

REFINEMENT OF THE CRYSTAL STRUCTURE OF SWEDENBORGITE

DANIELLE M.C. HUMINICKI AND FRANK C. HAWTHORNE[§]

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ABSTRACT

Swedenborgite, $(\text{Na}_{0.89}\text{Ca}_{0.04}\square_{0.07})\text{Be}_4\text{SbO}_7$, is hexagonal, unit-cell parameters a 5.4317(2), c 8.8571(4) Å, V 226.31(2) Å³, space group $P6_3mc$, $Z = 2$. The crystal structure was refined to an R index of 1.2% based on 290 unique observed reflections [$|F_o| > 5\sigma|F|$] collected with a single-crystal diffractometer and $\text{MoK}\alpha$ X-radiation. There is one *Sb* site occupied by Sb^{5+} and coordinated by an octahedron of O atoms, with a $\langle\text{Sb}-\text{O}\rangle$ distance of 1.97 Å. There are two *Be* sites that are each occupied by Be and coordinated by a tetrahedron of O atoms, with a grand $\langle\text{Be}-\text{O}\rangle$ distance of 1.64 Å. There is one *Na* site, coordinated by twelve O atoms and occupied primarily by Na. The structure consists of layers of corner-sharing (BeO_4) tetrahedra and (SbO_6) octahedra that link together to form a dense framework. The resulting arrangement consists of (SbO_6) octahedra alternating with $[\text{Be}_4\text{O}_{13}]$ clusters that are fragments of the bromellite (BeO) structure. Small amounts of Ca are incorporated into the structure via the substitution $\text{Ca} + \square \rightarrow 2\text{Na}$.

Keywords: swedenborgite, crystal structure, electron-microprobe analysis, beryllium mineral.

SOMMAIRE

La swédénborgite, $(\text{Na}_{0.89}\text{Ca}_{0.04}\square_{0.07})\text{Be}_4\text{SbO}_7$, est hexagonale, et ses paramètres réticulaires sont a 5.4317(2), c 8.8571(4) Å, V 226.31(2) Å³, groupe spatial $P6_3mc$, $Z = 2$. Nous en avons affiné la structure jusqu'à un résidu R de 1.2% en utilisant 290 réflexions uniques observées [$|F_o| > 5\sigma|F|$] mesurées sur cristal unique avec rayonnement $\text{MoK}\alpha$. Il y a un site *Sb*, qu'occupe le Sb^{5+} , coordonné par un octaèdre d'atomes d'oxygène, avec une longueur moyenne de liaison $\langle\text{Sb}-\text{O}\rangle$ de 1.97 Å. La structure possède deux sites *Be*, qu'occupent le Be en coordinence tétraédrique avec l'oxygène; la longueur de la liaison $\langle\text{Be}-\text{O}\rangle$ (moyenne globale) est 1.64 Å. Elle possède un site *Na*, en coordinence avec douze atomes d'oxygène et surtout peuplé d'atomes de Na. La structure contient des couches de tétraèdres (BeO_4) partageant des coins et des octaèdres (SbO_6) , liés ensemble pour former une trame dense. L'agencement qui en résulte contient une alternance d'octaèdres (SbO_6) et d'agroupements $[\text{Be}_4\text{O}_{13}]$, que l'on peut considérer des fragments de la structure de la bromellite (BeO). De faibles quantités de Ca sont incorporées dans la structure selon la substitution $\text{Ca} + \square \rightarrow 2\text{Na}$.

Mots-clés: swédénborgite, structure cristalline, analyse à la microsonde électronique, minéral de béryllium.

INTRODUCTION

Swedenborgite, a sodium beryllium antimonite, was first described by Aminoff (1924). It is transparent, colorless to pale yellow, with a hardness of approximately 8 and a basal cleavage. The mineral has been found only at the type locality, Långban, Sweden, where it is a constituent of skarns, associated with calcite, mangano-phyllite, bromellite, hematite and richterite. It forms very pale transparent, honey-yellow hexagonal prisms in massive calcite. Swedenborgite was first considered to be an Al-bearing antimonite, but was subsequently reported to contain Be in tetrahedral coordination, with the vertices of the BeO_4 group being linked to a [6]-coordinated Sb^{5+} . Pauling *et al.* (1935) solved the crystal structure of swedenborgite, and Povarennykh *et al.*

(1982) reported its infrared-absorption spectrum. The current study was done to provide more accurate structural parameters for swedenborgite.

