

PENOBSSQUISITE: A NEW BORATE MINERAL WITH A COMPLEX FRAMEWORK STRUCTURE

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ABSTRACT

Penobsquisite, a new mineral species 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, boracite, hilgardite, pringleite, trembathite, sellaita, fluorite, hematite and malachite. It occurs as euhedral, transparent, pale yellow, vitreous crystals ranging in size from 0.5 to 1.5 mm. Penobsquisite is biaxial positive, with indices of refraction α 1.550(2), β 1.554(2) and γ 1.592(2); $2V_{\text{meas.}} = 33(2)^\circ$, $2V_{\text{calc.}} = 36.6^\circ$. There is no dispersion and no pleochroism. The optical orientation is $Y = b$, $Z \wedge c = 16.6^\circ$ (in obtuse angle β). Penobsquisite is monoclinic, space group $P2_1$, a 11.63(4), b 9.38(1), c 8.735(9) Å, β 98.40(7)°, V 942.7(1) Å³ and $Z = 2$. The strongest lines of the X-ray powder-diffraction pattern [d in Å(hkl)] are: 8.65(3)(001), 7.29(10)(110), 5.32(2)(111), 4.50(2)(211), 2.958(3)(320,312,031), 2.744(2)(013,203) and 2.113(3)(114). Crystals are tabular on {100} and elongate on [010], with forms: pinacoids {100}, {101} and {101} and sphenoids {111}, {110}, {110}, {212} and {112}. Electron-microprobe analyses gave CaO 17.27(17.20–17.36), FeO 7.48(6.79–8.08), MgO 1.82(1.37–2.25), MnO 0.23(0.20–0.25), Cl 5.77(5.62–5.86), B₂O₃ 48.50(48.26–48.73) and H₂O 19.52(19.42–19.61), O = Cl –1.30, total 99.29 wt.%. H₂O and B₂O₃ were calculated by stoichiometry from the crystal-structure analysis. The empirical formula based on 24 anions is: Ca_{1.99}(Fe_{0.67}Mg_{0.29}Mn_{0.02})_{20.98}[B₉O_{12.95}(OH)_{5.99}]Cl_{1.05}·4.01H₂O, ideally Ca₂Fe[B₉O₁₃(OH)₆]Cl·4H₂O; $D_{\text{meas.}} = 2.26(3)$ g/cm³, $D_{\text{calc.}} = 2.27$ g/cm³. The IR spectrum, with absorption bands at 3336, 1646, 1345, 1205, 995, 693 and 548 cm⁻¹, indicates the presence of H₂O groups and complex borate groups. The crystal-structure determination refined to indices $R = 2.2\%$ and $R_w = 2.0\%$ for 2756 unique reflections. The borate framework of penobsquisite has sets of intersecting channels that parallel [010] and [001]. These large channels resemble the related borate structures of pringleite and ruitenbergitte. The framework consists of sheets of 12-membered rings of alternating triangular and tetrahedral borate polyhedra cross-linked by adjacent slabs of 3-membered rings having a crankshaft chain configuration.

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

SOMMAIRE

La pénobsquisite, nouvelle espèce minérale provenant de la mine exploitée par la Potash Corporation of Saskatchewan (division du Nouveau-Brunswick) à Penobsquis, comté de Kings, au Nouveau-Brunswick, a été découverte dans le membre dit "Upper Halite" de la séquence évaporitique, en association avec halite, boracite, hilgardite, pringléite, trembathite, sellaita, fluorite, hématite et malachite. Elle forme des cristaux idiomorphes, transparents, jaune pâle, à aspect vitreux, allant de 0.5 à 1.5 mm de diamètre. La pénobsquisite est biaxe positive, avec comme indices de réfraction α 1.550(2), β 1.554(2) and γ 1.592(2); $2V_{\text{mes.}} = 33(2)^\circ$, $2V_{\text{calc.}} = 36.6^\circ$. Il n'y aucune dispersion, ni de pléochroïsme. L'orientation optique est $Y = b$, $Z \wedge c = 16.6^\circ$ (dans l'angle obtus β). La pénobsquisite est monoclinique, groupe spatial $P2_1$, a 11.63(4), b 9.38(1), c 8.735(9) Å, β 98.40(7)°, V 942.7(1) Å³ et $Z = 2$. Les raies les plus intenses du cliché de diffraction X [méthode des poudres; d en Å(hkl)] sont: 8.65(3)(001), 7.29(10)(110), 5.32(2)(111), 4.50(2)(211), 2.958(3)(320,312,031), 2.744(2)(013,203) et 2.113(3)(114). Les cristaux sont tabulaires sur {100} et allongés sur [010], avec les formes suivantes: pinacoïdes {100}, {101} et {101}, et sphénoïdes {111}, {110}, {110}, {212} et {112}. Les analyses à la microsonde électronique ont donné CaO 17.27(17.20–17.36), FeO 7.48(6.79–8.08), MgO 1.82(1.37–2.25), MnO 0.23(0.20–0.25), Cl 5.77(5.62–5.86), B₂O₃ 48.50(48.26–48.73) et H₂O 19.52(19.42–19.61), O = Cl –1.30, pour un total de 99.29% (poids). La proportion de H₂O et B₂O₃ a été calculée par stœchiométrie à partir des résultats de l'analyse de la structure cristalline. La formule empirique, fondée sur un total de 24 anions, serait: Ca_{1.99}(Fe_{0.67}Mg_{0.29}Mn_{0.02})_{20.98}[B₉O_{12.95}(OH)_{5.99}]Cl_{1.05}·4.01H₂O ou, de façon idéale, Ca₂Fe[B₉O₁₃(OH)₆]Cl·4H₂O; $D_{\text{meas.}} = 2.26(3)$ g/cm³, $D_{\text{calc.}} = 2.27$ g/cm³. Le spectre infra-rouge, avec ses bandes d'absorption à 3336, 1646, 1345, 1205, 995, 693 et 548 cm⁻¹, indique la présence de groupes H₂O et de groupes boratés complexes. La structure cristalline a été affinée jusqu'à un résidu R de 2.2% ($R_w = 2.0\%$) en utilisant 2756 réflexions uniques. La trame boratée de la pénobsquisite contient des canaux parallèles à [010] et [001] qui se croisent. Ces canaux ressemblent à ceux des borates pringléite et ruitenbergitte. La trame est faite de feuillets d'anneaux à douze membres, qui sont des polyèdres boratés triangulaires et tétraédriques en alternance. Ces polyèdres sont interliés par des panneaux adjacents contenant des anneaux à trois membres ayant un agencement en chaîne semblable à un arbre coudé.

