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Bergslagite, a mineral with tetrahedral berylloarsenate sheet anions

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Abstract. The mineral bergslagite, ideal formula $CaBeAsO_4(OH)$, occurs in association with schefferite, tilasite, manganberzeliite, svabite, barite and calcite as veinlets in hematite ore from Långban, Sweden. Its structure has been determined from single crystal X-ray intensities by direct methods. Unit cell parameters: $a = 4.8818(9)$, $b = 7.809(1)$, $c = 10.127(1)$ Å, $\beta = 90.16(1)°$; $Z = 4$. The structure was refined with similar results in space groups $P\bar{1}$ and $P2_1/c$. With $P2_1/c$ symmetry, values of $R = 6.1\,\%$ and $R_w = 7.2\,\%$ were obtained. This mineral is isotypic with datolite, herderite etc. and the structure consists of tetrahedral sheet anions and Ca^{2+} layers stacked along **a**. Be and As atoms alternate at the nodes of the 4 and 8 ring tetrahedral net, except for a minor substitution of As^{5+} by Si^{4+} and probably Be^{2+}. The distances $T-O(nbr)$ are shorter than $T-O(br)$ for both AsO_4 and $BeO_3(OH)$ tetrahedra, but the As centred tetrahedra are more regular. Each $CaO_6(OH)_2$ polyhedron (distorted square antiprism) shares an edge with three more polyhedra to form a polyhedral layer in the *bc* plane. Berylloarsenates structurally related to silicates seem to be rare, in contrast to beryllophosphates.

Introduction

In August 1975 specimens of a hematite ore with thin, filled fissures were collected by one of the authors (SH) on the mine dumps at Långban in Värmland, Sweden. This particular section of the dumps has later been fenced off and is now closed to the public. An inconspicuous grey mineral was later recognized in the specimens by Mr. Samuel Hansen, Markaryd. It occurs as massive aggregates of intergrown crystals, associated with schefferite, tilasite, manganberzeliite, svabite, calcite and barite.

A qualitative EDX analysis with a Philips *EM* 400 electron microscope indicated major amounts of Ca and As, as well as traces of Si. The powder diffraction pattern did not correspond to any known calcium arsenate and therefore a single crystal X-ray structure analysis was undertaken in order to further characterize the material.

A mineralogical description is in preparation and will be published elsewhere. The new mineral having the name bergslagite has been approved by the Commission on New Minerals and Mineral names, IMA.

Experimental

Preliminary Weissenberg photographs yielded rough lattice constants and showed a diffraction symmetry lower than *mmm* with no systematic absences. Powder diffraction data were obtained with a Guinier-Hägg camera with Cu$K\alpha_1$ radiation. The first 51 lines could be indexed on a unit cell of monoclinic geometry and a least-squares refinement, employing 37 single indexed reflections, led to: $a = 4.8818(9)$, $b = 7.809(1)$, $c = 10.127(1)$ Å, $\beta = 90.16(1)^\circ$.

A relationship to datolite, $CaBSiO_4(OH)$ and herderite, $CaBePO_4F$ was indicated by the cell parameter quotients.

Intensity data were collected for one hemisphere ($h > 0$) in reciprocal space out to $\sin\theta/\lambda = 0.70$, with a crystal fragment ($0.062 \times 0.084 \times 0.172$ mm) mounted in a Nicolet *P*3*m* diffractometer, equipped with a graphite monochromator to give Mo$K\alpha$ radiation. Very weak reflections were omitted after a prescan. Peaks were monitored by ω scans with a constant width of 1.0° and a variable scan rate of $1.0 - 12.0^\circ$/min, while backgrounds were measured for a total period equal to the peak scan time. The experimental stability was checked by regular testing of two strong reflections. Data reduction of the intensities and their standard deviations included Lorentz, polarization and absorption corrections ($\mu = 10.5$ mm^{-1}, range of transmission factors $0.44 - 0.55$). When reflections with $|F_o| < 6\sigma(|F_o|)$ were considered unobserved, 2128 structural amplitudes remained.

Structure determination

The positions of 4 As and 4 Ca atoms were taken from the E-map with the highest combined figure of merit, produced by the MULTAN program in space group $P1$. Using least squares refinements based on $|F|$'s and difference Fourier syntheses the model was improved and all non-H atoms were located.

