

NATROLEMOYNITE, A NEW HYDRATED SODIUM ZIRCONOSILICATE FROM MONT SAINT-HILAIRE, QUEBEC: DESCRIPTION AND STRUCTURE DETERMINATION

ANDREW M. McDONALD[§]

Department of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

GEORGE Y. CHAO[¶]

Ottawa–Carleton Geoscience Centre, Department of Earth Sciences, Carleton University, Ottawa, Ontario K1S 5B6, Canada

ABSTRACT

Natrolemoynite is a new member of the lemoynite group found in altered or unaltered pegmatites cutting nepheline syenite at the Poudrette quarry, Mont Saint-Hilaire, Quebec. In altered pegmatites, it is associated with microcline, lemoynite, lepidocrocite, galena, sphalerite, calcite and pyrite, and in unaltered pegmatites, with biotite, microcline, albite, magnetite, a chlorite-group mineral, a burbankite-group mineral, an unidentified donnayite-(Y)-like mineral, zircon and pyrochlore. Crystals are colorless to white (occasionally with a slightly pink to red tinge), bladed to prismatic, elongate along [001], with maximum widths of 1 mm and lengths of 2 mm. The mineral typically develops in compact radial aggregates and spheres 4 mm in maximum diameter. It is transparent to translucent, with a vitreous to subadamantine luster and a white streak. The Mohs hardness is 3. Perfect {100} and {010} cleavages and a poor {001} cleavage are observed. D_{meas} is 2.47(1) g/cm³ and D_{calc} , 2.50 g/cm³. Natrolemoynite is biaxial negative, α 1.533(1), β 1.559(1), γ 1.567(1), $2V_{\text{meas.}}$ = 63(1)°, $2V_{\text{calc.}}$ = 57(1)°; dispersion is weak, with r and v crossed. The optical orientation is $X = b$, $Z \wedge a = 41^\circ$ (measured in the obtuse angle β). The average result of nineteen electron-microprobe analyses gave Na₂O 7.47, K₂O 1.29, CaO 0.37, MnO 0.12, Al₂O₃ 0.04, SiO₂ 54.51, TiO₂ 0.38, ZrO₂ 21.97, Nb₂O₅ 1.01 and H₂O (calc.) 14.72, total 101.88 wt.%, corresponding to (Na_{2.66}K_{0.30}Ca_{0.07}Mn_{0.02}) Σ 3.05 (Zr_{1.96}Nb_{0.08}Ti_{0.05}) Σ 2.09 (Si_{9.99}Al_{0.01}) Σ 10O_{25.79}•9H₂O on the basis of 10(Si + Al) or, ideally, Na₄Zr₂Si₁₀O₂₆•9H₂O. It is monoclinic, $C2/m$, a 10.5150(2), b 16.2534(4), c 9.1029(3) Å, β 105.462(2)°, V 1499.4(1) Å³, $Z = 2$. The structure was refined to $R = 4.2\%$ for 2133 reflections [$F_o > 4\sigma(F_o)$]. Six-membered rings of SiO₄ tetrahedra are linked along [001] by ZrO₆ octahedra to form a zirconosilicate framework. Channels parallel to [001] are occupied by Na and H₂O. Evidence is provided for limited Na \leftrightarrow H₃O⁺ substitution. Crystal-chemical and field relations indicate that paragenetically, natrolemoynite is one of the last sodium zirconosilicate hydrate phases to develop.

Keywords: natrolemoynite, new mineral species, zirconosilicate, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La natrolemoynite est un nouveau membre du groupe de la lemoynite, découverte dans des pegmatites altérées ou non recoupant des syénites néphéliniques dans la carrière Poudrette, au mont Saint-Hilaire, Québec. Dans le cas des pegmatites altérées, elle est associée à microcline, lemoynite, lepidocrocite, galène, sphalérite, calcite et pyrite; lui sont associés dans les pegmatites non altérées biotite, microcline, albite, magnétite, un minéral du groupe de la chlorite, un autre du groupe de la burbankite, un minéral non identifié ressemblant à la donnayite-(Y), zircon et pyrochlore. Les cristaux sont incolores à blanc (possiblement avec une teinte rosâtre ou rougeâtre), en lames ou en prismes, allongés selon [001], avec une largeur et une longueur maximales de 1 et 2 mm, respectivement. Le minéral se présente en amas compacts fibroradiés et en boules atteignant un diamètre de 4 mm. La natrolemoynite est transparente à translucide, avec un éclat vitreux ou sub-adamantin et une rayure blanche. La dureté de Mohs est 3. Les clivages {100} et {010} sont parfaits, et le clivage {001}, de piètre qualité. La densité mesurée est 2.47(1) g/cm³, et la densité calculée, 2.50 g/cm³. La natrolemoynite est biaxe négative, α 1.533(1), β 1.559(1), γ 1.567(1), $2V_{\text{mes.}}$ = 63(1)°, $2V_{\text{calc.}}$ = 57(1)°; la dispersion est faible, avec r et v croisés. L'orientation optique est $X = b$, $Z \wedge a = 41^\circ$ (mesuré dans l'angle β obtus). La moyenne des résultats de dix-neuf analyses à la microsonde électronique a donné Na₂O 7.47, K₂O 1.29, CaO 0.37, MnO 0.12, Al₂O₃ 0.04, SiO₂ 54.51, TiO₂ 0.38, ZrO₂ 21.97, Nb₂O₅ 1.01 et H₂O (calc.) 14.72, pour un total de 101.88% (poids), ce qui correspond à (Na_{2.66}K_{0.30}Ca_{0.07}Mn_{0.02}) Σ 3.05 (Zr_{1.96}Nb_{0.08}Ti_{0.05}) Σ 2.09 (Si_{9.99}Al_{0.01}) Σ 10O_{25.79}•9H₂O sur une base de 10(Si + Al) ou, idéalement, Na₄Zr₂Si₁₀O₂₆•9H₂O. Elle est monoclinique, $C2/m$, a 10.5150(2), b 16.2534(4), c 9.1029(3) Å, β 105.462(2)°, V 1499.4(1) Å³, $Z = 2$. La structure a été affinée jusqu'à un résidu R de 4.2% avec 2133 réflexions

[§] E-mail address: amcdonald@nickel.laurentian.ca

[¶] Present address: 2031 Delmar Drive, Ottawa, Ontario K1H 5P6, Canada.

