

**ROGERMITCHELLITE, Na<sub>12</sub>(Sr,Na)<sub>24</sub>Ba<sub>4</sub>Zr<sub>26</sub>Si<sub>78</sub>(B,Si)<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O,  
 A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC:  
 DESCRIPTION, STRUCTURE DETERMINATION AND RELATIONSHIP  
 WITH HFSE-BEARING CYCLOSILICATES**

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ABSTRACT

Rogermitchellite is a new, complex species of zirconosilicate found in igneous breccia at the Poudrette quarry, Mont Saint-Hilaire, Quebec. It is associated with aegirine, annite, galena, a labuntsovite-group mineral, manganoneptunite, microcline, pyrrhotite, sodalite and zircon. Paragenetically, the mineral crystallizes after aegirine and before microcline. Isolated, single crystals are colorless to grey, prismatic along [001], and slightly flattened perpendicular to this direction, with a maximum dimension of  $0.1 \times 0.25$  mm. It develops as euhedral crystals displaying the prominent forms prism {100} and pinacoid {001}, with a minor, very shallow ditrigonal scalenohedron {101}. The mineral is transparent with a vitreous luster and a white streak and is non-luminescent. The Mohs hardness is 5, and no cleavage is evident. It is brittle with a conchoidal to splintery fracture. The calculated density is  $3.34 \text{ g/cm}^3$ . Rogermitchellite is non-pleochroic, uniaxial positive, with  $\omega$  1.640(1) and  $\epsilon$  1.663(1). Four analyses made on one crystal gave, as an average: Na<sub>2</sub>O 3.45, CaO 0.10, SrO 18.54, BaO 5.18, B<sub>2</sub>O<sub>3</sub> (calc.) 2.34, SiO<sub>2</sub> 39.12, ZrO<sub>2</sub> 26.39, TiO<sub>2</sub> 0.63 and H<sub>2</sub>O (calc.) 6.96, for a total of 102.71 wt.%. The empirical formula, based on 288 anions and the sum of (Si + B) = 90 *apfu*, is: Na<sub>12</sub>(Sr<sub>21.16</sub>Na<sub>1.17</sub>Ca<sub>0.21</sub>)<sub>Σ22.54</sub>Ba<sub>4.00</sub>(Zr<sub>25.33</sub>Ti<sub>0.93</sub>)<sub>Σ26.26</sub>(Si<sub>77.02</sub>B<sub>0.98</sub>)<sub>Σ78</sub>B<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O or, ideally, Na<sub>12</sub>Sr<sub>24</sub>Ba<sub>4</sub>Zr<sub>26</sub>Si<sub>78</sub>B<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O. The mineral is trigonal, space group *P* $\bar{3}$ *c*1, *a* 26.509(4), *c* 9.975(2) Å, *V* 6070.6(1) Å<sup>3</sup> and *Z* = 1. The strongest six lines on the X-ray powder-diffraction pattern [*d* in Å(1)(*hkl*)] are: 2.760(100)(442), 3.761(90)(402), 1.991(70)(444), 3.150(50)(441), 5.762(40)(400) and 3.924(30)(312). The crystal structure was refined to *R* = 4.62% and *wR*<sup>2</sup> = 12.73% for 1588 reflections [*F*<sub>o</sub> > 4σ(*F*<sub>o</sub>)]. It consists of pairs (Si<sub>3</sub>O<sub>9</sub>) rings (offset 30° relative to one another along [001]) linked to isolated ZrO<sub>6</sub> octahedra in a motif similar to that in benitoite. Additional (Si<sub>3</sub>O<sub>9</sub>) and [Si<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>] rings along with ZrO<sub>6</sub> octahedra complete a three-dimensional heteropolyhedral framework. Channels along [001] within this framework are occupied by Ba, Na, (Sr + Na) and H<sub>2</sub>O. Rogermitchellite has chemical and crystal-structure features common to benitoite, wadeite and catapleite, and should be considered as a structural hybrid of these minerals. It possesses additional features (presence of essential B, Sr, H<sub>2</sub>O; trigonal symmetry) that make it unique.

*Keywords:* rogermitchellite, new mineral species, zirconosilicate, crystal structure, cyclosilicate, heteropolyhedral framework, benitoite, igneous breccia, Mont Saint-Hilaire, Quebec.

SOMMAIRE

Nous décrivons la rogermitchellite, nouvelle espèce de zirconosilicate découverte dans une brèche ignée à la carrière Poudrette, au mont Saint-Hilaire, Québec. Lui sont associés aegyrine, annite, galène, un minéral du groupe de la labuntsovite, manganoneptunite, microcline, pyrrhotite, sodalite et zircon. Le minéral cristallise après l'aegyrine et avant la microcline. Les monocristaux individuels sont incolores à gris, prismatiques selon [001], et légèrement aplatis perpendiculaire à cette direction, avec une dimension maximale de  $0.1 \times 0.25$  mm. Les cristaux idiomorphes montrent comme formes prédominantes le prisme {100} et le pinacoïde {001}, avec un scalénoèdre ditrigonal mineur {101} à inclinaison très faible. C'est un minéral transparent ayant un éclat vitreux et une rayure blanche; il est non-luminescent. La dureté de Mohs est 5, et aucun clivage n'est évident. C'est un minéral cassant, avec une fracture conchoïdale et esquilleuse. La densité calculée est  $3.34 \text{ g/cm}^3$ . La rogermitchellite est non pléochroïque, uniaxe positive, avec  $\omega$  1.640(1) et  $\epsilon$  1.663(1). Quatre analyses effectuées sur un cristal ont donné, en moyenne: Na<sub>2</sub>O 3.45, CaO 0.10, SrO 18.54, BaO 5.18, B<sub>2</sub>O<sub>3</sub> (calc.) 2.34, SiO<sub>2</sub> 39.12, ZrO<sub>2</sub> 26.39, TiO<sub>2</sub> 0.63 et

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H<sub>2</sub>O (calc.) 6.96, pour un total de 102.71% (poids). La formule empirique, fondée sur une base de 288 anions et la somme (Si + B) = 90 *apfu*, est: Na<sub>12</sub>(Sr<sub>21.16</sub>Na<sub>1.17</sub>Ca<sub>0.21</sub>)<sub>Σ22.54</sub>Ba<sub>4.00</sub> (Zr<sub>25.33</sub>Ti<sub>0.93</sub>)<sub>Σ26.26</sub>(Si<sub>77.02</sub>B<sub>0.98</sub>)<sub>Σ78</sub>B<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O ou, de façon idéale, Na<sub>12</sub>Sr<sub>24</sub>Ba<sub>4</sub>Zr<sub>26</sub>Si<sub>78</sub>B<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O. Le minéral est trigonal, groupe spatial *P3c1*, *a* 26.509(4), *c* 9.975(2) Å, *V* 6070.6(1) Å<sup>3</sup> et *Z* = 1. Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å(*hkl*)] sont: 2.760(100)(442), 3.761(90)(402), 1.991(70)(444), 3.150(50)(441), 5.762(40)(400) et 3.924(30)(312). Nous en avons affiné la structure cristalline jusqu'à un résidu *R* de 4.62%, *wR*<sup>2</sup> égal à 12.73%, avec 1588 réflexions observées [*F*<sub>o</sub> > 4σ(*F*<sub>o</sub>)]. Elle contient des paires d'anneaux Si<sub>3</sub>O<sub>9</sub> déplacés de 30° l'un par rapport à l'autre le long de [001], connectés à des octaèdres ZrO<sub>6</sub> isolés selon un motif semblable à celui de la bénomite. Des anneaux (Si<sub>3</sub>O<sub>9</sub>) et [Si<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>] et des octaèdres ZrO<sub>6</sub> additionnels complètent la charpente hétéropolyédrique tri-dimensionnelle. Des canaux de long de [001] dans cette charpente contiennent Ba, Na, (Sr + Na) et H<sub>2</sub>O. De par sa composition et sa structure, la rogermitchellite possède des points communs avec bénomite, wadeïte et catapléite, et devrait en être considérée comme structuralement hydride. Elle possède des attributs additionnels (présence de Ba, Sr, H<sub>2</sub>O essentiels; symétrie trigonale) qui la rendent unique.