Table 1. Atomic coordinates and thermal parameters, space group $P2_1/c$

	x	y	z	$B_{eq}(\text{Å}^2)$
Ca	0.9985(2)	0.1117(1)	0.3284(1)	0.73(2)
Be	0.5510(15)	0.4147(9)	0.3381(7)	0.62(10)[a]
As	0.4790(1)	0.27511(8)	0.07950(6)	0.41(1)
O(1)	0.2400(9)	0.4137(5)	0.0310(4)	0.99(9)
O(2)	0.6779(9)	0.2897(6)	0.4529(4)	0.97(8)
O(3)	0.6906(9)	0.3452(6)	0.1992(4)	0.93(8)
O(4)	0.3106(9)	0.1044(5)	0.1439(4)	0.99(9)
OH	0.2226(9)	0.4127(6)	0.3308(4)	0.94(9)

[a] B_{iso}

Four low density peaks were assigned to Be because (1) charge compensation required a divalent cation which (2) could not be detected by the qualitative EDX analysis and (3) had the appropriate tetrahedral T—O distances. Since a centre of symmetry was clearly indicated by the positional parameters the space group was changed to $P\bar{1}$, with the improvement that all isotropic temperature factors became positive. Refinement minimizing $\Sigma w(|F_o|-|F_c|)^2$ with weights $w^{-1}=\sigma^2(|F_o|)+(0.01|F_o|)^2+2.0$ and isotropic thermal parameters reached: $R=0.053$, $R_w=0.067$, $S=[\Sigma w(|F_o|-|F_c|)^2/(\text{number of reflections-number of parameters refined})]^{1/2}=1.61$ (66 parameters). Anisotropy led to nonpositive definite temperature factors for some atoms.

Again the coordinates showed a higher symmetry and the following refinements were undertaken in $P2_1/c$. Anisotropic refinement except for Be gave $R=0.062$, $R_w=0.074$, $S=1.81$ (68 parameters, 2106 reflections) after deletion of the weak (6–$20\sigma(|F_o|)$) reflections violating the extinction rules of $P2_1/c$. All temperature factors were positive definite and the e.s.d.'s were reduced. At this stage, a full quantitative chemical analysis had been completed and it gave a composition of $Ca_{1.00}Be_{1.08}Si_{0.08}As_{0.84}O_{3.70}(OH)_{1.30}$. As this formula indicates some substitution of As^{5+} by other ions, an occupancy refinement of the As site was finally undertaken. When the replacement of As by equal amounts of Be and Si was included in the refinement the occupancy factor of As became 0.907(7) and thus 0.093 for (Be+Si). With the occupancy factors fixed to refined values the anisotropic refinement finally converged to $R=0.061$, $R_w=0.072$ and $S=1.68$.

The last difference Fourier map has residual peaks with a maximum height of 2.1 e Å^{-3}. Resulting structural parameters are given in Table 1 and a selection of interatomic distances and angles is presented in Table 2.[1]

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[1] Additional material to this paper can be ordered referring to the no. CSD 50578, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Discussion

This study establishes that bergslagite, $CaBeAsO_4(OH)$, is a new member of the datolite group of structures, which crystallize in $P2_1/c$, with unit cells of nearly orthorhombic geometry. Members of this mineral group are: datolite, $CaBSiO_4(OH)$; bakerite, composition as datolite but ~25% of the SiO_4 tetrahedra are replaced by $BO_3(OH)$; herderite, $CaBePO_4F$; and hydroxyl-herderite $CaBePO_4(OH)$. Another group of minerals e.g. gadolinite, $Y_2Fe^{II}Be_2Si_2O_{10}$ (Foit and Gibbs, 1975); homilite, $Ca_2Fe^{II}B_2Si_2O_{10}$ etc. can be described as filled datolite structures, while drugmanite, $Pb_2(Fe^{III},Al)HP_2O_8(OH)_2$, in addition to the filled iron sites has vacant tetrahedra (King and Sengier-Roberts, 1983).

Our results are not conclusive as to whether bergslagite has the symmetry $P\bar{1}$ or $P2_1/c$. All of the four crystals we have tested so far, exhibit weak but distinct X-ray diffractions that should be absent for $P2_1/c$. The lower *R*-

Table 2. Selected interatomic distances (Å) and angles (°) for bergslagite (*b*). Some average values from hydroxylherderite (*h*) and datolite (*d*) are included for comparison

Symmetry code superscripts:

(none)	x, y, z	(v)	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$
(i)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	(vi)	$1+x, y, z$
(ii)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	(vii)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(iii)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$		
(iv)	$2-x, -\frac{1}{2}+y, \frac{1}{2}-z$		

a) sheet anion

TO_4		TO_3OH	
As–O(1)	1.664(4)	Be–OH	1.605(9)
As–O(3)	1.682(4)	Be–O(4^{iii})	1.638(8)
As–O(2^{ii})	1.688(4)	Be–O(2)	1.638(8)
As–O(4)	1.698(4)	Be–O(3)	1.657(8)
$\langle As-O\rangle_b$	1.683	$\langle Be-O\rangle_b$	1.634
$\langle P-O\rangle_h$	1.541	$\langle Be-O\rangle_h$	1.623
$\langle Si-O\rangle_d$	1.633	$\langle B-O\rangle_d$	1.480
O(3)–As–O(4)	106.0(2)	O(3)–Be–O(4^{iii})	102.7(4)
O(1)–As–O(4)	106.5(2)	O(2)–Be–O(3)	104.6(4)
O(2^{ii})–As–O(3)	106.9(2)	O(2)–Be–O(4^{iii})	107.8(5)
O(2^{ii})–As–O(4)	109.6(2)	O(3)–Be–OH	111.7(5)
O(1)–As–O(2^{ii})	112.0(2)	O(2)–Be–OH	113.8(5)
O(1)–As–O(3)	115.4(2)	O(4^{iii})–Be–OH	115.2(5)
$\langle O-As-O\rangle_b$	109.4	$\langle O-Be-O\rangle_b$	109.3

Table 2 continued

TO_4		TO_3OH	
O(1)–O(4)	2.694(6)	O(3)–O(4^{iii})	2.573(6)
O(3)–O(4)	2.699(6)	O(2)–O(3)	2.607(6)
O(2^{ii})–O(3)	2.707(6)	O(2)–O(4^{iii})	2.646(6)
O(2^{ii})–O(4)	2.767(6)	O(3)–OH	2.700(6)
O(1)–O(2^{ii})	2.780(6)	O(2)–OH	2.716(6)
O(1)–O(3)	2.829(6)	O(4^{iii})–OH	2.738(6)
⟨O–O⟩$_b$	2.746	⟨O–O⟩$_b$	2.663
⟨O–O⟩$_h$	2.514	⟨O–O⟩$_h$	2.648
⟨O–O⟩$_d$	2.662	⟨O–O⟩$_d$	2.417
	tetrahedral	connections	
Be–O(3)–As	117.7(4)	Be–As	2.858(7)
Be–O(2)–As^{i}	120.0(4)	Be–As^{i}	2.881(7)
Be–O(4^{iii})–As^{iii}	123.6(4)	Be–As^{iii}	2.939(7)
⟨Be–O–As⟩$_b$	120.4	⟨Be–As⟩$_b$	2.893
⟨Be–O–P⟩$_h$	123.3		
⟨B–O–Si⟩$_d$	124.3		

b) CaO_8 polyhedron

Ca–O(1^{v})	2.372(4)
Ca–O(1^{vii})	2.405(4)
Ca–O(4^{vi})	2.414(5)
Ca–O(2)	2.447(4)
Ca–OH^{vii}	2.483(4)
Ca–O(3^{iv})	2.591(5)
Ca–OH^{vi}	2.593(5)
Ca–O(3)	2.699(4)
⟨Ca–O⟩$_b$	2.500
⟨Ca–O⟩$_h$	2.491
⟨Ca–O⟩$_d$	2.486

values also favour $P\bar{1}$. The unit cell geometry, well-behaved refinement of anisotropic temperature factors and lower e.s.d.'s support the choice of $P2_1/c$. Finally, the atomic positions in $P\bar{1}$ differ from the higher symmetry only by a few e.s.d.'s and this is the crucial indication that the higher symmetry of the structure and diffraction pattern should be chosen (Herbstein and Marsh, 1982). As a result of the lattice geometry there are not less than eight possible twin laws and at least two were observed on large

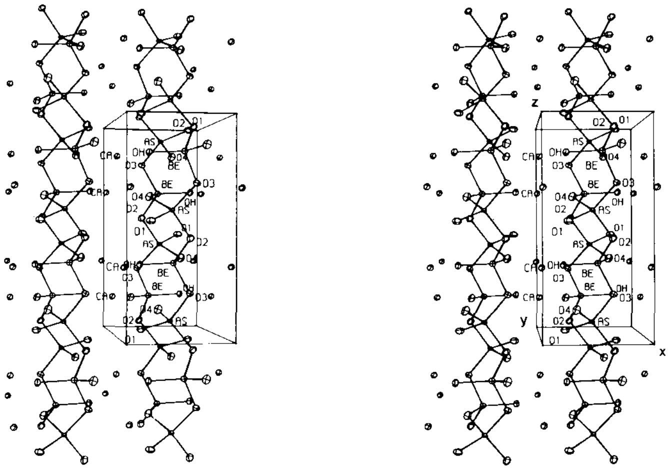

Fig. 1. Stereoplot of the bergslagite structure. Displacement ellipsoids are drawn at the 50% probability level

twinned crystals of hydroxylherderite from Brazil (Dunn et al., 1979). A small twin component is one of the possible explanations for the space group problem and the relatively high residual indexes.

