

THE CRYSTAL STRUCTURE OF ALFREDSTELZNERITE, $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$, A COMPLEX HYDROXY-HYDRATED CALCIUM BORATE MINERAL

MARK A. COOPER AND FRANK C. HAWTHORNE

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

MIGUEL A. GALLISKI AND MARÍA FLORENCIA MÁRQUEZ-ZAVALÍA

IANIGLA-CONICET, CCT-MENDOZA, Avda. Ruiz Leal s/n, Parque Gral. San Martín; C.C.330 (5.500) Mendoza, Argentina

ABSTRACT

The crystal structure of alfredstelznerite, $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$, orthorhombic, a 12.161(2), b 40.477(8), c 10.1843(17) Å, V 5013(3) Å³, $Z = 4$, has been solved by direct methods and refined to an R_1 value of 14.1% in space group $Pca2_1$. There are four Ca sites, each of which is fully occupied by Ca and coordinated by three O atoms, four (OH) groups and one (H_2O) group, with $\langle Ca-\Phi \rangle$ distances (Φ : unspecified anion) from 2.452 to 2.479 Å. There are sixteen B sites, each of which is occupied by B , forming eight $(B\Phi_3)$ triangles and eight $(B\Phi_4)$ tetrahedra. There are fifty-nine anion sites, of which sixteen are occupied by O^{2-} , twenty-four are (OH) groups, and nineteen are (H_2O) groups. The fundamental building block of the alfredstelznerite structure is the $[\text{B}_4\text{O}_4(\text{OH})_6]$ polyhedron cluster containing two $(B\Phi_3)$ triangles and two $(B\Phi_4)$ tetrahedra. One $(B\Phi_3)$ triangle and two $(B\Phi_4)$ tetrahedra form a three-membered ring that is decorated by an additional $(B\Phi_3)$ triangle sharing a vertex with a $(B\Phi_4)$ tetrahedron; the algebraic descriptor for this borate cluster is $\langle \Delta 2 \square \rangle \Delta$. In alfredstelznerite, there are four symmetrically distinct $[\text{B}_4\text{O}_4(\text{OH})_6]$ clusters that are strongly pseudosymmetric, both in terms of the stereochemistry of the cluster and in the linkage of Ca atoms to the cluster. The $[\text{B}_4\text{O}_4(\text{OH})_6]$ clusters link along $[100]$ and $[001]$ via $Ca-\Phi$ bonds to form undulating layers parallel to (010) with a composition $Ca(\text{H}_2\text{O})[\text{B}_4\text{O}_4(\text{OH})_6]$. Hydrogen bonds from (OH) and (H_2O) groups provides connectivity within and between the $Ca(\text{H}_2\text{O})[\text{B}_4\text{O}_4(\text{OH})_6]$ layers. There are three symmetrically distinct $Ca(\text{H}_2\text{O})[\text{B}_4\text{O}_4(\text{OH})_6]$ layers that repeat in the sequence $ABC B \dots$ along $[010]$. The three layers A , B and C are chemically equivalent and structurally similar, but differ in their relative stacking. The B and C layers nestle together with the hillocks and valleys of the undulating layers in mutual alignment, and an intervening sandwich of interstitial (H_2O) groups. The relative $a/2$ offset between the A and B layers along $[100]$ results in direct juxtaposition of hillock and valley that gives rise to a greater layer-separation and produces open tunnels that extend along $[001]$ and contain interstitial (H_2O) groups. The only other structure containing a borate cluster graphically identical to that in alfredstelznerite is synthetic $\text{Mg}(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_2$.

Keywords: alfredstelznerite, crystal structure, borate, $[\text{B}_4\text{O}_4(\text{OH})_6]$ cluster.

SOMMAIRE

Nous avons résolu la structure cristalline de l'alfredstelznerite, $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$, orthorhombique, a 12.161(2), b 40.477(8), c 10.1843(17) Å, V 5013(3) Å³, $Z = 4$, par méthodes directes, et nous l'avons affinée jusqu'à un résidu R_1 de 14.1% dans le groupe spatial $Pca2_1$. La structure contient quatre sites Ca ; chacun contient uniquement le Ca et est entouré de trois atomes d'oxygène, quatre groupes (OH) et un groupe (H_2O) ; Les distances $\langle Ca-\Phi \rangle$ (Φ : anion non spécifié) varient de 2.452 à 2.479 Å. Il y a seize sites B , chacun étant occupé par B , dont huit triangles $(B\Phi_3)$ et huit tétraèdres $(B\Phi_4)$. Il y a 59 sites anioniques, dont seize sont de l'oxygène, 24 sont des groupes (OH) , et 19 sont des groupes (H_2O) . Le bloc structural fondamental dans la structure, le module polyédrique $[\text{B}_4\text{O}_4(\text{OH})_6]$, contient deux triangles $(B\Phi_3)$ et deux tétraèdres $(B\Phi_4)$. Un triangle $(B\Phi_3)$ et deux tétraèdres $(B\Phi_4)$ forment un anneau à huit membres, décoré par un triangle $(B\Phi_3)$ additionnel partageant un sommet avec un tétraèdre $(B\Phi_4)$; l'expression algébrique pour décrire ce module boraté est $\langle \Delta 2 \square \rangle \Delta$. Dans l'alfredstelznerite, il se trouve quatre modules $[\text{B}_4\text{O}_4(\text{OH})_6]$ qui sont symétriquement distincts, mais fortement pseudosymétriques, aussi bien en termes de stéréochimie du module que des liaisons impliquant le Ca . Les groupes $[\text{B}_4\text{O}_4(\text{OH})_6]$ sont interconnectés le long

