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REFINEMENT OF THE CRYSTAL STRUCTURE OF AMINOFFITE

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ABSTRACT

Aminoffite, $(Ca_{2.95}Mn_{0.08}Pb_{0.01})(BeOH)_2(Si_{2.95}As_{0.03})O_{10}$, is tetragonal, $P4_2/n$, *a* 9.809(1), *c* 9.844(2) Å, *V* 947.3(3) Å^3, Z = 12. The structure was refined to an *R* index of 2.9% based on 1265 observed [$|F_o| > 5\sigma F$] reflections measured with a four-circle single-crystal diffractometer and Mo*K*α X-radiation. There are two *Si* sites and one *Be* site in the structure of aminoffite, each coordinated by four anions in a tetrahedral arrangement. There are two distinct *Ca* sites, coordinated by six O-atoms, and one and two (OH) groups, respectively, with <*Ca*–O> distances of 2.467 and 2.436 Å. The single H-atom is part of an (OH) group that is part of the $(Be\phi_4)$ (ϕ: unspecified anion) tetrahedron. The (SiO_4) groups link to form linear $[Si_3O_{10}]$ trimers that are linked by $(Be\phi_4)$ groups to form a sheet of tetrahedra parallel to (001). These sheets stack in the [001] direction and are linked together by interstitial Ca atoms and by hydrogen bonding. Details of the sheet topologies in Be minerals with two-dimensional structural units are examined; $(Be\phi_4)$ tetrahedra show a marked preference for trivalent vertices in two-dimensional nets. Bond-valence considerations show that such $(Be\phi_4)$ tetrahedra must have a monovalent anion [usually (OH)] at one vertex, and hence most such structures have acid $\{BeO_3(OH)\}$ groups.

Keywords: aminoffite, crystal structure, electron-microprobe analysis, beryllium mineral, structure topology, bond valence.

SOMMAIRE

L'aminoffite, $(Ca_{2.95}Mn_{0.08}Pb_{0.01})(BeOH)_2(Si_{2.95}As_{0.03})O_{10}$, est tétragonale, $P4_2/n$, *a* 9.809(1), *c* 9.844(2) Å, *V* 947.3(3) Å^3, *Z* = 12. Nous en avons affiné la structure jusqu'à un résidu *R* de 2.9% en utilisant 1265 réflexions observées [$|F_o| > 5\sigma F$] mesurées avec un diffractomètre à quatre cercles et un rayonnement Mo*K*α. Il y a deux sites *Si* et un site *Be* dans la structure, chacun coordonné par quatre anions en agencement tétraédrique. Il y a deux sites *Ca* distincts, coordonnés par six atomes d'oxygène, et un et deux groupes (OH), respectivement, avec des distances <*Ca*–O> de 2.467 et 2.436 Å. L'atome d'hydrogène, en une position cristallographiquement unique, fait partie du groupe (OH) des tétraèdres $(Be\phi_4)$ (ϕ: anion non spécifié). Les groupes (SiO_4) sont liés entre eux pour former des trimères linéaires $[Si_3O_{10}]$ rattachés par des groupes $(Be\phi_4)$ pour former un feuillet de tétraèdres parallèle à (001). Ces feuillets sont empilés le long de [001] et sont liés l'un à l'autre par des atomes de Ca interstitiels et par des liaisons hydrogène. Nous passons sous revue les détails topologiques des feuillets des minéraux de béryllium contenant des unités structurales à deux dimensions. Les tétraèdres $(Be\phi_4)$ montrent une préférence marquée pour des cations trivalents aux nodes d'un réseau bidimensionnel. Une considération des valences de liaison montre que de tels tétraèdres $(Be\phi_4)$ doivent avoir un anion monovalent, (OH) en général, à un vertex, et donc la plupart de telles structures contiennent des groupes acides $\{BeO_3(OH)\}$.

(Traduit par la Rédaction)

Mots-clés: aminoffite, structure cristalline, analyse à la microsonde électronique, minéral de béryllium, topologie de la structure, valences de liaison.

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INTRODUCTION

Aminoffite, a beryllium silicate mineral from Långban, Sweden, was first described by Hurlbut (1937). It occurs as euhedral crystals in cavities in massive magnetite and goethite associated with calcite, fluorite and barite. The structure of aminoffite was determined by Coda *et al.* (1967), who reported a revised chemical formula, $Ca_3(BeOH)_2Si_3O_{10}$, but did not provide new compositional data to confirm the details of the formula. Using bond-valence arguments, they interpreted the O(5) anion as an (OH) group, with a hydrogen bond to the O(6) anion, on the basis of an O(5)–O(6) distance of 2.87 Å (Coda *et al.* 1967). As part of a general study of Be minerals (Hawthorne & Huminicki 2002), we have refined the crystal structure of aminoffite, revised the stereochemical details of the hydrogen bonding, and provide results of an electron-microprobe analysis.