(Traduit par la Rédaction)

*Mots-clés:* rogermitchellite, nouvelle espèce minérale, zirconsilicate, structure cristalline, cyclosilicate, charpente hétéropolyédrique, bénomite, brèche ignée, mont Saint-Hilaire, Québec.

## INTRODUCTION

Cyclosilicates represent one of the most diverse classes of silicates found in highly alkaline to aegaitic environments. Although the latter are typically dominated by catapleite and eudialyte-group minerals, the list of new cyclosilicate species being discovered in these environments continues to grow. In the case of hyperaegaitic nepheline syenites at Mont Saint-Hilaire, Quebec, new additions include bobtraillite (McDonald & Chao 2008) and the focus of this present contribution, rogermitchellite. In addition, work is proceeding on another new species, provisionally labeled UK120, that appears to be chemically and structurally related to catapleite.

Rogermitchellite, Na<sub>12</sub>(Sr,Na)<sub>24</sub>Ba<sub>4</sub>Zr<sub>26</sub>Si<sub>78</sub>(B,Si)<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O, has only been found on a single sample. Shortly after its discovery and recognition that it potentially represented a new mineral species, it was tentatively labeled as UK99 (Wight & Chao 1995). Subsequent analyses confirmed that it is new to science. It has been named rogermitchellite after Dr. Roger Howard Mitchell (*b.* 1941), Professor Emeritus in the Department of Geology at Lakehead University, Thunder Bay, Ontario, Canada, in recognition of his outstanding contributions to the mineralogy and petrology of alkaline rocks. Dr. Mitchell authored or co-authored a trilogy of monographs devoted to the petrology of the various types of primary alkaline rocks and has published several papers relating to the mineralogy of these unusual rock types. Both the mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (2003–019). The holotype material, consisting of one matrix specimen and a single-crystal mount (used in the intensity-data collection for refinement of the crystal structure), is housed in the collection of the Canadian Museum of Nature, Ottawa, catalogue number CMNMC 860087.

## OCCURRENCE

Rogermitchellite was discovered on a specimen provided by Mr. Gilles Haineault, a local collector who has previously provided specimens of several new mineral species. The sample, measuring ~1 × 1.5 × 2 cm, appears to represent a late-stage igneous breccia in nepheline syenite from the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, Canada. The mineral occurs as free-standing crystals in vugs and is clearly a late-stage phase. Associated minerals include aegirine, annite, galena, a labuntsovite-group mineral, manganoneptunite, microcline, pyrrhotite, sodalite and zircon [the latter showing only the dipyrmaid {101}]. The vugs in the sample, measuring 1 to 2 mm across, are dominated by aegirine and microcline. In general, microcline appears to overgrow aegirine and in one situation, a crystal of rogermitchellite was found overgrowing aegirine. This suggests the paragenetic sequence: aegirine → rogermitchellite → microcline.

## PHYSICAL AND OPTICAL PROPERTIES

Crystals of rogermitchellite are prismatic, and elongate along [001] (Fig. 1). On the type specimen, five crystals in total were identified. They form individual, isolated grains, typically 0.05 × 0.1 mm, with the largest crystal measuring 0.1 × 0.25 mm. Crystals are colorless (smaller) to gray in color (larger) and euhedral; they exhibit as prominent forms the prism {100} and pinacoid {001}, with a very shallow ditrigonal scalenohedron {10} and {10} (very minor). Crystals are striated along their length; although roughly hexagonal in outline, they tend to be flattened perpendicular to [001], this flattening being more pronounced on smaller crystals. Rogermitchellite is transparent, has a vitreous luster, a white streak and shows no fluorescence in either short-, medium- or long-wave ultraviolet radiation. The

mineral has a Mohs hardness of 5 with no observable cleavage. It is very brittle with a conchoidal to splintery fracture. The density could not be determined owing to the small number of crystals available and their fine grain-size. The calculated density, 3.34(1) g/cm<sup>3</sup>, was determined using the empirical chemical formula and the unit-cell parameters derived from the crystal-structure analysis.

Rogermitchellite is non-pleochroic, uniaxial positive, with  $\omega$  1.640(1) and  $\varepsilon$  1.663(1) for  $\lambda = 589$  nm. A Gladstone–Dale calculation, using the empirical formula and the unit-cell parameters from the crystal-structure analysis, gave a compatibility index of 0.017, considered to be superior (Mandarino 1981).

#### CHEMICAL COMPOSITION

Rogermitchellite was analyzed using a Cambridge Microscan MK5 electron microprobe using an operating voltage of 15 kV, a beam current of 10 nA. Wavelength-dispersion data were collected using the following standards: albite (NaK $\alpha$ ), Kakanui hornblende (CaK $\alpha$ , SiK $\alpha$ , TiK $\alpha$ ), celestine (SrL $\alpha$ ), Ba glass (BaL $\alpha$ ) and zircon (ZrL $\alpha$ ). Also sought, but not detected, were Nb, P, F, K, Hf and Y. Four analyses made on one crystal gave as an average: Na<sub>2</sub>O 3.45 (3.40–3.50), CaO 0.10 (0.07–0.14), SrO 18.54 (18.44–18.73), BaO 5.18 (5.01–5.33), B<sub>2</sub>O<sub>3</sub> (calc.) 2.34, SiO<sub>2</sub> 39.12 (38.92–39.27), ZrO<sub>2</sub> 26.39 (25.99–26.80), TiO<sub>2</sub> 0.63 (0.56–0.68) and

H<sub>2</sub>O (calc.) 6.96, total 102.71 wt.%. The presence of H<sub>2</sub>O was confirmed by infrared spectroscopy (see below), and results of the crystal-structure analysis. The presence of boron was also initially identified from the results from the crystal-structure analysis, and its presence was subsequently confirmed by qualitative wavelength-dispersion scans. The empirical formula, based on 288 anions and the sum of (Si + B) = 90 *apfu*, is: Na<sub>12</sub>(Sr<sub>21.16</sub>Na<sub>1.17</sub>Ca<sub>0.21</sub>)<sub>Σ22.54</sub>Ba<sub>4.00</sub>(Zr<sub>25.33</sub>Ti<sub>0.93</sub>)<sub>Σ26.26</sub>(Si<sub>77.02</sub>B<sub>0.98</sub>)<sub>Σ78</sub>B<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O or, ideally, Na<sub>12</sub>Sr<sub>24</sub>Ba<sub>4</sub>Zr<sub>26</sub>Si<sub>78</sub>B<sub>12</sub>O<sub>246</sub>(OH)<sub>24</sub>•18H<sub>2</sub>O. The presence of a relatively high proportion of Sr  $\leftrightarrow$  Na substitution in crystallographic sites assigned to Sr is confirmed by results of the single-crystal X-ray-diffraction study (discussed below). The low analytical totals for the sites assigned to Sr may be due to element migration under the electron beam or, possibly, to the presence of structural vacancies (although the latter is not borne out in results from the crystal-structure analysis). The mineral does not effervesce in 1:1 HCl at room temperature.

#### INFRARED ANALYSIS

The infrared spectrum of rogermitchellite (Fig. 2) was obtained using a Bomem Michelson MB-120 Fourier transform infrared spectrometer equipped with a mercury–cadmium telluride (MCT) detector. A single crystal was mounted in a Spectra-Tech low-pressure diamond-anvil microsample cell. The spectrum was obtained over the range 4000–660 cm<sup>-1</sup> from a total of 200 co-added scans. A digital version of this spectrum is available from the Depository of Unpublished Data



FIG. 1. Photograph of rogermitchellite (taken by AMM). Note the associated aegirine. Crystal is 0.25 mm in length.

