

SZAIBÉLYITE: CRYSTAL-STRUCTURE ANALYSIS AND HYDROGEN BONDING

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ABSTRACT

Szaibélyite, ideally $\text{MgBO}_2(\text{OH})$, from the Potash Corporation of Saskatchewan (New Brunswick Division) mine at Penobscus, Kings County, New Brunswick, occurs in the Upper Halite member of the Windsor Group evaporites, and is associated with halite, sylvite, anhydrite, hilgardite, volkovskite, hydroboracite, walkerite and pringleite. Electron-microprobe analysis, supported by a single-crystal analysis of its structure, yielded: MgO 47.92 (46.28–48.71), FeO 0.74 (0.22–3.05), MnO 0.04 (0.00–0.08), (ideal B_2O_3) 41.77 and (ideal H_2O) 10.81, for a total of 101.18 wt.%. The empirical formula based on three anions is $(\text{Mg}_{0.99}\text{Fe}_{0.01})\text{B}_1\text{H}_1\text{O}_3$. Szaibélyite is monoclinic, $P2_1/a$, with refined unit-cell parameters a 12.586(1), b 10.415(1), c 3.1340(3) Å, β 95.923(2)°, V 408.6(1) Å³, Z = 8. The crystal structure refined to an R index of 0.031 using 1,191 unique reflections. The corrugated (100) sheets of $[\text{MgO}_6]$ octahedra are cross-linked by isolated clusters of $[\text{B}_2\text{O}_4(\text{OH})]$ polyhedra. The [OH] groups strengthen the cross-linkage with hydrogen bonding. The fundamental building block (FBB) within the structure, $2\Delta:2\Delta$, is compared to that in the structures of other borates, such as suanite and clinokurchatovite.

Keywords: szaibélyite, crystal structure, borate, finite cluster, evaporite, hydrogen bonding.

SOMMAIRE

La szaibélyite, de composition idéale $\text{MgBO}_2(\text{OH})$, est présente dans le membre Halite Supérieure des évaporites du groupe de Windsor à la mine exploitée par la Potash Corporation of Saskatchewan (division du Nouveau-Brunswick) à Penobscus, comté de Kings, au Nouveau-Brunswick, en association avec halite, sylvite, anhydrite, hilgardite, volkovskite, hydroboracite, walkerite et pringleite. Les résultats des analyses à la microsonde électronique et de l'analyse de la structure cristalline ont donné: MgO 47.92 (46.28–48.71), FeO 0.74 (0.22–3.05), MnO 0.04 (0.00–0.08), (B_2O_3 idéal) 41.77 et (H_2O idéal) 10.81, pour un total de 101.18% (poids). La formule empirique calculée sur une base de trois anions est $(\text{Mg}_{0.99}\text{Fe}_{0.01})\text{B}_1\text{H}_1\text{O}_3$. La szaibélyite est monoclinique, $P2_1/a$, avec paramètres réticulaires affinés a 12.586(1), b 10.415(1), c 3.1340(3) Å, β 95.923(2)°, V 408.6(1) Å³, Z = 8. La structure cristalline a été affinée jusqu'à un résidu R de 0.031 en utilisant 1,191 réflexions uniques. Les feuillettes (100) ondulants d'octaèdres $[\text{MgO}_6]$ sont interliés par des groupements isolés de polyèdres $[\text{B}_2\text{O}_4(\text{OH})]$. Les groupes [OH] renforcent les interliaisons grâce à des liaisons hydrogène. Le bloc structural fondamental de la structure, $2\Delta:2\Delta$, est ici comparé avec celui d'autres borates, par exemple suanite et clinokurchatovite.

(Traduit par la Rédaction)

Mots-clés: szaibélyite, structure cristalline, borate, groupement isolé, évaporite, liaison hydrogène.

INTRODUCTION

Szaibélyite, ideally $\text{MgBO}_2(\text{OH})$, from the Potash Corporation of Saskatchewan (New Brunswick Division) mine at Penobscus, Kings County, New Brunswick, occurs in the Upper Halite member of the Windsor Group evaporites, associated with halite, sylvite, anhydrite, hilgardite, volkovskite, hydroboracite, walkerite and pringleite (Grice *et al.* 2005). The evaporites are Mississippian in age and occur in the Moncton sub-

basin, in the eastern part of the Maritimes Basin, a northeasterly trending depositional trough extending through southern New Brunswick, Nova Scotia and western Newfoundland (Waugh & Urquhart 1983, Webb & Roulston 1994). Szaibélyite forms in the middle of the crystallization sequence of borate minerals. The presence of borate minerals within two potash mines in the Penobscus–Sussex area of New Brunswick was first noted in the early 1980s in residue from the drilling operations (Roulston & Waugh 1981).