(Traduit par la Rédaction)

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

INTRODUCTION

Penobsquisite is the latest in a series of new borate minerals to be described from the evaporite deposits of southern New Brunswick. The others include trembathite (Burns *et al.* 1992), and pringleite and ruitenbergitte (Roberts *et al.* 1993). Penobsquisite was discovered during a systematic examination of residue obtained from the dissolution of halite drill-core from the mine operated by the Potash Corporation of Saskatchewan (New Brunswick Division) (formerly Potash Company of America), at Penobsquis, Cardwell Parrish, Kings County, New Brunswick. Euhedral crystals showing an unusual morphology 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.

Penobsquisite (pronounced penob'skwisait) is named for the locality. Although the origin of the name is uncertain, it was probably coined by M.H. Perley in 1857 from the Maliseet, *penobsq sips*, meaning "stone brook", to replace the name of Stones Brook, a local village (Rayburn 1975). 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 81524.

OCCURRENCE

Penobsquisite occurs in the lower third of the Upper Halite member, within a thick sequence of evaporite in the Windsor Group. The stratigraphy and geological setting of the evaporite deposits are described by Roulston & Waugh (1981). The evaporites are Mississippian in age and occur in the Moncton sub-basin, part of the Fundy epigeosyncline, a north-easterly 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, ruitenbergitte, trembathite, strontioiginorite, congolite, tyretskite, ginorite, inyoite

and penobsquisite. Other minerals found with the borate assemblage include anhydrite, sellaite, fluorite, nickeline, pyrite, chalcocopyrite, 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.

Penobsquisite was found in only one piece of drill core from the lower third of the Upper Halite member of the Potash Corporation of Saskatchewan mine, and is intimately associated with halite, boracite, hilgardite, pringleite, trembathite, sellaite, fluorite, hematite and malachite. Approximately 100 crystals in the size range 0.5 – 1.5 mm, with a total approximate weight of 30 mg, were separated.

PHYSICAL AND OPTICAL PROPERTIES

Penobsquisite belongs to the monoclinic sphenoidal class, 2, a class rare in the mineral kingdom. It exhibits an unusual morphology. The crystals are equidimensional to tabular on {100}, often slightly elongate on [010], triangular in shape and euhedral, up to 1.5 mm in width. The following forms were observed and measured on a reflecting goniometer: pinacoids {100}, {101} and $\{10\bar{1}\}$, and the sphenoids {111}, $\{110\}$, $\{1\bar{1}0\}$, $\{2\bar{1}2\}$ and $\{\bar{1}\bar{1}2\}$ (Fig. 1). No twinning was

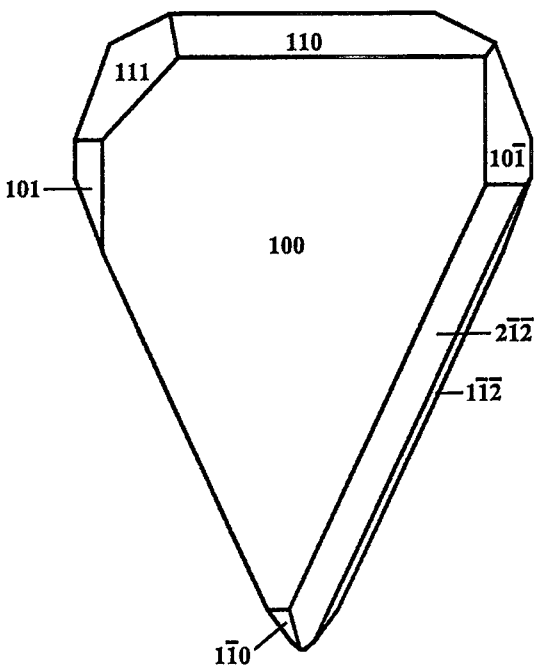


FIG. 1. Penobsquisite: crystal drawing.

observed. The crystals are transparent to translucent, pale yellow, with a white streak and vitreous luster. Penobsquisite shows no fluorescence with either short-wave or long-wave ultraviolet light. It has an approximate hardness of 3 (Mohs hardness scale), is brittle, devoid of cleavage and has a conchoidal fracture. The density of $2.26(3) \text{ g/cm}^3$ was measured by suspension in bromoform and agrees well with the calculated density of 2.27 g/cm^3 .

Penobsquisite is biaxial positive, with indices of refraction α 1.550(2), β 1.554(2) and γ 1.592(2) (for $\lambda = 590 \text{ nm}$); $2V_{\text{meas.}} = 33(2)^\circ$, $2V_{\text{calc.}} = 36.6^\circ$. There is no dispersion and no pleochroism. The optical orientation is $Y = b$, $Z \wedge c = 16.6^\circ$ (in obtuse angle β).

