, the varennesite structure need only be compared to those that have layers of unbranched tetrahedra of the type $[Si_2O_5]^{2-}$ alternating with layers of octahedra. Liebau (1985) derived a good method of showing the influence of the cation composition of the octahedrally coordinated layer on the distribution of tetrahedra in the silicate layer. The average radius of the octahedrally coordinated cation [$\langle r_M \rangle$, using the values of Shannon (1976)] and the ratio of octahedrally coordinated to tetrahedrally coordinated cations (n_M:n_T) both influence the distribution of silica tetrahedra. As these parameters increase, the mesh size of the layer of octahedra effectively spreads out in area, thus requiring the layer of tetrahedra to compensate its fit. The compensation in fit may be achieved by: 1) rotation, tilting, or inversion of the tetrahedra, 2) variation in the topological linkages within the layer, or 3) curvature of layers. For varennesite, $\langle r_M \rangle$ = 1.00 Å and n_M:n_T = 1.00. These values are close to those of two Mn-silicates, manganpyrosmalite, $Mn_8[Si_6O_{15}](OH,Cl)_{10}$, with $\langle r_M \rangle$ = 0.83 Å and n_M:n_T = 1.33, and bementite, $Mn_7[Si_6O_{15}](OH)_8$, with $\langle r_M \rangle$ = 0.83 Å and n_M:n_T = 1.17. Apophyllite, $KCa_4[Si_4O_{10}](F,OH)\cdot 8H_2O$, also has similar values, with $\langle r_M \rangle$ = 1.08 Å (note that K and Ca are in 8- and 7-fold coordination, respectively), and

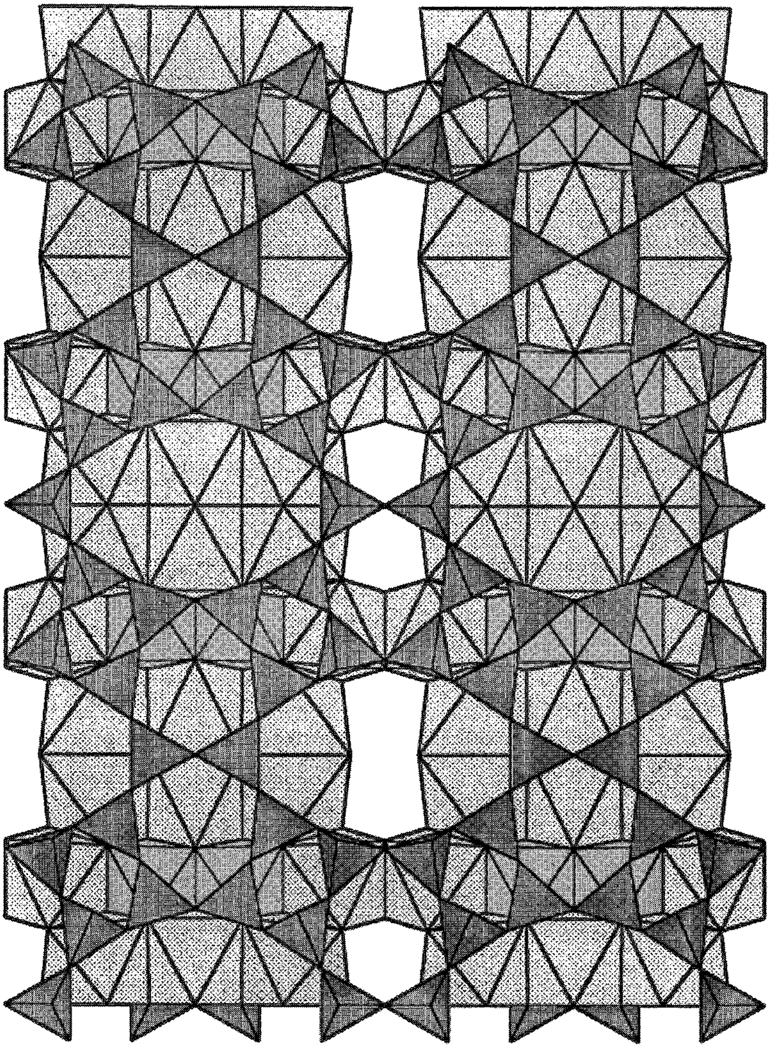


FIG. 5. Varennesite, (010) silicate layer overlying the layer of octahedra.