EXPERIMENTAL

X-ray diffraction

The sample used in this work is from Långban, Sweden. The aminoffite crystals are transparent, pale yellow, subhedral, 300–400 μm across in massive magnetite with an iron oxide coating, and are associated with euhedral calcite crystals. The fragment used for analysis, with dimensions 0.10 × 0.10 × 0.20 mm, was taken from a dipyramidal crystal associated with iron oxide minerals. The unit-cell dimensions were determined using a Siemens *P*4 automated four-circle diffractometer with a graphite monochromator and a Mo$K\alpha$ X-ray tube. Twenty-five reflections between 23 and 30°2θ were centered, and a constrained tetragonal cell was determined from the setting angles and refined using a least-squares technique (Table 1). Single-crystal intensity data were measured from 4 to 60°2θ over the range $0 \le h \le 13$, $\overline{13} \le k \le 13$, $\overline{13} \le l \le 13$, with a scan range of 1.2° and scan-speeds from 2.5 to 29.3°/min. A total of 5829 intensities was measured over four asymmetric units. Psi-scan data were measured on 20 reflections out to 60°2θ at increments of 5°; an absorption correction, with the crystal modeled as a triaxial ellipsoid, reduced *R*(azimuthal) from 3.8 to 1.6%. Intensities were corrected for Lorentz, polarization and background effects, and then reduced to structure factors; of the 1385 unique reflections, 1265 were classed as observed ($|F_o| > 5\sigma F$).

TABLE 1. MISCELLANEOUS INFORMATION FOR AMINOFFITE

a (Å)	9.8093(14)	crystal size (mm)	0.08 x 0.10 x 0.14
c	9.8444(17)	radiation	Mo$K\alpha$/graphite
V (Å^3)	947.31(31)	Total no. of *I*	5658
Sp. Gr.	$P4_2/n$	No. of *F*	1385
Z	12	No. $|F_o| > 5\sigma F$	1265
μ (mm^{-1})	2.14	*R* (merge) %	3.7
		R (obs)	2.9
		wR (obs) %	2.9

$R = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$

$wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$, $w = 1$

Chemical analysis

The crystal used for X-ray diffraction was mounted in a 2.5 cm perspex disc, ground, polished, coated with carbon and analyzed using a Cameca SX–50 electron microprobe. Aminoffite has the general formula $Ca_3(BeOH)_2Si_3O_{10}$. Energy-dispersion spectrometry (EDS) indicated the presence of Ca, Si, Mn, As and Pb. The crystal was analyzed for these elements, plus Al, Na and F. Ten points were analyzed in wavelength-dispersion mode with the following conditions: excitation voltage: 15 kV, specimen current: 20 nA, beam size: 5 μm, peak count-time: 20 s, background count-time: 10 s. The standards and crystals used for $K\alpha$ X-ray lines were as follows: F: fluorine analogue of riebeckite, TAP; Al: andalusite, TAP; Si: diopside, TAP; Mn: spessartine, LiF; Na: albite, TAP; Ca: diopside, PET; As: cobaltite, TAP; and Pb: PbTe, PET. The chemical composition and unit formula are given in Table 2; the BeO and H_2O contents were calculated on the basis of stoichiometry: Be = 2 *apfu* (atoms per formula unit) and OH = 2 *pfu*.

CRYSTAL-STRUCTURE REFINEMENT

All calculations were done using the Siemens SHELXTL PC^{TM} Plus software for crystal-structure determination and refinement. Structure refinement was initiated with the coordinates of Coda *et al.* (1967); the *R* index converged rapidly to a value of 3.0% for a model including anisotropic-displacement parameters for all atoms. At this stage of the refinement, a difference-Fourier map was calculated, and the coordinates

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

CaO	39.19	Ca	2.94
MnO	1.27	Mn^{2+}	0.07
PbO	0.66	Pb^{2+}	0.01
SiO_2	42.09	Σ	3.02
BeO**	11.87		
As_2O_5	0.7	Si	2.95
H_2O**	4.28	As^{5+}	0.03
Σ†	100.06	Σ	2.98
		Be	2

