

BRIANROULSTONITE: A NEW BORATE MINERAL WITH A SHEET STRUCTURE

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ABSTRACT

Brianroulstonite from the Potash Corporation of Saskatchewan (New Brunswick Division) mine at Penobsquis, Kings County, New Brunswick, occurs in the Upper Halite member of the evaporite sequence, associated with halite, hilgardite, pringleite, trembathite, sellaïte, fluorite, hematite, muscovite, penobsquisite and a clay-group mineral. It occurs as thin, transparent to translucent, colorless to white, vitreous, cleavable masses to $2 \times 1 \times 1$ mm. Brianroulstonite is biaxial negative, with indices of refraction α 1.506(2), β 1.527(2) and γ 1.532(2); $2V_{\text{meas.}} = 56(1)^\circ$, $2V_{\text{calc.}} = 51.4^\circ$. There is no dispersion and no pleochroism. The optical orientation is $Z = b$, $X \wedge c = 30^\circ$ (in the obtuse angle β). Brianroulstonite is monoclinic, space group Pa , with cell parameters refined from X-ray powder-diffraction data: a 17.42(4), b 8.077(5), c 8.665(6) Å, β 121.48(7)°, V 1040(2) Å³ and $Z = 2$. The strongest six lines of the X-ray powder-diffraction pattern [d in Å(hkl)] are: 8.10(10)(010), 4.04(4)(020), 3.56(2)(221), 2.834(2)(601,203), 2.535(2)(230,031) and 2.276(2)(231). The crystals have a micaceous habit, with a perfect parting plane on {010}, which is also the composition plane for the 2-fold rotational twin on [102]. Electron-microprobe analyses gave (in wt.%) CaO 32.85 (29.24–34.50), K₂O 0.05 (0.05–0.06), Cl 13.79 (13.28–14.31), B₂O₃ 33.92 and H₂O 40.44, O = Cl –3.11, total 117.99%. The proportion of H₂O and B₂O₃ was calculated by stoichiometry from the results of the crystal-structure analysis. The empirical formula based on 23 anions is: (Ca_{3.00}K_{0.01})_{Σ3.01}[B₅O₆(OH)₆](OH)Cl_{1.99}·8H₂O or, ideally, Ca₃[B₅O₆(OH)₆](OH)Cl₂·8H₂O; $D_{\text{meas.}} = 1.97(3)$ g/cm³, $D_{\text{calc.}} = 1.93$ g/cm³. The IR spectrum, with absorption bands at 3363, 1640, 1384, 1295, 1153, 920, 790, 720, 556 and 408 cm⁻¹, indicates the presence of H₂O groups and complex borate groups. The crystal-structure determination refined to $R = 3.9\%$ for 2945 unique reflections. The (010) borate sheet of brianroulstonite consists of edge-sharing 12-membered rings. The 12-membered rings of alternating triangular and tetrahedral borate polyhedra are cross-linked by slabs of Cl anions bonded to H atoms in the H₂O groups. The Ca polyhedra are centered in the rings and bond the borate sheets to the H₂O groups. Sheets of 12-membered borate rings are also found in the minerals penobsquisite, pringleite and rutenbergite, all found in the Sussex evaporite. Differing patterns of cross-linkage of these sheets gives rise to distinct structures.

Keywords: brianroulstonite, new mineral species, crystal structure, borate, polymerization, evaporite, Penobsquis, New Brunswick.

SOMMAIRE

La brianroulstonite, nouvelle espèce minérale, a été découverte dans la mine de la Potash Corporation of Saskatchewan (division du Nouveau-Brunswick), à Penobsquis, comté de Kings, au Nouveau-Brunswick. Elle se trouve dans le membre supérieur "Upper Halite" de la séquence évaporitique, en association avec halite, hilgardite, pringleïte, trembathite, sellaïte, fluorite, hématite, muscovite, penobsquisite, et un minéral du groupe des argiles. Elle se présente en masses clivables minces, transparentes à translucides, incolores à blanches, à aspect vitreux, mesurant jusqu'à $2 \times 1 \times 1$ mm. La brianroulstonite est biaxe négative, avec les indices de réfraction α 1.506(2), β 1.527(2), et γ 1.532(2); $2V$ mesuré est égal à $56(1)^\circ$, et $2V$ calculé, 51.4° . Il n'y a aucune dispersion et aucun pléochroïsme. L'orientation optique est $Z = b$, $X \wedge c = 30^\circ$ (dans l'angle β obtus). Elle est monoclinique, groupe spatial Pa , avec les paramètres suivants, affinés à partir de données de diffraction X (méthode des poudres): a 17.42(4), b 8.077(5), c 8.665(6) Å, β 121.48(7)°, V 1040(2) Å³ et $Z = 2$. Les six raies les plus intenses du spectre de diffraction [d en Å(hkl)] sont: 8.10(10)(010), 4.04(4)(020), 3.56(2)(221), 2.834(2)(601,203), 2.535(2)(230,031), et 2.276(2)(231). Les cristaux ont un aspect micacé, avec un plan de séparation parfait sur {010}, qui est aussi le plan de composition d'une maille de rotation d'ordre 2 sur [102]. Les analyses à la microsonde électronique ont donné (en poids) CaO 32.85 (29.24–34.50), K₂O 0.05 (0.05–0.06), Cl 13.79 (13.28–14.31), B₂O₃ 33.92 et H₂O 40.44, O = Cl –3.11, pour un total de 117.99%; la proportion de H₂O et de B₂O₃ a été calculée selon la stoechiométrie découlant de l'affinement de la structure cristalline. La formule empirique, fondée sur une base de 23 anions, est (Ca_{3.00}K_{0.01})_{Σ3.01}[B₅O₆(OH)₆](OH)Cl_{1.99}·8H₂O ou, de façon idéale, Ca₃[B₅O₆(OH)₆](OH)Cl₂·8H₂O; la densité mesurée est de 1.97(3), et la densité calculée, 1.93. Le spectre d'absorption dans l'infra-rouge montre des bandes d'absorption à 3363, 1640, 1384, 1295, 1153, 920, 790, 720, 556 et 408 cm⁻¹, et indique la présence de groupes H₂O et de groupes de borates complexes. La structure cristalline a été affinée jusqu'à un résidu R de 3.9% en utilisant les intensités de 2945 réflexions uniques. Le feuillet (010) de la brianroulstonite contient des anneaux à douze groupes partageant des arêtes. Ces anneaux à groupes de borate triangulaire et tétraédrique en alternance sont interliés par des panneaux