§ E-mail address: frank_hawthorne@umanitoba.ca

de [100] et de [001] grâce à des liaisons Ca- Φ , pour former des couches ondulantes parallèles à (010), avec une composition $\text{Ca}(\text{H}_2\text{O})[\text{B}_4\text{O}_4(\text{OH})_6]$. Les liaisons hydrogène provenant des groupes (OH) et (H₂O) fournissent la connectivité requise au sein des couches $\text{Ca}(\text{H}_2\text{O})[\text{B}_4\text{O}_4(\text{OH})_6]$ et entre les couches. Trois couches $\text{Ca}(\text{H}_2\text{O})[\text{B}_4\text{O}_4(\text{OH})_6]$ sont symétriquement distinctes et se répètent dans la séquence *ABC*B... le long de [010]. Les trois couches *A*, *B* et *C* sont chimiquement équivalentes et semblables dans leurs structures, mais elles diffèrent dans leur mode d'empilement. Les couches *B* et *C* sont emboîtées, les monticules et les vallées des couches ondulantes en alignement mutuel, avec une intercalation de groupes (H₂O) interstitiels. Le décalage relatif de *a*/2 entre les couches *A* et *B* le long de [100] a pour effet de juxtaposer directement monticules et vallées, ce qui mène à une plus grande séparation entre les couches, et des canaux ouverts allongés selon [001]; ceux-ci contiennent les groupes (H₂O) interstitiels. La seule autre structure contenant un module boraté graphiquement identique à celui de l'alfredstelnznerite est celle du composé synthétique $\text{Mg}(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_2$.

Mots-clés: alfredstelnznerite, structure cristalline, borate, module $[\text{B}_4\text{O}_4(\text{OH})_6]$.

INTRODUCTION

Alfredstelnznerite is a new borate mineral species of composition $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$. It was discovered at the Santa Rosa mine, a Tertiary borate deposit in Sijes, Salta, northwestern Argentina (Galliski *et al.* 2010), where it is associated with colemanite, hydroboracite, ulexite, inyoite, gypsum and anhydrite, and minor meyerhofferite, nobleite, gowerite, inderborite, inderite, orpiment and realgar. As part of our general interest in borate minerals (Cooper & Hawthorne 1998, Cooper *et al.* 1994, Hawthorne *et al.* 1996, Grice *et al.* 1994, 1999, Burns & Hawthorne 1994a, b, 1995, Burns *et al.* 1994, 1995, Schindler & Hawthorne 2001a, b, c), we have solved the crystal structure of alfredstelnznerite and present the results here.

EXPERIMENTAL

The collection of X-ray data

Many crystals of alfredstelnznerite were examined. They show a milky appearance characteristic of partial dehydration. A transparent crystal was attached to a tapered glass fiber and mounted on a Bruker *P4* diffractometer equipped with a Smart 1K CCD detector (MoK α radiation). The diffraction from the crystal was weak, and no data were observed above 42° 2 θ . In addition, the *b* cell-dimension was supported by only a few weak reflections that were streaked in the *b* direction. However, only one crystal suitable for single-crystal diffraction was available after several years of searching, and this crystal was used in this study. The intensities of 33,873 reflections (16,779 in the Ewald sphere) were collected to 42° 2 θ using 120 s per 0.3° frame. An empirical absorption correction (SADABS: Shelldrick 1998) was applied, and the data were corrected for Lorentz, polarization and background effects, and averaged to give 4795 unique reflections. The refined unit-cell parameters were obtained from 3723 reflections with *I* > 10 σ (*I*). Miscellaneous data-collection information is given in Table 1.

All structure calculations were done with the SHELXTL PC (version 5.1) system of programs using

neutral scattering factors from the International Tables for X-ray Crystallography (1992); *R* indices are of the form given in Table 1 and are expressed as percentages. The structure was solved by direct methods and repeated difference-Fourier synthesis, and refined on *F*² to *R*₁ = 14.1% for 3795 independent observed (*|F_o|* > 4 σ (*F*)) reflections. The initial model produced meaningless isotropic-displacement parameters. A more robust convergence was obtained by constraining the isotropic-displacement parameters to be equal at chemically similar sites, and allowing the displacement parameters for the O atoms of interstitial (H₂O) groups to refine independently of each other. At this stage of the refinement, there was a large dispersion in the individual B–O distances (1.24–1.49 Å for [³B] and 1.35–1.59 Å for [⁴B]), with fairly large standard deviations (~0.03 Å). For well-refined borate structures, the reported dispersion is 1.336–1.404 Å for [³B]–O distances and 1.426–1.526 Å for [⁴B]–O distances, at a 2 σ cutoff (Hawthorne *et al.* 1996). We attribute this large dispersion in our observed B–O distances to low accuracy in the refined coordinates of the “light” B atoms. In order to attain a more chemically realistic model, we included a soft constraint that the [³B]–O distances refine to ~1.37 Å, and the [⁴B]–O distances, to ~1.48 Å, with a standard deviation of 0.03 Å. This treatment had no effect on the final *R* value, but resulted in more reasonable [³B]–O and [⁴B]–O distances, 1.32–1.41 and 1.43–1.52 Å, respectively. The final *R*₁ value, 14.1%, is high; two contributing factors are likely responsible: (1) a large unit-cell containing

TABLE 1. MISCELLANEOUS INFORMATION FOR ALFREDSTELNZNERITE

<i>a</i> (Å)	12.161(2)	crystal size (μm)	16 × 24 × 350
<i>b</i>	40.477(8)	radiation	MoK α /Graphite
<i>c</i>	10.1843(17)	total no. of <i>I</i>	33873
<i>V</i> (Å ³)	5013.0(3)	No. in Ewald sphere	16779
Space group	<i>Pca</i> 2 ₁	No. unique reflections	4795
<i>Z</i>	4	<i>R</i> (merge) %	8.1
<i>D</i> _{calc.} (g.cm ⁻³)	1.775	No. with (<i> F_o </i> > 4 σ)	3795
<i>R</i> ₁ %	14.1	<i>wR</i> ₂ %	36.9