[$F_o > 4\sigma(F_o)$]. Des anneaux de tétraèdres SiO_4 à six membres sont liés le long de [001] par des octaèdres ZrO_6 pour former une trame zirconsilicatée. Des canaux parallèles à [001] sont le site de Na et de H_2O . Nous présentons de l'évidence favorisant une substitution limitée $\text{Na} \leftrightarrow \text{H}_3\text{O}^+$. D'après les propriétés cristallographiques et les relations de terrain, la natrolemoynite semble être la dernière des phases zirconsilicatées hydratées de sodium à cristalliser.

(Traduit par la Rédaction)

Mots-clés: natrolemoynite, nouvelle espèce minérale, zirconsilicate, structure cristalline, mont Saint-Hilaire, Québec.

INTRODUCTION

Lemoynite, ideally $(\text{Na,K})_2\text{CaZr}_2\text{Si}_{10}\text{O}_{26} \cdot 5-6\text{H}_2\text{O}$, is a rare mineral originally described from Mont Saint-Hilaire, Quebec by Perrault *et al.* (1969). During the course of a re-investigation of the structure of this mineral, a number of specimens were found to contain a phase that macroscopically resembles lemoynite, but which produces an X-ray powder-diffraction pattern distinct from that of lemoynite. Subsequent chemical and crystal-structure analyses of this phase indicated it to be a Na-dominant polymorph of lemoynite. It has been named *natrolemoynite* in allusion to its relationship to lemoynite. Both the mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, IMA. The holotype material is housed in the collection of the Canadian Museum of Nature, Ottawa, catalogue number CNMMI 81534.

OCCURRENCE

Natrolemoynite occurs on specimens of an intensely altered pegmatite cutting nepheline syenite and exposed in the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec. This pegmatite, now microcline-dominant, was originally encountered in 1964–1965, at which point small quantities of material containing lemoynite-group minerals were recovered. It was intersected once more in 1985, at which time the largest quantities of these minerals were collected (Horváth & Gault 1990). Samples containing natrolemoynite that were analyzed during the course of this study were originally collected by the late Mr. A. Vogg, of Arnprior, Ontario, and are believed to have been derived from the 1985 find.

Natrolemoynite has a paragenesis similar to that of lemoynite (both species may in fact be found on the same specimen), both occurring as late-stage phases in interstices between coarse, intergrown crystals of microcline perthite, possibly crystallizing from fluids modified by the alteration of pre-existing zirconsilicates (*e.g.*, eudialyte-group minerals) or Zr-bearing silicates (*e.g.*, aegirine, arfvedsonite; Rubin *et al.* 1993, Piilonen *et al.* 1998). Associated minerals include microcline, lemoynite, lepidocrocite [identified by a combination of semiquantitative energy-dispersion spectrometry and Fourier-transform infrared-absorption spectroscopy; previously described as a “reddish brown

resinous material” by Horváth & Gault (1990)], galena, sphalerite, calcite and pyrite.

Following application to the CNMMN, IMA, a new occurrence of natrolemoynite at Mont Saint-Hilaire was recorded by the senior author. The mineral was found as fine acicular sprays (<0.5 mm in length; Fig. 1) on quartz in a pegmatite block recovered from the northeast corner of the Poudrette quarry on the so-called eighth level in July, 1998. Associated minerals include biotite, microcline, albite, magnetite, a chlorite-group mineral, a burbankite-group mineral [possibly remondite-(Ce)], an unidentified donnayite-(Y)-like mineral (temporarily designated UK109), zircon and pyrochlore.

Natrolemoynite is chemically and structurally related to both lemoynite and altsite (Khomyakov *et al.* 1995). We propose that all three minerals be included in what will be henceforth referred to as the lemoynite group.

PHYSICAL AND OPTICAL PROPERTIES

Crystals of natrolemoynite are bladed to prismatic, elongate along [001], with maximum widths of 1 mm and lengths of 2 mm. They typically develop in compact radial aggregates and spheres of maximum diameter 4 mm (Fig. 2). Growth from a common point of nucleation and development of the resulting radial texture may be evidence of rapid crystallization. The dominant forms observed include {100}, {010} and {001}, with minor, unidentified pinacoid-like forms also being present in some cases. The mineral is colorless to white and may have a slightly pink to red tinge, possibly owing to inclusions of lepidocrocite. It has a vitreous to subadamantine luster (the latter most notable in samples from the 1998 discovery), is transparent to translucent, has a white streak, and shows no fluorescence in either short- or long-wave ultraviolet radiation. The mineral has a Mohs hardness of 3, perfect {100} and {010} cleavages along with a poor {001} cleavage. It is brittle and has an uneven fracture. The density, measured by the float-sink method using a pycnometer and bromoform diluted with acetone, is 2.47(1) g/cm³, which agrees very favorably with the calculated value of 2.50 g/cm³.

Natrolemoynite is nonpleochroic, biaxial negative, α 1.533(1), β 1.559(1), γ 1.567(1) (for $\lambda = 590$ nm), $2V_{\text{meas.}} = 63(1)^\circ$, $2V_{\text{calc.}} = 57(1)^\circ$. The dispersion is weak with r and v crossed. The optical orientation is $X = b$, $Z \wedge a = 41^\circ$ (measured in the obtuse angle β). A



FIG. 1. Photograph of natrolemoynite from unaltered pegmatite. The spray is 0.5 mm across.

Gladstone–Dale calculation gave a compatibility index of -0.027 , excellent (Mandarino 1981).

CHEMICAL COMPOSITION

Chemical analyses were conducted on a CAMEBAX SX-50 electron microprobe using an operating voltage of 15 kV, a beam current of 10 nA and a beam diameter of approximately 10 μm . The rather small beam-diameter was necessitated by the large length:width ratio of the crystals. Sample degradation under the electron beam was severe, requiring the beam to be rastered along grains being analyzed. Energy-dispersion data were collected using the following standards: wadeite ($\text{ZrL}\alpha$, $\text{KK}\alpha$), wollastonite ($\text{CaK}\alpha$), synthetic MnTiO_3 ($\text{MnK}\alpha$, $\text{TiK}\alpha$), synthetic FeNb_2O_6 ($\text{NbL}\alpha$), and synthetic Al_2O_3 ($\text{AlK}\alpha$). In addition, wavelength-dispersion data were collected using wadeite ($\text{SiK}\alpha$) and albite ($\text{NaK}\alpha$) as standards. Also sought, but not detected,