CHEMICAL COMPOSITION

Electron-microprobe analysis

Chemical analysis was performed on a JEOL 733 electron microprobe in wavelength-dispersion (WD) mode using Tracor Northern 5500 and 5600 automation. 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 $0.20 \mu\text{A}$. Standards used in the probe analysis were danburite ($\text{CaK}\alpha$), dolomite ($\text{MgK}\alpha$), rhodochrosite ($\text{MnK}\alpha$), siderite ($\text{FeK}\alpha$) and scapolite ($\text{ClK}\alpha$). Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. All three crystals mounted for analysis showed concentric, oscillatory Fe–Mg zonation using the back-scatter electron detector; several zones were found to be large enough to allow analysis with a $50\text{-}\mu\text{m}$ beam to prevent sample degradation. Minor inclusions of fluorite and sellaite were noted in the crystals. 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 atomic number greater than 8, other than those reported here; F, Sr and K were sought but not detected. An attempt to analyze the material for boron with the WD system was made. The presence of boron was confirmed, but the combined problems of the overlap of a chlorine peak on that of boron and severe degradation of the sample precluded accurate analysis. The presence of H_2O was confirmed by infrared spectroscopy. An average result of three determinations (with ranges) gave $\text{CaO } 17.27(17.20\text{--}17.36)$, $\text{FeO } 7.48(6.79\text{--}8.08)$,

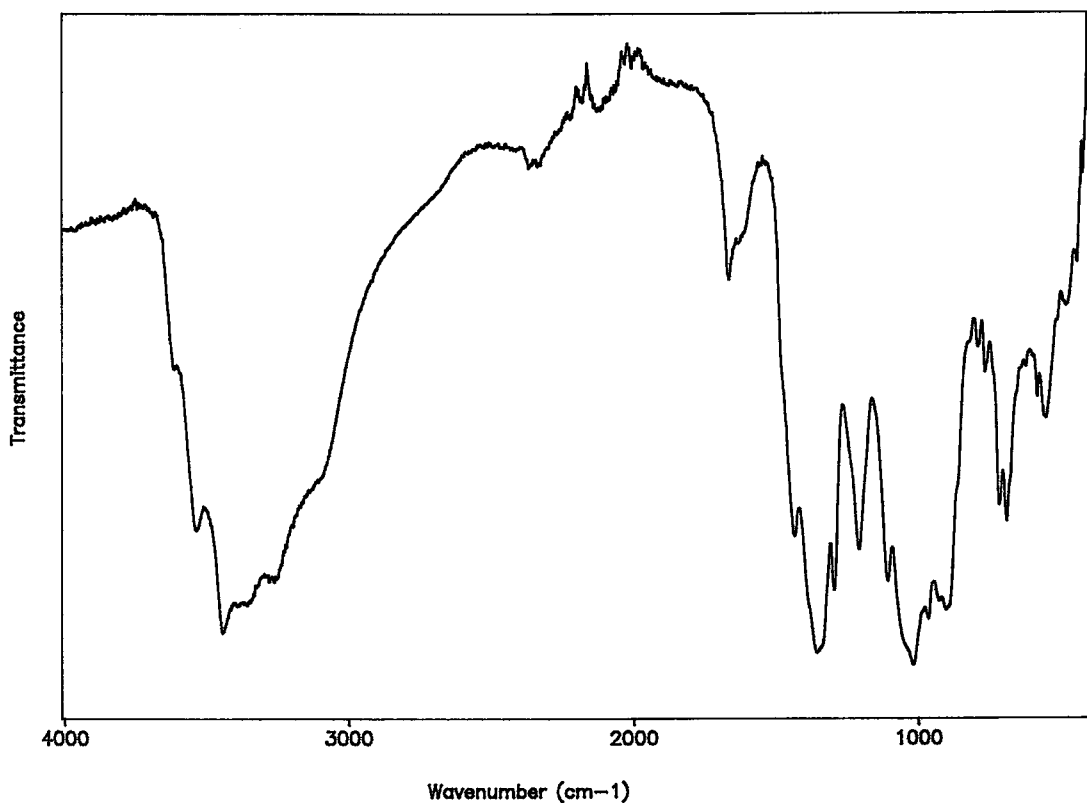


FIG. 2. Penobsquisite: infrared spectrum.

MgO 1.82(1.37–2.25), MnO 0.23(0.20–0.25), Cl 5.77(5.62–5.86), B₂O₃ 48.50(48.26–48.73) and H₂O 19.52(19.42–19.61), O = Cl –1.30, total 99.29 wt.%. H₂O and B₂O₃ were calculated by stoichiometry from the results of the crystal-structure analysis. Hawthorne & Grice (1990) have demonstrated the strength of crystal-structure analysis as a chemical analytical method for light elements. The empirical formula based on 24 anions is Ca_{1.99}(Fe_{0.67}Mg_{0.29}Mn_{0.02})_{Σ0.98}Cl_{1.05}[B₉O_{12.95}(OH)_{5.99}]•4.01H₂O or, ideally, Ca₂(Fe)Cl[B₉O₁₃(OH)₆]•4H₂O.

Infrared analysis

The infrared spectrum (Fig. 2) of penobsquisite 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 3336 cm⁻¹ region, the O–H stretching frequency, indicates the presence of OH⁻ anions or H₂O groups. The broadness and fine structure of the peak indicate a variety of distinct OH or H₂O groups in the structure. The peak centered at 1646 cm⁻¹ is attributed to H–O–H bending, which confirms the presence of H₂O groups. As a result of a comparison of the remaining complex part of the spectrum to spectra given in Farmer (1974), the following frequency regions are assigned modes: 1400–1300 cm⁻¹: asymmetric stretching (BO₃), 1200 cm⁻¹: O–H in-plane bending, 1100–900 cm⁻¹: asymmetric stretching (BO₄) and symmetric stretching (BO₃), 800–700 cm⁻¹: symmetric stretching (BO₄), and 600–400 cm⁻¹: bending modes of (BO₃) and (BO₄).