* Calculated based on 12 anions *pfu*

** Calculated assuming 2 Be and 2 (OH) *pfu*

† Al, Na and F were not detected

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR AMINOFFITE

Site	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca(1)	0.06286(5)	0.04403(5)	0.25852(5)	0.0096(1)	0.0111(2)	0.0099(2)	0.0079(2)	–0.0025(2)	–0.0009(2)	0.0043(2)
Ca(2)	¼	¾	0.25956(7)	0.0070(2)	0.0075(3)	0.0067(3)	0.0068(3)	0	0	0.0004(2)
Si(1)	0.03770(6)	0.76281(6)	0.02968(7)	0.0066(2)	0.0065(3)	0.0068(3)	0.0066(3)	0.0001(2)	–0.0010(2)	–0.0006(2)
Si(2)	¼	¼	0.01020(9)	0.0063(2)	0.0063(4)	0.0057(4)	0.0069(4)	0	0	0.0000(3)
Be	0.0371(3)	0.7674(3)	0.5268(3)	0.0093(7)	0.0071(13)	0.0127(13)	0.0082(13)	–0.0001(11)	0.0020(10)	0.0003(11)
O(1)	0.3733(2)	0.6099(2)	0.0874(2)	0.0086(4)	0.0086(7)	0.0090(7)	0.0082(7)	0.0003(6)	0.0002(6)	–0.0016(6)
O(2)	0.1054(2)	0.6243(2)	0.0934(2)	0.0088(4)	0.0079(7)	0.0097(7)	0.0088(8)	0.0007(6)	0.0004(6)	0.0026(6)
O(3)	0.2328(2)	0.3865(2)	0.1010(2)	0.0080(4)	0.0094(7)	0.0061(7)	0.0084(8)	–0.0004(6)	0.0014(6)	–0.0004(6)
O(4)	0.6185(2)	0.7272(2)	0.0903(2)	0.0092(4)	0.0058(7)	0.0136(8)	0.0083(8)	0.0007(6)	0.0005(6)	–0.0006(6)
O(5)	0.7898(2)	0.4656(2)	0.1360(2)	0.0126(5)	0.0215(9)	0.0082(8)	0.0080(8)	0.0005(6)	0.0005(7)	0.0013(7)
O(6)	0.9669(2)	0.2339(2)	0.1341(2)	0.0091(4)	0.0102(8)	0.0102(8)	0.0070(7)	–0.0011(6)	–0.0006(6)	0.0003(6)
H	0.756(4)	0.548(2)	0.181(3)	0.0245(96)						

of the H position were determined. Full-matrix least-squares refinement of all variables, including H-atom coordinates with the soft constraint that O–H ≈ 0.98 Å, converged to a final *R* index of 2.9% for 1265 observed reflections. Final refined atom-parameters 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

Cation polyhedra

There are two *Si* sites, *Si*(1) and *Si*(2), that are tetrahedrally coordinated by O atoms at mean distances of 1.631 and 1.630 Å, respectively (Table 4). These distances are in accord with the absence of Al in the chemical composition (Table 1). There is one *Be* site that is tetrahedrally coordinated by three O atoms and one (OH) group, and has a <*Be*–O> distance of 1.645 Å, which is slightly larger than the grand <*Be*–O> distance of 1.633 Å reported by Hawthorne & Huminicki (2002) for Be minerals. There are two *Ca* sites, *Ca*(1) and *Ca*(2), that are [7]- and [8]-coordinated, respectively, by six O atoms and one and two (OH) groups, respectively. The <Ca–O> distances are 2.467 and 2.436 Å for *Ca*(1) and *Ca*(2), respectively. These values are rather curious, as *Ca*(1) is [7]-coordinated and *Ca*(2) is [8]-coordinated, and yet <*Ca*(1)–O> at 2.467 Å is larger than <*Ca*(2)–O> at 2.436 Å. It is significant that the equivalent isotropic-displacement factor at *Ca*(1), 0.0096(1), is significantly larger than the analogous value at *Ca*(2), 0.0070(2). This suggests a "rattling" of *Ca*(1) in a polyhedron that is slightly too large for its constitutent-cation size, although the incident bond-valence sums at *Ca*(1) and *Ca*(2) (Table 5) suggest that the <*Ca*(2)–O> distance is anomalously short, rather than <*Ca*(1)–O> being anomalously long.