were F, Hf and S. Nineteen analyses of four different crystals gave as an average: Na_2O 7.47 (5.89–9.22), K_2O 1.29 (0.92–1.72), CaO 0.37 (0.22–0.57), MnO 0.12 (0–0.21), Al_2O_3 0.04 (0–0.19), SiO_2 54.51 (53.62–55.27), TiO_2 0.38 (0.11–0.56), ZrO_2 21.97 (20.84–22.83), Nb_2O_5 1.01 (0.66–1.51) and H_2O (calc.) 14.72 (14.49–14.91), total 101.88 wt.%. The presence of H_2O was confirmed by infrared spectroscopy (see below), and results of the crystal-structure analysis, the latter serving as the basis for calculation of the stoichiometric proportion of H_2O . The empirical formula based on 10($\text{Si} + \text{Al}$) is: $(\text{Na}_{2.66}\text{K}_{0.30}\text{Ca}_{0.07}\text{Mn}_{0.02})_{\Sigma 3.05}(\text{Zr}_{1.96}\text{Nb}_{0.08}\text{Ti}_{0.05})_{\Sigma 2.09}(\text{Si}_{9.99}\text{Al}_{0.01})_{\Sigma 10}\text{O}_{25.79} \cdot 9\text{H}_2\text{O}$, ideally $\text{Na}_4\text{Zr}_2\text{Si}_{10}\text{O}_{26} \cdot 9\text{H}_2\text{O}$. The low total for the alkali site may be due to a combination of element migration under the electron beam, the presence of vacancies and the presence of hydronium ions, as noted in lemoynite (Le Page & Perrault 1976). The mineral does not effervesce in 1:1 HCl at room temperature.

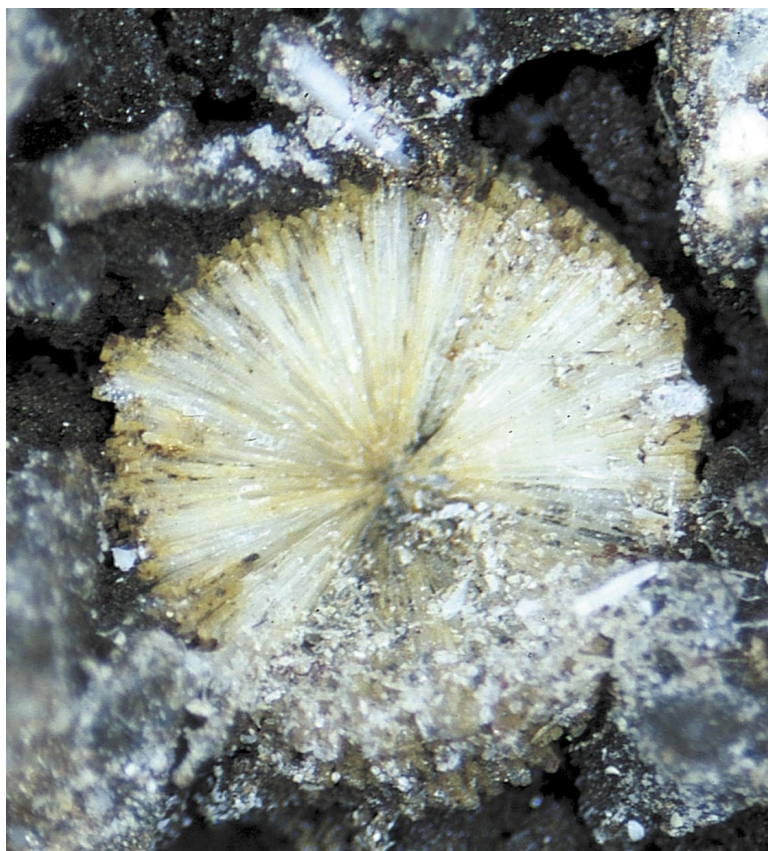


FIG. 2. Photograph of natrolemoynite from altered pegmatite. The radial spray is 3 mm in diameter.

INFRARED ANALYSIS

The infrared spectrum of natrolemoynite (Fig. 3) was obtained with a pressed KBr pellet containing approximately 15 mg of material on a Perkin-Elmer Fourier-transform infrared spectrometer. The spectrum was collected over a range of $4000\text{--}400\text{ cm}^{-1}$. It shows a broad peak centered in the 3435 cm^{-1} region (O-H stretching) and a relatively sharp peak at 1641 cm^{-1} (H-O-H bending), suggesting the presence of molecular H_2O . The asymmetric nature of the peaks is a reflection of the presence of four crystallographically distinct H_2O molecules (one of which shows a high degree of positional disorder and partial occupancy), as indicated by results of the crystal-structure analysis. The spectrum also shows a series of strong, sharp bands in the $1200\text{--}950\text{ cm}^{-1}$ region (asymmetric O-Si-O stretching) and in the $800\text{--}700\text{ cm}^{-1}$ (symmetric Si-O-Si stretching). Absorption bands in the remainder of the spectra could not be unequivocally assigned.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray powder-diffraction data were collected with a 114.6 diameter Debye-Scherrer camera employing Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). Intensities were visually estimated. Whether or not an hkl plane contributed to a reflection was determined from the powder pattern calculated using the atomic parameters determined in the crystal-structure analysis and the program POWDERCELL (Nolze & Kraus 1998). Overall agreement between the observed and calculated patterns is very good (Table 1). Distinguishing between natrolemoynite and lemoynite on the basis of X-ray powder-diffraction patterns can be readily accomplished by comparison of the two largest d -values: 8.832 and 8.132 \AA for natrolemoynite versus 9.0 and 8.01 \AA for lemoynite (Perrault *et al.* 1969).

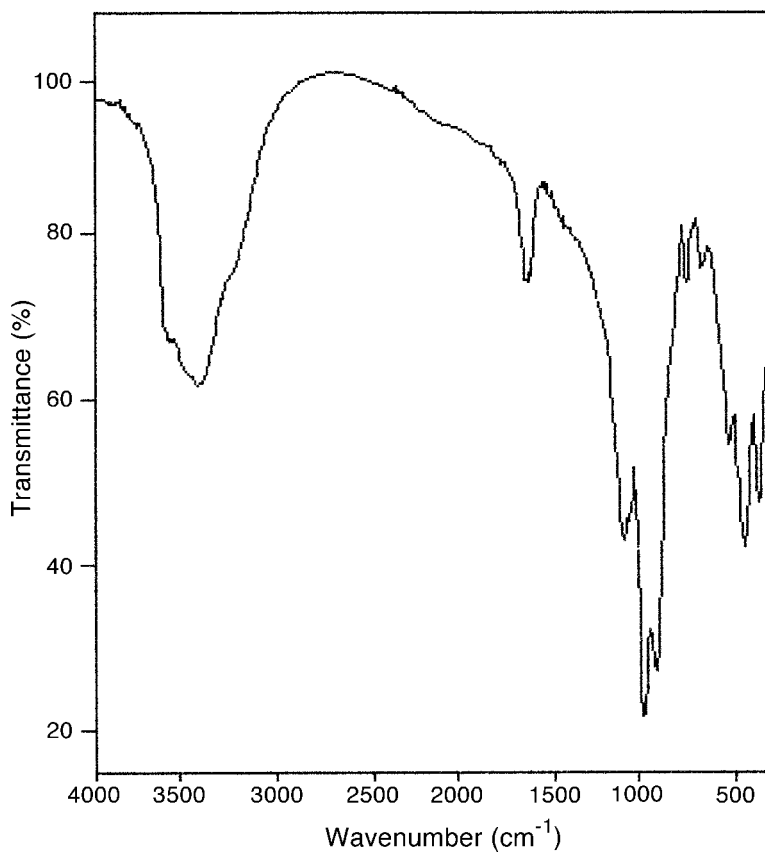


FIG. 3. Infrared spectrum of natrolemoynite.