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Szaibélyite was found in four samples of the Penobscuis deposit, in the central and eastern portions of the body, just above the sylvite zone. This would make szaibélyite late in the crystallization sequence. This deposit has been dramatically folded.

The initial features of the crystal structure were determined by means of a two-dimensional refinement of film data collected on a crystal from Kitai, China (Peng *et al.* 1963). No *R* index was given for this structure determination. Takéuchi & Kudoh (1975) better refined the structure of szaibélyite using a crystal from the Königshall–Hindenberg potash mine, Reyershausen, Germany. They were able to refine the structure to an *R* index of 5.9% on a twinned crystal, but were unable to determine the positions of the hydrogen atoms. Using detailed IR spectroscopy on szaibélyite, Marincea (2001) has explained some of the features of the $[B_2O_4(OH)]$ group, but a single-crystal analysis of the structure is necessary to establish the molecular geometry. Discovery of good crystals of this rare mineral in the Penobscuis deposit gave the possibility of improving the structural characterization of the phase.

CHEMICAL COMPOSITION

Electron-microprobe analysis

The chemical analyses were performed with a JEOL 733 electron microprobe in wavelength-dispersion (WD) mode using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine (Pouchou & Pichoir 1984) in XMAQNT (C. Davidson, CSIRO, pers. commun.). The operating voltage was 15 kV, and the beam current was 20 nA. The beam diameter varied from 20 to 40 μm . The following standards were used: periclase ($MgK\alpha$), almandine ($FeK\alpha$) and tephroite ($MnK\alpha$). Several 100-s energy-dispersion (ED) scans were made, and indicated no additional elements with *Z* > 8 other than those reported here. Calcium, Sr and Cl were sought, but not detected. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. Twenty electron-microprobe analyses were performed on seven different grains. The quantities of hydrogen and B were not established, but their presence was confirmed by crystal-structure analysis. The chemical composition is:

MgO 47.92 (46.28–48.71), FeO 0.74 (0.22–3.05), MnO 0.04 (0.00–0.08), (ideal B_2O_3) 41.77 and (ideal H_2O) 10.81, for a total of 101.18 wt.%. The empirical formula based on three anions is $(Mg_{0.99}Fe_{0.01})B_1H_1O_3$. Totals exceeding 100% were obtained even with different standards for Mg: periclase, dolomite and forsterite. There apparently are some problems in the correction factors for B and Mg.

CRYSTAL-STRUCTURE DETERMINATION

Szaibélyite crystals from Penobscuis are clear, colorless or white and usually fibrous, elongate on the *c* axis and, in some cases, developed as blades flattened on (100). There was no evidence of twinning, but subparallel growth along [001] is common. Subparallel growths were avoided; these crystals afforded excellent material for a crystal-structure refinement. The single crystal of szaibélyite used for the collection of X-ray intensity data measures $0.20 \times 0.12 \times 0.08$ mm. Intensity data were collected on a fully automated Siemens P4 four-circle diffractometer equipped with an APEX 4K CCD detector and operated at 50 kV, 40 mA, with graphite-monochromated $MoK\alpha$ radiation. A full sphere of intensity data was collected up to $2\theta = 60^\circ$ using 30 s frames at frame widths of 0.15° . With these operating conditions, no deterioration in the degree of crystallinity was evident in the final analysis of the reflections used as intensity standards. Information relevant to the data collection and structure determination is given in Table 1. The three-dimensional data were corrected for Lorentz, polarization, and background effects, and multiply-measured reflections were averaged using the Bruker program SAINT. An empirical absorption-correction was applied (SADABS, Sheldrick 1998), which reduced the internal residual for merging data with diffraction symmetry $2/m$ from 3.0% before the absorption correction to 2.2% after the absorption correction. All calculations were done with the Siemens SHELXTL 5.1 system of programs (Sheldrick 1997), with scattering factors of neutral atoms taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.960, which suggests the centrosymmetric space-group $P2_1/a$. The initial coordinates assigned to the atoms were those of Takéuchi & Kudoh (1975), except for the hydrogen atoms, which were located on difference-Fourier maps in subsequent refinements. Site occupancies of the two Mg sites were allowed to refine using Mg and Fe scattering curves to final values of 12.76(4) and 11.90(2) e^- , respectively, with an average of 12.33 e^- . The total electrons per formula unit (*epfu*) from the electron-microprobe analysis, 12.14, agrees within 1.5% of that determined from crystal-structure analysis. The H atoms were refined with an isotropic displacement factor and without constraints on the O–H distances. The addition