Unit-cell contents: 4 [Ca₂(H₂O)₄[B₄O₄(OH)₆]₄(H₂O)₁₅].
*R*₁ = $\Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; *wR*₂ = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

numerous weakly bonded (H₂O) groups (41.7 wt.% H₂O), with the considerable scattering of a large number of H atoms not represented in the final model; (2) a high degree of pseudosymmetry and probable stacking disorder (streakiness in diffraction maxima along [010]) among the structural layers. Nevertheless, the structural model clearly establishes the correct chemical formula and bond connectivity for alfredstelznerite. Details of the data collection and structure refinement are given in Table 1, final atom parameters are listed in Table 2, and selected interatomic distances and angles in Table 3. A table of structure factors may be obtained from the Depository of Unpublished Data on the MAC website [document Alfredstelznerite CM48_129].

Chemical composition

All (H₂O) groups are fully occupied and show a variable degree of positional disorder (*cf.* isotropic-displacement parameters, which were refined without constraints). Counting the atoms in the unit cell gives the formula [Ca₄(H₂O)₄ B₁₆O₁₆(OH)₂₄ (H₂O)₁₅], with Z = 4. The presence of one additional interstitial (H₂O) group would produce a simpler formula (*i.e.*, one divisible by 4); however, none of the 50 most significant peaks in the final difference-Fourier map were at a reasonable location for consideration as an additional (H₂O) group. The structure model was input into the CAVITIES search routine in the program ATOMS (Dowty 2000) to search for voids within the structure that could possibly accommodate an additional interstitial (H₂O) group (*i.e.*, >4 Å from Ca, >3 Å from B, and >2.6 Å from O atoms). Only one such location was found: O, 0.1333, 0.9800; however, there was no significant electron-density at this position after its inclusion in the refinement model with a variable occupancy-factor. The calculated density, 1.775, is in very close agreement with the measured density, 1.77(1), and all significant electron density is accounted for in the structure model, suggesting that the chemical formula from structure refinement is complete.

DESCRIPTION OF THE STRUCTURE

Sites

There are four Ca sites, each of which is fully occupied by Ca and coordinated by three O atoms, four (OH) groups and one (H₂O) group, with <Ca-Φ> distances (Φ: unspecified anion) from 2.45 to 2.50 Å (Table 3). There are sixteen B sites, each of which is occupied by B, forming eight (BΦ₃) triangles and eight (BΦ₄) tetrahedra. Every B site is coordinated to at least one (OH), and four BΦ₃ triangles and four BΦ₄ tetrahedra are each coordinated by two (OH) groups.

There are fifty-nine O sites, of which O(1)–O(16) are occupied by O²⁻, O(17)–O(40) are (OH) groups, and O(41)–O(59) are (H₂O) groups. The correct designation