X-ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using a prismatic crystal mounted so as to rotate about c . Data measurement and reduction (Lorentz, polarization, background, scaling) were carried out using the NRCVAX package of computer programs (Gabe *et al.* 1989). A set of 25 reflections permuted four ways ($\pm h$ at $\pm 2\theta$) was used to give the refined unit-cell dimensions provided in Table 2. In light of the fact that lemoynite crystallizes in the space group $C2/c$ but exhibits strong $C2/m$ pseudosymmetry (Le Page & Perrault 1976), a careful analysis of $h0l$ reflections in natrolemoynite was undertaken prior to collection of intensity data. This failed to support the presence of a c -glide perpendicular to b . A full sphere of X-ray intensity data out to $2\theta = 60^\circ$ was collected using a $\theta:2\theta$ scan-mode, with scan speeds inversely proportional to intensity. Information pertinent to the data collection and structure determination is provided in Table 2.

Solution and refinement of the crystal structure were accomplished using the SHELX-93 package of pro-

grams (Sheldrick 1993). The crystal structure was solved using direct methods with scattering curves taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. Phasing of a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.857; considering the observed morphology of the crystals, the refined structures of other lemoynite-group minerals and the clear presence of a m -plane rather c -glide perpendicular to b , the centrosymmetric space-group $C2/m$ was selected. The phase-normalized factors were used to give an E -map on which were located the Zr, one Na, three Si and several O sites. The remaining Na and O sites were located on subsequent difference-maps. Determination of those O sites likely occupied by H₂O was made on the basis of calculated bond-valence sums. Anisotropic refinement of this model indicated that the Na2 and OW11 sites have lower-than-ideal site-occupancy factors (SOF). In natrolemoynite, the zirconosilicate framework [(Zr₄Si₂₀O₅₂)] has a net unsatisfied charge of -8 that must be compensated for by intraframework ions, principally Na. Na1 occupies a

TABLE 1. NATROLEMOYNYTE: X-RAY POWDER-DIFFRACTION DATA

<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>hkl</i>	<i>l</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>hkl</i>
30	8.832	8.773	001	1	2.064	2.062	$\bar{1}72$
100	8.132	8.127	020	15	2.032	2.032	080
25	6.998	6.982	$\bar{1}11$	20	1.995	1.995	262
40	5.975	5.962	021			1.990	243
15	5.560	5.546	111	10	1.986	1.987	063
10	5.058	5.067	200	15	1.933	1.933	404
15	5.011	5.004	$\bar{2}01$	15	1.925	1.921	422
2	4.805	4.778	130	20	1.886	1.886	461
10	4.443	4.437	$\bar{1}31$			1.886	280
5	4.324	4.324	$\bar{1}12$	5	1.858	1.856	511
5	4.265	4.261	$\bar{2}21$			1.850	460
3	4.077	4.063	040	5	1.844	1.844	$\bar{1}73$
35	3.974	3.955	201			1.842	204
10	3.866	3.860	022	5	1.806	1.807	281
30	3.693	3.687	041	5	1.779	1.778	442
40	3.564	3.556	221	5	1.747	1.747	$\bar{6}01$
35	3.490	3.491	$\bar{2}22$	7	1.729	1.728	$\bar{2}64$
5	3.459	3.455	$\bar{1}32$			1.727	514
10	3.350	3.402	$\bar{3}11$	5	1.707	1.705	064
2	3.177	3.170	240			1.703	403
20	3.053	3.051	$\bar{3}12$	2	1.686	1.683	353
		3.046	132	10	1.670	1.668	083
10	2.986	2.982	$\bar{1}13$	5	1.634	1.634	$\bar{6}23$
10	2.931	2.927	$\bar{3}31$	7	1.611	1.607	481
15	2.891	2.888	203	7	1.574	1.573	464
25	2.846	2.847	151			1.571	443
		2.834	241	5	1.554	1.553	604
30	2.804	2.801	$\bar{2}42$	10	1.544	1.548	$\bar{3}55$
15	2.778	2.773	222	5	1.525	1.524	0102
15	2.715	2.721	$\bar{2}23$	7	1.504	1.503	2101
		2.709	060	15	1.476	1.475	404
15	2.634	2.632	$\bar{1}52$			1.474	641
		2.628	401			1.473	065
10	2.503	2.501	$\bar{4}21$	7	1.440	1.442	463
1	2.457	2.437	152	15	1.421	1.421	$\bar{2}46$
25	2.391	2.391	422	10	1.363	1.363	$\bar{4}102$
		2.388	260	7	1.324	1.325	681
		2.387	242			1.324	2103
5	2.329	2.327	333			1.323	$\bar{2}66$
2	2.283	2.283	203	15	1.298	1.300	680
5	2.237	2.235	261			1.300	591
		2.232	403			1.298	226
20	2.200	2.198	223	10	1.283	1.284	$\bar{2}27$
		2.193	004			1.282	$\bar{3}113$
8	2.157	2.152	423			1.281	2121
10	2.120	2.118	024	15	1.252	1.256	4102
10	2.100	2.096	$\bar{1}34$				

special position with multiplicity 4, and *Na2* occupies a general position of multiplicity 8. However *Na2* has a refined *SOF* of ~0.25, leaving a total unsatisfied charge of -2 on the framework. This charge discrepancy could be compensated by hydronium (H_3O^+), and the substitution $Na \rightleftharpoons H_3O^+$ has been suggested to occur in lemoynite (Le Page & Perrault 1976) and the sodium titanium silicate hydrate vinogradovite (Kalsbeek & Rønso 1992). Both *Na1* and *Na2* are separated by a short distance of ~2 Å, suggesting that the two sites cannot be occupied simultaneously, but rather on an alternating basis. Anisotropic refinement also indicated a lower-than-ideal *SOF* for the *OW11* site, combined with a high anisotropic positional displacement behavior. The site was therefore refined isotropically, with a positional displacement factor fixed at 0.1, a value consistent with those observed for other sites unequivocally assigned