TABLE 1. SZAIBÉLYITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Space group	$P2_1/a$	Measured reflections	4004
<i>a</i> (Å)	12.586(1)	Unique reflections	1191
<i>b</i> (Å)	10.415(1)	Observed reflections [$> 4\sigma(F)$]	1162
<i>c</i> (Å)	3.1340(3)	<i>R</i> (int) (%)	1.8
α (°)	90	Goodness of fit on F^2	1.05
β (°)	95.923(2)	<i>R</i> index (%) for all data	3.1
γ (°)	90	wR^2 (%) for all data	7.9
<i>V</i> (Å ³)	408.6(1)	Refinement by full-matrix least squares on F^2	
Ideal unit-cell contents	$8[MgBO_2(OH)]$	$\mu = 1.41 \text{ mm}^{-1}$	

of an isotropic extinction-correction did not improve the refinement, nor was there any evidence of twinning. The maximum and minimum electron-densities in the final cycle of refinement were +0.41 and -0.29 e⁻/Å³. The final positional and anisotropic displacement parameters of atoms are given in Table 2, and selected bond-lengths and angles, in Table 3. Tables listing the observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, on the MAC website [szaibelyite CM46_671].

DESCRIPTION OF THE STRUCTURE

Szaibélyite has a finite-cluster borate structure (Grice *et al.* 1999) isostructural with that of sussexite (Hoffman & Armbruster 1995). The Mg atoms are arranged in planes parallel to (100) and linked through edges and vertices of the [MgO₆] octahedra. These sheets are cross-linked by borate polyanions and H-bonding (Fig. 1). The sheet structure is in accord with the (100) platy habit and good cleavage. It would also constitute the twin plane noted by Takéuchi & Kudoh (1975).

Borate polyanion

The borate polyanion consists of two crystallographically distinct borate groups, both of which are triangularly coordinated. There are two types of triangular coordination, the common [BO₃] and the rarer [BO₂(OH)]. There are no H₂O groups bonded to B in any borate mineral structure. The fundamental building block (FBB) given by Grice *et al.* (1999) is: 2Δ:2Δ. This sequence of symbols (Burns *et al.* 1995) denotes two triangular groups shared by a corner.

Mg polyhedra

The two crystallographically distinct Mg polyhedra are both octahedra. Each Mg forms a ribbon of edge-sharing octahedra parallel to [001]. The two sets of ribbons share corners, giving an undulating surface parallel to (100) (Fig. 2). This planar surface is cross-linked into a framework by [B₂O₄(OH)] groups and hydrogen bonds.

TABLE 2. SZAIBÉLYITE: COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS (Å)³

Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
Mg1	0.50433(3)	0.13724(3)	0.2348(1)	0.0074(2)	0.0071(2)	0.0092(2)	-0.0001(1)	0.0006(1)	0.0002(1)	0.00791(8)
Mg2	0.41242(3)	0.42083(3)	0.7103(1)	0.0073(2)	0.0078(2)	0.0090(2)	0.0004(1)	0.0007(1)	0.0005(1)	0.00806(8)
B1	0.13788(8)	0.1681(1)	0.7590(3)	0.0077(4)	0.0083(4)	0.0073(4)	0.0005(3)	0.0007(3)	0.0006(3)	0.0079(2)
B2	0.30629(8)	0.0479(1)	0.6212(3)	0.0085(4)	0.0078(4)	0.0093(4)	0.0012(3)	0.0013(3)	-0.0008(4)	0.0085(2)
O1	0.07618(5)	0.06199(7)	0.7800(2)	0.0077(3)	0.0076(3)	0.0108(3)	-0.0000(2)	0.0013(2)	-0.0004(2)	0.0087(1)
O2	0.10053(6)	0.29133(7)	0.7743(2)	0.0084(3)	0.0067(3)	0.0116(3)	0.0000(2)	0.0013(2)	0.0005(2)	0.0089(1)
O3	0.24772(5)	0.15513(7)	0.7185(2)	0.0070(3)	0.0074(3)	0.0171(3)	-0.0015(2)	0.0027(2)	-0.0001(2)	0.0104(2)
O4	0.24785(6)	0.44956(7)	0.6062(2)	0.0075(3)	0.0093(3)	0.0152(3)	0.0036(2)	0.0003(2)	-0.0004(2)	0.0108(2)
O5	0.41400(5)	0.04335(7)	0.7182(2)	0.0065(3)	0.0080(3)	0.0113(3)	-0.0004(2)	0.0004(2)	0.0007(2)	0.0086(1)
O6	0.40869(5)	0.29482(7)	0.2074(2)	0.0073(3)	0.0082(3)	0.0114(3)	-0.0000(2)	0.0009(2)	-0.0005(2)	0.0090(1)
H4	0.197(2)	0.387(2)	0.679(7)	0.042(5)						
H6	0.348(1)	0.266(2)	0.154(6)	0.028(4)						