TABLE 2. FINAL PARAMETERS OF ATOMS IN ALFREDSTELZNERITE

Site	x	y	z	U _{iso}
Ca(1)	0.6291(4)	0.28603(10)	0	0.0072(6)
Ca(2)	0.3727(4)	0.25068(9)	0.5036(6)	0.0072(6)
Ca(3)	0.3751(4)	0.48287(10)	0.4737(6)	0.0072(6)
Ca(4)	0.3789(4)	0.01816(10)	0.4861(6)	0.0072(6)
B(1)	0.7719(18)	0.3525(5)	0.157(2)	0.0063(13)
B(2)	0.9306(15)	0.3374(5)	0.292(2)	0.0063(13)
B(3)	0.7846(16)	0.2940(5)	0.223(2)	0.0063(13)
B(4)	0.6132(16)	0.2735(6)	0.337(2)	0.0063(13)
B(5)	0.2451(18)	0.1828(4)	0.182(2)	0.0063(13)
B(6)	0.4178(16)	0.1968(5)	0.301(2)	0.0063(13)
B(7)	0.2825(16)	0.2412(5)	0.226(2)	0.0063(13)
B(8)	0.1124(16)	0.2609(6)	0.341(2)	0.0063(13)
B(9)	0.2435(19)	0.0869(4)	0.809(2)	0.0063(13)
B(10)	0.4124(15)	0.0726(5)	0.690(2)	0.0063(13)
B(11)	0.2815(16)	0.0276(5)	0.763(2)	0.0063(13)
B(12)	0.1145(17)	0.0049(6)	0.651(2)	0.0063(13)
B(13)	0.2770(18)	0.4159(5)	0.823(2)	0.0063(13)
B(14)	0.4378(15)	0.4307(5)	0.683(2)	0.0063(13)
B(15)	0.2861(15)	0.4741(5)	0.752(2)	0.0063(13)
B(16)	0.1204(16)	0.4952(6)	0.635(2)	0.0063(13)
O(1)	0.7320(12)	0.3214(3)	0.1468(16)	0.0124(7)
O(2)	0.8555(11)	0.3616(3)	0.2330(16)	0.0124(7)
O(3)	0.8939(11)	0.3035(3)	0.2669(17)	0.0124(7)
O(4)	0.7176(12)	0.2862(3)	0.3405(16)	0.0124(7)
O(5)	0.2310(12)	0.2141(3)	0.1483(16)	0.0124(7)
O(6)	0.3270(11)	0.1736(3)	0.2679(16)	0.0124(7)
O(7)	0.3922(11)	0.2318(3)	0.2713(17)	0.0124(7)
O(8)	0.2153(12)	0.2468(3)	0.3414(19)	0.0124(7)
O(9)	0.2275(12)	0.0534(3)	0.8435(17)	0.0124(7)
O(10)	0.3160(11)	0.0942(3)	0.7117(16)	0.0124(7)
O(11)	0.3880(11)	0.0376(3)	0.7198(17)	0.0124(7)
O(12)	0.2168(12)	0.0199(3)	0.6429(17)	0.0124(7)
O(13)	0.2354(12)	0.4479(3)	0.8279(16)	0.0124(7)
O(14)	0.3622(11)	0.4069(3)	0.7476(16)	0.0124(7)
O(15)	0.3965(12)	0.4653(3)	0.7089(17)	0.0124(7)
O(16)	0.2247(12)	0.4818(3)	0.6312(17)	0.0124(7)
O(17)	0.7221(12)	0.3761(3)	0.0780(16)	0.0124(7)
O(18)	0.9320(12)	0.3419(4)	0.4356(16)	0.0124(7)
O(19)	0.0413(11)	0.3420(3)	0.2342(16)	0.0124(7)
O(20)	0.7860(12)	0.2661(3)	0.1320(16)	0.0124(7)
O(21)	0.5563(12)	0.2714(4)	0.2192(16)	0.0124(7)
O(22)	0.5698(12)	0.2621(4)	0.4510(16)	0.0124(7)
O(23)	0.1808(12)	0.1587(3)	0.1248(16)	0.0124(7)
O(24)	0.4374(12)	0.1955(4)	0.4448(16)	0.0124(7)
O(25)	0.5150(11)	0.1874(3)	0.2293(16)	0.0124(7)
O(26)	0.2886(12)	0.2695(3)	0.1343(16)	0.0124(7)
O(27)	0.0560(12)	0.2638(4)	0.2233(16)	0.0124(7)
O(28)	0.0665(12)	0.2734(4)	0.4537(16)	0.0124(7)
O(29)	0.1727(12)	0.1088(3)	0.8603(16)	0.0124(7)
O(30)	0.5115(11)	0.0827(3)	0.7640(16)	0.0124(7)
O(31)	0.4423(12)	0.0742(4)	0.5451(16)	0.0124(7)
O(32)	0.2835(12)	-0.0018(4)	0.8507(17)	0.0124(7)
O(33)	0.0563(12)	0.0028(4)	0.7671(16)	0.0124(7)
O(34)	0.0618(12)	-0.0058(4)	0.5406(16)	0.0124(7)
O(35)	0.2272(12)	0.3932(3)	0.9079(16)	0.0124(7)
O(36)	0.5491(12)	0.4286(3)	0.7297(17)	0.0124(7)
O(37)	0.4323(12)	0.4259(4)	0.5409(16)	0.0124(7)
O(38)	0.2863(12)	0.5031(3)	0.8380(16)	0.0124(7)
O(39)	0.0620(12)	0.4941(4)	0.7520(16)	0.0124(7)
O(40)	0.0657(12)	0.5056(4)	0.5289(16)	0.0124(7)
O(41)	0.6341(12)	0.2294(3)	-0.0454(16)	0.0124(7)
O(42)	0.3851(12)	0.3095(3)	0.4871(17)	0.0124(7)
O(43)	0.3968(12)	0.5453(3)	0.4749(16)	0.0124(7)
O(44)	0.3727(12)	-0.0379(4)	0.5583(16)	0.0124(7)
O(45)	0.3760(16)	0.3605(4)	0.086(2)	0.034(5)
O(46)	0.622(2)	0.4045(6)	0.405(2)	0.059(7)
O(47)	0.7685(14)	0.2072(4)	0.7582(19)	0.026(4)
O(48)	0.4421(18)	0.1899(5)	0.957(2)	0.052(6)
O(49)	0.2554(17)	0.3259(4)	0.262(2)	0.039(5)
O(50)	0.7086(15)	0.1354(5)	0.988(2)	0.042(5)
O(51)	0.5579(16)	0.1195(5)	0.200(2)	0.039(5)
O(52)	0.6354(15)	0.1785(4)	0.570(2)	0.034(5)
O(53)	0.528(3)	0.3463(7)	0.325(3)	0.092(9)
O(54)	0.7307(14)	0.4405(4)	0.2048(18)	0.024(4)
O(55)	0.7296(16)	0.0613(5)	0.732(2)	0.041(5)
O(56)	0.4424(17)	0.0794(5)	0.037(2)	0.050(6)
O(57)	0.477(3)	0.4208(8)	0.158(4)	0.109(11)
O(58)	0.5592(16)	0.1467(5)	0.799(2)	0.043(5)
O(59)	0.635(2)	0.0892(6)	0.415(3)	0.066(7)

of anions was made using Pauling bond-strength arguments and is summarized in Figure 1 for the fifty-nine anion sites. All O atoms that link two adjacent B atoms receive between 1.75 and 2.00 *vu* (valence units) from B (\pm Ca) and are O atoms that receive up to one additional hydrogen-bond. All O atoms that link to only one B atom receive between 0.75 and 1.25 *vu* from B (\pm Ca) and are (OH) groups that receive up to two additional hydrogen-bonds. All O atoms that do not bond to any B atoms are (H₂O) groups that receive up to two (or more) additional hydrogen-bonds. The resulting structural formula for alfredstelnznerite is Ca₄(H₂O)₄ [B₄O₄(OH)₆]₄ (H₂O)₁₅, and this is in agreement with the chemical composition reported by Galliski *et al.* (2010).

