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FLUORINE–HYDROXYL VARIATION IN HAMBERGITE: A CRYSTAL-STRUCTURE STUDY

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ABSTRACT

The structure of five crystals of hambergite, *a* 9.654(2) – 9.776(3), *b* 12.194(2) – 12.364(4), *c* 4.430(1) – 4.440(2) Å, *V* 528.1(2) – 530.5(2) $Å^3$, space group *Pbca*, has been refined to *R* indices in the range 3.2 – 4.2% and *wR* indices 3.3 – 5.4% for 555 – 770 observed $[|F| \geq 5\sigma|F|]$ unique reflections collected using graphite-monochromated Mo$K\alpha$ X-radiation. The structure of hambergite contains two unique $BeO_3(OH)$ tetrahedra and one BO_3 triangle, which share anions to form modulated sheets parallel to (100); these sheets link to form a framework structure by sharing OH anions, and hydrogen bonds link adjacent OH positions. Considerable F ↔ OH substitution is exhibited by hambergite. The range 0 to 0.5 F atoms per formula unit is observed. The F ↔ OH substitution causes a linear decrease of the *a* unit-cell dimension, and a linear increase in the *b* and *c* dimensions. Bond-length variations with F ↔ OH substitution are in good agreement with expected trends from sums of ionic radii. The F ↔ OH mechanism of substitution predicts a maximum of approximately 50% replacement of OH by F in the structure, in accord with the maximum F content encountered in nature.

Keywords: hambergite, borate, beryllium, hydrogen bond, crystal structure.

SOMMAIRE

Nous avons déterminé la structure de cinq cristaux de hambergite, *a* 9.654(2) – 9.776(3), *b* 12.194(2) – 12.364(4), *c* 4.430(1) – 4.440(2) Å, *V* 528.1(2) – 530.5(2) $Å^3$, groupe spatial *Pbca*, jusqu'à un résidu *R* entre 3.2 et 4.2% (*wR* entre 3.3 et 5.4%) en utilisant entre 555 et 770 réflexions observées $[|F| \geq 5\sigma|F|]$ avec rayonnement Mo$K\alpha$ (monochromatisation au graphite). La structure contient deux tétraèdres $BeO_3(OH)$ uniques et un triangle BO_3 qui forment des feuillets modulés parallèles à (100) par partage d'anions; ces feuillets sont liés pour former une charpente par partage d'anions OH et par liaisons hydrogène impliquant les positions OH adjacentes. Cette espèce fait preuve d'une substitution F ↔ OH importante, allant de 0 à 0.5 atomes F par unité formulaire. La substitution F ↔ OH est responsable d'une diminution dans le paramètre *a*, et d'une augmentation linéaire des paramètres *b* et *c*. Les variations en longueurs de liaisons avec le degré de substitution F ↔ OH concordent bien avec celles qui sont attendues selon la somme des rayons ioniques. Le mécanisme de substitution F ↔ OH prédit jusqu'à environ 50% de remplacement de OH par F dans la structure, ce qui concorde bien avec le taux d'incorporation maximum observé dans la nature.

(Traduit par la Rédaction)

Mots-clés: hambergite, borate, béryllium, liaison hydrogène, structure cristalline.

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INTRODUCTION

Hambergite, $Be_2(BO_3)(OH,F)$, occurs in granitic pegmatites at several localities, including near Halgaråen, Langesundsfjord, Norway, at Anjanabanoana, Madagascar, at Sušice, Ctidružice and Kracovice, Czech Republic, the Little Three and Himalaya mines in San Diego County, California, in gem gravels from Kashmir, India, and in several pocket pegmatites with abundant elbaite in Russia, Pakistan, Italy and the U.S.A. The crystal structure of hambergite was solved by Zachariasen (1931) and later refined by Zachariasen *et al.* (1963), and Vergnoux & Ginouvès (1955) reported infrared spectra for hambergite. Switzer *et al.* (1965) examined hambergite crystals from several localities, and found that considerable F may substitute for OH in the structure. Samples of hambergite from the Little Three mine have the highest reported F content at 6.0 wt%.