TABLE 3. SZAIBÉLYITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Mg1-O6	2.0320(8)	Mg2-O6	2.0413(8)	D-H...A	O4-H4...O2	O6-H6...O3	
Mg1-O2	2.1109(7)	Mg2-O6	2.0477(8)				
Mg1-O2	2.1126(8)	Mg2-O1	2.0579(8)	D-H (Å)	0.955	0.829	
Mg1-O5	2.1189(7)	Mg2-O4	2.0849(8)	D-A (Å)	2.575	2.816	
Mg1-O5	2.1412(8)	Mg2-O1	2.1420(8)	H-A (Å)	1.624	2.100	
Mg1-O5	2.2135(8)	Mg2-O1	2.1649(8)	∠D-H...A (°)	173.6	144.4	
(Mg1-O)	(2.1215)	(Mg2-O)	(2.0898)				
B1-O1	1.356(1)	O1-B1-O2	124.17(9)	B2-O5	1.359(1)	O5-B1-O4	121.03(9)
B1-O2	1.370(1)	O1-B1-O3	119.93(9)	B2-O4	1.386(1)	O5-B1-O3	121.23(9)
B1-O3	1.408(1)	O2-B1-O3	115.90(8)	B2-O3	1.389(1)	O4-B2-O3	117.58(8)
(B1-O)	(1.378)	(O-B1-O)	(120.00)	(B2-O)	(1.378)	(O-B2-O)	(119.95)

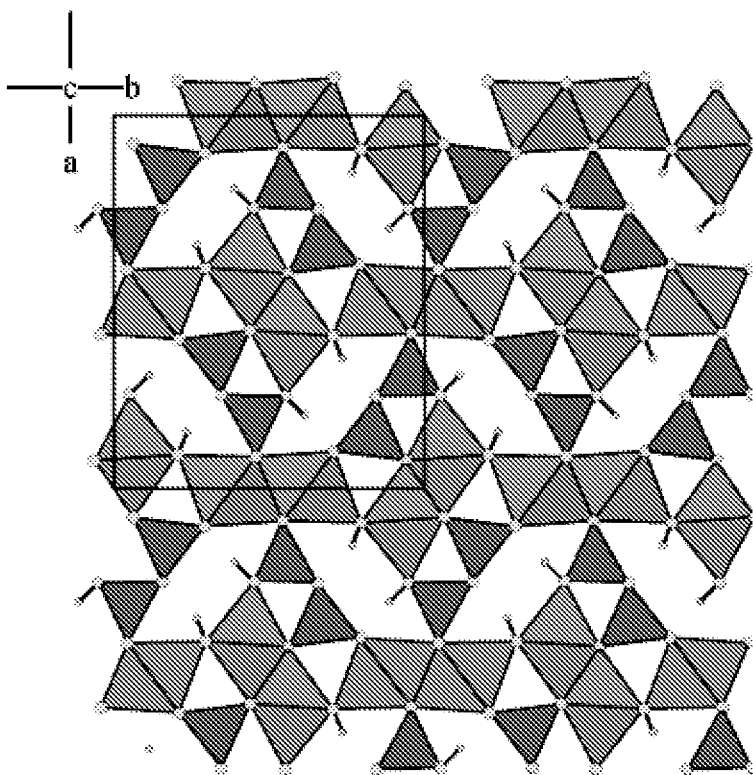


FIG. 1. The structure of szaibélyite projected along [001]. Red triangles represent $[BO_3]$ polyhedra, the $[MgO_6]$ octahedra are orange, and the H atoms are grey.