The datolite structure type was first described by Ito and Mori (1953) and the members of this mineral group have been the subject of several investigations. Structural data for comparison with bergslagite were taken from the latest refinements of datolite (Foit et al., 1973) and hydroxylherderite (Lager and Gibbs, 1974). These authors also present theoretical evaluations of $T-O$ distance variations as well as literature references.

One part of the bergslagite structure consists of a sheet of corner-connected $BeO_3(OH)$ and AsO_4 tetrahedra situated at $x \sim 0.5$. Between two of these sheets, a layer of Ca^{2+} ions at $x \sim 0$ is sandwiched, see Fig. 1. The anion $[BeAsO_4(OH)]_n^{2n-}$ has T_2O_5 stoichiometry and forms a three-connected two-dimensional net with Be and As alternating at the nodes, Fig. 2. This type of net is well known among the phyllosilicates. Berylloarsenate structures analogous with silicates seem to be rare, while several beryllophosphate minerals containing tetrahedral anions with varying degrees of corner-sharing have been described. Asbecasite, $Ca_3(Ti,Sn)As_6Si_2Be_2O_{20}$, has a layer anion, but it is built of BeO_4 and SiO_4 tetrahedra plus $As^{III}O_3$ triangular pyramids, not $As^{V}O_4$ tetrahedra (Cannillo et al., 1969). The structures of bearsite, $Be_2AsO_4(OH) \cdot 4H_2O$ and the isotypic moraesite $Be_2PO_4(OH) \cdot 4H_2O$ are unknown.

Chemical and structural analyses of bergslagite indicate the replacement of some AsO_4^{3-} tetrahedra with $SiO_3(OH)^{3-}$ and $BeO(OH)_3^{3-}$. This is comparable to the substitution of SiO_4^{4-} with $BO_3(OH)^{4-}$ in bakerite, but the

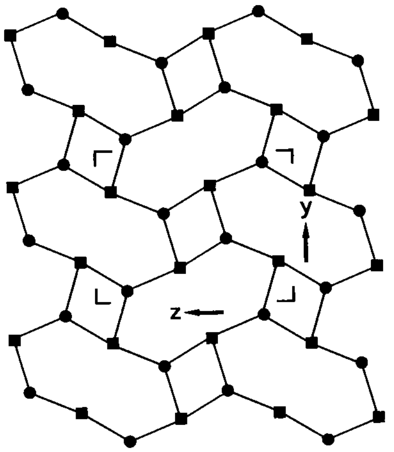

Fig. 2. The three-connected 2D-net of the anion. Only the tetrahedral nodes are included, dots for Be and squares for As atoms

introduction of $BeO(OH)_3^{3-}$ for AsO_4^{3-} in bergslagite leads to Be-(OH)-Be connections between tetrahedra, an arrangement existing in β-$Be(OH)_2$ which has a structure with a tetrahedral framework of cristobalite type (Seitz et al., 1950). The small influence of this solid solution on bond lengths etc. is neglected in the following discussion.