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

Ca(1)–O(1)a	2.347(2)		O(1)–*Si*(1)–O(2)	106.6(1)
Ca(1)–O(2)	2.421(2)		O(1)–*Si*(1)–O(4)	109.1(1)
Ca(1)–O(3)a	2.624(2)		O(1)–*Si*(1)–O(6)	110.4(1)
Ca(1)–O(3)d	2.364(2)		O(2)–*Si*(1)–O(4)	106.7(1)
Ca(1)–O(5)j	2.716(2)		O(2)–*Si*(1)–O(6)	114.3(1)
Ca(1)–O(6)j	2.419(2)		O(4)–*Si*(1)–O(6)	109.6(1)
Ca(1)–O(6)k	2.380(2)			
<*Ca*(1)–O>	2.467		O(3)–*Si*(2)–O(3)a	112.9(1)
			O(3)–*Si*(2)–O(4)e	107.6(1)
Ca(2)–O(1),b	2.494(2)	x2	O(3)–*Si*(2)–O(4)g	111.3(1)
Ca(2)–O(2),b	2.491(2)	x2	O(3)a –*Si*(2)–O(4)e	111.3(1)
Ca(2)–O(5)d,h	2.383(2)	x2	O(3)a –*Si*(2)–O(4)g	107.6(1)
Ca(2)–O(6)d,h	2.377(2)	x2	O(4)e –*Si*(2)–O(4)g	105.9(1)
<*Ca*(2)–O>	2.436			
			O(1)–*Be*–O(2)	105.2(2)
Si(1)–O(1)b	1.627(2)		O(1)–*Be*–O(5)	118.4(2)
Si(1)–O(2)	1.637(2)		O(1)–*Be*–O(3)	103.0(2)
Si(1)–O(4)b	1.647(2)		O(2)–*Be*–O(5)	107.4(2)
Si(1)–O(6)e	1.614(2)		O(2)–*Be*–O(3)	106.8(2)
<*Si*(1)–O>	1.631		O(3)–*Be*–O(5)	115.2(2)
Si(2)–O(3),a	1.619(2)	x2	H–O(5)	0.98(3)
Si(2)–O(4)e,g	1.641(2)	x2	H–O(4)	2.39(3)
<*Si*(2)–O>	1.630		H–O(4)l	2.36(3)
Be–O(1)c	1.664(4)		O(5)–H···O(4)	129(3)
Be–O(2)c	1.649(4)		O(5)–H···O(4)l	131(3)
Be–O(3)c	1.648(3)			
Be–O(5)d	1.618(4)			
<*Be*–O>	1.645			

Symmetry operators: a = $-x+½, -y+½, z$; b = $-x+½, -y+1½, z$; c = $y-½, -x+1, z+½$; d = $-y+½, x, -z+½$; e = $-x+1, -y+1, -z$; f = $-x+½, -y+½, -z$; g = $x-½, y-½, -z$; h = $y, -x+1½, -z+½$; i = $-y+½, x-1, -z+½$; j = $x-1, y, z$; k = $-y+½, x-½, -z+½$; l = $-y+1½, x, -z+½$.

Hydrogen bonding

The O(5) atom is located at the apex of the (*Be*ϕ_4) tetrahedron and bonds to two interstitial Ca atoms (in addition to H). Coda *et al.* (1967) assigned (OH) to the

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

	Ca(1)	*Ca*(2)	*Si*(1)	*Si*(2)	*Be*	H	Σ
O(1)	0.36	$0.24^{\times2}\downarrow$	0.99		0.47		2.06
O(2)	0.29	$0.24^{\times2}\downarrow$	0.97		0.48		1.98
O(3)	0.17 0.34			$1.01^{\times2}\downarrow$	0.49		2.01
O(4)			0.94	$0.96^{\times2}\downarrow$		$0.03^{\times2}\downarrow\rightarrow$	1.96
O(5)	0.13	$0.32^{\times2}\downarrow$			0.53	0.94	1.92
O(6)	0.29 0.33	$0.33^{\times2}\downarrow$	1.03				1.98
Σ	1.91	2.26	3.93	3.94	1.97	1.00	

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

O(5) anion on the basis of bond-strength sums and the short O(5)–O(6) bond distance: the bond-strength sum around O(5) from bonding to [7]- and [8]-coordinated Ca atoms and a [4]-coordinated Be atom is 1/2 + 2/7 + 2/8 = 1.04 *vu*; thus according to the valence-sum rule, the O(5) anion requires additional bond-valence from the H atom.

In the present refinement, the H-atom was located on a difference-Fourier map, ~1 Å from the donor atom, O(5). This result is in agreement with that of Coda *et al.* (1967) and is in accord with the calculated bond-valences (Table 5). The acceptor atom was determined to be the O(4) atom, on the basis of valence-sum rule and the bond lengths and angles associated with H and the O(4) anion (Table 4). The H–O(4) distance of 2.36 Å is typical for a weak hydrogen bond (Baur 1972), and the low incident bond-valence sum at O(4) from the Si atoms is also in accord with O(4) as a hydrogen-bond acceptor. The hydrogen bond is apparently bifurcated between two symmetrically equivalent O(4) atoms (Fig. 1), although the large U_{11} value for O(5) suggests either static disorder or, possibly, dynamic switching of a hydrogen bond between the two O(4) anions.