EXPERIMENTAL

The specimen of swedenborgite used in this work was obtained from the Royal Ontario Museum. The crystal used for structure work was ground to a spheroid with dimensions $0.17 \times 0.17 \times 0.19$ mm.

X-ray diffraction

The unit-cell dimensions were determined using a Siemens P4 automated four-circle diffractometer with a graphite monochromator and a $\text{MoK}\alpha$ X-ray source.

[§] E-mail addresses: frank_hawthorne@umanitoba.ca

Twenty-five reflections between 25 and 35°2θ were centered, and a constrained hexagonal cell was determined from the setting angles and refined using the method of least-squares (Table 1). Single-crystal intensity data were measured from 4 to 60°2θ over the range to 7 7 1̄2, with a 2θ scan range of 1.1° and scan-speeds from 2.5 to 29.3°/min. A total of 2478 intensities was measured over eight octants. Psi-scan data were measured for 20 reflections out to 60°2θ at increments of 5°, and corrected for absorption; we modeled the crystal as a triaxial ellipsoid, which reduced *R*(azimuthal) from 1.2 to 0.8%. Intensities were corrected for Lorentz, polarization and background effects, and then reduced to structure factors; of the 292 unique reflections, 290 were classed as observed ($|F_o| > 5\sigma|F|$).

Chemical analysis

The crystal used for X-ray diffraction was mounted in a perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX-50 electron microprobe operating under the following conditions in wavelength-dispersion mode: excitation voltage: 15 kV, specimen current: 20 nA, beam size: 5 μm, peak count-time: 20 s, background count-time: 10 s. The following standards and crystals were used for *Kα* X-ray lines for the elements sought: Al: andalusite, TAP; Si: diopside, PET/TAP; Na: albite, TAP; Ca: diopside, PET; Sb: Sb₂O₃, PET. No other elements were detected in energy-dispersion mode. Four points were analyzed, and the mean chemical composition and unit formula are given in Table 2; the proportion of BeO was calculated assuming four Be *apfu* (atoms per formula unit) for seven anions *pfu*. The sum of the oxides is somewhat high; this may be connected with the calculation of the BeO content (~35 wt.% of the composition) from stoichiometric considerations.

STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PCTM Plus (Version 4.2) system of programs; *R* indices are of the form listed in Table 1, and are given as percentages. The refinement converged to an *R* index of 2.1% using the atom coordinates of Pauling *et al.*

(1935). The atom displacements were allowed to refine anisotropically; an extinction correction was also refined, and the final *R* index converged to a value of 1.2%. The refined coordinates and anisotropic-displacement factors are listed in Table 3, and selected interatomic distances are given in Table 4. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Beryllium minerals with infinite frameworks of (*Tφ*₄) tetrahedra form seven main groups, based on the type of linkage (Hawthorne & Huminicki 2001). These are: (1) structures with (*Beφ*₄)–(*Beφ*₄) linkages, (2) structures with (*Beφ*₄)–(*Bφ*_n) linkages, (3) structures with (*Beφ*₄)–(*Beφ*₄) / (*Liφ*₄)–(*Siφ*₄) linkages, (4) struc-

TABLE 1. DATA-COLLECTION INFORMATION FOR SWEDENBORGITE

Space group	<i>P6₃mc</i>	Radiation	MoKα/graphite
<i>a</i> (Å)	5.4317(2)	Total no. of <i>I</i>	2478
<i>c</i>	8.8571(4)	No. of $ F $	292
<i>V</i> (Å ³)	226.31(2)	No. of $ F_o > 5\sigma$	290
<i>Z</i>	2	<i>R</i> (merge) %	1.8
μ (mm ⁻¹)	6.17	<i>R</i> (obs) %	1.2
		<i>wR</i> (obs) %	1.2
$R = \Sigma(F_o - F_c) / \Sigma F_o $			
$wR = [\Sigma w(F_o - F_c)^2 / \Sigma F_o^2]^{1/2}$, $w = 1/\sigma^2(F)$			