In order to investigate the effects of F↔OH substitution upon the crystal structure of hambergite, and to assess the possibility of a complete solid-solution series from $Be_2(BO_3)OH$ to $Be_2(BO_3)F$, we have undertaken a crystal-structure study of five crystals. Four of the crystals studied are from pegmatites in the Czech Republic: Sušice (HM2), Ctidružice (HM3) and Kracovice (HM4, HM5). The other crystal is from the Himalaya mine, California (HM1).

EXPERIMENTAL

Collection of X-ray data

Each of the five crystals of hambergite was mounted on a Nicolet $R3m$ automated four-circle diffractometer. For each crystal, approximately thirty reflections in the range $8° \leq 2\theta \leq 58°$ were centered using graphite-monochromated Mo$K\alpha$ X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the automatically aligned reflections by least-squares techniques. Data were collected using the θ–2θ scan mode with a 2.2° 2θ scan range and a variable scan-rate ranging from 4° to 29.3° 2θ/min. A total of 1799–2115 reflections was measured over the range $3° \leq 2\theta \leq 60°$; the index ranges $0 \leq h \leq 13$, $-17 \leq k \leq 17$, $0 \leq l \leq 6$ were covered, giving two asymmetric units. Two standard reflections were measured every 50 reflections; no significant change in their intensities occurred during data collection. An empirical absorption-correction based on 36 psi-scans for each of nine to eleven reflections over the range $10° \leq 2\theta \leq 60°$ was applied; the resulting R azimuthal values range from 1.2 to 2.2% (Table 1). The data were corrected for Lorentz, polarization and background effects, and symmetry-equivalent reflections were merged, giving R_{INT} values ranging from 1.1 to 5.4%

TABLE 1. MISCELLANEOUS INFORMATION FOR HAMBERGITE

	HM1	HM2	HM3	HM4	HM5
Locality	Himalaya	Sušice	Ctidružice	Kracovice	Kracovice
a (Å)	9.776(3)	9.754(2)	9.678(2)	9.663(4)	9.654(2)
b (Å)	12.194(2)	12.231(2)	12.313(2)	12.364(4)	12.347(2)
c (Å)	4.430(1)	4.4340(9)	4.439(1)	4.440(2)	4.4364(9)
V (Å^3)	528.1(2)	529.0(1)	528.9(2)	530.5(2)	528.8(2)
Space Group	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*
Z	8	8	8	8	8
R_{az} (%)	1.3→1.1	1.3→1.2	3.7→1.7	1.7→1.6	4.1→2.2
Total Ref.	1799	2115	1809	1802	1813
$\lvert F_o\rvert \geq 5\sigma\lvert F\rvert$	645	555	645	770	611
R_{INT} (%)	5.4	1.1	2.9	2.3	3.1
Final R (%)	4.2	3.2	3.4	3.2	3.2
Final wR (%)	5.4	3.3	3.7	3.5	3.4
Final S	1.04	0.70	0.70	0.73	0.68

$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$

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

$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m - n)]^{½}$, for m observations and n parameters