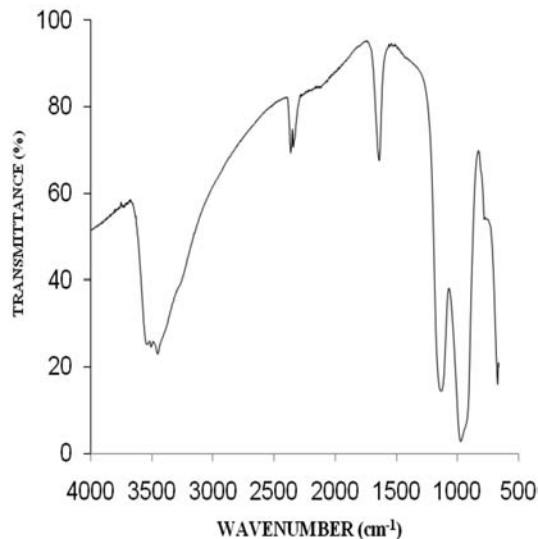


FIG. 2. The infrared spectrum of rogermitchellite. The artifact at 2400 cm<sup>-1</sup> corresponds to O stretching in atmospheric CO<sub>2</sub>.

on the MAC website [document Rogermitchellite CM48\_267]. The absorption bands were identified using data from Farmer (1974). The spectrum shows a medium-intensity band centered at the 3508  $\text{cm}^{-1}$  composed of three weaker bands (3533, 3508, 3453  $\text{cm}^{-1}$ ; O–H stretching) and a relatively weak band at 1638  $\text{cm}^{-1}$  (H–O–H bending). The spectrum also shows a strong, sharp band at 1129 and 971, with a shoulder at 918  $\text{cm}^{-1}$  (asymmetric O–Si–O, O–B–O stretching). A moderately strong, sharp band is also observed at 777  $\text{cm}^{-1}$  (symmetric Si–O–Si, O–B–O stretching). It should be noted that as the ranges in frequency modes for the  $\text{BO}_4$  and  $\text{SiO}_4$  tetrahedra directly overlap [asymmetric stretching: 1100–850  $\text{cm}^{-1}$  for  $\text{BO}_4$  versus 1200–900  $\text{cm}^{-1}$  for  $\text{SiO}_4$ ; symmetric stretching: 850–700  $\text{cm}^{-1}$  for  $\text{BO}_4$  versus 800–400  $\text{cm}^{-1}$  for  $\text{SiO}_4$ ; Farmer (1974)], it is not possible to unequivocally assign absorption bands in these regions.

#### X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray powder-diffraction data were collected with a Debye–Scherrer camera 114.6 mm diameter employing Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Intensities were visually estimated using a scanned image of the powder pattern. Whether or not an  $hkl$  plane significantly contributes to a reflection was determined from the powder pattern calculated using the atom parameters derived from the crystal-structure analysis and the program POWDERCELL (Nolze & Kraus 1998). Overall agreement between the observed and calculated patterns is very good (Table 1).

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

$l_{\text{meas}}$	$l_{\text{calc}}$	$d_{\text{meas}}$	$d_{\text{calc}}$	$h$	$k$	$l$	$l_{\text{meas}}$	$l_{\text{calc}}$	$d_{\text{meas}}$	$d_{\text{calc}}$	$h$	$k$	$l$
10	10	6.392	6.367	3	1	0	70	40	1.991	1.992	4	4	4
40	35	5.762	5.739	4	0	0	3	2	1.948	1.953	9	3	2
5	6	5.491	5.520	2	2	1	20	28	1.916	1.913	12	0	0
5	5	5.393	5.367	3	1	1	15	11	1.882	1.882	8	0	4
3	6	4.986	4.988	0	0	2	15	15	1.786	1.786	12	0	2
25	12	3.968	3.985	2	2	2	3	4	1.764	1.767	8	2	4
30	18	3.924	3.926	3	1	2	3	1	1.722	1.720	12	1	2
90	64	3.761	3.765	4	0	2	25	10	1.701	1.703	8	3	4
15	12	3.534	3.534	4	1	2	1	4	1.656	1.657	8	8	0
25	28	3.310	3.314	4	4	0	10	9	1.637	1.637	8	4	4
50	37	3.150	3.145	4	4	1	5	6	1.616	1.614	11	4	2
5	3	3.022	3.041	7	1	0	5	4	1.595	1.597	4	0	6
4			3.036	6	0	2	15	12	1.571	1.572	8	8	2
5	7	3.013	3.010	4	3	2	15	10	1.517	1.518	12	0	4
3	4	2.952	2.947	3	1	3	6			1.516	12	4	2
5	10	2.874	2.870	8	0	0	25	18	1.4854	1.4860	4	4	6
100	100	2.760	2.760	4	4	2	1	3	1.4091	1.4083	11	4	4
20	16	2.489	2.494	0	0	4	15	10	1.3796	1.3800	8	8	4
3	3	2.284	2.287	4	0	4	5	4	1.3277	1.3295	12	7	2
5	8	2.168	2.169	8	4	0	5	3	1.2535	1.2549	12	0	6
1	2	2.075	2.081	4	3	4	4			1.2524	16	4	0
3	2	2.028	2.021	8	5	0	5	5	1.2459	1.2469	0	0	8
							5	8	1.2143	1.2147	16	4	2

X-ray intensity data were collected on a Bruker P4 diffractometer equipped with a SMART 1K CCD detector and a crystal-to-detector distance of 4.045 cm. A total of 58748 reflections were measured out to  $2\theta = 60^\circ$  using framewidths  $0.2^\circ \omega$  and count times of 90 s per frame. Of the 3571 unique reflections, 1588 were considered as observed [ $|F_o| \geq 4\sigma F$ ]; the low number of unique reflections is attributable to the paucity of observable data beyond  $2\theta = 50^\circ$ . The data were corrected for Lorentz, polarization and background effects using the program SAINT. Absorption corrections were applied using the program SADABS, the crystal being modeled as an ellipse. All reflection data were then merged using the program XPREP. 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 programs (Sheldrick 1993). The crystal structure was solved using direct methods, with scattering curves and anomalous scattering factors 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 1.007. Although the calculated mean values are  $|E^2 - 1|$  of 0.968 (centric) and 0.736 (acentric), based on the symmetry observed in benitoite and other related minerals, the noncentrosymmetric space-group  $P6_3cm$  (#185) was selected as the preferred choice from a listing of potential space-groups. The phase-normalized structure-factors were used to give an  $E$ -map on which were located three Zr, two Sr and one Ba, three Si and several O sites. The remaining Na, Si, and O sites were located on subsequent difference-maps. Results from this model indicated two of the tetrahedral sites to have bond distances of  $\sim 1.51 \text{ \AA}$ , too short for a Si–O bond length, but consistent with that of B–O. In light of this, a qualitative wavelength-dispersion scan was made, which confirmed the presence of B. On the basis of these

TABLE 2. MISCELLANEOUS INFORMATION  
CONCERNING ROGERMITCHELLITE

Space Group	$P\bar{3}c1$ (# 165)	Diffractometer	Bruker P4
$a$ (Å)	26.509(4)*	Radiation	$\text{MoK}\alpha$ (50 kV, 40 mA)
$c$ (Å)	9.975(2)*	Monochromator	Graphite
$V$ (Å <sup>3</sup> )	6070.6(1)	Crystal size	$0.05 \times 0.08 \times 0.10 \text{ mm}$
Z	1	$\mu$ (MoK $\alpha$ )	7.57 $\text{mm}^{-1}$
Chemical Formula	$\text{Na}_{12}(\text{Sr}, \text{Na})_{24}\text{Ba}_4\text{Zr}_{26}\text{Si}_{18}(\text{B}, \text{Si})_{12}\text{O}_{246}(\text{OH})_{24} \cdot 18\text{H}_2\text{O}$		
Intensity-data collection	9:20 scan mode		
$2\theta$ limit	50°		
Number of unique reflections	3571		
Number of observed reflections	1588		
Criterion for observed reflections	$F_o > 4\sigma(F_o)$		
Goof	0.858		
Final $R$ for all observed reflections	4.62%		
Final $wR^2$ for all observed reflections	12.73%		

\* values refined from four-circle diffractometer data.

data, B has thus been assigned to the sites in question. Determination of those *O* sites likely occupied by OH or H<sub>2</sub>O was made on the basis of bond-valence calculations in conjunction with charge-balance considerations. This model refined to  $R \approx 4\%$  and overall, made very reasonable crystal-chemical sense except for two of the tetrahedral sites assigned to Si, namely *Si*(2) and *Si*(5). These had two normal Si–O bond distances of  $\sim 1.64$  Å but also two very unusual ones, one  $\sim 1.4$  and the other  $\sim 1.7$  Å. Such unusual Si–O bond distances were also observed in refinement of the crystal structure of bobtraillite (McDonald & Chao 2005), and in that case, were resolved by reducing the space group selected from  $P6_3cm$  to  $P\bar{3}c1$ . A similar approach was taken for rogermitchellite (*i.e.*, refinement of the crystal structure in an alternative space-group). As this proved successful (*i.e.*, producing reasonable Si–O bond distances),  $P\bar{3}c1$  was selected as the correct space-group. Final least-squares refinement of this model gave residuals of  $R = 4.62\%$  and  $wR^2 = 12.73\%$ , and the difference map calculated at this stage did not reveal any positive maxima greater than  $\sim 1 e^{-}/\text{Å}^3$ . It should be noted that refinement of this model indicated non-positive definite behavior for several of the assigned atoms; however, the magnitudes of such displacements are considered to be very minor.