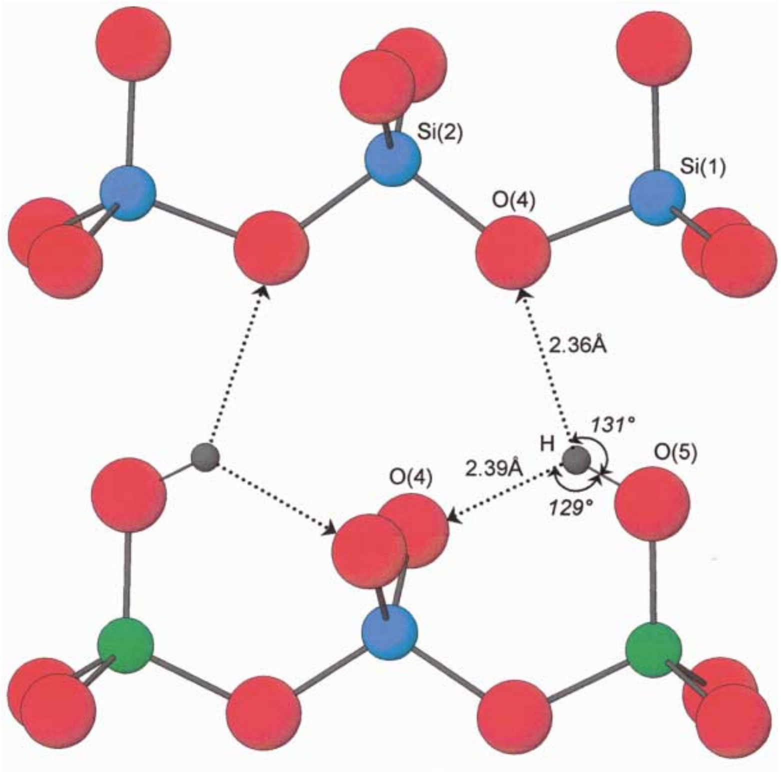


FIG. 1. Perspective view of bond lengths and angles for the hydrogen position. The hydrogen bond is bifurcated between two symmetrically equivalent O(4) atoms. Green circles: Be atoms; blue circles: Si atoms; orange circles: O atoms; small black circles: H atoms; hydrogen bonds are shown as dotted lines.

BOND TOPOLOGY

In aminoffite, (SiO_4) groups form linear [Si_3O_{10}] trimers that are linked by ($Be\phi_4$) groups into a sheet of tetrahedra parallel to (001) (Fig. 2). The central (SiO_4) group of each [Si_3O_{10}] trimer, *Si*(2), is four-connected, whereas all other (SiO_4) and ($Be\phi_4$) tetrahedra of the sheet are three-connected, that is, they each have one anion that does not bridge between tetrahedra (Fig. 2). There are four-membered rings of alternating ($Be\phi_4$) and (SiO_4) tetrahedra, and these are linked through the four-connected (SiO_4) tetrahedra to form six-membered rings of tetrahedra. The four-membered rings connect in rows such that their apices alternately point in the +*c* and –*c* directions. The sheets of tetrahedra stack in the [001] direction (Fig. 3), and are linked together by interstitial Ca atoms and by hydrogen bonding between donor O(5) and acceptor O(4) anions of adjacent sheets (Fig. 1).

CHEMICAL FORMULA OF AMINOFFITE

The unit formula derived from the results of electron-microprobe analysis shows that Pb, Mn and As are incorporated into the ideal $Ca_3Be(OH)_2Si_3O_{10}$ structure (Table 2). There is minor compositional zonation in the crystal, with Pb and As varying sympathetically. The data are in reasonable accord with the minor substitutions $Pb^{2+} \rightarrow Ca$, $Mn^{2+} \rightarrow Ca$ and $As^{5+} \rightarrow Si$, although the charge-balance mechanism for the last substitution is not apparent.

Sheet topologies in beryllium minerals

Figure 4 shows graphs of the ($Be\phi_4$)–($T\phi_4$) sheets in minerals, arranged in terms of increasing complexity; *i.e.*, number of distinct vertices and size of the constituent circuits. We will refer to these graphs as "nets" to accord with common usage (*e.g.*, Smith 1977). There