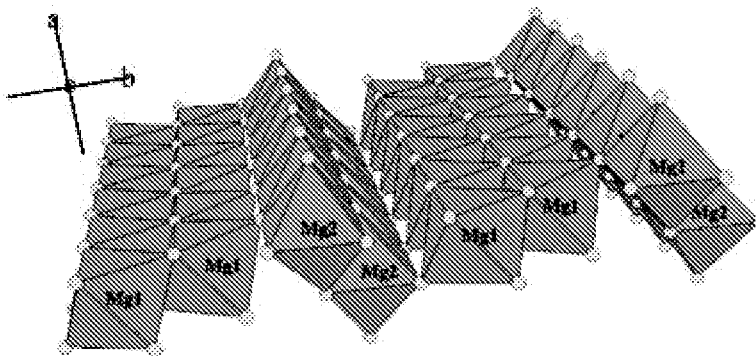


FIG. 2. The undulating (100) layer of $[MgO_6]$ octahedra in the szaibélyite structure.

OH groups and hydrogen bonding

In szaibélyite, there are two (OH) groups; one group is bonded solely to two $[MgO_6]$ octahedra, and

the remaining (OH) group is shared by Mg2 and B2 polyhedra. Figure 3 shows the hydrogen-bonding relationships for the (OH) groups, and Table 3 gives the appropriate bond-lengths for both the H-bond donor

polyhedra. In suanite, this sheet is flat and discontinuous (Fig. 5). The sheet consists of slabs, four octahedra wide and running parallel to the **b** axis. There is a gap of one octahedron between each slab. The borate layer consisting of $[B_2O_5]$ blocks is also flattened relative to their orientation in szaibélyite. This flattening condenses the structure; the density increases from 2.61 g/cm^3 in szaibélyite to 2.92 g/cm^3 in suanite.

Schindler & Hawthorne (2001) have formulated a method to determine the conditions of formation of borate minerals. They have calculated the topology of a $\text{pH} - \log[\text{H}_2\text{O}]$ diagram incorporating each of the borate structural units. Overlain on this topology, they have constructed two additional figures using the parameters (a) average basicity (AB), and (b) percentage of tetrahedrally coordinated B ($^{(4)}\text{B}$). For the mineral assemblage at Sussex, New Brunswick, the AB (in valence units, *vu*) and $^{(4)}\text{B}$ (%) for each mineral are: hilgardite (0.33, 60), trembathite (0.38, 86), volkovskite (0.23, 54), hydroboracite (0.37, 66) walkerite (0.23, 54), pringleite (0.32, 54), and szaibélyite (0.64, 0). Applying these numbers to the relevant $\text{pH} - \log[\text{H}_2\text{O}]$ activity–activity diagram covers a significant proportion of the entire range of pH and $\log[\text{H}_2\text{O}]$. What is unique about szaibélyite is that it occurs in the highest pH range, above that normally

encountered in evaporite deposits and more in keeping with a skarn deposit. It is known that the Windsor Group evaporites have been folded, but the degree of metamorphism has never been established. The presence of szaibélyite may provide the first indicator mineral of this metamorphism.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the cooperation of, and samples provided by, Brian Roulston, Potash Corporation of Saskatchewan (New Brunswick Division). I thank Frank Hawthorne, University of Manitoba, for the use of the four-circle diffractometer. Bob Gault and Glenn Poirier carried out the electron-microprobe analyses. Helpful comments from an anonymous referee, Associate Editor André-Mathieu Franolet and Robert F. Martin, improved the quality of the manuscript.

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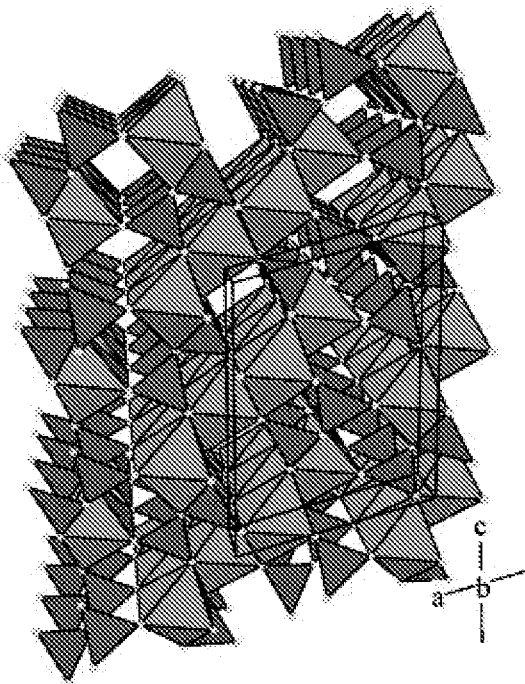


FIG. 5. The structure of suanite (Guo *et al.* 1995), with red triangles representing $[BO_3]$ polyhedra; $[MgO_6]$ octahedra are shown in orange.

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Received June 19, 2007, revised manuscript accepted May 15, 2008.