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d'anions Cl formant des liaisons avec les atomes H des groupes H₂O. Les polyèdres Ca sont centrés sur les anneaux et joignent les feuillets de borate aux groupes H₂O. De tels feuillets de borate à douze membres sont aussi présents dans la penobsquiste, pringleite et rutenbergite, tous découverts dans la même séquence évaporitique. Ce sont les schémas de liaisons entre les anneaux qui distinguent leurs structures.

(Traduit par la Rédaction)

Mots-clés: brianroulstonite, nouvelle espèce minérale, structure cristalline, borate, polymérisation, évaporite, Penobsquis, Nouveau-Brunswick.

INTRODUCTION

Brianroulstonite is the latest in a series of new borate minerals to be described from the evaporite deposits of southern New Brunswick. Others in this series include trembathite (Burns *et al.* 1992), pringleite and rutenbergite (Roberts *et al.* 1993) and penobsquiste (Grice *et al.* 1996). Brianroulstonite was discovered during a systematic examination of residue obtained from the dissolution of halite-sylvite-bearing drill-core from the mine operated by the Potash Corporation of Saskatchewan (New Brunswick Division), at Penobsquis, New Brunswick. Micaceous crystals were noted in the residue. Subsequent X-ray and electron-microprobe analysis clearly indicated that this was an unknown phase. The data presented here establish this mineral as a new species.

The examination of drill core from this area forms part of a Canadian Museum of Nature project of wider scope by the senior author of this paper (JDG), which includes the structural classification of all borate minerals.

Brianroulstonite is named for Brian V. Roulston (b. 1948). Mr. Roulston has been actively involved in the study of the geology of evaporite deposits for over 20 years. He is credited with the interpretation of the complex stratigraphy and structure of the Sussex deposits and has authored many papers on the subject. He was the first geologist to advocate and use borate minerals as stratigraphic markers in the New Brunswick evaporite deposits. 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 CMNMI 81500.

OCCURRENCE

Brianroulstonite was discovered in a piece of drill core from the Potash Corporation of Saskatchewan mine (New Brunswick Division), formerly the Potash Company of America mine, 5 km east of Penobsquis, Cardwell Parish, Kings County, New Brunswick. The drill core comes from the lower third of the Upper Halite member within a thick sequence of Windsor Group evaporites. The stratigraphy and geological setting of the evaporite deposits are described by Roulston & Waugh (1981) and by Roulston *et al.* (1995). The evaporites are Mississippian in age and occur in the Moncton sub-basin, part of the Fundy

epigeosyncline, a northeasterly trending depositional trough extending through southern New Brunswick, Nova Scotia and western Newfoundland.

Borate minerals from two potash mines in the Penobsquis-Sussex area of New Brunswick were first noted in the early 1980s in residue from the drilling operations, and were subsequently identified in the mining companies' laboratories and at various institutions (Roulston & Waugh 1981). The list of borate minerals compiled from these earlier investigations and from our study includes boracite, veatchite, colemanite, danburite, hilgardite-1A, hilgardite-4M, howlite, hydroboracite, priceite, szaibelyite, ulexite, volkovskite, pringleite, rutenbergite, trembathite, strontiongorite, congolite, tyretskite, ginorite, inyoite and penobsquiste. Other minerals found with the borate assemblage include anhydrite, sellaite, fluorite, nickeline, pyrite, chalcopyrite, sphalerite, halite, sylvite, microcline, diopside, quartz, a mica-group mineral, a clay-group mineral, hematite, limonite, magnesite, calcite, dolomite, monohydrocalcite and malachite. Organic material is present in several sections of core.

Brianroulstonite is intimately associated with halite, hilgardite, pringleite, trembathite, sellaite, fluorite, hematite, muscovite, penobsquiste and a clay-group mineral. Only a few cleavage masses, with a total approximate weight of 10 mg, were separated.