Table 3 contains the final positional and displacement parameters; selected interatomic distances are listed in Table 4, and bond-valence sums, in Table 5. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data on the MAC website [document Rogermitchellite CM48\_267].

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of rogermitchellite is rather complex, consisting of nine tetrahedral, three octahedral and four sites dominated by alkali and alkaline-earth elements with coordination numbers ranging from [6] to [10]. The tetrahedral sites include seven unique Si sites and two of mixed (B,Si) composition (the latter two dominated by B, with the B:Si ratios being determined from the refined structure). The SiO<sub>4</sub> tetrahedra all have normal <Si–O> bond distances, with average values ranging from 1.61 to 1.63 Å (Table 4). The mixed B + Si sites are present as [XO<sub>2</sub>(OH)<sub>2</sub>]<sup>4+</sup> complexes with average <X–O> bond distances of 1.50 and 1.52 Å. As noted with bobtraillite (McDonald & Chao 2005), the longest distances in these tetrahedral complexes correspond to X–(OH) bonds, and the presence of such bonds explain the lower-than-ideal bond-valence sum calculated for B (Table 5). All tetrahedra are linked into three-membered rings, details of which are discussed below.

There are three MO<sub>6</sub> octahedra present, identified as Zr(1)O<sub>6</sub>, Zr(2)O<sub>6</sub> and Zr(3)O<sub>6</sub>. All exhibit normal <Zr–O> bond distances (Table 4), with Zr(2)O<sub>6</sub> having a greater dispersion in individual bond-lengths and a

shorter average <Zr–O> bond distance; these characteristics may reflect preferential Zr ↔ Ti substitution in this octahedron.

There are four sites dominated by alkaline and alkaline-earth elements. One [8]-coordinated site has been assigned to Na; site-occupancy refinement indicates complete occupancy. Strontium has been assigned to two [10]-coordinated sites; a site-occupancy refinement suggests lower-than-ideal values if one assumes only Sr for both; in light of this, and in accordance with mineral-composition data, Na was also assigned to these sites. The results (Table 3) indicate Sr:Na ratios from refinement of the crystal structure ( $\sim 9:1$ ) that are reasonably consistent with those obtained by electron-microprobe analyses. The final site, with a coordination number of 12, has been ascribed wholly to Ba.

Although the crystal structure of rogermitchellite is simplistic in the sense that it is based on a heteropolyhedral framework of octahedra and tetrahedra, the relatively large number of unique octahedral and tetrahedral sites involved and the correspondingly large unit-cell result in a complex arrangement.

Rogermitchellite is a cyclosilicate containing two basic kinds of three-membered rings, (Si<sub>3</sub>O<sub>9</sub>)<sup>6-</sup> and [Si<sub>2</sub>BO<sub>8</sub>(OH)]<sup>6-</sup>, the same as those observed in bobtraillite. If viewed along [001], a simple pinwheel motif may be envisioned (Fig. 3). This consists of a central <sup>112</sup>Ba surrounded by two sets of three-membered silicate rings [namely, Si(5)O<sub>4</sub> + Si(3)O<sub>4</sub> and Si(1)O<sub>4</sub> + Si(2)O<sub>4</sub>; the two sets being rotated relative to one another by 30° along [001]) that are, in turn, linked to two different sets of three ZrO<sub>6</sub> octahedra ([Zr(1)O<sub>6</sub> in the interior, Zr(2)O<sub>6</sub> at the exterior). A heteropolyhedral framework consisting of three-membered rings and MO<sub>6</sub> octahedra is observed in all minerals related to wadeite and benitoite. The particular arrangement observed in rogermitchellite is distinct from that observed in bobtraillite (wherein six [Si<sub>3</sub>O<sub>9</sub>]<sup>6-</sup> rings are *radially* distributed about a central ZrO<sub>6</sub> octahedron). As discussed by McDonald & Chao (2005), such a motif is similar to a component of the basic motif found in benitoite and will be referred to as the Benitoite Pinwheel Motif (BPM). However, the BPM in rogermitchellite also is distinct; it is primarily linked to other such units by three-membered rings of tetrahedra, either [Si<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>]<sup>5-</sup> or (Si<sub>3</sub>O<sub>9</sub>)<sup>6-</sup>, rather than by a combination of three-membered silicate rings and TiO<sub>6</sub> octahedra as in benitoite (Fig. 4). In rogermitchellite, there are two BPM in each unit cell, with three-membered [Si(4)<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>]<sup>5-</sup> rings serving as the principal bridges, *via* linkages made between these rings and both Zr(1)O<sub>6</sub> and Zr(2)O<sub>6</sub> octahedra in adjacent BPM. At the same time, three-membered [Si(6)<sub>2</sub>Si(7)O<sub>9</sub>]<sup>6-</sup> rings serve to reinforce the bridging *via* linkages made with Zr(2)O<sub>6</sub> octahedra in adjacent BPM and with Zr(3)O<sub>6</sub> octahedra, the latter being located at the periphery of the unit cell.

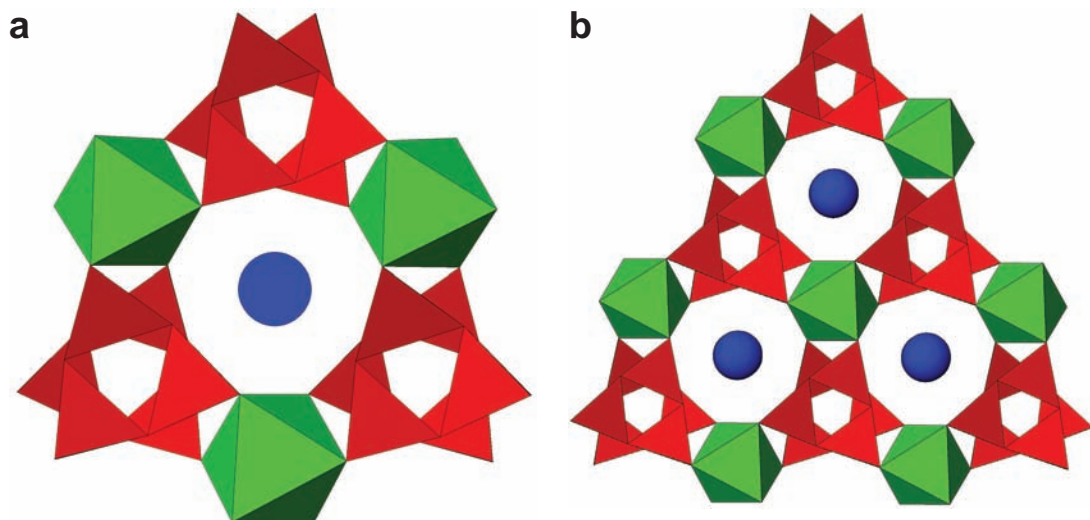


FIG. 3. The  $[(\text{Zr}:\text{Ti})\text{Si}_5\text{O}_{13}]^{2-}$  pinwheel motifs in (a) rogermitchellite and (b) benitoite projected along [001]. The  $\text{Zr}(1)\text{O}_6$  octahedra are shown in green,  $\text{SiO}_4$  tetrahedra in red, and Ba atoms as blue spheres.