TABLE 2. MISCELLANEOUS INFORMATION ABOUT NATROLEMOYNYTE

Space group	C2/m (# 12)	Diffractometer	Enraf Nonius CAD4
<i>a</i> (Å)	10.5150(2)*	Radiation	MoK α (50 kV, 40 mA)
<i>b</i>	16.2534(4)*	Monochromator	graphite
<i>c</i>	9.1029(3)*	Crystal shape	prismatic, elongate on [001]
β (°)	105.462(2)*	μ (MoK α)	0.98 mm ⁻¹
Crystal size	0.8 × 0.04 × 0.07 mm		
<i>V</i> (Å ³)	1499.4(1)		
<i>Z</i>	2		
Chemical formula		Chemical formula	Na ₂ Zr ₇ Si ₁₀ O ₂₆ •9H ₂ O
Intensity-data collection		θ :2 θ scan mode	
2 θ limit			60°
Number of unique reflections			2266
Number of observed reflections			2125
Criterion for observed reflections			$F_o > 4\sigma(F_o)$
GoOF			1.217
Final <i>R</i> for all observed reflections			4.6%
Final <i>wR</i> ² for all observed reflections			13.6%

* values refined from four-circle diffractometer data.

as H_2O (*OW8*, 9 and 10). Refinement of this model resulted in a *SOF* of 0.28(1) for *OW11*, which corresponds to 2.24 H_2O molecules *pfu*. Combining this with the sum derived from the other three H_2O sites (*OW8*, 9 and 10) gives a net sum of 18.24 H_2O molecules *pfu*, or ideally nine H_2O molecules for *Z* = 2. The *OW11* site is within a reasonable distance for bonding to *Na1* [2.87(2) Å], but unreasonably close to *Na2* [2.02(2) Å]. Given these distances, the low *SOF* for the *OW11* site and the possible mutually exclusive occupation of the *Na1* and *Na2* sites, the *OW11* site is considered to be concomitantly occupied with *Na1*. Final least-squares refinement of this model gave residuals of *R* = 4.6% and *wR*² = 13.6%. An isotropic-extinction factor was applied but did not change the residuals substantially.

Table 3 contains the final positional and displacement parameters; selected interatomic distances are presented in Table 4, and bond-valence sums in Table 5. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, K1A 0S2, Canada.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

There are three crystallographically distinct SiO_4 tetrahedra in the structure. The $\langle Si-O \rangle$ decreases in length, $Si(3)-O < Si(1)-O < Si(2)-O$, this being primarily a function of the number of observed tetrahedral linkages [$Si(3)O_4$ is joined to four other tetrahedra, $Si(1)O_4$ to three and $Si(2)O_4$ to two]. In general, the shortest $Si-O$ distances involve those oxygen atoms shared with ZrO_6 octahedra (*i.e.*, *O2,6,7*). The ZrO_6 octahedron is quite regular, with its axial bonds being only slightly longer than its equatorial ones (2.092 *versus* 2.061 and 2.077 Å, respectively). The *Na1* site is coordinated by six oxygen atoms in a distorted octahedral arrangement. The *Na2* site is coordinated by four

TABLE 3. POSITIONAL AND DISPLACEMENT PARAMETERS FOR NATROLEMOYNITE

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Na1	0	0.3926	½	0.0054(2)	0.0044(2)	0.0107(3)	0	0.0004(2)	0	0.0072(1)
Na2	0.1801	0.4296	0.6210	0.0108(2)	0.0055(7)	0.0063(7)	-0.0016(6)	0.0028(7)	0.0017(7)	0.0074(4)
Zr	¼	¼	½	0.0008(1)	0.0012(1)	0.0015(1)	0.0005(1)	0.0001(1)	0.0000(1)	0.0012(1)
Si1	0.26452(8)	0.09667(5)	-0.25035(9)	0.0008(1)	0.0006(1)	0.0011(1)	0.0000(1)	0.0001(1)	0.0000(1)	0.0009(1)
Si2	0.06154(8)	0.22752(5)	0.74688(1)	0.0009(1)	0.0011(1)	0.0015(1)	-0.0001(1)	0.0002(1)	0.0003(1)	0.0012(1)
Si3	½	0.16734(8)	0	0.0008(1)	0.0009(1)	0.0011(1)	0	-0.0001(1)	0	0.0010(1)
O1	0.1433(2)	0.1411(2)	-0.2017(3)	0.0015(1)	0.0013(1)	0.0024(1)	0.0002(1)	0.0001(1)	0.0002(1)	0.0017(1)
O2	0.1316(2)	0.2790(2)	0.6402(1)	0.0016(1)	0.0013(1)	0.0024(1)	0.0002(1)	0.0007(1)	0.0002(1)	0.0017(1)
O3	0.2294(3)	0	-0.2612(4)	0.0016(1)	0.0006(1)	0.0022(1)	0	0.0000(1)	0	0.0016(1)
O4	0.3969(2)	0.1072(1)	-0.1125(2)	0.0015(1)	0.0016(1)	0.0022(1)	-0.0005(1)	-0.0004(1)	-0.0002(1)	0.0020(1)
O5	0.0781(3)	0.2761(1)	0.9082(3)	0.0024(1)	0.0022(1)	0.0020(1)	-0.0007(1)	0.0004(1)	0.0006(1)	0.0022(1)
O6	0.2827(3)	0.1318(2)	-0.4070(3)	0.0026(1)	0.0016(1)	0.0019(1)	0.0008(1)	0.0010(1)	0.0006(1)	0.0020(1)
O7	0.0907(2)	0.2073(2)	0.3293(3)	0.0010(1)	0.0029(1)	0.0024(1)	-0.0003(1)	0.0000(1)	0.0000(1)	0.0022(1)
OW8	0.0973(7)	0	-0.6174(6)	0.0082(5)	0.0088(6)	0.04343(4)	0	0.0011(4)	0	0.0076(2)
OW9	0.1717(6)	0.1093(5)	0.1215(6)	0.0092(4)	0.0116(5)	0.0052(3)	0.007(3)	0.0028(2)	0.0055(4)	0.0085(2)
OW10	0.0115(9)	0	-0.1214(10)	0.0066(5)	0.0154(10)	0.0068(5)	0	0.0032(4)	0	0.0094(3)
OW11	0.1003(22)	½	0.75563(24)							0.0100