n_M:n_T = 1.25. The silicate layer for each of these structures is shown in Figure 6. Manganpyrosmalite and bementite have identical (r_M) values, but the increase of n_M:n_T from bementite to manganpyrosmalite is compensated for by a topological rearrangement of the six-membered rings, giving rise to larger holes in the layer of tetrahedra in manganpyrosmalite. Apophyllite shows a large increase in (r) over the Mn-silicates, which is the cause of a shift to a four-membered ring. Varennesite, with its intermediate values, is a compromise, with each pair of six-membered rings having a common edge. In order to compensate for the decrease in (r) from apophyllite to varennesite, the layer of octahedra in the former is flat, whereas in the latter it is corrugated. In Figure 7, note the similarity in arrangement of octahedrally coordinated cations, H_2O molecules and silicate layers in the two structures.

To date, three other hydrated Na–Mn silicates are known to be close in composition to varennesite, $Na_8Mn_2(Si_{10}O_{25})(OH,Cl)_2 \cdot 12H_2O$. These are raite, $Na_4Mn_4Si_8(O,OH)_{24} \cdot 9H_2O$, shafranovskite, $Na_2MnSi_3O_8 \cdot 3H_2O$, and zakharovite, $Na_4Mn_5Si_{10}O_{24}(OH)_6 \cdot 6H_2O$. These minerals occur in the peralkaline Lovozero massif or Khibina massif, Kola peninsula, in Russia. Raite and zakharovite also are found at Mont Saint-Hilaire. Unfortunately, the crystal structure of these minerals has not been determined, but it is