PHYSICAL AND OPTICAL PROPERTIES

Brianroulstonite occurs as cleavable masses to $2 \times 1 \times 1$ mm, with individual crystals of micaceous habit approximately $0.5 \times 0.25 \times 0.1$ mm in size. The thin colorless to white {010} lamellae are flexible, transparent to translucent, with a vitreous luster and a white streak. Brianroulstonite is nonfluorescent in either long- or short-wave ultraviolet light. Merohedral twinning, with [102] as twin axis and (010) as composition plane, is ubiquitous but not observable, even under high-power magnification. It has an approximate hardness of 5 (Mohs hardness scale) and a perfect (010) cleavage. The density, $1.97(3)$ g/cm³, was measured by suspension in bromoform; it is slightly high compared with the calculated density of 1.93 g/cm³ owing to minute inclusions of an unknown Ca-, Sr-, and Cl-bearing phase.

Brianroulstonite is biaxial negative, with indices of refraction α 1.506(2), β 1.527(2) and γ 1.532(2) (for $\lambda = 590$ nm); $2V_{\text{meas.}} = 56(1)^\circ$, $2V_{\text{calc.}} = 51.4^\circ$. There is no

dispersion and no pleochroism. The optical orientation is $X \wedge c = 30^\circ$ (in obtuse angle β), $Y = a$, and $Z = b$.

CHEMICAL COMPOSITION

Electron-microprobe analysis

Chemical analyses were performed on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. The wavelength-dispersion (WD) mode was used. Data reduction was 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 μ A. Four analyses were performed on three separate grains using a beam 40 μ m in diameter. Data for all 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. F was sought but not detected. A wavelength-dispersion scan of the boron peak confirmed the presence of boron; however, the combined problems of the overlap of chlorine on boron and severe degradation of the sample precluded an accurate analysis for boron. Even using a broad beam and rastering across the sample, severe burn-up resulted in the high totals reported here. The relative count-rates of the two major ions detectable by the microprobe (Ca and Cl), during a series of 3-s counts, remained unchanged, resulting in stoichiometric results for those two elements. The presence of H₂O was confirmed by infrared spectroscopy. Standards were used in the electron-microprobe analyses: danburite (CaK α), microcline

(KK α) and scapolite (ClK α). Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. The four determinations (with ranges) gave, as average result, CaO 32.85(29.24–34.50), K₂O 0.05(0.05–0.06), Cl 13.79(13.28–14.31), B₂O₃ 33.92 and H₂O 40.44, O = Cl–3.11, total 117.99 wt.%. H₂O and B₂O₃ were calculated by stoichiometry from the results of the crystal-structure analysis. The empirical formula based on 23 anions is (Ca_{3.00}K_{0.01})_{Σ3.01}B₅O₆(OH)₇Cl_{1.99}·8H₂O or, ideally, Ca₃B₅O₆(OH)₇Cl₂·8H₂O. Clearly, the quality of the crystal-structure analysis was essential in the description of this species (Hawthorne & Grice 1990).

Infrared analysis

The infrared spectrum (Fig. 1) of brianroulstonite was obtained using a Bomem Michelson MB–120 Fourier-transform infrared spectrometer with a diamond-anvil cell microsampling device. The broad peak centered in the 3363 cm^{-1} region, the O–H stretching frequency, indicates the presence of (OH)[–] anions or H₂O groups. The broadness of the peak indicates a variety of distinct OH or H₂O groups in the structure. The peak centered at 1640 cm^{-1} is attributed to H–O–H bending, which confirms the presence of H₂O groups. Comparing the remaining complex part of the spectrum to spectra given in Farmer (1974), the following peaks are assigned modes: 1384 and 1295 cm^{-1} : asymmetric stretching, [BO₃]; 1153 and 920 cm^{-1} : asymmetric stretching, [BO₄]; 790 and 720 cm^{-1} : symmetric stretching, [BO₄], and 56 and 408 cm^{-1} : bending modes, [BO₃] and [BO₄].

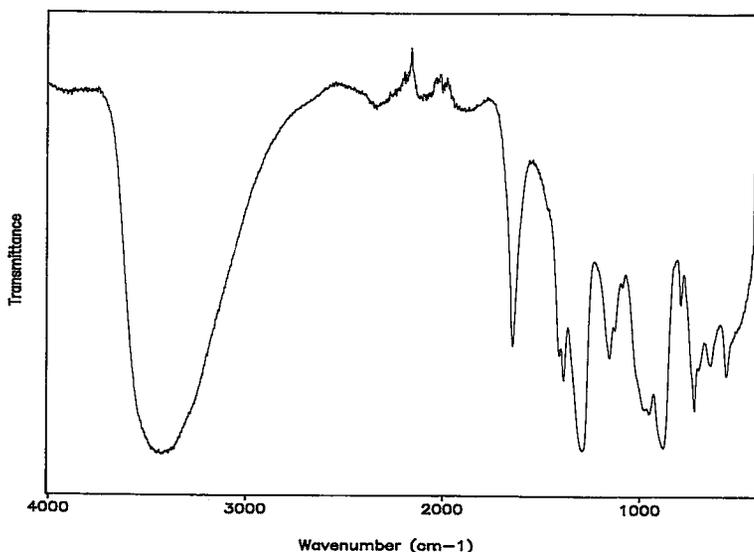


FIG. 1. Brianroulstonite: infrared spectrum.