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN NATROLEMOYNITE

Na(1)O ₆ polyhedron		Na(2)O ₄ polyhedron	
Na1	-O2 × 2 -O6 × 2 -OW11 × 2	Na2	-O6 -O2 -OW9 -OW8 -O>
	2.453 (4) 2.672 (3) 2.874 (17)		2.315 (13) 2.516 (15) 2.528 (15) 2.614 (20) 2.453
<Na1	-O>	<Na2	-O>
	2.666		
ZrO ₆ octahedron		Si(1)O ₄ tetrahedron	
Zr	-O2 × 2 -O7 × 2 -O6 × 2	Si1	-O6 -O3 -O4 -O1 -O>
	2.061 (3) 2.077 (3) 2.092 (2)		1.591 (3) 1.611 (1) 1.615 (3) 1.626 (2) 1.611
<Zr	-O>	<Si1	-O>
	2.077		
Si(2)O ₄ tetrahedron		Si(3)O ₄ tetrahedron	
Si2	-O7 -O2 -O5 -O1	Si3	-O5 × 2 -O4 × 2
	1.600 (3) 1.602 (3) 1.635 (3) 1.648 (3)		1.608 1.609
<Si2	-O>	<Si3	-O>
	1.621		1.608

oxygen atoms in a distorted planar arrangement. Four-coordinated Na is rather unusual, but has been observed in a number of Na-bearing phases from highly alkaline environments including kogarkoite (Fanfani *et al.* 1980), vlasovite (Voronkov *et al.* 1974) and vuonnemite (Ercit *et al.* 1998). The plausibility and occurrence of NaO₄ have been discussed by Ercit *et al.* (1998). These authors presented a grand mean <Na–O> of 2.432 Å, in good agreement with a <Na2–O> of 2.492 Å obtained in this study.

The SiO₄ tetrahedra are joined into two types of six-membered rings: one is composed of two Si(3)O₄ and

TABLE 5. EMPIRICAL BOND-VALENCES (v.u.) FOR NATROLEMOYNITE*

	Na1	Na2	Zr	Si1	Si2	Si3	ΣV
O1				0.995	0.937		1.932
O2	0.171 ⁺²¹	0.144 ⁺²¹	0.715 ⁺²¹		1.061		2.091
O3				1.036 ⁺²¹			2.072
O4				1.025		1.000 ⁺²¹	2.025
O5					0.971	1.003 ⁺²¹	2.024
O6	0.095 ⁺²¹	0.249	0.658 ⁺²¹	1.093			2.095
O7			0.685 ⁺²¹		1.067		1.752
OW8		0.111 ⁺²¹					0.222
OW9		0.141					0.141
OW10							0
OW11	0.055 ⁺²¹						0.112
ΣV	0.642	0.645	4.116	4.149	4.036	4.006	

* Parameters from Brese & O'Keeffe (1991).

four Si(1)O₄ tetrahedra linked to rings of the same type *via* Si(2)O₄ tetrahedra (Fig. 4) and the other is composed of two Si(1)O₄, two Si(2)O₄ and two Si(3)O₄ tetrahedra directly linked *via* Si(3)O₄ tetrahedra to two adjacent rings of the same type (Fig. 5). The two types of rings are joined to form a composite silicate slab of thickness ~7 Å, parallel to [010] (Fig. 5). Adjacent silicate slabs are linked along [001] *via* ZrO₆ octahedra, producing a three-dimensional zirconosilicate framework of composition [ZrSi₅O₁₃]²⁻ (Fig. 5). The framework contains channels parallel to [001] that are occupied by Na1, Na2 and H₂O molecules (Fig. 6). Alternatively, the structure can be regarded as a loop-branched single-chain silicate of periodicity four, with Na as the “soft” cation and Zr as the “hard” cation (Liebau 1985). The chains are joined *via* direct linkages of tetrahedra to form loops of

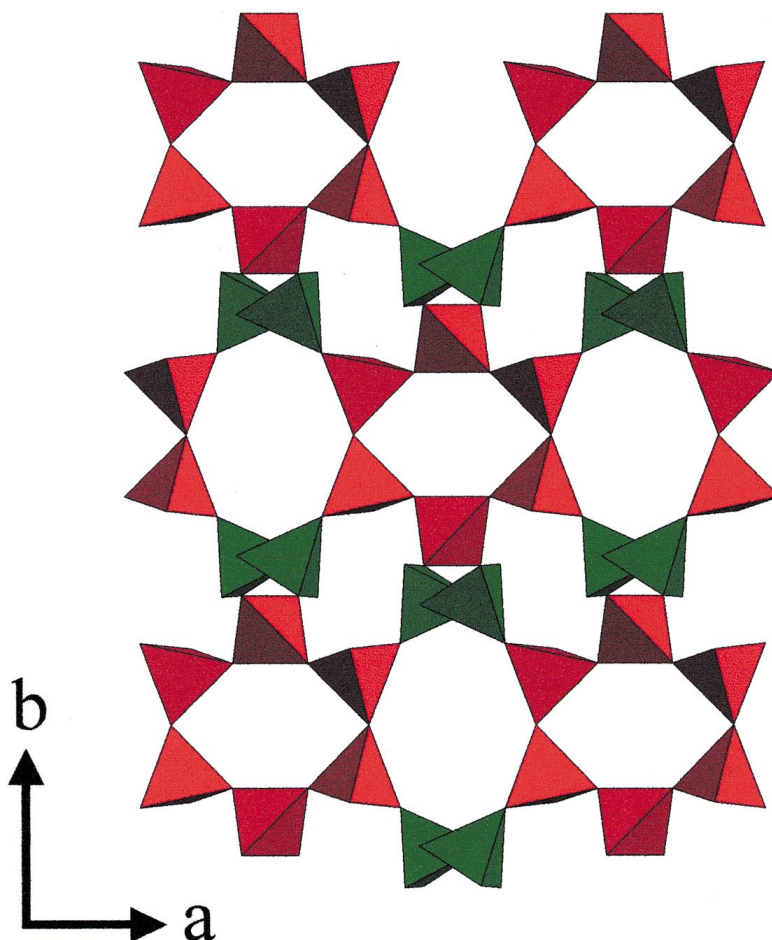


FIG. 4. Six-membered silicate rings in natrolemoynite, projected along [001]. The $\text{Si}(1)\text{O}_4$ and $\text{Si}(3)\text{O}_4$ tetrahedra are shown in red, the $\text{Si}(2)\text{O}_4$ tetrahedra in green.

ten-membered rings. Such rings give rise to channels parallel to [102] that are occupied by Na and H_2O molecules, a feature identical to that described in altsite (Ferraris *et al.* 1995).