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*)* FOR SWEDENBORGITE

Na ₂ O	9.66	Na	0.89
CaO	0.68	Ca	0.04
Sb ₂ O ₅	57.32	Σ	0.93
BeO **	35.15		
Σ	102.87	Sb ⁵⁺	1.01
		Be	4

* calculated based on 7 anions *pfu*;

** calculated on the basis of stoichiometry.

TABLE 3. ATOMS COORDINATES AND DISPLACEMENT PARAMETERS FOR SWEDENBORGITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Sb	1/3	2/3	0	0.0033(1)	0.0033(1)	0.0033(1)	0.0032(1)	0	0	0.0017(1)
Na	1/3	2/3	0.6245(3)	0.0154(6)	0.0154(2)	0.0154(6)	0.0152(10)	0	0	0.0077(4)
Be(1)	0	0	0.0629(9)	0.0038(12)	0.0035(14)	0.0035(14)	0.0044(21)	0	0	0.0017(7)
Be(2)	0.1664(4)	0.8336(4)	0.3126(4)	0.0053(9)	0.0047(10)	0.0047(10)	0.0059(13)	-0.0009(7)	0.0009(7)	0.0019(20)
O(1)	0	0	0.3728(5)	0.0045(7)	0.0056(9)	0.0056(9)	0.0056(9)	0	0	0.0028(5)
O(2)	0.4961(3)	0.5039(3)	0.3706(2)	0.0057(5)	0.0046(5)	0.0046(5)	0.0080(7)	0.0023(5)	-0.0023(5)	0.0020(6)
O(3)	0.1616(2)	0.8384(2)	0.1269(2)	0.0058(6)	0.0077(7)	0.0077(7)	0.0049(8)	0.0002(4)	-0.0002(4)	0.0060(8)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SWEDENBORGITE

<i>Sb</i> –O(2)e,g,i	x3	1.972(2)	O(1)–Be(1)–O(3)	x3	110.4(3)
<i>Sb</i> –O(3)c,d	x3	1.968(1)	O(3)–Be(1)–O(3)′	x3	108.5(3)
< <i>Sb</i> –O>		1.97			
<i>Na</i> –O(2)c,d	x3	2.721(3)	O(1)–Be(1)–O(2)	x2	111.4(2)
<i>Na</i> –O(2)f,h,j	x3	2.707(3)	O(1)–Be(1)–O(3)		107.3(2)
<i>Na</i> –O(3)m,n,o,p,q,r	x6	2.716(1)	O(2)–Be(1)–O(2)′		108.5(2)
< <i>Na</i> –O>		2.715	O(2)–Be(1)–O(3)	x2	109.1(2)
Be(1)–O(1)b		1.684(9)	O(2)–Sb–O(2)	x3	89.6(1)
Be–O(3)c,k,l	x3	1.622(3)	O(2)–Sb–O(3)	x6	89.9(1)
<Be(1)–O>		1.638	O(3)–Sb–O(3)	x3	90.6(1)
Be(2)–O(1)a		1.654(2)			
Be(2)–O(2)c,d	x2	1.635(3)			
Be–O(3)		1.645(4)			
<Be(2)–O>		1.642			

Symmetry operators: a = *x*, *y*+1, *z*; b = *x*, *y*, *z*–½; c = *x*, –2*y*, *z*; d = –2*x*+1, *y*+1, *z*; e = –*x*+1, –*y*, *z*–½; f = –*x*+1, –*y*, *z*+½; g = –*x*+1, 2*y*+2, *z*–½; h = –*x*+1, 2*y*+2, *z*+½; i = 2*x*+1, –*y*, *z*–½; j = 2*x*+1, –*y*, *z*+½; k = *x*, *y*, *z*; l = –2*x*, *y*, *z*; m = –*x*+1, –*y*+1, *z*+½; n = –*x*, –*y*, *z*+½; o = –*x*, 2*y*+1, *z*+½; p = –*x*+1, 2*y*+1, *z*+½; q = 2*x*, –*y*+1, *z*+½; r = 2*x*, –*y*, *z*+½.