X-RAY CRYSTALLOGRAPHY AND
CRYSTAL-STRUCTURE DETERMINATION

X-ray precession photographs show brianroulstonite to be pseudohexagonal with $a \approx 17 \text{ \AA}$ and $c \approx 8 \text{ \AA}$. Careful inspection of the precession photographs showed a strong subcell on one of the pseudohexagonal axes, indicating that $a \neq b$; thus the true symmetry of the mineral is monoclinic, diffraction symmetry $2/m$, with $a \approx 17$, $b \approx 8$ and $c \approx 17/2 \text{ \AA}$ and $\beta \approx 120^\circ$. From the conditions of systematic extinction, possible space-groups include $P2_1/a$ (space group #13) and Pa (space group #7). X-ray powder-diffraction data collected with a 114.6-mm-diameter Debye-Scherrer camera with $\text{CuK}\alpha$ (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 coordinates determined in the crystal-structure analysis.

The single crystal of brianroulstonite used for the collection of X-ray-diffraction intensity data (catalogue number CMNMI 81500) measures $0.5 \times 0.25 \times 0.1 \text{ mm}$. Intensity data were collected on a fully automated Siemens P3 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $\text{MoK}\alpha$ radiation. A set of 32 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Only one asymmetric unit of intensity data was collected

TABLE 1. BRIANROULSTONITE: X-RAY POWDER DIFFRACTION DATA

<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{cal} *	<i>hkl</i>	<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{cal} *	<i>hkl</i>
10	8.10	8.07	010	2	2.535	2.531	230
1	7.06	7.09	110			2.530	031
<1	5.90	5.91	$\bar{1}11$	<1	2.468	2.476	600
1	5.49	5.45	011			2.463	003
		5.45	210	<1	2.412	2.411	$\bar{2}13$
<1	4.61	4.58	111	<1	2.363	2.365	330
1	4.33	4.35	$\bar{2}01$			2.356	013
		4.33	$\bar{2}02$	<1	2.319	2.321	$\bar{2}21$
4	4.04	4.03	020			2.311	$\bar{2}23$
<1	3.80	3.83	$\bar{3}11$	2	2.276	2.273	231
		3.82	$\bar{2}12$	<1	2.179	2.180	430
<1	3.69	3.714	400			2.177	$\bar{3}02$
		3.695	002			2.176	032
2**	3.56	3.564	$\bar{2}21$	<1	2.099	2.102	$\bar{3}12$
<1	3.43	3.432	$\bar{3}12$			2.101	$\bar{3}03$
<1	3.37	3.374	410			2.095	$\bar{6}04$
		3.360	012			2.091	$\bar{4}14$
<1	3.15	3.173	$\bar{3}11$	<1	2.052	2.053	412
1	2.932	2.925	221	<1	1.961	1.961	$\bar{6}32$
2**	2.834	2.836	$\bar{6}01$			1.957	$\bar{4}33$
		2.819	$\bar{2}03$	<1	1.889	1.895	$\bar{3}04$
<1	2.726	2.734	420	<1	1.824	1.822	630
		2.726	022			1.817	033
<1	2.648	2.649	130	<1	1.807	1.810	810
<1	2.626	2.634	411			1.801	014
		2.628	212	1	1.651	1.650	$\bar{6}42$
						1.648	$\bar{4}43$

- 114.6 mm Gandolfi camera, $\text{CuK}\alpha$ radiation (Ni filtered)

- intensities estimated visually

* refined cell parameters $a = 17.42(4)$, $b = 8.077(5)$, $c = 8.665(6) \text{ \AA}$, $\beta = 121.48(7)^\circ$

** enhanced *I* due to included halite

(i.e., $hk \pm l$ for the centrosymmetric space-group) up to $2\theta = 60^\circ$ using a $\theta:2\theta$ scan-mode with scan speeds inversely proportional to intensity, varying from 4 to $29.3^\circ/\text{minute}$. Data pertinent to the intensity-data collection are given in Table 2.

Reduction of the intensity data, structure determination and structure refinement (in the early stages of refinement) were done with the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included corrections for background, scaling, Lorentz, polarization and linear absorption. For the ellipsoidal absorption-correction, eleven intense diffraction-maxima in the range 5 to $45^\circ 2\theta$ were chosen for Ψ diffraction-vector scans after the method of North *et al.* (1968). The merging *R* for the Ψ -scan data set (396 reflections) decreased from 4.99% before the absorption correction to 1.66% after the absorption correction.

Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.816, indicating a noncentrosymmetric space-group. A direct-method solution for the noncentrosymmetric space-group *Pa* gave a good combined figure of merit of 0.029. The *E*-map coordinates for the noncentrosymmetric model were assigned with appropriate scattering curves, and the structure model refined to $R = 24\%$. The difference-Fourier maps of subsequent refinements required a rearrangement of some of the assigned sites and the addition of new sites. With all of the sites assigned the correct scattering curves, the model refined to $R = 12.2\%$ with isotropic displacement-factors. At this point in the refinement, a rotational twin law on $[102]$ was introduced using the computer program SHELXL-93 (Sheldrick, in prep.). This reduced the residual factor, *R*, to 6.4%. In the final least-squares refinement, the position of all atoms was refined, with anisotropic displacement-factors, to a final residual *R* of 3.9%. The addition of an isotropic extinction-correction did not improve the refinement. Every attempt was made to locate H atoms, but residual background electron densities, of the order of 0.5 to 1.1 electrons/ \AA^3 , were too high to do this unequivocally. The refined fractional contribution of the second component of the twin is 0.405(1). The final positional and isotropic displacement-parameters are given in Table 3, and selected bond-lengths and angles, in Table 4. Tables listing the observed and calculated structure-factors may be obtained from the

TABLE 2. BRIANROULSTONITE: DATA COLLECTION INFORMATION

Space Group	<i>Pa</i> (# 7)	Measured / unique reflections	6678 / 4659
<i>a</i> (Å)	17.367(4)	Observed reflections [$> 3\sigma(F)$]	2945
<i>b</i> (Å)	8.079(2)	Min. / Max. transmission	0.958/ 0.670
<i>c</i> (Å)	8.693(2)	μ (mm^{-1})	1.15
β (°)	121.56(2)	Refined parameters	279
V (Å ³)	1039.3(6)	<i>R</i> [observed / all reflections] (%)	3.9 / 5.2
Unit-cell contents $2[\text{Ca}_3[\text{B}_3\text{O}_6(\text{OH})_6](\text{OH})\text{Cl}_2 \cdot 8\text{H}_2\text{O}]$			

Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

The pseudosymmetry in brianroulstonite was most effectively explored with the computer program MISSYM (Le Page 1987). With all atom positions disordered (*i.e.*, a complete disregard for chemical types of atoms), the symmetry of the structure is $6/mmm$.

Considering the B atom sites only, the symmetry is $62m$, whereas the Cl and O (without regard to OH or H₂O groups) sites lose the 6-fold axis, but retain the $2m$ symmetry aspect. The Ca sites effectively destroy all pseudosymmetry. Thus the cause of the pseudohexagonal cell and the twin law are easily understandable in light of these quasi symmetry elements.

DESCRIPTION OF THE STRUCTURE

TABLE 3. BRIANROULSTONITE: ATOMIC COORDINATES AND ISOTROPIC DISPLACEMENT FACTORS ($\text{\AA}^2 \times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ca1	1/2	0.4976(1)	0	124(2)
Ca2	0.8880(1)	0.2995(1)	0.5255(1)	140(2)
Ca3	0.1204(2)	0.5290(1)	0.7562(2)	130(2)
Cl1	0.3266(2)	0.0109(2)	0.9132(2)	336(5)
Cl2	0.0894(2)	0.0056(2)	0.4194(2)	314(4)
B1	0.8466(4)	0.4608(7)	0.1206(4)	128(9)
B2	0.6821(4)	0.4715(7)	0.4502(4)	127(9)
B3	0.2354(4)	0.4896(6)	0.2264(4)	129(8)
B4	0.5162(5)	0.4998(5)	0.3616(6)	134(12)
B5	0.3015(4)	0.5326(7)	0.7890(4)	93(9)
O1	0.8200(2)	0.4501(5)	0.2447(3)	136(6)
O2	0.9362(3)	0.4802(5)	0.1775(3)	172(8)
O3	0.2846(3)	0.5490(5)	0.9387(3)	149(6)
O4	0.7446(3)	0.4587(5)	0.3995(3)	152(6)
O5	0.7095(3)	0.4600(5)	0.6281(3)	157(6)
O6	0.5914(3)	0.4911(4)	0.3248(3)	150(8)
OH1	0.1544(2)	0.5606(4)	0.0688(2)	124(5)
OH2	0.2266(2)	0.3103(4)	0.2034(2)	198(6)
OH3	0.5122(3)	0.3520(5)	0.4551(3)	153(7)
OH4	0.5253(3)	0.6346(5)	0.4805(3)	143(7)
OH5	0.3611(3)	0.6639(4)	0.7917(3)	139(6)
OH6	0.3492(3)	0.3813(4)	0.7992(3)	153(7)
OH7	0.9873(3)	0.4838(3)	0.7321(3)	74(5)
W1	0.1627(4)	0.2463(6)	0.8483(3)	346(9)
W2	0.1399(4)	0.8266(5)	0.8270(4)	416(12)
W3	0.9829(3)	0.0784(5)	0.7214(3)	338(8)
W4	0.5545(3)	0.7839(5)	0.0700(3)	273(8)
W5	0.8903(3)	0.0854(6)	0.3224(3)	347(9)
W6	0.5144(3)	0.1977(5)	0.0451(3)	351(10)
W7	0.7751(4)	0.0875(6)	0.4519(5)	574(16)
W8	0.8825(3)	0.7793(5)	0.5444(3)	275(9)