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray precession photographs show penobsquisite to be monoclinic, with possible space-groups *P*2₁ (space group #4) and *P*2₁/*m* (space group #11). Space group *P*2₁ is consistent with the crystal morphology. X-ray powder-diffraction data collected with a 114.6-mm-diameter Debye–Scherrer camera with CuKα (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 penobsquisite used for the collection of X-ray-diffraction intensity data (catalogue number CMNMI 81524) is a ground sphere of radius 0.11 mm. Intensity data were collected on a fully automated Siemens *P*3 four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated MoKα radiation. A set of 25 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Only one asymmetric unit of intensity data was collected (for the acentric space-group)

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

<i>l</i>	<i>d</i> Å _{meas}	<i>d</i> Å _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> Å _{meas}	<i>d</i> Å _{calc}	<i>hkl</i>
3	8.65	8.62	001	<1	2.442	2.441	421
10	7.29	7.27	110	<1	2.426	2.426	330
1	6.37	6.35	011	<1	2.355	2.353	213
1	5.75	5.74	200	<1	2.304	2.304	140
2	5.32	5.32	111	<1	2.259	2.258	422
1	4.89	4.90	210	<1	2.239	2.232	510
2	4.50	4.51	211			2.205	332
		3.854	102	<1	2.198	2.203	403
<1	3.822	3.830	300			2.179	104
		3.800	121	<1	2.174	2.176	240
<1	3.723	3.727	202	3	2.113	2.123	114
<1	3.539	3.547	310	1	2.030	2.034	332
1	3.449	3.452	311	<1	1.998	2.006	431
<1	3.237	3.245	221			2.004	340
		3.154	122	<1	1.990	1.995	423
1	3.132	3.132	311			1.968	522
		3.103	302	<1	1.965	1.967	314
<1	3.046	3.052	212			1.949	521
		3.025	130	<1	1.948	1.947	333
3	2.958	2.969	320			1.942	503
		2.947	312	<1	1.916	1.921	233
		2.947	031	<1	1.892	1.892	611
1	2.813	2.820	131			1.876	610
		2.752	230	<1	1.874	1.874	512
2	2.744	2.750	013			1.874	342
		2.740	203	<1	1.848	1.850	324
<1	2.692	2.696	103	<1	1.818	1.819	440
<1	2.631	2.631	213	<1	1.787	1.789	250
1	2.567	2.569	231	<1	1.769	1.767	251
<1	2.521	2.516	411				
<1	2.478	2.484	303				
		2.483	412				

Debye-Scherrer 114.6 mm powder camera, Ni-filtered CuKα radiation
Indexed on XRPD refined parameters; *a* 11.63(4), *b* 9.38(1), *c* 8.735(9) Å, β 98.40(7)°

up to 2θ = 60° using a θ:2θ scan-mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Data pertinent to the intensity-data collection are given in Table 2.

Reduction of the intensity data, structure determination and structure 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,

TABLE 2. PENOBSQUISITE: DATA COLLECTION INFORMATION

Space Group	<i>P</i> 2 ₁	Measured unique reflections	2756
<i>a</i> (Å)	11.620(3)	Observed reflections [<i>I</i> > 4σ(<i>I</i>)]	2633
<i>b</i> (Å)	9.407(2)	Minimum transmission	0.738
<i>c</i> (Å)	8.726(1)	Maximum transmission	0.747
β (°)	98.58(2)	<i>R</i> / <i>R</i> _w (%)	2.2/2.0
<i>V</i> (Å ³)	943.2(3)	<i>R</i> _w = [Σw(<i>F</i> _o - <i>F</i> _c) ² / Σw <i>F</i> _o ²] ^{1/2}	w = [σ ² (<i>F</i> _o)] ⁻¹
Unit-cell contents	2[Ca ₂ Fe[B ₉ O ₁₃ (OH) ₆]Cl • 4H ₂ O]		μ = 1.41 mm ⁻¹