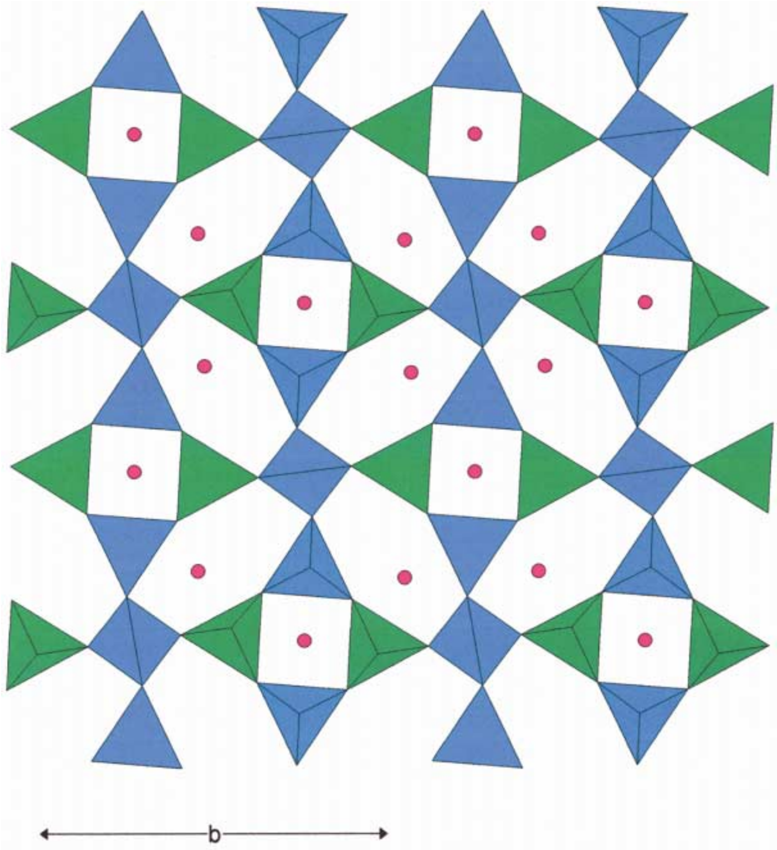


FIG. 2. The sheet of tetrahedra in aminoffite, projected onto (001). ($Be\phi_4$) (green) and ($Si\phi_4$) (blue) tetrahedra link together to form a sheet, the tightly bonded structural unit. The weakly bonded interstitial Ca atoms (small red circles) are at z = ¼ and ¾.

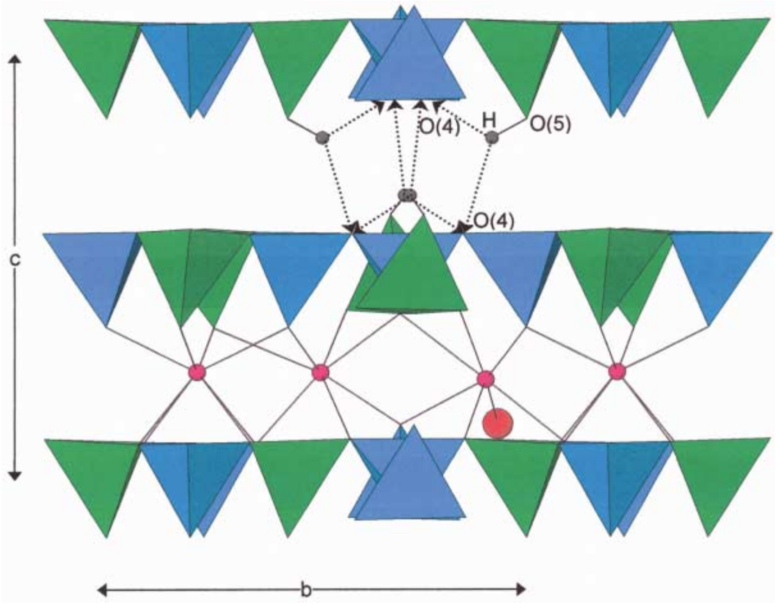
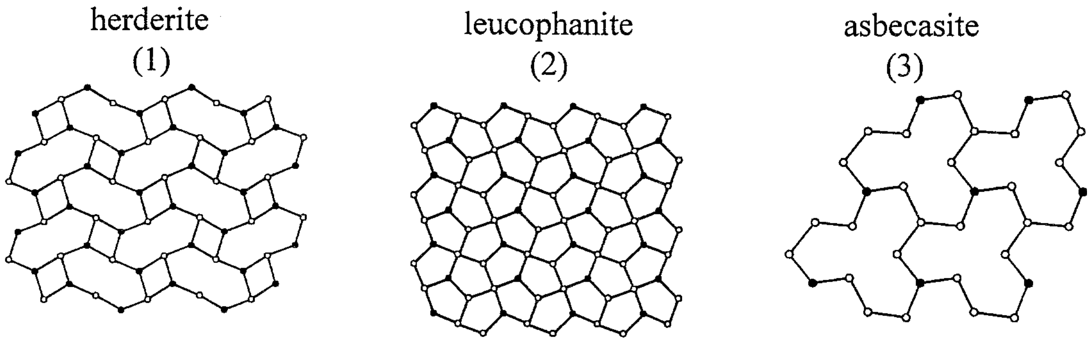