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

Ca1-O2	2.336(4)	Ca2-O1	2.411(4)	Ca3-O3	2.442(4)		
Ca1-O6	2.409(3)	Ca2-O4	2.490(4)	Ca3-O5	2.339(4)		
Ca1-OH1	2.467(3)	Ca2-OH4	2.664(4)	Ca3-OH1	2.472(3)		
Ca1-OH3	2.516(4)	Ca2-OH5	2.606(4)	Ca3-OH3	2.480(4)		
Ca1-OH6	2.450(4)	Ca2-OH7	2.273(3)	Ca3-OH4	2.464(4)		
Ca1-OH7	2.226(5)	Ca2-W3	2.423(4)	Ca3-OH7	2.233(5)		
Ca1-W4	2.452(4)	Ca2-W5	2.486(4)	Ca3-W1	2.406(5)		
Ca1-W6	2.447(4)	Ca2-W7	2.424(4)	Ca3-W2	2.461(5)		
(Ca1-O)	2.413	(Ca2-O)	2.472	(Ca3-O)	2.412		
B1-O1	1.382(6)	O1-O2	120.4(5)	B2-O4	1.373(7)	O4-O5	119.6(5)
B1-O2	1.372(7)	O1-O3	120.3(4)	B2-O5	1.363(7)	O4-O6	121.5(5)
B1-O3	1.372(6)	O2-O3	118.7(5)	B3-O6	1.377(8)	O5-O6	118.8(5)
(B1-O)	1.376	(O-O)	120.0	(B2-O)	1.371	(O-O)	119.9
B3-O1	1.474(8)	O1-O4	103.0(3)	B4-O2	1.479(9)	O2-O6	101.8(5)
B3-O4	1.488(8)	O1-OH1	112.6(5)	B4-O6	1.501(9)	O2-OH3	113.5(5)
B3-OH1	1.473(6)	O1-OH2	111.7(5)	B4-OH3	1.467(7)	O2-OH4	112.3(4)
B3-OH2	1.459(5)	O4-OH1	112.0(5)	B4-OH4	1.452(7)	O6-OH3	112.2(4)
(B3-O)	1.474	O4-OH2	111.4(5)	(B4-O)	1.475	O6-OH4	113.9(5)
		OH1-OH2	106.2(3)			OH3-OH4	103.3(6)
		(O-O)	109.3			(O-O)	109.6
B5-O3	1.482(6)	O3-O5	102.4(4)				
B5-O5	1.474(7)	O3-OH5	112.4(4)				
B5-OH5	1.474(6)	O3-OH6	113.0(4)				
B5-OH6	1.453(6)	O5-OH5	112.9(4)				
(B5-O)	1.471	O5-OH6	113.3(4)				
		OH5-OH6	103.3(4)				
		(O-O)	109.6				
Cl1-OH5	3.162(7)	Cl2-W2	3.487(7)	W1-OH2	2.728(7)	W7-W8	2.959(8)
Cl1-OH6	3.240(7)	Cl2-W4	3.250(7)	W3-W4	2.832(8)	W8-OH2	2.871(8)
Cl1-W1	3.217(7)	Cl2-W5	3.167(7)	W3-W8	2.905(8)	W8-OH3	2.939(7)
Cl1-W2	3.278(7)	Cl2-W6	3.248(7)	W4-OH2	2.689(8)	W8-OH5	2.874(7)
Cl1-W3	3.220(7)	Cl2-W7	3.178(7)			W8-OH7	2.926(7)
Cl1-W6	3.213(7)	(Cl2-O)	3.266				
(Cl1-O)	3.222						

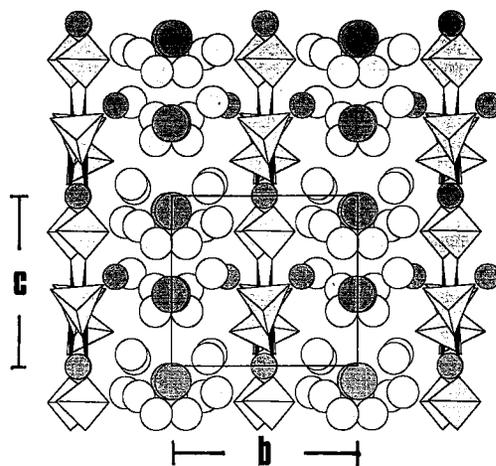


FIG. 2. Brianroulstonite: a [100] projection showing the borate sheets of triangular and tetrahedral polyhedra. Between the borate sheets and Ca atoms (smaller circles with dark shading) is a layer of Cl atoms (larger circles with dark shading) and H₂O groups (medium-sized circles with lighter shading).

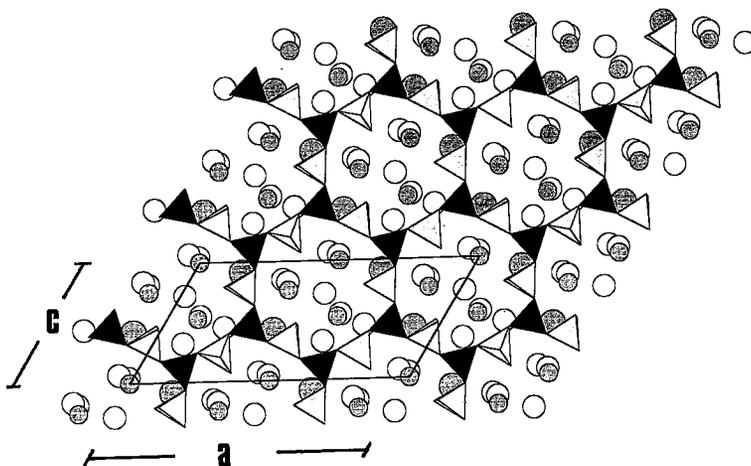


FIG. 3. Brianroulstonite: (010) sheet showing 12-membered rings of borate polyhedra: FBB $6\Delta 6\Box: < \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box >$. $[\text{BO}_2]$ triangles have dark shading, and $[\text{BO}_2(\text{OH})_2]$ tetrahedra have lighter shading. Ca atoms are small circles with dark shading, H_2O groups are small circles with light shading, and Cl atoms are large circles with dark shading.