The major topological features observed in the natrolemoynite structure, including the zirconosilicate framework, are virtually identical to those found in lemoynite (Le Page & Perrault 1976) and altsite (Ferraris *et al.* 1995). All these minerals occur in highly alkaline environments (lemoynite and natrolemoynite at Mont Saint-Hilaire, altsite in the Khibina complex, Kola Peninsula, Russia) and principally differ in composition. Lemoynite (space-group $C2/c$; Le Page & Perrault 1976) is chemically and structurally very close to natrolemoynite, but contains ordered Ca at one alkali site and disordered (Na,K, H_2O) or (Na,K, \square) in the oth-

ers. It shows a pronounced subcell with $c' = c/2$ and a strong $C2/m$ pseudosymmetry, violated principally by positioning of the Ca ions. Le Page & Perrault (1976) also considered the sites occupied by alkalis, alkaline earths and H_2O molecules as being linked into chains that ideally have space-group symmetry Cc . When potential absences in this chain are considered, a two-fold axis is produced and statistically, $C2/c$ symmetry results. The implication is therefore that the structure proposed for lemoynite may in fact be a superstructure. Furthermore, there is evidence (A.M. McDonald, unpubl. data) that lemoynite crystallizes in a space group of symmetry lower than $C2/c$, the possibility of which is currently under study. In altsite (space group $C2/m$), one of the three tetrahedral sites is occupied by Al, there is essential Ti (rather than Zr) in the octahedrally coordinated

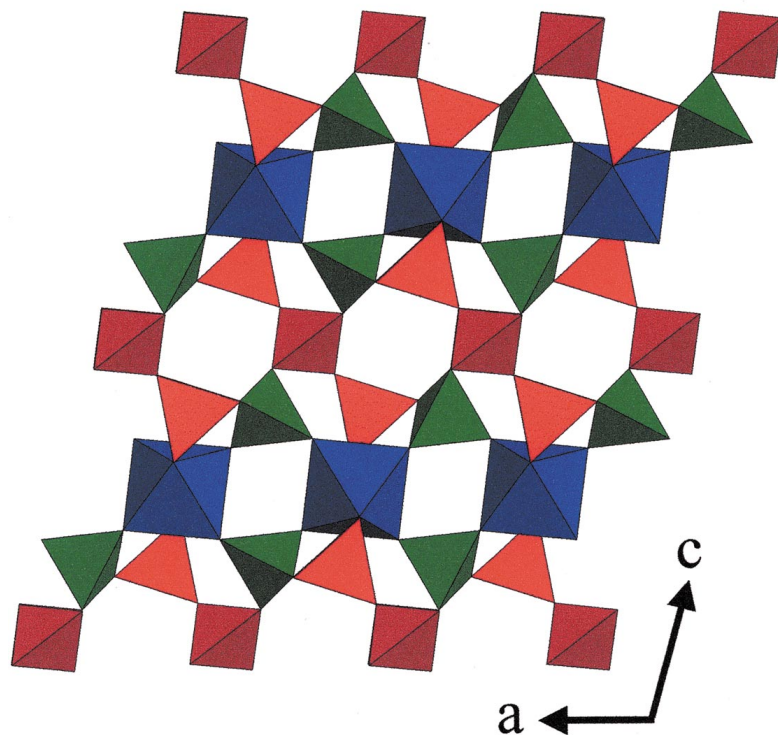


FIG. 5. The $[\text{ZrSi}_5\text{O}_{13}]^{2-}$ framework in natrolemoynite, projected onto (010). Legend as in Figure 4 with ZrO_6 octahedra shown in dark blue.

high-field-strength-element (*HFSE*) site, in addition to the presence of ordered K, Na, and essential Cl (substituting for selected H_2O molecules found in lemoynite and natrolemoynite).

Natrolemoynite is the sixth known sodium zirconosilicate hydrate found at Mont Saint-Hilaire (Table 6), clear evidence of the variability of products in the system $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2-\text{H}_2\text{O}$. In general, most of these minerals are late-stage products forming in interstices, vugs or miarolitic cavities. They may arise through late-stage hydrothermal fluids, which promote the remobilization of Zr from pre-existing phases (*e.g.*, aegirine, arfvedsonite; Rubin *et al.* 1993) or they may be primary minerals crystallizing from an extremely evolved, incompatible-element-rich “melt” or segregation. The exact conditions [P - T - $f(\text{O}_2)$] under which these minerals crystallize still remain largely unknown. Synthesis experiments have been conducted in the system $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2-\text{H}_2\text{O}$ (*e.g.*, Christophe-Michel-Lévy 1961, Baussy *et al.* 1974, Lazutkina *et al.* 1980), but only one has succeeded in producing reversible subsolidus reactions (Currie & Zaleski 1985). These authors noted conditions of formation for elpidite to be ~ 595 – 640°C at 1–2 kbars, which likely represents the upper limit of

formation of a sodium zirconosilicate hydrate. Marr & Wood (1992) attempted to unravel some of the complexities associated with the paragenesis of these minerals *via* an analysis of petrogenetic grids for the system $\text{SiO}_2-\text{Na}_2\text{ZrO}_3-\text{H}_2\text{O}$, based on calculated P - $\mu(\text{H}_2\text{O})$ phase diagrams. Although they were hampered by the lack of information relating to both experimental phase-equilibria and free-energy data for these minerals, they predicted that vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$) is the anhydrous zirconosilicate stable to high- T and intermediate- to low- P conditions, with parakeldyshite ($\text{Na}_2\text{ZrSi}_2\text{O}_7$) + quartz being the high- T , high- P assemblage. These predictions are consistent with the data of Gardinier (1980) and Lazutkina *et al.* (1980), who demonstrated (experimentally) that parakeldyshite and vlasovite are stable up until incongruent melting ($T > 1200^\circ\text{C}$). Hence most of the sodium zirconosilicates encountered at Mont Saint-Hilaire must be relatively low- T , late-stage products, a feature consistent with field observations.