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

ATOM	x	y	z	U(eq)
CA1	0.63456(4)	0.28302(9)	0.47322(5)	102(1)
CA2	0.65876(4)	0.48751(9)	0.09093(5)	108(1)
FE	0.93944(4)	0.59614(8)	-0.07485(5)	134(1)
CL	0.98111(6)	0	0.29606(8)	232(2)
B1	0.8966(3)	0.3404(3)	0.3122(3)	106(8)
B2	0.6114(2)	0.5806(3)	-0.3044(3)	90(7)
B3	0.4616(3)	0.7360(3)	0.1648(3)	106(7)
B4	0.1575(2)	0.6538(3)	0.1801(3)	93(8)
B5	0.8831(2)	0.3442(3)	0.0269(3)	91(7)
B6	0.4685(3)	0.2360(3)	0.0994(3)	110(8)
B7	0.0729(3)	0.4010(3)	0.2008(3)	100(7)
B8	0.7225(3)	0.3678(3)	-0.1977(3)	83(7)
B9	0.5439(2)	0.5887(3)	-0.5904(3)	104(7)
O1	0.8288(2)	0.3293(2)	0.1697(2)	108(5)
O2	0.0110(2)	0.3706(2)	0.3326(2)	127(5)
OH3	0.8380(2)	0.3258(3)	0.4385(2)	174(6)
O4	0.6768(2)	0.4628(2)	-0.3244(2)	97(5)
O5	0.5551(2)	0.6479(2)	-0.4319(2)	123(5)
O6	0.6053(2)	0.6277(2)	-0.1577(2)	151(5)
O7	0.5328(2)	0.6873(2)	0.0640(2)	135(5)
O8	0.6270(2)	0.3244(2)	-0.1104(2)	111(5)
O9	0.5234(2)	0.1989(2)	-0.3174(2)	127(5)
O10	0.7679(2)	0.2444(2)	-0.2691(2)	103(5)
O11	0.1485(2)	0.5218(2)	0.2388(2)	138(5)
O12	0.0984(2)	0.6988(2)	0.0378(2)	113(5)
O13	0.8083(2)	0.4344(2)	-0.0826(2)	89(5)
O14	0.9917(2)	0.4221(2)	0.0594(2)	97(5)
OH15	0.5863(2)	0.2437(3)	0.1914(2)	173(6)
OH16	0.4213(2)	0.3782(3)	0.0972(2)	308(8)
OH17	0.8560(2)	0.7706(2)	-0.1776(2)	158(5)
OH18	0.6533(2)	0.5499(2)	0.3554(2)	136(5)
OH19	0.4807(2)	0.4531(2)	0.4003(2)	149(5)
W20	0.7105(2)	0.0362(3)	0.4648(3)	222(7)
W21	0.7159(2)	0.9951(4)	0.1420(3)	482(10)
W22	0.8714(3)	0.6798(3)	0.4426(3)	351(8)
W23	0.8311(2)	0.6689(3)	0.1294(3)	265(7)
H3	0.882(4)	0.347(5)	0.520(5)	500
H15	0.620(4)	0.166(5)	0.162(5)	500
H16	0.409(4)	0.395(5)	0.182(5)	500
H17	0.199(4)	0.283(6)	0.186(5)	500
H18	0.713(4)	0.597(6)	0.405(5)	500
H19	0.426(4)	0.462(5)	0.434(5)	500
H20	0.768(4)	0.037(5)	0.547(5)	500
H20a	0.724(4)	0.010(6)	0.390(5)	500
H21	0.229(4)	0.511(6)	-0.131(5)	500
H21a	0.323(4)	0.456(5)	0.466(5)	500
H22	0.088(4)	0.121(5)	0.497(5)	500
H22a	0.117(4)	0.257(6)	0.540(5)	500
H23	0.817(4)	0.751(5)	0.109(5)	500
H23a	0.861(4)	0.678(5)	0.222(5)	500

nine intense diffraction-maxima in the range 6 to 50° 2 θ 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 1.19% before the absorption correction to 1.17% after the absorption correction. This small correction is indicative of a near-perfect sphere.

Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.695, suggesting the space group $P2_1$. The E -map coordinates were assigned with appropriate scattering curves, and the structure model refined to $R = 13.6\%$. 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 $R = 5.9\%$ with isotropic displacement-factors. By inverting the structure to the enantiomorph, the residual dropped to $R = 5.7\%$. In the final least-squares refinement, all non-H atomic positions were refined with anisotropic displacement-factors to final residuals of $R = 2.2\%$ and $R_w = 2.0\%$. The weighting scheme is inversely proportional to $\sigma^2(F)$. The addition of an isotropic extinction-correction did not improve the refinement. 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 as well as the anisotropic displacement-parameters may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION OF THE STRUCTURE

The crystal structure of penobsquisite is a three-dimensional borate framework consisting of nine crystallographically distinct borate polyhedra, four of which are triangular [(BO_3) groups] and five of which are tetrahedral [(BO_4) groups]. There are two types of triangular coordination, the common $[\text{BO}_3]$ and the much rarer $[\text{BO}_2(\text{OH})]$. There are also two types of tetrahedral coordination, $[\text{BO}_4]$ and $[\text{BO}_2(\text{OH})_2]$ (Table 4). Those O atoms bonded to two B atoms are O^{2-} anions, whereas O atoms bonded to one B atom are part of an $(\text{OH})^-$ group. There are no H_2O groups bonded to B. The Ca, Fe and Cl atoms and the H_2O groups lie within the channels of the borate framework (Fig. 3). Both Ca sites have [9]-coordination, with very similar polyhedra, each having an equatorial plane, (001), with five ligands and a [001] alignment with three O atoms at one vertex and an OH group at the other vertex (Fig. 4). The Ca1 and Ca2 polyhedra are related by a pseudo-center of symmetry. The Fe atom has octahedral coordination, with an elongate axis bonded to a Cl and an H_2O group; the equatorial plane of the distorted octahedron is defined by three O atoms and an OH group (Table 4). Two of the H_2O groups (W21 and W22) are H-bonded within the structure to Cl atoms at distances of $\sim 3.1 \text{ \AA}$ (Table 4). This is consistent with O—H...Cl bond lengths observed in other borates (Grice *et al.* 1994). W20 is also H-bonded within the structure, but W23 is not. W23 is bonded to both the Fe and Ca2 atoms (Table 4).

The polymerization of the borate polyhedra may be described as slabs on (100). A slab 8 \AA thick at a height $a/2$ (Fig. 5) shows a sheet of 12-membered rings, with the rings stretched parallel to [001]. Within the 12-membered rings, triangular and tetrahedral borate polyhedra alternate. The fundamental building block (FBB) for this layer is $6\Delta 6\Box < \Delta \Delta \Delta \Delta \Delta \Delta \Delta \Delta \Delta \Delta \Delta \Delta >$ (Burns *et al.* 1995). This sheet of rings is cross-linked by an adjacent slab of crankshaft chains with double-