the remaining two $(\text{OH})^-$ anions on the other side of the polyhedron but above and below the (010) plane. On the contrary, the Ca2 atom has a (010) plane of three H_2O groups above the Ca, the two O atoms and one OH group below the Ca, and the remaining two OH groups in the Ca (010) plane. All but one of the eight H_2O groups are bonded to one Ca atom. The exception, W8, is H-bonded within the structure (Table 4). The Cl⁻ anions play an important role within the structure, cross-linking the borate–Ca slabs through H atoms in the H_2O groups or $(\text{OH})^-$ anions at distances of $\sim 3.2 \text{ \AA}$ (Table 4). This is consistent with O–H–Cl bond lengths observed in other borates (Grice *et al.* 1994, 1996).

The polymerization of borate polyhedra in brianroulstonite may be described as (010) sheets of edge-sharing rings (Fig. 3). The fundamental building block (FBB) for this sheet is $6\Delta 6\Box: < \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box >$ or $6\Delta 6\Box: < \Delta \Box \bullet >$ (Burns *et al.* 1995). This FBB indicates that the 12 boron polyhedra involved form a 12-membered ring of alternating triangles and tetrahedra, and each ring shares three borate polyhedra with adjacent rings. This configuration can best be seen (Fig. 4) using boron–boron connectivity diagrams (Grice *et al.* 1994), in which each polyhedron is represented by its central B atom, and lines between B atoms are those sharing an oxygen atom (note: the O atoms are not shown in such diagrams).

The edge-sharing 12-membered rings seem common in newly described minerals from the Sussex, New Brunswick evaporites, but had never before been documented until this occurrence (Grice *et al.* 1996). The polymorphs pringleite and ruitenbergitte (Grice *et al.* 1994) and penobsquiste (Grice *et al.* 1996) all have this structural

feature, although the rings may be distorted, as in pringleite (Fig. 5). It is interesting that in all these structures, the sheets of rings are interconnected to form distinct arrangements. Brianroulstonite has the simplest, fundamental relationship, in that the borate sheets are cross-linked through Cl atoms and H-bonding, whereas in the other minerals, the borate sheets are cross-linked by other borate polyhedra forming a framework. Figure 6 shows the three-dimensional framework of the borate polyhedra in the pringleite structure, which is essentially the same in the ruitenbergitte structure, with an overall

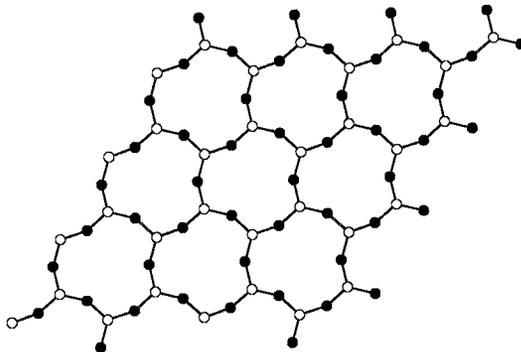


FIG. 4. Brianroulstonite: (010) sheet showing B–B connectivity. The 12-membered rings have alternating B polyhedra in triangular coordination (open circles) and tetrahedral coordination (filled circles).

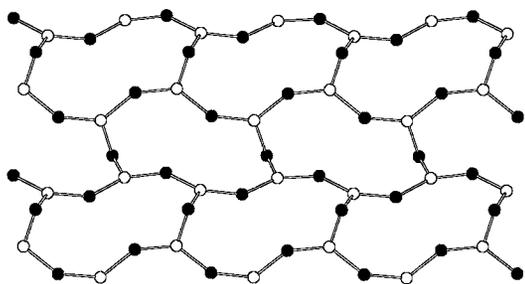


FIG. 5. Pringleite: (110) sheet showing B-B connectivity. The 12-membered rings have alternating B polyhedra in triangular coordination (open circles) and tetrahedral coordination (filled circles).

FBB $8\Delta 7\square := \langle \Delta \square \Delta \square \Delta \square \Delta \square \Delta \square \rangle \langle 2\Delta \square \rangle \Delta$. The (110) sheets of 12-membered rings are cross-linked by a $\langle \Delta 2 \square \rangle \Delta$ group. The structure of penobsquisite has an overall FBB $10\Delta 11\square := \langle \Delta \square \Delta \square \Delta \square \Delta \square \Delta \square \rangle \langle 2\Delta \square \rangle \langle \Delta 2 \square \rangle$, and the 12-membered ring sheet on (100) is cross-linked by the $\langle 2\Delta \square \rangle \langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle$ portion (Fig. 7). This cross-linkage FBB, $\langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle$, consists of two three-membered rings with a single borate polyhedron, through corner sharing of an anion (hence no “-” between the double rings in the FBB).