If one considers the six sodium zirconosilicate hydrates found at Mont Saint-Hilaire in terms of molar ratios (Table 6), a number of features become apparent: 1) the $\text{Na}_2\text{O}:\text{ZrO}_2$ ratio is constant and equal to 1, 2) the $(\text{Na}_2\text{O} + \text{ZrO}_2):\text{SiO}_2$ ratio is variable (0.167–0.333), 3)

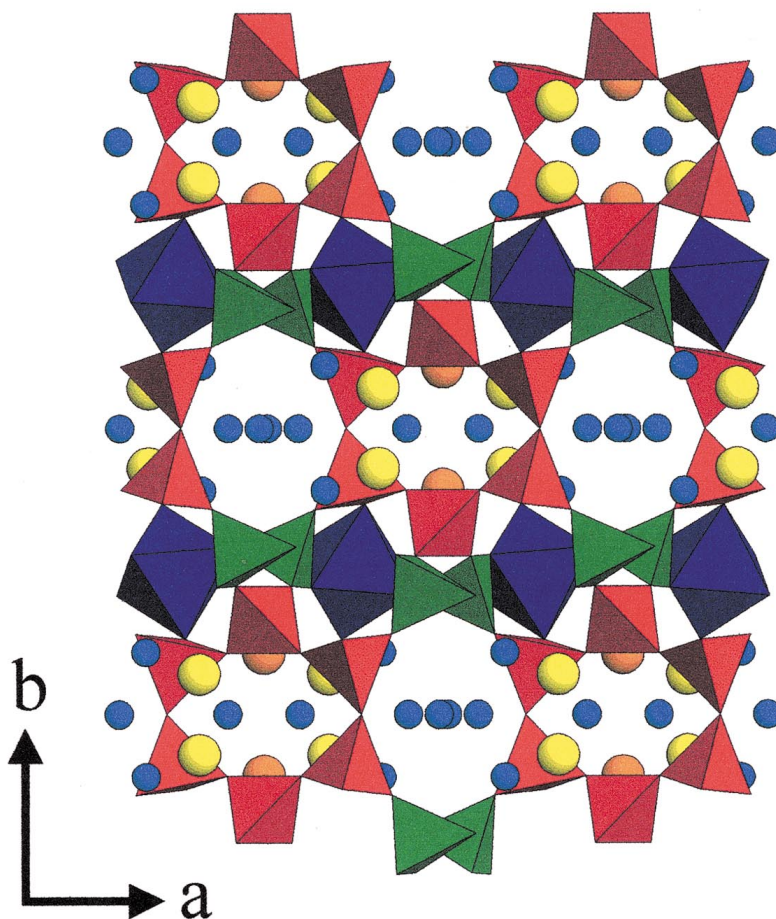


FIG. 6. The $[\text{ZrSi}_5\text{O}_{13}]^{2-}$ framework in natrolemoynite, projected onto (001). Legend as in Figures 4 and 5, with Na(1) atoms shown in orange, Na(2) atoms in yellow and O atoms of H_2O molecules in light blue.

the $\text{SiO}_2\text{:H}_2\text{O}$ ratio is variable (2 to 1.11), but generally decreases when considered in a paragenetic context (*e.g.*, hilairite found overgrowing elpidite). The fact that all these sodium zirconosilicate minerals are hydrated is not surprising. Studies on the complexation of Zr indicate that $\text{Zr}(\text{OH})_{4(\text{aq})}$ is the dominant species over a wide range of pH conditions ($\sim 2\text{--}10$), varying only if the activities of competing ligands (*e.g.*, F, SO_4) are high (Aja *et al.* 1995). Given the similarity in $\text{SiO}_2\text{:H}_2\text{O}$ ratio for natrolemoynite *versus* hilairite (1.11 *versus* 1, respectively), the implication is that variations in T , P or activity of the fluid may also play critical roles in determining which of these phases crystallizes. Lastly, it is interesting to compare the silicate topologies of the six Na zirconosilicate hydrates (Table 6). Elpidite, gaidonnayite, hilairite and catapleite are all unbranched chain silicates (Liebau 1985) with differing periodicities

or chain topologies (elpidite, gaidonnayite, hilairite *versus* the silicate ring in catapleite). Tumchaite (Subbotin *et al.* 2000) is also unbranched, but is classified as a sheet silicate, whereas natrolemoynite is classified as loop-branched silicate. The crystal structures of both tumchaite and natrolemoynite are characterized by higher Si:O ratios, relative to those of more simple unbranched silicates (Table 6). In general, the higher Si:O ratio reduces the overall negative charge per tetrahedron, thus reducing the repulsive forces between adjacent tetrahedra and further stabilizing their respective crystal-structures relative to those of the unbranched silicates. Considering the $(\text{Na}_2\text{O} + \text{ZrO}_2)\text{:SiO}_2$ ratios of sodium zirconosilicate hydrates found at Mont Saint-Hilaire (Table 6), natrolemoynite represents a paragenetically intermediate phase between elpidite and the others. If one considers the high degree of SiO_4 polymerization

TABLE 6. DATA FOR SODIUM ZIRCONOSILICATES FOUND AT MONT SAINT-HILAIRE, QUEBEC

Mineral, Formula	Space Group	Na ₂ O/ ZrO ₂ :SiO ₂	SiO ₂ / H ₂ O	Silicate classification*
Elpidite Na ₂ ZrSi ₃ O ₁₃ •3H ₂ O	<i>Pbcm</i>	1:1.6	2	UB double chain (<i>P</i> = 3)
Catapleite Na ₂ ZrSi ₃ O ₉ •2H ₂ O	<i>I2/c</i>	1:1.3	1.5	UB ring (three-membered)
Gaidonnayite Na ₂ ZrSi ₃ O ₉ •2H ₂ O	<i>P2₁nb</i>	1:1.3	1.5	UB single chain (<i>n</i> = 6)
Hilairite Na ₂ ZrSi ₃ O ₉ •3H ₂ O	<i>R32</i>	1:1.3	1	UB single chain (<i>n</i> = 2)
Tumchaite Na ₂ ZrSi ₄ O ₁₁ •2H ₂ O	<i>P2₁/c</i>	1:1.4	2	UB unbranched single sheet (<i>n</i> = 4)
Natrolemoynite Na ₄ Zr ₂ Si ₁₀ O ₂₆ •9H ₂ O	<i>C2/m</i>	1:1.5	1.11	IB loop-branched (<i>n</i> = 2)

* Based on the classification scheme of Liebau (1985).

exhibited and the complexity of its crystal structure, natrolemoynite must be one of the last sodium zirconosilicate hydrate minerals to form. In general, it is not uncommon to find several sodium zirconosilicate hydrates in the same sample (*e.g.*, elpidite, catapleite, gaidonnayite, *etc.*). Natrolemoynite, however, has not been found in association with any other such phases in either of the two distinct occurrences at Mont Saint-Hilaire, suggesting that it does not coexist with other sodium zirconosilicate hydrates. In any case, the occurrence of this mineral is exceedingly rare relative to that of other sodium zirconosilicate hydrates found at Mont Saint-Hilaire, indicating that the conditions which led to its formation must clearly have been rather unique.

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