TABLE 5. BOND-VALENCE TABLE (*vu*) FOR SWEDENBORGITE

	<i>Sb</i>	<i>Na</i>	Be(1)	Be(2)	Σ
O(1)			0.48	0.48 ^{xs}	1.88
O(2)	0.92 ^{xs}	0.08 ^{xs} 0.09 ^{xs}		0.50 ^{xs}	2.09
O(3)	0.93 ^{xs}	0.09 ^{xs}	0.52 ^{xs}	0.49	2.12
Σ	5.55	1.05	2.04	1.97	

* Bond valences calculated using the curves of Brown & Altermatt (1985).

tures with (Be ϕ_4)–(Si ϕ_4) linkages, (5) structures with (Be ϕ_4)–(Si ϕ_4)–(Si ϕ_4)–(Al ϕ_4) linkages, (6) structures with (Be ϕ_4)–(Si ϕ_4)–(Si ϕ_4) linkages, and (7) structures with (Be ϕ_4)–(P ϕ_4) linkages. The structure of swedenborgite belongs to the first group, as its framework structure consists of (Be ϕ_4)–(Be ϕ_4) linkages. The strongly bonded (Be ϕ_4)–(Be ϕ_4) linkages form the main framework, together with (Sb ϕ_6) octahedra.

Cation polyhedra

There is one *Sb* site surrounded by six anions in an octahedral arrangement and at an average distance of 1.97 Å. This stereochemistry is typical for Sb⁵⁺, and the electroneutrality principle requires that *Sb* occur in the pentavalent state. The sum of the bond valences at the *Sb* site is rather high (5.55 *vu*), but this is not an unusual feature of heavy high-valence cations. There are two *Be* sites, Be(1) and Be(2), both of which are occupied solely by *Be* and are surrounded by four anions in tetrahedral arrangements, with an average bond-distance of 1.64 Å (Table 4). There is one *Na* atom surrounded by twelve anions at an average distance of 2.72 Å.

The oxygen atoms surrounding *Sb* are O(2), O(3) and their symmetry equivalents. Thus, each oxygen atom that is bonded to *Sb* will receive a bond valence of 5/6 *vu* from the *Sb* atom, and will need an additional bond-valence of 1 1/6 *vu* to satisfy the valence-sum rule (Table 5). The oxygen atoms that are bonded to Sb⁵⁺ obtain an additional 1 *vu* from two *Be* atoms (~0.5 *vu* each) and ~0.08 *vu* from each of two [12]-coordinated *Na* atoms.

Bond topology

The structure of swedenborgite may be described conveniently in terms of layers of polyhedra. The *A* layer (Fig. 1a) consists of alternating (SbO₆) octahedra and (BeO₄) tetrahedra placed at the vertices of a 6³ net and linked by sharing corners. Thus each polyhedron shares three corners with adjacent polyhedra, leaving one tetrahedron and three octahedron vertices that are not linked within this layer. The *B* layer (Fig. 1b) consists of (BeO₄) tetrahedra and vacancies placed at the vertices of a 3⁶ net. There are two types of rows of tetrahedra in this layer: (1) continuous rows of corner-sharing tetrahedra, and (2) rows in which tetrahedra and vacancies alternate; these rows alternate within the *B* layer. The vacancies in the *B* layer correspond with the (SbO₆) octahedron of the *A* layer (Fig. 1b). The *A* and *B* layers alternate in the *c* direction (Fig. 2). Sequential *A* layers (and *B* layers) are rotated 180° (compare the *A* and *A*′ layers in Fig. 2). The resulting structure (Fig. 3) has large icosahedral interstices that contain *Na* atoms.