Borate minerals with FBBs of this magnitude are quite rare. In a tabulation of all the structures of borate minerals (Hawthorne *et al.* 1996), the only ones with

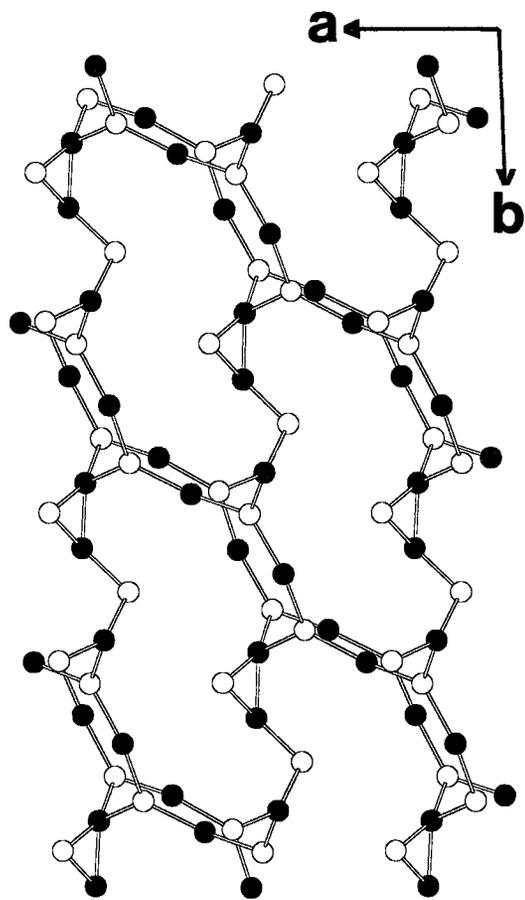


FIG. 6. Pringleite: [001] projection showing the B-B connectivity framework with large “S”-shaped channels. The (110) sheets of 12-membered rings are cross-linked by $\langle \Delta 2 \square \rangle \Delta$ groups. Polyhedra with B in triangular coordination are shown by open circles, and those with B in tetrahedral coordination are shown by filled circles.

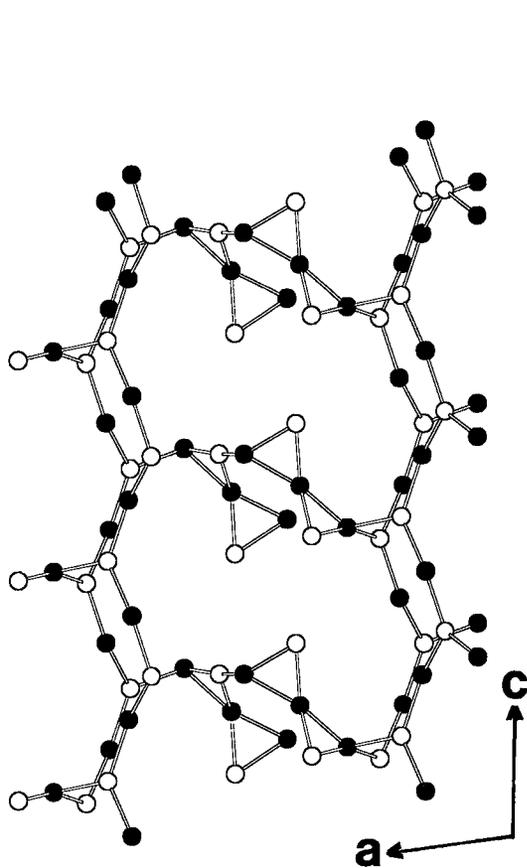


FIG. 7. Penobsquisite: [010] projection showing the B-B connectivity framework, characterized by large “S”-shaped channels. The (100) sheets of 12-membered rings are cross-linked by $\langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle \langle \Delta 2 \square \rangle$ chains. Polyhedra with B in triangular coordination are shown by open circles, and those with B in tetrahedral coordination are shown by filled circles.

FBBs greater than six are: kernite, with a chain structure, strontiorborite, ginorite, johachidolite and preobrazhenskite, with sheet structures, and the boracite series (boracite, chambersite, congolite, ericaite and trembathite), pringleite, ruitenbergitte and penobsquisite, with framework structures. All of these minerals, except johachidolite, have within their structure the very common three-membered ring of boron polyhedra (Burns *et al.* 1995). Brianroulstonite, pringleite, ruitenbergitte and penobsquisite are the only examples of structures with twelve-membered rings of borate polyhedra.

Brianroulstonite provides yet another example of the complex polymerization present in minerals of marine evaporite sequences. Grice *et al.* (1994) attributed this structural complexity to the presence of Cl⁻ anions, but it is also known that the Sussex deposits have been intensely folded (Roulston *et al.* 1995). As the effects of metamorphism on borate minerals is not yet known, it is premature to propose a correlation between metamorphism and highly polymerized structures among the borate minerals.

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