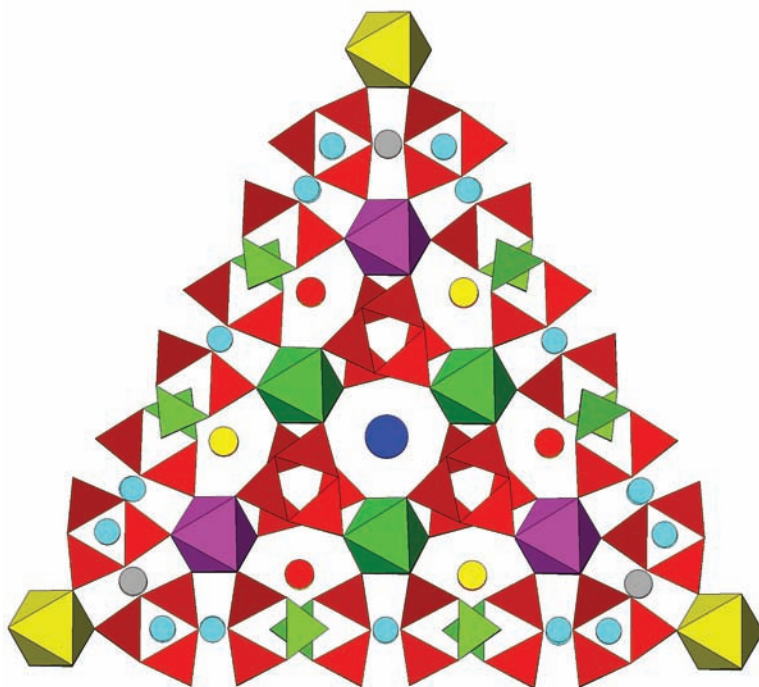


FIG. 4. The crystal structure of rogermitchellite (one-half of the unit cell) projected along [001]. Legend as in Figure 3, with  $\text{Zr}(2)\text{O}_6$  octahedra in purple,  $\text{Zr}(3)\text{O}_6$  octahedra in yellow,  $\text{BO}_4$  tetrahedra in green, Na ions as grey spheres, Sr(1) ions as yellow spheres, Sr(2) ions as red spheres, and  $\text{H}_2\text{O}$  as light blue spheres.

TABLE 3. POSITIONAL AND DISPLACEMENT PARAMETERS FOR ROGERMITCHELLITE

	x	y	z	sof	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Na1	0.9184(7)	0.8370(3)	0.499(1)	1.00	0.046(7)	0.048(5)	0.088(7)	-0.016(6)	-0.016(6)	0.026(6)	0.059(2)
Sr1	0.67649(9)	0.5817(1)	0.5005(3)	0.91(1)	0.014(2)	0.017(2)	0.017(2)	-0.002(1)	0.000(2)	0.006(2)	0.017(1)
Na2				0.09(1)							
Sr2	0.9051(1)	0.5816(1)	0.4997(3)	0.89(1)	0.015(2)	0.015(2)	0.018(2)	0.003(1)	0.003(2)	0.008(1)	0.016(1)
Na3				0.11(1)							
Ba	2/3	1/3	0.5000(2)	0.33	0.0158(6)	0.0158(6)	0.027(1)	0	0	0.0079(3)	0.0196(5)
Zr1	0.83860(1)	0.4193(1)	0.5000(1)	1.00	0.0088(8)	0.013(1)	0.0087(8)	0.000(1)	0.0005(7)	0.005(1)	0.0105(4)
Zr2	0.8389(1)	0.67753(6)	0.4999(2)		1.00	0.012(2)	0.0120(9)	0.0087(8)	0.0001(7)	0.002(2)	0.006(2)
	0.0109(4)										
Zr3	0	0	1/2	0.17	0.010(1)	0.010(1)	0.001(2)	0	0	0.0052(6)	0.0073(8)
Si1	0.9355(2)	0.6769(2)	0.2501(5)	1.00	0.006(2)	0.004(3)	0.016(3)	0.000(2)	0.000(2)	-0.001(2)	0.010(1)
Si2	0.6802(2)	0.4470(2)	0.2501(5)	1.00	0.009(3)	0.002(2)	0.011(3)	0.000(2)	0.000(2)	0.005(2)	0.007(1)
Si3	0.8086(2)	0.4892(2)	0.2498(5)	1.00	0.009(3)	0.008(3)	0.010(3)	0.000(2)	0.000(2)	0.005(2)	0.009(1)
Si4	0.9354(2)	0.4192(2)	0.2500(5)	1.00	0.010(3)	0.014(3)	0.010(3)	-0.001(2)	0.001(2)	0.006(2)	0.011(1)
Si5	0.7670(2)	0.5764(2)	0.2502(5)	1.00	0.008(2)	0.009(3)	0.012(3)	0.001(2)	-0.001(2)	0.004(2)	0.010(1)
Si6	0.9341(2)	0.7716(2)	0.7496(5)	1.00	0.016(2)	0.013(3)	0.014(3)	-0.003(2)	-0.001(2)	0.006(2)	0.014(1)
Si7	0	0.9042(2)	3/4	0.50	0.011(4)	0.014(3)	0.004(4)	0.000(1)	-0.001(3)	0.005(2)	0.010(2)
B1	0	0.6148(9)	1/4	0.39(2)	0.03(2)	0.15(5)	0.07(3)	0.08(3)	0.02(2)	0.08(4)	0.07(2)
Si8				0.11(2)							
B2	0	0.6443(7)	3/4	0.36(2)	0.02(1)	0.02(2)	0.07(3)	0.07(2)	-0.11(1)	0.00(2)	0.05(1)
Si9				0.14(2)							
O1	0.7727(4)	0.3561(4)	0.384(1)	1.00	0.022(6)	0.008(6)	0.000(7)	-0.009(5)	-0.011(5)	0.008(5)	0.010(3)
O2	0.9025(4)	0.4156(4)	0.387(1)	1.00	0.014(6)	0.015(7)	0.007(8)	0.002(5)	0.006(5)	0.004(5)	0.014(4)
O3	0.7030(4)	0.5183(4)	0.250(1)	1.00	0.002(6)	0.000(6)	0.022(7)	0.002(5)	0.004(6)	-0.010(5)	0.013(3)
O4	0.7723(4)	0.6120(4)	0.384(1)	1.00	0.012(6)	0.005(6)	0.031(9)	-0.009(5)	-0.001(6)	-0.002(5)	0.019(3)
O5	0	0.5222(5)	3/4	0.50	0.013(8)	0.010(6)	0.006(9)	-0.001(3)	-0.002(7)	0.006(4)	0.009(4)
O6	0.8403(4)	0.6124(4)	0.617(1)	1.00	0.015(6)	0.004(6)	0.025(8)	0.003(5)	0.009(5)	0.003(5)	0.016(3)
O7	0.9010(4)	0.6729(4)	0.386(1)	1.00	0.016(7)	0.006(6)	0.016(8)	0.000(5)	0.007(5)	0.008(5)	0.012(3)
O8	0.9468(5)	0.5827(4)	0.751(1)	1.00	0.018(7)	0.007(6)	0.022(8)	0.002(5)	0.001(5)	0.010(6)	0.014(3)
O9	0.8399(4)	0.4839(4)	0.119(1)	1.00	0.021(6)	0.006(6)	0.009(7)	0.000(5)	0.005(5)	0.008(5)	0.011(3)
O10	0.7384(4)	0.4409(4)	0.251(1)	1.00	0.000(5)	0.009(6)	0.018(8)	0.001(5)	0.004(5)	0.000(5)	0.010(3)
O11	0.8403(4)	0.4842(5)	0.380(1)	1.00	0.017(6)	0.012(6)	0.012(8)	-0.002(5)	-0.001(5)	0.006(6)	0.014(3)
O12	0.9997(4)	0.9353(5)	0.616(1)	1.00	0.023(7)	0.022(7)	0.014(7)	0.006(6)	0.003(6)	0.010(6)	0.020(3)
O13	0.8149(4)	0.5537(4)	0.249(1)	1.00	0.011(6)	0.003(6)	0.023(8)	-0.003(5)	0.001(5)	0.006(5)	0.011(3)
O14	0.6434(4)	0.4162(4)	0.117(1)	1.00	0.010(6)	0.010(6)	0.009(8)	0.001(5)	-0.009(5)	0.001(5)	0.011(3)
O15	0.9026(5)	0.4874(5)	0.612(1)	1.00	0.019(7)	0.022(7)	0.005(8)	-0.003(5)	0.000(5)	0.011(6)	0.015(3)
O16	0	0.7359(6)	1/4	0.50	0.000(8)	0.014(7)	0.02(1)	0.001(3)	0.002(6)	0.000(4)	0.014(4)
O17	0.9458(4)	0.6204(4)	0.250(1)	1.00	0.012(6)	0.013(6)	0.015(7)	0.003(5)	0.001(5)	0.008(6)	0.012(2)
O18	0	0.7798(6)	3/4	0.50	0.013(9)	0.010(6)	0.03(1)	0.001(3)	0.003(8)	0.006(4)	0.017(4)
O19	0.9007(4)	0.6727(4)	0.114(1)	1.00	0.014(6)	0.006(6)	0.012(8)	0.005(5)	-0.009(5)	0.006(5)	0.010(3)
O20	0.9016(5)	0.7411(5)	0.615(1)	1.00	0.019(7)	0.028(7)	0.017(8)	-0.018(6)	-0.014(6)	0.012(6)	0.021(3)
O21	0.9426(4)	0.8380(4)	0.751(1)	1.00	0.000(5)	0.013(6)	0.041(8)	0.005(6)	0.002(5)	0.005(5)	0.022(3)
O22	0.8392(5)	0.7410(5)	0.384(1)	1.00	0.024(8)	0.028(7)	0.013(8)	0.017(6)	0.003(5)	0.016(6)	0.020(3)
OH23	0.9995(5)	0.5848(5)	0.377(1)	1.00	0.042(9)	0.020(7)	0.02(1)	0.016(7)	-0.003(8)	0.019(7)	0.028(4)
OH24	0.0000(5)	0.6728(6)	0.617(1)	1.00	0.003(6)	0.040(9)	0.03(1)	0.002(7)	0.003(7)	0.001(6)	0.029(4)
OW25	0.9999(8)	0.8332(7)	0.411(2)	1.00	0.08(1)	0.06(1)	0.07(1)	-0.01(1)	-0.01(1)	0.04(1)	0.067(7)
OW26	0	1/2	1/2	0.20(2)							0.1
OW27	0.999(1)	0.758(1)	0.961(3)	0.42(3)							0.1