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

Ca1-OH3	2.461(2)	Ca2-O1	2.487(2)	Fe-O12	2.184(2)	Cl-O12	97.2(1)
Ca1-O4	2.442(2)	Ca2-O6	2.536(2)	Fe-O13	2.148(2)	Cl-O13	93.6(1)
Ca1-O5	2.523(2)	Ca2-O7	2.372(2)	Fe-O14	2.052(2)	Cl-O14	92.4(1)
Ca1-O9	2.517(2)	Ca2-O8	2.320(2)	Fe-OH17	2.044(2)	Cl-OH17	99.3(1)
Ca1-O10	2.558(2)	Ca2-O13	2.519(2)	Fe-W23	2.429(3)	Cl-W23	170.3(1)
Ca1-OH15	2.467(2)	Ca2-OH15	2.638(2)	Fe-Cl	2.435(1)	O13-O14	66.5(1)
Ca1-OH18	2.734(2)	Ca2-OH16	2.953(3)	<Fe-O> _{eq}	2.107	O14-O12	86.4(1)
Ca1-OH19	2.413(2)	Ca2-OH18	2.391(2)	<Fe-φ> _{sp}	2.432	O12-OH17	99.0(1)
Ca1-W20	2.489(3)	Ca2-W23	2.614(3)			OH17-O13	105.5(1)
<Ca1-O>	2.512	<Ca2-O>	2.537			O13-O12	151.2(1)
						O14-OH17	166.3(1)
B1-O1	1.373(3)	O1-O2	124.0(2)	B2-O4	1.369(4)	O4-O5	118.7(2)
B1-O2	1.344(3)	O1-OH3	115.4(2)	B2-O5	1.361(3)	O4-O6	119.3(2)
B1-OH3	1.387(4)	O2-OH3	120.6(2)	B2-O6	1.366(3)	O5-O6	122.0(2)
<B-O>	1.368	<O-O>	120.0	<B-O>	1.365	<O-O>	120.0
B3-O7	1.373(4)	O7-O8	118.7(2)	B4-O10	1.372(3)	O10-O11	115.7(2)
B3-O8	1.353(3)	O7-O9	122.6(2)	B4-O11	1.353(4)	O10-O12	120.1(2)
B3-O9	1.363(3)	O8-O9	118.7(2)	B4-O12	1.392(3)	O11-O12	124.1(2)
<B-O>	1.363	<O-O>	120.0	<B-O>	1.372	<O-O>	120.0
B5-O1	1.485(3)	O1-O12	109.3(2)	B6-O6	1.471(4)	O6-O7	101.2(2)
B5-O12	1.507(4)	O1-O13	108.5(2)	B6-O7	1.495(3)	O6-OH15	112.7(2)
B5-O13	1.463(3)	O1-O14	110.4(2)	B6-OH15	1.481(3)	O6-OH16	113.9(2)
B5-O14	1.449(3)	O12-O13	112.7(2)	B6-OH16	1.445(4)	O7-OH15	114.2(2)
<B-O>	1.476	O12-O14	111.4(2)	<B-O>	1.473	O7-OH16	108.8(2)
		O13-O14	104.5(2)			OH15-OH16	106.2(2)
		<O-O>	109.5			<O-O>	109.5
B7-O2	1.473(4)	O2-O11	108.9(2)	B8-O4	1.459(3)	O4-O8	109.8(2)
B7-O11	1.444(4)	O2-O14	111.0(2)	B8-O8	1.494(4)	O4-O10	106.2(2)
B7-O14	1.451(3)	O2-OH17	106.8(2)	B8-O10	1.453(3)	O4-O13	113.3(2)
B7-OH17	1.510(4)	O11-O14	112.6(2)	B8-O13	1.448(3)	O8-O10	110.2(2)
<B-O>	1.470	O11-OH17	109.8(3)	<B-O>	1.464	O8-O13	104.6(2)
		O14-OH17	107.2(2)			O10-O13	112.8(2)
		<O-O>	109.5			<O-O>	109.5
B9-O5	1.478(3)	O5-O9	102.3(2)	OH3-H3	0.83(4)	Cl-H3	2.54(4)
B9-O9	1.464(3)	O5-OH18	115.8(2)	OH15-H15	0.88(5)	Cl-OH3	3.319(3)
B9-OH18	1.468(4)	O5-OH19	110.6(2)	OH16-H16	0.79(5)	Cl-H21	2.64(4)
B9-OH19	1.468(4)	O9-OH18	114.6(2)	OH17-H17	0.64(4)	Cl-W21	3.173(3)
<B-O>	1.470	O9-OH19	111.3(2)	OH18-H18	0.88(4)	Cl-H22	2.29(4)
		OH18-OH19	102.5(2)	OH19-H19	0.74(4)	Cl-W22	3.135(3)
		<O-O>	109.5				
W20-H20	0.91(4)	W21-H21	0.68(5)	W22-H22	0.86(5)	W23-H23	0.81(5)
W20-H20a	0.74(5)	W21-H21a	0.83(4)	W22-H22a	0.75(5)	W23-H23a	0.84(4)
H20-O11	1.977(4)	W21-H15	1.98(5)	W22-H18	1.98(4)		
W20-O11	2.851(3)	W21-H20a	2.15(4)	W22-H23a	1.91(4)		
		W21-OH16	2.668(3)	W22-OH18	2.814(3)		
		W21-W20	2.853(3)	W22-W23	2.705(3)		

ring borate polyhedra (Fig. 6). This chain has the FBB $2\Delta 3\Box : \langle \Delta 2\Box \rangle : \langle \Delta 2\Box \rangle$ (Burns *et al.* 1995). The dimorphic structures pringleite and rutenbergite have similar sheets of 12-membered rings (Grice *et al.* 1994), but the sheets in these structures are cross-linked by a $\langle \Delta 2\Box \rangle \Delta$ group.