The structure can also be described as [Be₄O₁₃] clusters and (SbO₆) octahedra placed at the vertices of a 6³ net, and linked by sharing polyhedron vertices. Significant in this description is the fact that the [Be₄O₁₃] cluster (Fig. 4) is a fragment of the bromellite (BeO) structure (Wells 1984). Bromellite has the wurtzite structure and consists of identical layers of corner-sharing (BeO₄) tetrahedra that occupy the vertices of a 3⁶ net. If we remove three *Be* and one *O* atoms per unit cell for such a layer, we obtain the pattern of (BeO₄) in the *A* layer of swedenborgite. If we remove one *Be* atom per unit cell from a BeO layer, we obtain the *B* layer of swedenborgite. Addition of Sb⁵⁺ and *Na* to the interstices of these layers results in the swedenborgite structure: Be₈O₈–Be₄–O + Sb⁵⁺ + *Na* → *Na* Be₄ Sb⁵⁺ O₇.

CHEMICAL COMPOSITION OF SWEDENBORGITE

A general formula for swedenborgite can be written as *A* T₄ O B O₆, where *A* = *Na*, *Ca* and □, *T* = *Be*, and *B* = Sb⁵⁺. The cation sum at the *Na* site in the crystal examined here is 0.93 *apfu* (Table 2), indicating a vacancy content of 0.07 *pfu*. This suggests that *Ca* is incorporated into the swedenborgite structure *via* the substitution *Ca* + □ → 2*Na*.

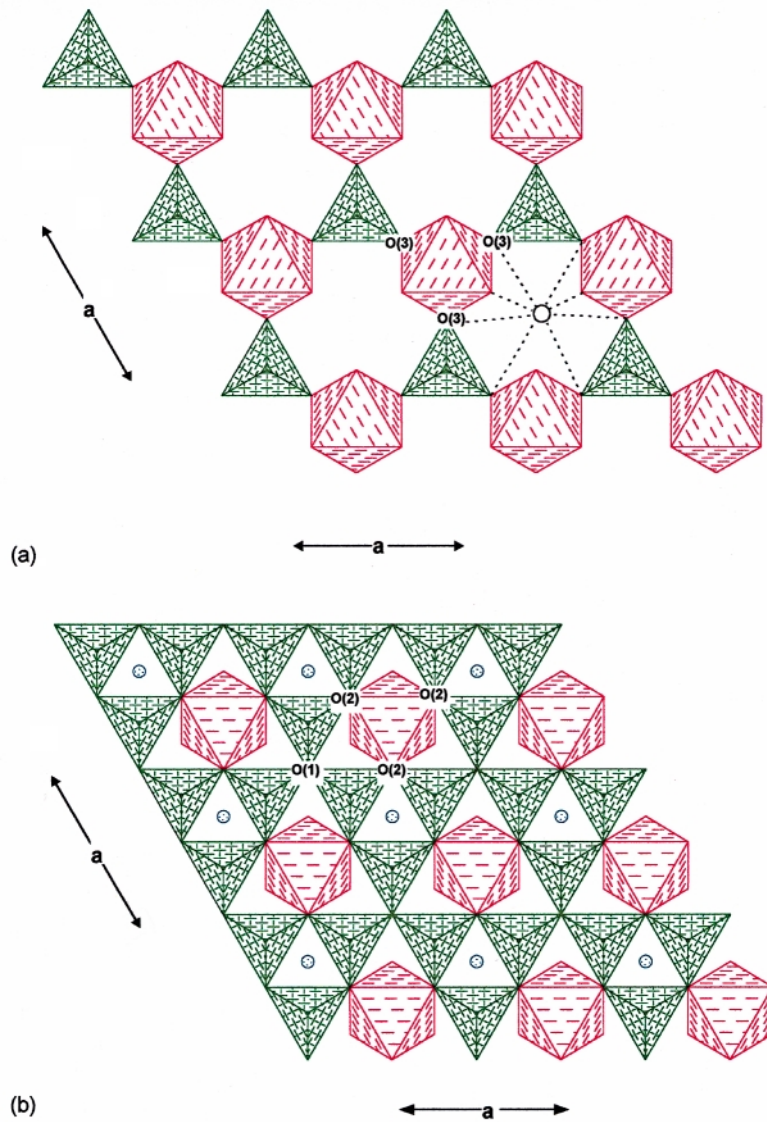


FIG. 1. The *A* and *B* layers in swedenborgite, projected down [001], consisting of (a) the *A* layer, a corner-sharing array of (SbO_6) and $\{Be(1)O_4\}$ tetrahedra, and (b) the *B* layer, a dense corner-sharing array of $\{Be(2)O_4\}$ tetrahedra, and linking (SbO_6) octahedra in the underlying *A*-layer; (BeO_4) groups are shaded with green hatching, (SbO_6) groups are shaded with red broken lines, Na are shown by the dot-shaded green circles.