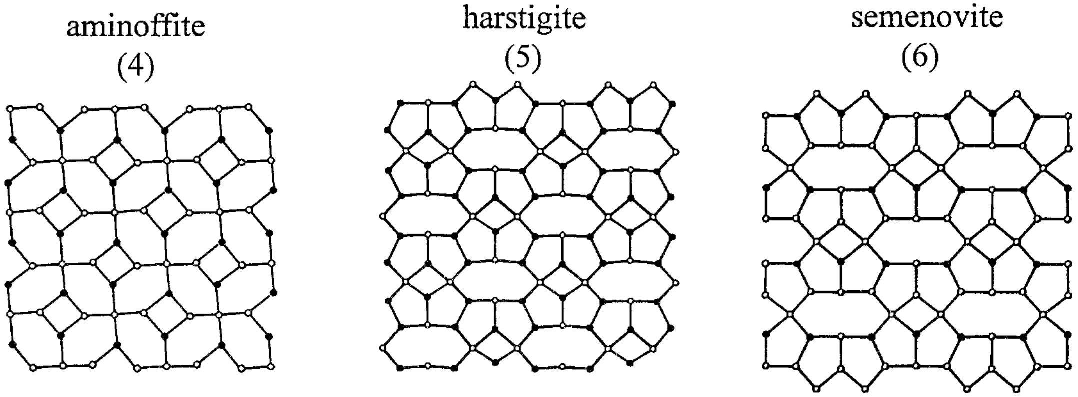
FIG. 3. The structure of aminoffite projected down the *a* axis. Legend as in Figures 1 and 2.

is one net with just one type of vertex, the (4.8^2) net in herderite. The portrayal of this net (1) in Figure 4 does not resemble the usual representations of this net (*e.g.*, Hawthorne & Smith 1988) as we have retained the geometrical arrangement of the polyhedra in the original sheet. However, the Schäffli-type symbol of the net makes this correspondence clear, as the net is actually a graph, and its geometrical characteristics are of no significance. Net (2) is found in leucophanite and has two types of vertices in the ratio of 1:2, $(5^4)\ (5^3)_2$; it is made up of pentagons. Ideal pentagons cannot form a planar two-dimensional net, and the pentagons show significant angular distortion from their holosymmetric form. Net (3) occurs in asbecasite and has two types of vertices in the ratio 3:2, $(12^2)_3\ (12^3)_2$; it is the only net with a two-connected vertex, and is made up of a stellate form of dodecagon. This is an extremely unusual net, but seems somewhat less exotic when one realizes that it can also be described as a 6^3 net with one-sixth of the vertices omitted (Hawthorne & Huminicki 2002). Net (4) occurs in aminoffite; it has two types of vertices in the ratio 1:4, $(6^4)\ (4.6^2)_4$, and consists of squares and hexagons.

Net (5) occurs in harstigite and has three types of vertices in the ratio 1:3:1; it has the symbol $(4.5^2)\ (5^2.8)_3$ (4.5.8.5). It consists of squares, pentagons and octagons, and $(Be\phi_4)$ tetrahedra occupy the (4.5^2) and $(5^2.8)$ vertices. Net (6) of semenovite is also $(4.5^2)\ (5.8^2)_3$ (4.5.8.5), but is colored differently from net (5) [*i.e.*, the $(Be\phi_4)$ and $(T\phi_4)$ tetrahedra correspond to different sets of vertices]. Net (7) of uralolite has four types of vertices in the ratio 2:2:2:1, and consists of triangles, squares and octagons. In the structure of uralolite, the corresponding sheet is quite corrugated in order to maintain reasonable anion–anion distances between tetrahedra. Net (8) of ehrleite has four types of vertices in the ratio 1:2:1:1, and consists of squares and dodecagons. Net (9) of samfowlerite has six types of vertices in the ratio 2:1:5:1:2:1, and consists of squares, pentagons and octagons.

In Table 6, we have indicated which vertices correspond to $(Be\phi_4)$ tetrahedra and which vertices correspond to other $(T\phi_4)$ tetrahedra. In most of the nets, $(Be\phi_4)$ tetrahedra occupy trivalent vertices; only in nets (7) and (8) do they occupy tetravalent vertices. On the other hand, the $(T\phi_4)_2$ tetrahedra occupy divalent, trivalent and tetravalent vertices (in the proportions 2:12:8). Hence we may conclude that $(Be\phi_4)$ tetrahedra have a strong preference for trivalent vertices in two-dimensional nets. This has very interesting crystal-chemical consequences for the identities of the anions coordinating Be. For those anions that bridge tetrahedra in a net, the sum of the incident bond-valences from the net cations is 0.50 (from Be) + 1.00 (from Si) or 1.25 (from As or P) = 1.50 or 1.75 *vu*. The remaining bond-valence required is easily supplied from the interstitial cations. However, for that anion that does not bridge tetrahedra in a net (*i.e.*, for a trivalent vertex, there is one per tetrahedron), the sum of the bond valence incident from the net cations is only 0.50 *vu* (from Be). The remaining


herderite (1) leucophanite (2) asbecasite (3)


aminoffite (4) harstigite (5) semenovite (6)