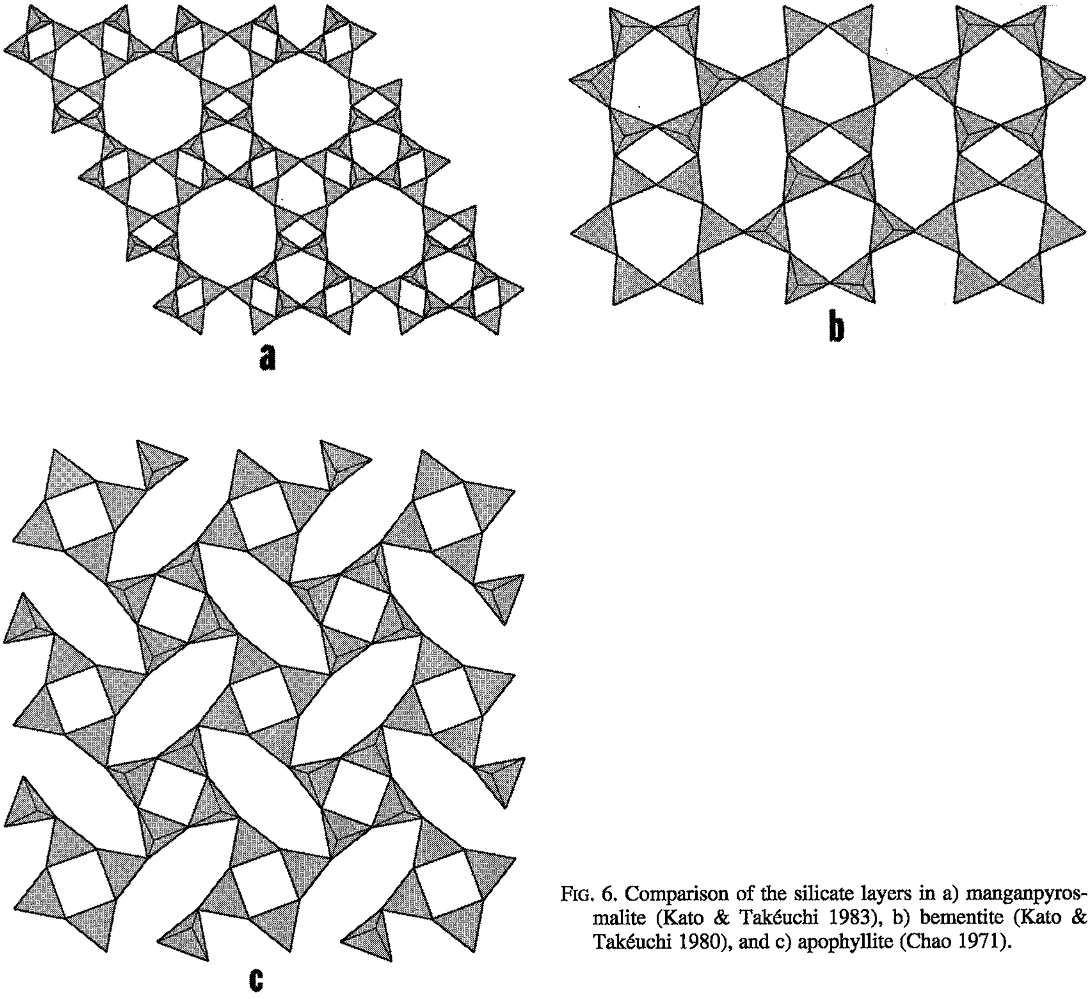


FIG. 6. Comparison of the silicate layers in a) manganpyrosmalite (Kato & Takéuchi 1983), b) bementite (Kato & Takéuchi 1980), and c) apophyllite (Chao 1971).

evident that all form during the late stages of crystallization of peralkaline rocks. Varennesite is by far the most strongly alkaline of all the phases, and its stability is due to the ability of Na to adopt novel schemes of coordination.

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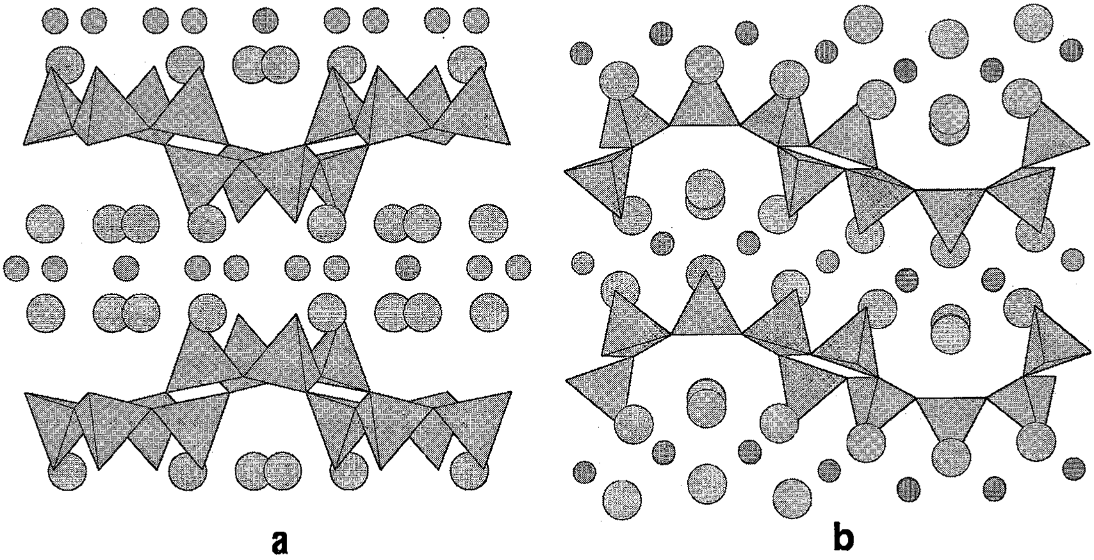

FIG. 7. Comparison of the layering of silicate tetrahedra, H_2O molecules (lighter-shaded circles) and octahedrally coordinated cations (darker-shaded circles) in a) apophyllite and b) varennesite.

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