Figure 7 shows the 3-dimensional framework of the borate polyhedra in the penobsquisite structure with an overall FBB $14\Delta 16\Box$:

$\langle \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \Delta \Box \Delta \Box \Delta \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \Delta \Box \Delta \Box \Delta \Delta 2\Box \rangle \langle \Delta 2\Box \rangle$. This FBB outlines an "S"-shaped channel in Figure 7. A similar, but not identical, channel is found in the pringleite and rutenbergite structures (Fig. 8). Borate minerals with FBBs of this magnitude are quite rare. Having tabulated all the borate mineral structures, the only ones with FBBs greater than six are: kernite with a chain structure, strontiorborite, ginorite, johachidolite

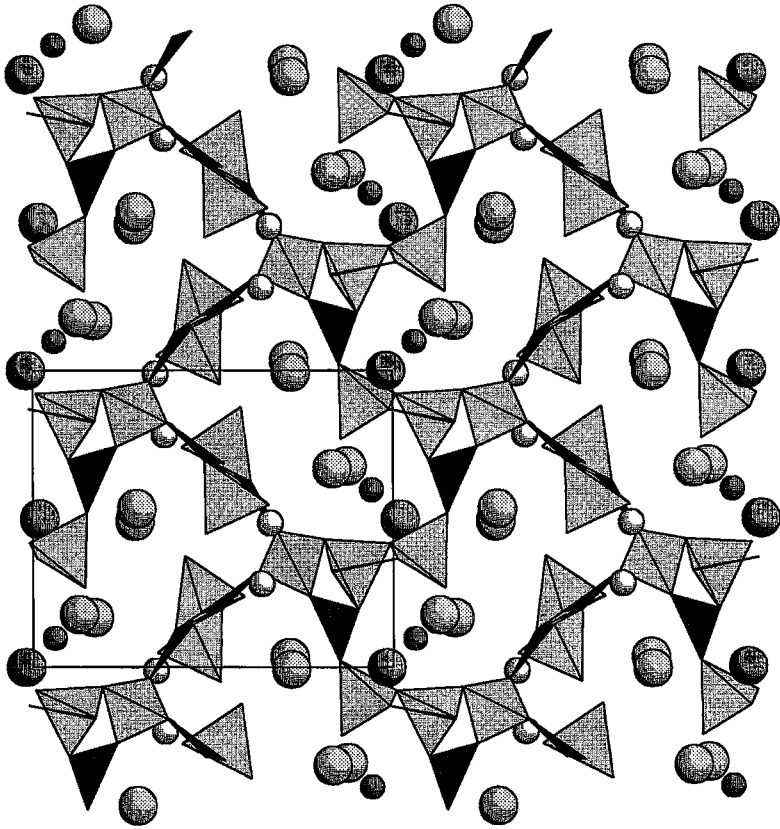


FIG. 3. Penobsquidite: a [001] projection showing the borate framework of triangular and tetrahedral polyhedra. In the channels are Ca atoms (smaller circles with lighter shading), Fe atoms (smaller circles with darker shading), Cl atoms (larger circles with darker shading) and H₂O groups (larger circles with lighter shading). The unit cell is outlined with $b < a$.

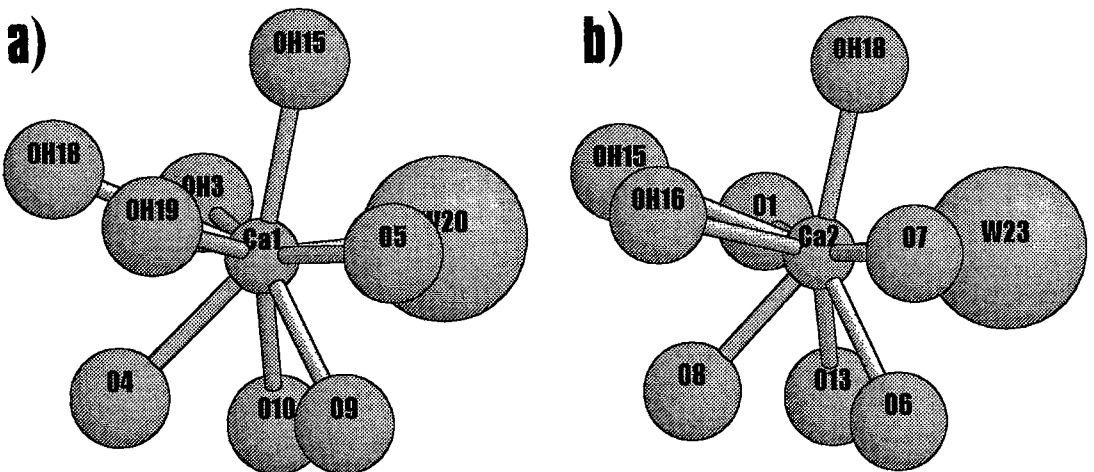


FIG. 4. Penobsquidite: Ca coordination: (a) Ca1 coordination projected along [100] with +[001] vertical; (b) Ca2 coordination projected along [100] with -[001] vertical.

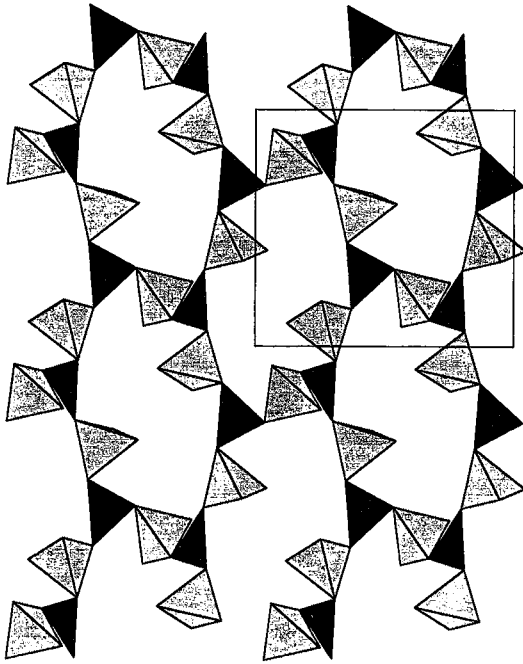


FIG. 5. Penobsquisite: (100) layer at height $a/2$ showing sheets of 12-membered rings of borate polyhedra: FBB $6\Delta 6\Box$: $\langle \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box \Delta \Box \rangle$. The unit cell is outlined with $b < c$.