The series datolite, hydroxyl-herderite and bergslagite shows an increasing unit cell volume: 354, 360, 386 Å^3, which can be compared to the variation of tetrahedral dimensions in Table 2. If the regularity of tetrahedra is estimated by the tetrahedral angle variance, $\sigma^2 = \left[\sum_{i=1}^{6} (\theta_i - 109.47°)^2\right] / 5$ (Robinson et al., 1971) the result is: datolite $\sigma_B^2 = 3.5$, $\sigma_{Si}^2 = 17.9$ deg^2; hydroxyl-herderite, $\sigma_{Be}^2 = 12.9$, $\sigma_P^2 = 5.3$ deg^2; bergslagite, $\sigma_{Be}^2 = 25.8$, $\sigma_{As}^2 = 13.8$ deg^2. In the latter two the $TO_3(OH)$ tetrahedron is less regular than the TO_4 tetrahedron, while in datolite the situation is the reverse. Datolite also differs when $T-O$ distances, involving bridging and non-bridging O atoms, are compared. In bergslagite we have: As$-$O(nbr) = 1.664, $\langle$As$-$O(br)$\rangle_3$ = 1.689, Be$-$O(nbr) = 1.605, $\langle$Be$-$O(br)$\rangle_3$ = 1.644 Å and similarly in hydroxyl-herderite: P$-$O(nbr) = 1.513, $\langle$P$-$O(br)$\rangle_3$ = 1.550, Be$-$O(nbr) = 1.602, $\langle$Be$-$O(br)$\rangle_3$ = 1.630 Å, i.e. the distance to a non-bridging O atom is shorter than the distance to a bridging O atom. In datolite Si$-$O(nbr) = 1.570, $\langle$Si$-$O(br)$\rangle_3$ = 1.653 Å follows the pattern, while for the B centred tetrahedron $\langle$B$-$O(br)$\rangle_3$ = 1.475 Å is shorter than B$-$O(nbr) = 1.496 Å.

A very accurate prediction of the distance As$-$Be is obtained from the sum of non-bonded radii: $R(\mathrm{As}) + R(\mathrm{Be}) = (1.54 + 1.35)$ Å $= 2.89$ Å (O'Keeffe and Hyde, 1981) since the average As – Be distance observed in this mineral is 2.893 Å.

Ca coordinates six O atoms and two OH groups in a distorted square antiprism. Each CaO_8 polyhedron shares an edge with three other polyhedra of the same kind and thus a polyhedral layer in the *bc* plane is formed. The ⟨Ca – O⟩ distances show little variation in the three structures.

Note added in proof

Further chemical analyses gave a slightly modified composition: $Ca_{0.99}Be_{1.02}Si_{0.08}As_{0.87}O_{3.70}(OH)_{1.30}$ (Hansen et al., 1984). This formula shows a better agreement with the occupancy factor (0.91) for As, as obtained in the least-squares refinements, but it also indicates that the degree of substitution of As^{5+} by Be^{2+} is negligible.

References

Cannillo, E., Giuseppetti, G., Tadini, C.: The crystal structure of asbecasite. Atti. Accad. Naz. Lincei. R. C., Cl. Sci. fis. mat. nat., **46**, 457 – 467 (1969)

Dunn, P. J., Wolfe, C. W., Leavens, P. B., Wilson, E. W.: Hydroxyl-herderite from Brazil and a guide to species nomenclature for the herderite/hydroxylherderite series. Mineralogical Record, **10**, 5 – 11 (1979)

Foit Jr., F. F., Gibbs, G. V.: Refinement of $NiYb_2Be_2Si_2O_{10}$, a gadolinite-type structure. Z. Kristallogr. **141**, 375 – 386 (1975)

Foit Jr., F. F., Phillips, M. W., Gibbs, G. V.: A refinement of the crystal structure of datolite, $CaBSiO_4(OH)$. Am. Mineral. **58**, 909 – 914 (1973)

Hansen, S., Fälth, L., Petersen, O. V., Johnsen, O.: Bergslagite, a new mineral species from Långban, Sweden. Neues Jahrb. Mineral. Monatsh. (in press)

Herbstein, F. H., Marsh, R. E.: Changes in space and Laue groups of some published crystal structures. Acta Crystallogr. **B38**, 1051 – 1055 (1982)

Ito, T., Mori, H.: The crystal structure of datolite. Acta Crystallogr. **6**, 24 – 32 (1953)

King, G. S. D., Sengier-Roberts, L.: Crystal structure of drugmanite, $Pb_2(Fe^{3+}, Al)H(PO_4)_2(OH)_2$. Eight European Crystallographic Meeting, abstracts, p. 111, Liège 1983

Lager, G. A., Gibbs, G. V.: A refinement of the crystal structure of herderite, $CaBePO_4OH$. Am. Mineral. **59**, 919 – 925 (1974)

O'Keeffe, M., Hyde, B. G.: The role of nonbonded forces in crystals. In: *Structure and bonding in crystals*, part I (Eds. M. O'Keeffe and A. Navrotsky), p. 227 – 254. New York: Academic Press 1981

Robinson, K., Gibbs, G. V., Ribbe, P. H.: Quadratic elongation: A quantitative measure of distortion in coordination polyhedra. Science, **172**, 567 – 570 (1971)

Seitz, A., Rösler, U., Schubert, K.: Kristallstruktur von β-$Be(OH)_2$. Z. Anorg. Chem. **261**, 94 – 105 (1950)