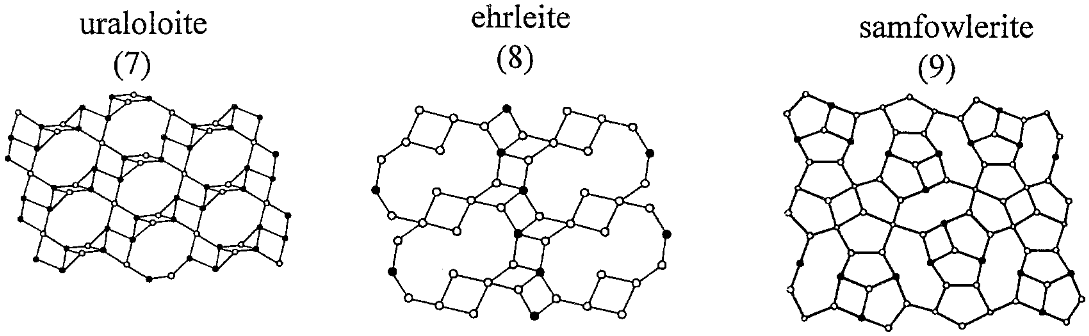

uraloloite (7) ehrleite (8) samfowlerite (9)

FIG. 4. Graphical representations of ($Be\phi_4$)–($T\phi_4$) sheets in Be-bearing minerals; black vertices represent ($Be\phi_4$) tetrahedra, and white vertices represent other ($T\phi_4$) tetrahedra.

TABLE 6. DETAILS OF THE NETS (GRAPHICAL REPRESENTATIONS) OF THE SHEETS IN BERYLLIUM MINERALS WITH TWO-DIMENSIONAL STRUCTURAL UNITS

Mineral	Graph symbol	No. of distinct vertices	$(Be\varphi_4)$	$(T\varphi_4)$
(1) Herderite	(4.8^2)	1	(4.8^2)	(4.8^2)
(2) Leucophanite	$(5^4)\ (5^3)_2$	2	(5^3)	$(5^3)\ (5^4)$
(3) Asbecasite	$(12^2)_2\ (12^3)_3$	2	(12^3)	$(12^2)\ (12^3)$
(4) Aminoffite	$(6^4)\ (4.6^2)_4$	2	(4.6^2)	$(4.6^2)\ (6^4)$
(5) Harstigite	$(4.5^2)\ (5^2.8)_3\ (4.5.8.5)$	3	$(4.5^2)\ (5^2.8)$	$(5^2.8)\ (4.5.8.5)$
(6) Semenovite	$(4.5^2)\ (5^2.8)_3\ (4.5.8.5)$	3	$(4.5^2)\ (5^2.8)$	$(4.5^2)\ (5^2.8)\ (4.5.8.5)$
(7) Uralolite	$(3.4.8)_2\ (3.4^2.8)_2\ (3.4.8.4)_2\ (4.8.4.8)$	4	$(3.4^2.8)\ (3.4.8.4)$	$(3.4.8)\ (4.8.4.8)$
(8) Ehrleite	$(4.12)\ (4^2.12)_2\ (4^3.12)\ (4.12.4.12)$	4	$(4^3.12)$	$(4.12)\ (4^2.12)\ (4.12.4.12)$
(9) Samfowlerite	$(4.5^2)_2\ (4.8^2)\ (5^2.8)_5\ (5^2.8^2)\ (4.5.8)_2\ (4.5.8.5)$	6	$(5^2.8)\ (4.5.8)$	$(4.5^2)\ (4.8^2)\ (5^2.8)\ (5^2.8^2)\ (4.5.8.5)$

1.50 *vu* required by the anion cannot be supplied solely by the interstitial cations as they do not have sufficiently high Lewis acidities to do so. Hence this anion *must* be monovalent, *i.e.*, (OH) or a halogen. Thus in most of the structures of Table 6, the $(Be\phi_4)$ groups are actually acid $\{BeO_3(OH)\}$ groups (*e.g.*, see Table 5 for aminoffite). This type of subtle interaction between structure topology and chemical composition is an area that needs much more extensive investigation.

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