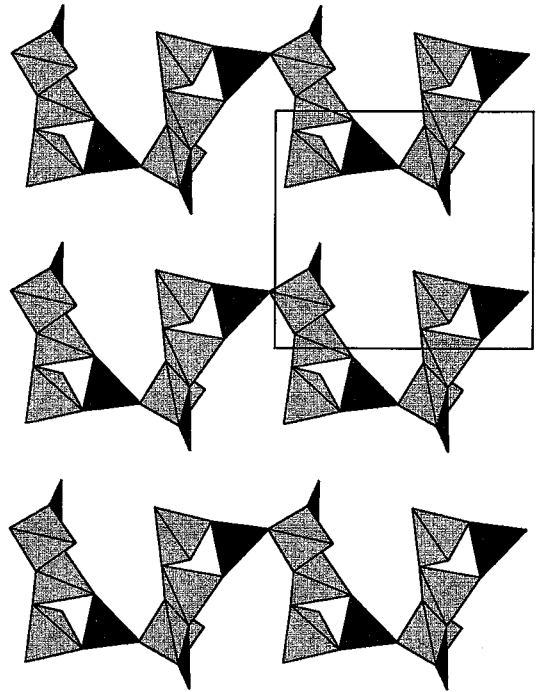
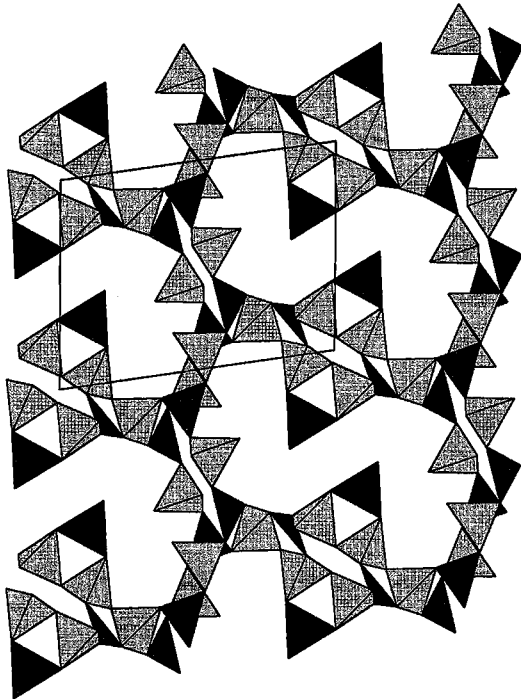


FIG. 6. Penobsquisite: (100) layer at a height $x = 0$ showing crankshaft chains of double 3-membered rings of borate polyhedra, FBB $2\Delta 3\Box$: $\langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle$. The unit cell is outlined with $b < c$.



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). Pringleite, ruitenbergitte and penobsquisite are unique in that they are the only examples of structures with twelve-membered rings of borate polyhedra.

FIG. 7. Penobsquisite: a [010] projection showing the borate framework of triangular and tetrahedral polyhedra and large "S"-shaped channels: FBB $14\Delta 16\Box$: $\langle \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \Delta \Box \Delta \Box \Delta \Box \Delta \Box \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \Delta \Box \Delta \Box \Delta \Box \langle \Delta 2\Box \rangle \langle \Delta 2\Box \rangle \rangle$. The unit cell is outlined with $c < a$.

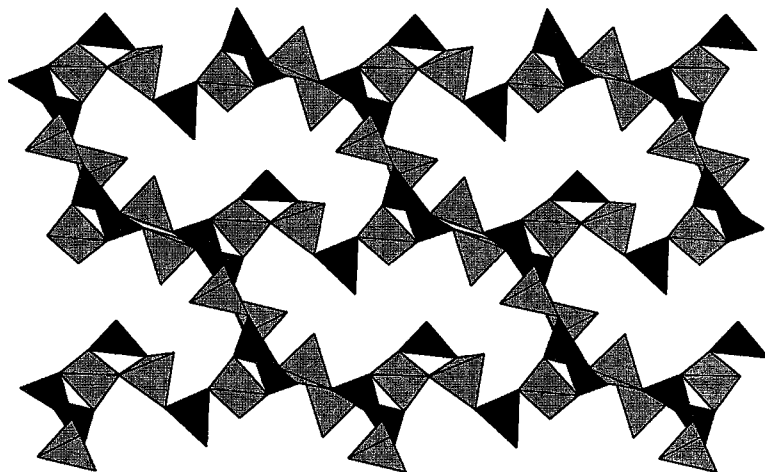


FIG. 8. Pringleite: [001] projection showing the borate framework of triangular and tetrahedral polyhedra and large "S"-shaped channels: FBB $8\Delta 7\Box$: $\triangle \Box \triangle \Box \triangle \Box \triangle \Box \triangle$ $\Box \Box \Box \triangle \Box \triangle \Box \triangle$.

Penobsquisite provides yet another example of the complex polymerization present in marine evaporate 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 (Waugh & Urquhart 1983). The effects of regional metamorphism on borate minerals is not yet known, so it would not be appropriate at this time to make a correlation between metamorphism and highly polymerized structures of the borate minerals.

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