Topology of the structure

The fundamental building block of the alfredstelnznerite structure is the [B₄O₄(OH)₆] polyhedron cluster formed from two (BΦ₃) triangles and two (BΦ₄) tetrahedra. The individual borate components

comprising each of the four [B₄O₄(OH)₆] clusters are segregated into the four vertical columns in Table 3. One (BΦ₃) triangle and two (BΦ₄) tetrahedra form a three-membered ring that is decorated by an additional (BΦ₃) triangle sharing a vertex with a (BΦ₄) tetrahedron (Fig. 2a). The algebraic descriptor for this borate cluster is <Δ2□>Δ (Burns *et al.* 1995). In alfredstelnznerite, there are four symmetrically distinct [B₄O₄(OH)₆] clusters that are strongly pseudosymmetric, both in terms of the stereochemistry of the cluster and in the linkage of Ca atoms to the cluster. This is shown in Figure 3, where the (BΦ₃) triangle of the three-membered ring is oriented exactly in the plane of the page for each [B₄O₄(OH)₆] cluster; there is strong pseudomirror symmetry between the upper two structural components (Figs. 3a, b) and lower two structural components (Figs. 3c, d). The [B₄O₄(OH)₆] clusters link along [100] and [001] *via* Ca–Φ bonds (Fig. 4a) to form undulating layers parallel to (010) with a composition Ca(H₂O) [B₄O₄(OH)₆] (Fig. 5). Additional hydrogen-bonding (not shown) from the

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN ALFREDSTELZNERITE

[CaΦ ₆]							
Ca(1)–O(1)	2.420(15)	Ca(2)–O(5)b	2.439(16)	Ca(3)–O(13)c	2.453(15)	Ca(4)–O(9)c	2.398(16)
Ca(1)–O(3)a	2.493(17)	Ca(2)–O(7)	2.498(17)	Ca(3)–O(15)	2.513(17)	Ca(4)–O(11)	2.510(17)
Ca(1)–O(4)a	2.472(16)	Ca(2)–O(8)	2.530(18)	Ca(3)–O(16)	2.434(16)	Ca(4)–O(12)	2.519(17)
Ca(1)–O(18)a	2.470(15)	Ca(2)–O(22)	2.499(15)	Ca(3)–O(37)	2.503(15)	Ca(4)–O(31)	2.477(15)
Ca(1)–O(20)	2.469(16)	Ca(2)–O(24)	2.443(15)	Ca(3)–O(38)c	2.536(16)	Ca(4)–O(32)c	2.522(16)
Ca(1)–O(21)	2.473(17)	Ca(2)–O(26)b	2.489(16)	Ca(3)–O(39)c	2.426(17)	Ca(4)–O(33)c	2.454(17)
Ca(1)–O(28)c	2.480(15)	Ca(2)–O(27)b	2.457(17)	Ca(3)–O(40)e	2.430(15)	Ca(4)–O(34)d	2.369(15)
<Ca(1)–Φ>	2.452	Ca(2)–O(42)	2.390(14)	Ca(3)–O(43)	2.540(14)	Ca(4)–O(44)	2.387(15)
		<Ca(2)–Φ>	2.468	<Ca(3)–Φ>	2.479	<Ca(4)–Φ>	2.455
[BΦ ₃]							
B(1)–O(1)	1.35(2)	B(5)–O(5)	1.32(2)	B(13)–O(13)	1.39(2)	B(9)–O(9)	1.41(2)
B(1)–O(2)	1.33(2)	B(5)–O(6)	1.38(2)	B(13)–O(14)	1.34(2)	B(9)–O(10)	1.36(2)
B(1)–O(17)	1.38(2)	B(5)–O(23)	1.38(2)	B(13)–O(35)	1.40(2)	B(9)–O(29)	1.34(2)
<B(1)–Φ>	1.35	<B(5)–Φ>	1.36	<B(13)–Φ>	1.38	<B(9)–Φ>	1.37
B(4)–O(4)	1.37(2)	B(8)–O(8)	1.34(2)	B(16)–O(16)	1.38(2)	B(12)–O(12)	1.39(2)
B(4)–O(21)	1.39(2)	B(8)–O(27)	1.39(2)	B(16)–O(39)	1.38(2)	B(12)–O(33)	1.38(2)
B(4)–O(22)	1.36(2)	B(8)–O(28)	1.37(2)	B(16)–O(40)	1.34(2)	B(12)–O(34)	1.37(2)
<B(4)–Φ>	1.37	<B(8)–Φ>	1.37	<B(16)–Φ>	1.37	<B(12)–Φ>	1.38
[BΦ ₄]							
B(3)–O(1)	1.50(2)	B(7)–O(5)	1.49(2)	B(15)–O(13)	1.45(2)	B(11)–O(9)	1.48(2)
B(3)–O(3)	1.45(2)	B(7)–O(7)	1.46(2)	B(15)–O(15)	1.46(2)	B(11)–O(11)	1.43(2)
B(3)–O(4)	1.48(2)	B(7)–O(8)	1.47(2)	B(15)–O(16)	1.48(2)	B(11)–O(12)	1.49(2)
B(3)–O(20)	1.46(2)	B(7)–O(26)	1.48(2)	B(15)–O(38)	1.46(2)	B(11)–O(33)	1.49(2)
<B(3)–Φ>	1.47	<B(7)–Φ>	1.48	<B(15)–Φ>	1.46	<B(11)–Φ>	1.47
B(2)–O(2)	1.46(2)	B(6)–O(6)	1.49(2)	B(14)–O(14)	1.49(2)	B(10)–O(10)	1.48(2)
B(2)–O(3)	1.46(2)	B(6)–O(7)	1.48(2)	B(14)–O(15)	1.51(2)	B(10)–O(11)	1.48(2)
B(2)–O(18)	1.48(2)	B(6)–O(24)	1.49(2)	B(14)–O(36)	1.45(2)	B(10)–O(30)	1.48(2)
B(2)–O(19)f	1.48(2)	B(6)–O(25)	1.44(2)	B(14)–O(37)	1.46(2)	B(10)–O(31)	1.52(2)
<B(2)–Φ>	1.47	<B(6)–Φ>	1.48	<B(14)–Φ>	1.48	<B(10)–Φ>	1.49

a: $\bar{x} + 3/2, y, z - 1/2$; b: $\bar{x} + 1/2, y, z + 1/2$; c: $\bar{x} + 1/2, y, z - 1/2$; d: $x + 1/2, \bar{y}, z$; e: $x + 1/2, \bar{y} + 1, z$; f: $x + 1, y, z$.