The large three-dimensional, heteropolyhedral framework of tetrahedra and octahedra observed in rogermitchellite produces numerous channels along [001] that house a variety of occupants. The inner ring of the BPM, formed by Zr(1)O<sub>6</sub> and three-membered silicate rings, gives rise to the largest void present in the mineral (~5 Å) and is occupied by <sup>112</sup>Ba. As in benitoite, the Ba site in rogermitchellite shows a distinct asymmetry with six short bonds (~2.81 Å) and six long bonds (~3.54 Å) with oxygen. Moving

outward from the BPM, irregular channels bounded by Zr(1)O<sub>6</sub>, Zr(2)O<sub>6</sub> octahedra and both three-membered [Si<sub>3</sub>O<sub>9</sub>]<sup>6-</sup> and [Si<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>]<sup>5-</sup> rings, are occupied by <sup>110</sup>Sr(1) and <sup>110</sup>Sr(2), the two occupying alternate channels in a 30° rotation about [001]. As noted, there are two BPM present in the unit cell of rogermitchellite. Bridging between them, *via* two SiO<sub>4</sub> tetrahedra from the [Si<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>]<sup>5-</sup> rings with Zr(1)O<sub>6</sub> octahedra and two SiO<sub>4</sub> tetrahedra from both the [Si<sub>2</sub>BO<sub>7</sub>(OH)<sub>2</sub>]<sup>5-</sup> and [Si<sub>3</sub>O<sub>9</sub>]<sup>6-</sup> rings with Zr(2)O<sub>6</sub> octahedra, creates rectan-

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å)  
IN ROGERMITCHELLITE

Na(1)O <sub>6</sub> polyhedron		(Sr1,Na2)O <sub>6</sub> polyhedron	
Na1	– OW25 2.38 (2)	(Sr1,Na2)	– O4 2.53 (1)
	– OW25' 2.39 (2)		– O9 2.57 (1)
	– O21 2.55 (1)		– O17 2.70 (1)
	– O21' 2.59 (1)		– O8 2.72 (1)
	– O22 2.61 (1)		– O19 2.72 (1)
	– O20 2.62 (1)		– O2 2.72 (1)
	– O12 2.68 (1)		– OH24 2.73(1)
	– O12' 2.68 (1)		– OH23 2.77(1)
<Na1	– O> 2.56	<Sr1,Na2	– O> 2.68
(Sr2,Na3)O <sub>6</sub> polyhedron		BaO <sub>6</sub> octahedron	
(Sr2,Na3)	– O6 2.53 (1)	Ba	– O1 ×3 2.81 (1)
	– O11 2.57 (1)		– O14 ×3 2.81 (1)
	– O17 2.70 (1)		– O10 ×3 3.54 (1)
	– O15 2.71 (1)		– O10' ×3 3.55 (1)
	– O7 2.72 (1)	<Ba	– O> 3.18
	– O8 2.73 (1)		
	– OH24 2.73 (1)	Zr(3)O <sub>6</sub> octahedron	
	– OH23 2.75 (1)	Zr3	– O12 ×6 2.07(1)
<Sr2,Na3	– O> 2.68	<Zr3	– O> 2.07
Zr(1)O <sub>6</sub> octahedron		Zr(2)O <sub>6</sub> octahedron	
Zr1	– O14 2.06(1)	Zr2	– O20 2.03(1)
	– O1 2.07(1)		– O22 2.03(1)
	– O9 2.07(1)		– O7 2.06(1)
	– O11 2.07(1)		– O19 2.06(1)
	– O15 2.07(1)		– O4 2.10(1)
	– O2 2.08(1)		– O6 2.10(1)
<Zr1	– O> 2.07	<Zr2	– O> 2.06
Si(1)O <sub>4</sub> tetrahedron		Si(2)O <sub>4</sub> tetrahedron	
Si1	– O7 1.60 (1)	Si2	– O1 1.61 (1)
	– O19 1.61 (1)		– O14 1.61 (1)
	– O16 1.643 (8)		– O10 1.63 (1)
	– O17 1.65 (1)		– O3 1.67 (1)
<Si1	– O> 1.63	<Si2	– O> 1.63
Si(3)O <sub>4</sub> tetrahedron		Si(4)O <sub>4</sub> tetrahedron	
Si3	– O9 1.59 (1)	Si4	– O2 1.60 (1)
	– O11 1.59 (1)		– O15 1.60 (1)
	– O13 1.63 (1)		– O8 1.63 (1)
	– O10 1.65 (1)		– O5 1.638 (8)
<Si3	– O> 1.62	<Si4	– O> 1.62
Si(5)O <sub>4</sub> tetrahedron		Si(6)O <sub>4</sub> tetrahedron	
Si5	– O4 1.60 (1)	Si6	– O20 1.58 (1)
	– O6 1.60 (1)		– O22 1.58 (1)
	– O3 1.62 (1)		– O18 1.648 (8)
	– O13 1.65 (1)		– O21 1.66 (1)
<Si5	– O> 1.62	<Si6	– O> 1.62
Si(7)O <sub>4</sub> tetrahedron		(B1,Si8)O <sub>2</sub> (OH) <sub>2</sub> tetrahedron	
Si7	– O12 ×2 1.57 (1)	(B1,Si8)	– OH23 ×2 1.49 (1)
	– O21 ×2 1.65 (1)		– O17 ×2 1.52 (1)
<Si7	– O> 1.61	<B1,Si8	– O> 1.50
(B2,Si9)O <sub>2</sub> (OH) <sub>2</sub> tetrahedron			
(B2,Si9)	– OH24 ×2 1.52 (1)		
	– O8 1.53 (1)		
<B2,Si9	– O> 1.52		

gular channels ( $\sim 2 \times 4 \text{ \AA}$ ), similar to those observed in wadeite, benitoite and the related species, catapleite. Although vacant in wadeite and benitoite, this particular void is occupied by H<sub>2</sub>O in rogermitchellite, just as in bobtraillite and catapleite. Additional H<sub>2</sub>O groups are located in channels at the centers of [Si<sub>3</sub>O<sub>9</sub>]<sup>6-</sup> rings that link two Zr(2)O<sub>6</sub> and one Zr(3)O<sub>6</sub> octahedra. Finally, rectangular channels are also formed between [Si<sub>3</sub>O<sub>9</sub>]<sup>6-</sup> rings and both Zr(2)O<sub>6</sub> and Zr(3)O<sub>6</sub> octahedra, and these are occupied by <sup>18</sup>Na.