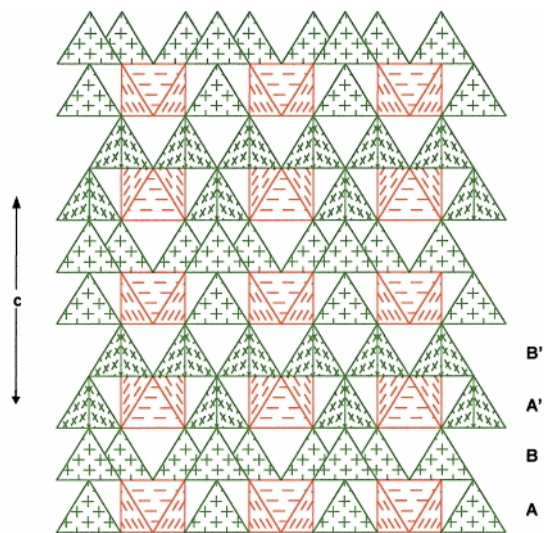


FIG. 2. The structure of swedenborgite projected onto (010); legend as in Figure 1. The *A* and *B* layers are identified to the right of the figure.

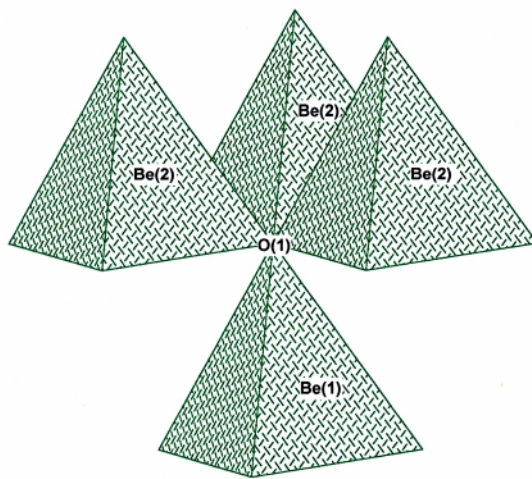


FIG. 4. Oblique view of the $[Be_4O_{13}]$ cluster in swedenborgite; legend as in Figure 1.

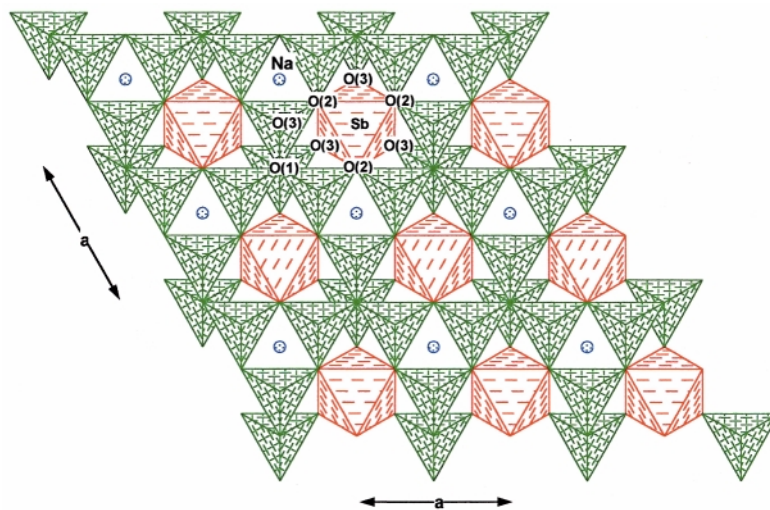


FIG. 3. The structure of swedenborgite projected down [001]; legend as in Figure 1.

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