O^{2-} : O(1) – O(16)	(OH): O(17) – O(40)	(H ₂ O): O(41) – O(59)
$Ca^{0.25} O^{2-} \begin{matrix} \nearrow^{1.00} B^{[3]} \\ \searrow_{0.75} B^{[4]} \end{matrix}$ $\Sigma = 2.00$	$Ca^{0.25} (OH)^{1.00} B^{[3]}$ $\Sigma = 1.25$	$Ca^{0.25} (H_2O)$ $\Sigma = 0.25$
$Ca^{0.25} O^{2-} \begin{matrix} \nearrow_{0.75} B^{[4]} \\ \searrow_{0.75} B^{[4]} \end{matrix}$ $\Sigma = 1.75$	$Ca^{0.25} (OH)^{0.75} B^{[4]}$ $\Sigma = 1.00$	
$O^{2-} \begin{matrix} \nearrow^{1.00} B^{[3]} \\ \searrow_{0.75} B^{[4]} \end{matrix}$ $\Sigma = 1.75$	$(OH)^{1.00} B^{[3]}$ $\Sigma = 1.00$	
	$(OH)^{0.75} B^{[4]}$ $\Sigma = 0.75$	(H_2O) $\Sigma = 0.00$

FIG. 1. Anion coordinations and designations in alfredstelznerite. Values are Pauling bond strengths (νu).

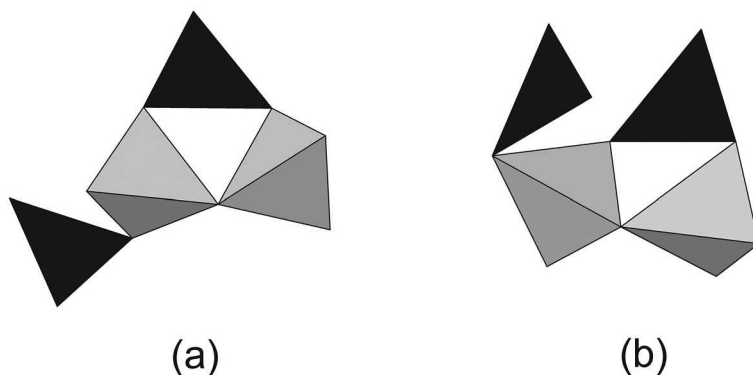


FIG. 2. The $[B_4O_4(OH)_6]$ cluster in (a) alfredstelznerite, and (b) synthetic $Mg(H_2O)_4[B_4O_4(OH)_6](H_2O)_2$. The $(B\Phi_3)$ triangles are shaded black, whereas the $(B\Phi_4)$ tetrahedra are shaded grey.

(OH) and (H₂O) groups provides further connectivity within and between $Ca(H_2O)[B_4O_4(OH)_6]$ layers. There are three symmetrically distinct $Ca(H_2O)[B_4O_4(OH)_6]$ layers that repeat in the sequence *ABC*... along [010] (Fig. 5). There are *a*-glide planes parallel to (010) at $y = 0, \frac{1}{2}$ that act on the proximal $Ca(4) + B(9-12)$ and $Ca(3) + B(13-16)$ components to produce the *A* and *C* layers, respectively. Midway between the *a*-glide planes at $y = \frac{1}{4}, \frac{3}{4}$ are the $Ca(1,2) + B(1-8)$ components that

meld to form the composite *B* layer. The three layers (*A*, *B*, *C*) are chemically equivalent and structurally very similar, but differ in their relative stacking. The *B* and *C* layers nestle together with the hillocks and valleys of the undulating layers in mutual alignment, and an intervening sandwich of interstitial (H₂O) groups. The relative *a*/2 offset between the *A* and *B* layers along [100] results in direct juxtaposition of hillock and valley that gives rise to a greater layer-separation, 10.86 Å (as

compared to 9.38 Å between *B* and *C*), and produces open tunnels that extend along [001] and contain interstitial (H_2O) groups.

Related structures

The only other structure containing the graphically identical borate cluster as in alfredstelznerite is synthetic $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$ (Abdullaev *et al.* 1984) (Fig. 2b). In that compound, $[\text{B}_4\text{O}_4(\text{OH})_6]$ clusters are linked into chains parallel to [010] by [7]-coordinated Mg (Fig. 4b, forming layers of composition $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6]$ that extend parallel to (100) (Fig. 4b). In synthetic $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$, these layers are more compact than in alfredstelznerite, and the layer separation is only 6.85 Å (Fig. 6). Alfredstelznerite and synthetic $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$ are

compared in Table 4. The Ca atoms in alfredstelznerite are each coordinated by one (H_2O) group, whereas the Mg atoms in synthetic $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$

TABLE 4. COMPARISON OF ALFREDSTELZNERITE AND SYNTHETIC $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$

	alfredstelznerite	synthetic phase
formula	$\text{Ca}_4(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6]_4$ (H_2O) ₁₆	$\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6]_4$ (H_2O) ₂
Z	4	4
Cell volume (Å ³)	5013.0	1012.85
D ^{calc.}	1.775	2.241
wt.%H ₂ O	41.7	47.5
($\text{H}_2\text{O}_{\text{interstitial}} / \text{H}_2\text{O}_{\text{total}}$) (%)	79	33
structural layer separation (Å)	9.38, 10.86	6.85