In summary, rogermitchellite is a cyclosilicate containing three-membered rings of both SiO<sub>4</sub> and BO<sub>2</sub>(OH)<sub>2</sub> tetrahedra. These tetrahedra are joined to ZrO<sub>6</sub> octahedra to produce a three-dimensional, heteropolyhedral framework of tetrahedra and octahedra, somewhat reminiscent of that found benitoite. Channels generated by this arrangement are occupied by a variety of alkalis, alkaline earths and H<sub>2</sub>O groups.

## RELATED STRUCTURES

Cyclosilicates from highly alkaline to apaitic environments represent a large, diverse group of minerals (Table 6). The majority of the crystal structures of these minerals are based on heteropolyhedral tetrahedron–octahedron frameworks, typically with the tetrahedra linked into three-membered rings (predominantly SiO<sub>4</sub>, but also with BO<sub>4</sub>, as is in bobtraillite and rogermitchellite) linked to isolated M<sup>4+</sup>O<sub>6</sub> octahedra (M = Zr, Ti, Sn) in pinwheel-like motifs. The frameworks produce large channels that are occupied by alkalis (Na,Ca), alkaline earths (Ba, Sr) and H<sub>2</sub>O groups. Although there has been no formal designation for this group of minerals, they have been informally included in the benitoite group of minerals (Hawthorne 1987, McDonald & Chao 2005). Such a group should also include related minerals (*e.g.*, hilairite, komkovite, *etc.*) whose structures are based on infinite (Si<sub>3</sub>O<sub>9</sub>) helical chains.

All minerals included in this benitoite group are hexagonal or pseudo-hexagonal in symmetry, this being strongly influenced by the cyclosilicate features present in these minerals. As noted by McDonald & Chao (2005), there are effectively two basic types of silicate-ring arrangements in these minerals: those where the rings directly superimpose over one another (*e.g.*, as in wadeite), and those in which the superimposed rings are rotated 30° relative to one another, typically about [001] (*e.g.*, benitoite). Rogermitcheillite represents the second example of a mineral related to benitoite that contains essential B, the other being bobtraillite. It is also unique among those minerals related to benitoite in that it is the first to contain (effectively) ordered Sr and Ba. Dimensionally, all are based on a the same basic unit-cell of dimensions  $\sim 7 \times 10 \text{ \AA}$ . For most, crystal-



TABLE 5. EMPIRICAL BOND-VALENCES ( $\nu u$ ) FOR ROGERMITCHELLITE\*

	Na1	Sr1*	Sr2*	Ba1	Zr1	Zr2	Zr3	Si1	Si2	Si3	Si4	Si5	Si6	Si7	B1*	B2*	$\Sigma V^{**}$
O1				0.245 <sup>*3</sup>	0.698				1.039								1.982
O2		0.181			0.679						1.067						1.927
O3									0.883			1.011					1.894
O4		0.312				0.644						1.067					2.023
O5											0.958						1.916
O6			0.312			0.644						1.067					2.023
O7			0.186			0.717		1.067									1.970
O8		0.186	0.181								0.984					0.829 <sup>*2</sup>	2.180
O9		0.279			0.698					1.096							2.073
O10				0.034 <sup>*3</sup>					0.984	0.932							1.983
				0.033 <sup>*3</sup>													2.073
O11			0.216		0.698					1.096							2.073
O12	0.093 <sup>*2</sup>						0.698 <sup>*8</sup>							1.157 <sup>*2</sup>			1.948
O13										0.984		0.932					1.916
O14				0.245 <sup>*3</sup>	0.717				1.039								2.029
O15			0.197		0.679						1.067						1.943
O16								0.958									1.916
O17		0.197	0.197					0.932							0.812 <sup>*2</sup>		2.138
O18													0.932				1.864
O19		0.186				0.717		1.039									1.942
O20	0.109					0.778							1.126				2.013
O21	0.132												0.907	0.932 <sup>*2</sup>			2.089
	0.118																
O22	0.112					0.757							1.126				1.995
OH23		0.181	0.181												0.881 <sup>*2</sup>		1.243
OH24		0.163	0.181													0.852 <sup>*2</sup>	1.196
OW25		0.209 <sup>*2</sup>															
$\Sigma V$	1.075	1.803	1.651	1.671	4.169	4.257	4.188	3.996	3.945	4.108	4.076	4.077	4.091	4.178	3.386	3.362	

\* Parameters from Brese & O'Keeffe (1991). Calculated using the refined site-occupancy factors as indicated in Table 3.

structure variations in the form of differing types of three-membered rings or crystallographically distinct  $MO_6$  octahedra results in multiplication of  $a_{\text{benitoite}}$ , with  $c_{\text{benitoite}}$  remaining constant. For example, the unit cell for bobtrillite is tripled along [100] ( $a_{\text{bobtrillite}} = 19.720 \text{ \AA}$ , *i.e.*,  $\sim 3a_{\text{benitoite}}$ ) and quadrupled in the case of rogermitchellite ( $a_{\text{rogermitchellite}} = 26.509 \text{ \AA}$ , *i.e.*,  $\sim 4a_{\text{benitoite}}$ ). The latter feature also results in this mineral having the largest unit-cell among all the benitoite-related minerals. Given the existence of rogermitchellite and bobtrillite and the chemical and geometrical aspects common to these minerals, along with those of both benitoite and wadeite, the possibility that other chemical and structural variants will be found in nature must be considered high.

#### ORIGIN, WITH COMMENTS ON THE OCCURRENCE OF CYCLOSILICATES IN HYPERAGPAITIC ENVIRONMENTS

Cyclosilicates containing essential Zr or Ti are common constituents of hyperagpaite and lamproitic rocks. Most are considered to develop under relatively

low pressure, typically <1 GPa, although some may develop over a larger range (1–3 GPa, as suggested for synthetic  $K_2TiSi_3O_9$ ; Gulliver *et al.* 1998). Temperatures of formation are generally considered to be low (<500°C), although higher-temperature anhydrous forms have also been synthesized [*e.g.*, those belonging to the  $K_2TiSi_3O_9$  (wadeite) –  $K_2ZrSi_3O_9$  join; Orlando *et al.* 2000]. The preponderance of cyclosilicates in hyperagpaite and lamproitic rocks rather than the structurally related ino- and phyllosilicates is a function of many factors, including a relatively high deficiency in silica and the ability of high-field-strength elements (HFSE) like Zr and Ti to polymerize with  $SiO_4$  tetrahedra to form heteropolyhedral frameworks of octahedra and tetrahedra. In many cases (particularly at relatively higher temperatures), the  $SiO_4$  tetrahedra are linked into three-membered rings that share all their free vertices with octahedra hosting the high-field-strength elements (HFSE), but in other cases, the  $SiO_4$  tetrahedra can be linked into infinite helical chains that necessarily share a more limited number of vertices with HFSE octahedra (*e.g.*, hilairite,  $Na_2ZrSi_3O_9 \cdot 3H_2O$ ). Generally, the latter situation appears to exist for zirconosilicates developing