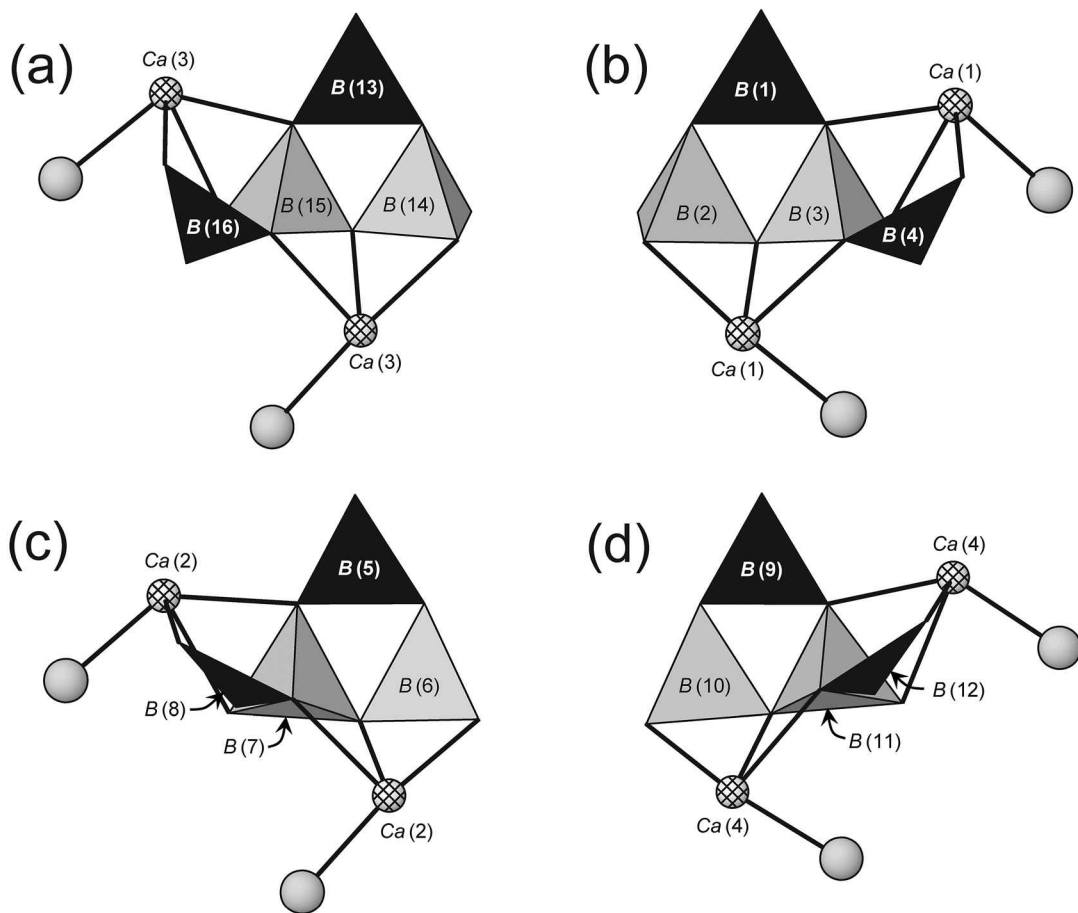


FIG. 3. The four symmetrically distinct $[\text{B}_4\text{O}_4(\text{OH})_6]$ clusters in alfredstelznerite, with the 3Δ triangle parallel to the page. Legend as in Figure 2, with Ca atoms as circles with cross-hatching, Ca- Φ bonds as thin lines, and (H_2O) groups as shaded circles.

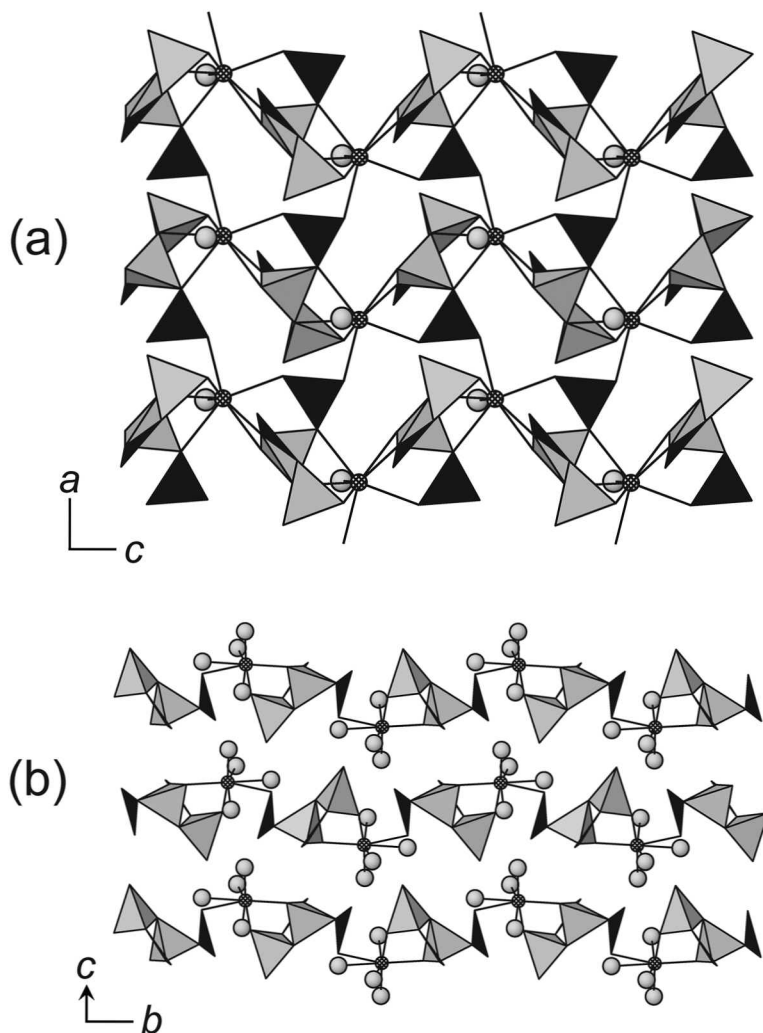


FIG. 4. The principal structural layer in (a) alfredstelnznerite projected down [010], (b) synthetic $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$ projected down [100]. Legend as in Figures 2 and 3, with Mg atoms shown as circles with cross-hatching.

are coordinated by four (H_2O) groups. Both compounds contain the $[\text{B}_4\text{O}_4(\text{OH})_6]^{2-}$ cluster in a 1:1 ratio with a divalent cation. The greater ratio of interstitial (H_2O) to total (H_2O) and the less compact structural layer in alfredstelnznerite gives rise to an expanded (H_2O)-rich interlayer region in the latter structure. Thus, although synthetic $\text{Mg}(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6] (\text{H}_2\text{O})_2$ contains a greater content of (H_2O), its density is appreciably greater than alfredstelnznerite due to architectural differences in structure that result from the different roles of interstitial and bonded (H_2O) groups.

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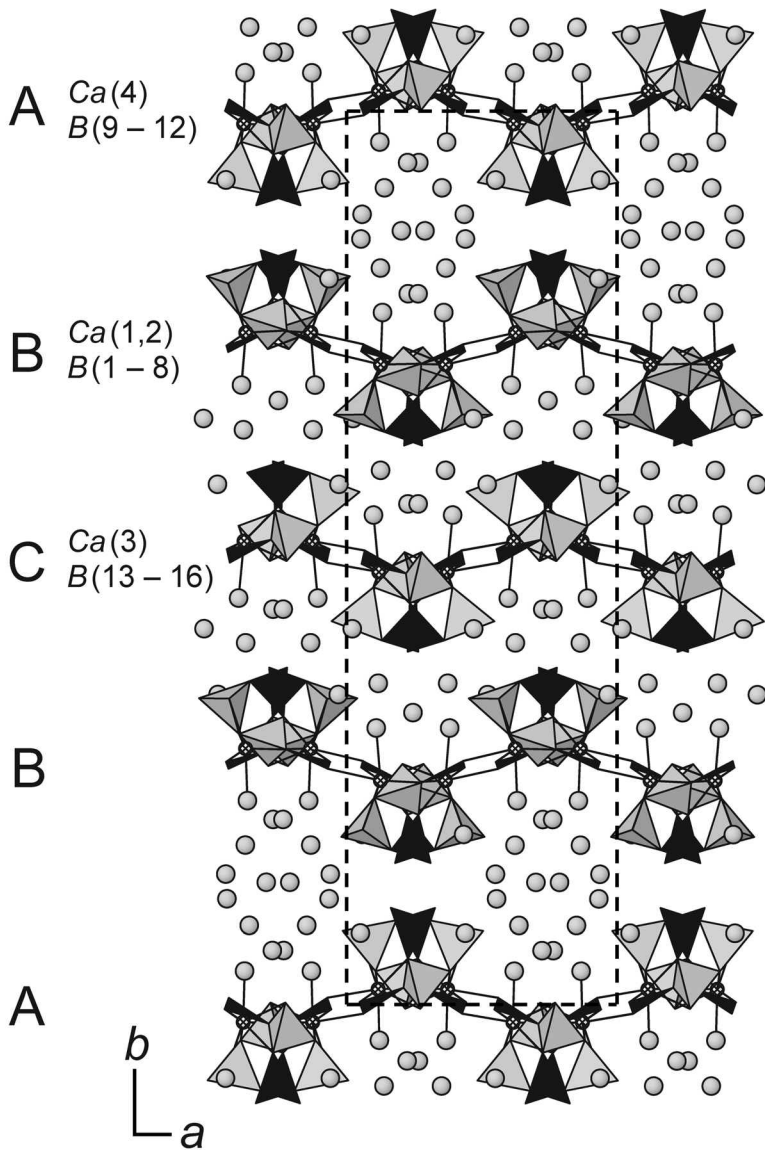


FIG. 5. The crystal structure of alfredstelnite projected down [001]; legend as in Figures 2 and 3. The unit cell is shown by dashed lines.

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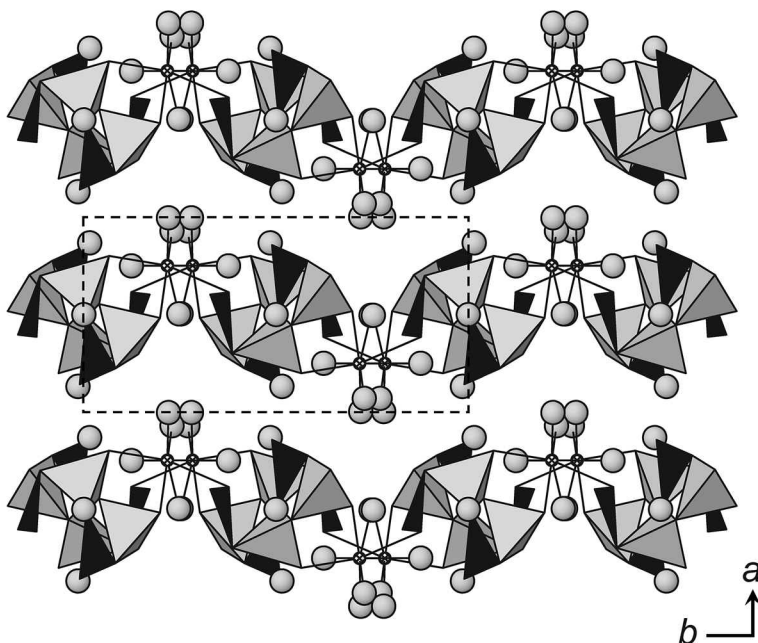


FIG. 6. The crystal structure of synthetic $\text{Mg}(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_2$ projected down [001]; legend as in Figures 2 and 3. The unit cell is shown by dashed lines.

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