TABLE 6. DATA FOR BENITOITE AND RELATED MINERALS

Mineral	Formula	Space Group	a (Å)	b (Å)	c (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	Ref.
Benitoite	BaTiSi <sub>3</sub> O <sub>9</sub>	<i>P</i> 6̄2 <i>c</i>	6.6410(7)		9.760(1)				(1)
Bazirite	BaZrSi <sub>3</sub> O <sub>9</sub>	<i>P</i> 6̄2 <i>c</i>	6.742(1)		9.930(2)				(2)
Pabstite	BaSnSi <sub>3</sub> O <sub>9</sub>	<i>P</i> 6̄2 <i>c</i>	6.7307(7)		9.824(2)				(2)
Wadeite	K <sub>2</sub> ZrSi <sub>3</sub> O <sub>9</sub>	<i>P</i> 6̄ or <i>P</i> 6 <sub>3</sub> / <i>m</i>	6.918(2)		10.151(3)				(3, 4)
Bobtrillite	(Na,Ca) <sub>13</sub> Sr <sub>11</sub> (Zr,Y,Nb) <sub>14</sub> Si <sub>42</sub> B <sub>6</sub> O <sub>132</sub> (OH) <sub>12</sub> •12H <sub>2</sub> O	<i>P</i> 3̄ <i>c</i> 1	19.720(1)		9.9788(5)				(5)
Rogermitchellite	Na <sub>12</sub> (Sr,Na) <sub>24</sub> Ba <sub>4</sub> Zr <sub>26</sub> Si <sub>175</sub> (B,Si) <sub>112</sub> O <sub>246</sub> (OH) <sub>24</sub> •18H <sub>2</sub> O	<i>P</i> 3̄ <i>c</i> 1	26.509(3)		9.975(1)				(this work)
Komkovite	BaZrSi <sub>3</sub> O <sub>9</sub> •3H <sub>2</sub> O	<i>R</i> 32	10.526(6)		15.736(9)				(6)
Hilairite	Na <sub>2</sub> ZrSi <sub>3</sub> O <sub>9</sub> •2H <sub>2</sub> O	<i>R</i> 32	10.556(1)		15.855(2)				(7)
Calcium catapleite	CaZrSi <sub>3</sub> O <sub>9</sub> •2H <sub>2</sub> O	<i>P</i> <i>bnn</i>	7.378(1)	12.779(1)	10.096(1)				(8)
Catapleite	Na <sub>2</sub> ZrSi <sub>3</sub> O <sub>9</sub> •2H <sub>2</sub> O	<i>B</i> 2/ <i>b</i>	23.917(2)	20.148(2)	7.432(1)		147.46(1)		(9)
Margarosanite	Ca <sub>3</sub> PbSi <sub>3</sub> O <sub>9</sub>	<i>P</i> 1̄	6.768(4)	9.575(4)	6.718(5)	69.40(3)	102.98(4)	96.98(5)	(10)
Walstromite	Ca <sub>3</sub> BaSi <sub>3</sub> O <sub>9</sub>	<i>P</i> 1̄	6.743(5)	9.607(5)	6.687(5)	69.85	102.23	96.11	(11)
Pseudo- wollastonite	CaSiO <sub>3</sub>	<i>P</i> 1̄ or <i>C</i> 2/ <i>c</i>	6.8394(5)	11.8704(9)	19.6313(9)		90.667(6)		(12, 13)

References: (1) Fischer (1969), (2) Hawthorne (1987), (3) Blinov *et al.* (1977), (4) Sakai *et al.* (2000), (5) McDonald & Chao (2005), (6) Sokolova *et al.* (1991), (7) Ilyushin *et al.* (1981a), (8) Merlino *et al.* (2004), (9) Ilyushin *et al.* (1981b), (10) Freed & Peacor (1969), (11) Alfors *et al.* (1965), (12) Yamanaka & Mori (1981), (13) Yang & Prewitt (1999).

at very low temperatures (*i.e.*, 200–250°C; Zubkova *et al.* 2007).

Some of the factors influencing the genesis of minerals containing essential HSFE and possessing structures based on frameworks of mixed octahedra and tetrahedra (termed mesoporous heterosilicate minerals, MHM) have been discussed by Pekov & Chukanov (2005). In short, they noted that MHM are derivatives of “magmatogenic” precursors (*e.g.*, eudialyte) from highly alkaline environments, the principal geochemical factor associated with their formation being fluids enriched in Na, K or Ba (Ca or Sr may be associated, but alone, fluids enriched in these particular elements are not conducive to the formation of MHM). These authors also noted a decrease in framework densities in MHM relative to primary minerals, a factor that may enhance the processes of cation leaching, hydration and ion exchange, all of which favor MHM formation. Considering the limited size of the specimen on which rogermitchellite was found makes it difficult to develop a concise pattern relating to its origin and paragenesis. However, consideration of: a) its bulk composition, b) the crystal-structure relationships with zirconosilicates, and c) observations made on the mineralogy of hyperagpaitic environments in general and of Mont Saint-Hilaire in particular, certain conjectures may be made. In many hyperagpaitic environments, including that at Mont Saint-Hilaire, the predominant high-temperature zirconosilicate of sodium is believed to be a eudialyte-group mineral (EGM). Such EGM are considered as orthomagmatic phases in several

hyperagpaitic settings (*e.g.*, Pilansberg, South Africa; Tamazeght, Morocco) but can easily undergo subsolidus transformations to form a relatively large and diverse group of secondary zirconosilicates (*e.g.*, catapleite, hilairite, *etc.*). Whereas the replacement of orthomagmatic phases including EGM, vlasovite, lāvenite and dalyite has been documented by other investigators (*e.g.*, Birkett *et al.* 1992, Moreau *et al.* 1996, Chakmouradian & Mitchell 2002), only EGM occur in any significant abundance at Mont Saint-Hilaire. On this basis, an EGM is considered as the most likely precursor of zirconosilicates like catapleite and rogermitchellite. Replacement of pre-existing EGM can also produce distinctive associated mineral assemblages that are directly relevant to the formation of rogermitchellite. At Pilansberg, for example, Liferovich & Mitchell (2006) documented the replacement of orthomagmatic EGM by Na zirconosilicates (possibly catapleite) *via* cation exchange with alkaline fluids. In addition, the minerals stronalsite, fluorstrophite and lamprophyllite were produced. This process, termed type-2 alteration by Liferovich & Mitchell (2000), involves reactions of orthomagmatic EGM at subsolidus conditions (<450°C) with deuterium- and chlorine-bearing fluids. The reaction has important implications with respect to the formation of rogermitchellite: first, the crystal-structure link between catapleite and this mineral suggests a similarity in the conditions of formation between the two, *i.e.*, subsolidus alteration of orthomagmatic EGM. Secondly, the mineral assemblage observed at Pilansberg is dominated by Sr-bearing minerals, an

important consideration in light of the essential Sr contained within rogermitchellite. The association of Sr enrichment during alteration and recrystallization of secondary Na-zirconosilicates after orthomagmatic EGM has also been observed at Tamazeght, Morocco (Schilling *et al.* 2009). The implication is therefore that formation of rogermitchellite may be related to the breakdown of earlier-formed EGM at temperatures <450°C, in a process comparable to the type-2 alteration described by Liferovich & Mitchell (2006).

Given the clear crystal-chemical similarities between catapleiite and rogermitchellite, it is worthwhile to discuss the conditions under which catapleiite has been synthesized. Catapleiite,  $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$ , is known to crystallize in two modifications, one hexagonal ( $P6_3/mmc$ ) and one monoclinic ( $I2/c$ ). The hexagonal form has been synthesized at 700 bars over the range 300–700°C (Baussy *et al.* 1974). Although monoclinic catapleiite has not been directly synthesized, results obtained during a study of the thermal behavior of synthetic catapleiite indicate that the hexagonal  $\rightarrow$  monoclinic transformation occurs at 155°C with the reverse occurring at 145°C (Ilyushin & Dem'yanets 1988). Considering these temperatures, along with that indicated in the above discussion, we suggest that rogermitchellite likely formed over the temperature range of 300–450°C at less than 1 GPa.

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