TABLE 2. ATOMIC PARAMETERS FOR HAMBERGITE

		HM1	HM2	HM3	HM4	HM5
Be(1)	x	0.0030(3)	0.0028(2)	0.0033(3)	0.0039(3)	0.0040(2)
	y	0.1885(3)	0.1887(2)	0.1894(2)	0.1893(2)	0.1893(2)
	+z	0.2632	0.2632	0.2632	0.2632	0.2632
	*$U_{eq.}$	70(7)	76(5)	102(5)	80(6)	81(5)
Be(2)	x	0.2376(3)	0.2374(3)	0.2384(3)	0.2386(3)	0.2383(2)
	y	0.0679(3)	0.0675(2)	0.0667(2)	0.0666(2)	0.0660(2)
	z	0.2767(7)	0.2773(5)	0.2798(5)	0.2812(6)	0.2800(5)
	$U_{eq.}$	75(7)	77(5)	100(5)	80(6)	80(5)
B	x	0.1063(3)	0.1063(2)	0.1077(2)	0.1079(2)	0.1081(2)
	y	0.1072(2)	0.1074(2)	0.1090(2)	0.1096(2)	0.1093(1)
	z	0.7729(6)	0.7739(5)	0.7762(4)	0.7780(5)	0.7775(4)
	$U_{eq.}$	62(6)	67(5)	99(5)	81(5)	75(4)
O(1)	x	0.0372(2)	0.0377(1)	0.0375(1)	0.0376(2)	0.0375(1)
	y	0.1877(1)	0.1879(1)	0.1885(1)	0.1887(1)	0.1887(1)
	z	0.6192(4)	0.6201(3)	0.6235(3)	0.6244(3)	0.6244(3)
	$U_{eq.}$	79(5)	78(3)	104(3)	86(4)	84(3)
O(2)	x	0.1009(2)	0.1017(1)	0.1033(1)	0.1039(1)	0.1039(1)
	y	0.1026(1)	0.1032(1)	0.1045(1)	0.1052(1)	0.1052(1)
	z	0.0825(4)	0.0830(3)	0.0857(3)	0.0868(3)	0.0867(3)
	$U_{eq.}$	76(4)	76(3)	103(3)	87(3)	86(3)
O(3)	x	0.1871(2)	0.1870(1)	0.1880(1)	0.1884(1)	0.1883(1)
	y	0.0342(1)	0.0346(1)	0.0363(1)	0.0366(1)	0.0367(1)
	z	0.6175(4)	0.6177(3)	0.6209(3)	0.6215(3)	0.6215(3)
	$U_{eq.}$	79(5)	78(3)	109(3)	94(4)	90(3)
O(4)	x	0.3400(2)	0.3409(1)	0.3442(1)	0.3451(1)	0.3449(1)
	y	0.1731(2)	0.1716(1)	0.1672(1)	0.1659(1)	0.1660(1)
	z	0.2952(4)	0.2950(3)	0.2950(3)	0.2951(4)	0.2951(3)
	$U_{eq.}$	0.96(5)	103(4)	140(4)	127(4)	131(3)
H	x	0.814(4)	0.816(3)	0.808(4)	0.812(6)	0.816(5)
	y	0.216(4)	0.214(2)	0.205(4)	0.196(4)	0.195(4)
	z	0.075(11)	0.077(8)	0.121(10)	0.094(15)	0.046(14)
	+$U_{eq.}$	200	200	200	200	200

*$U_{eq.} = U_{equiv.}$x10^4
\+ fixed during refinement

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR HAMBERGITE

	HM1	HM2	HM3	HM4	HM5
Be(1)-O(1)	1.612(2)	1.619(1)	1.634(1)	1.637(2)	1.635(1)
Be(1)-O(2)	1.629(3)	1.632(3)	1.628(2)	1.621(3)	1.619(2)
Be(1)-O(1)a	1.672(4)	1.673(3)	1.660(2)	1.662(2)	1.658(2)
Be(1)-O(4)b	1.625(4)	1.613(3)	1.585(3)	1.583(3)	1.584(3)
<Be(1)-O>	1.634	1.634	1.627	1.626	1.624
Be(2)-O(2)	1.644(4)	1.639(3)	1.633(3)	1.633(3)	1.629(3)
Be(2)-O(3)	1.641(4)	1.637(3)	1.634(3)	1.630(3)	1.630(3)
Be(2)-O(4)	1.629(4)	1.627(3)	1.608(3)	1.603(3)	1.609(3)
Be(2)-O(3)c	1.609(4)	1.614(3)	1.616(3)	1.622(3)	1.614(3)
<Be(2)-O>	1.631	1.629	1.623	1.622	1.620
B-O(1)	1.373(3)	1.371(2)	1.370(2)	1.373(3)	1.374(2)
B-O(3)	1.375(3)	1.375(2)	1.372(2)	1.379(3)	1.372(2)
B-O(2)d	1.374(3)	1.372(3)	1.375(2)	1.373(3)	1.373(2)
<B-O>	1.374	1.373	1.372	1.375	1.373
H-O(4)f	0.81(5)	0.81(3)	0.69(4)	0.69(6)	0.84(6)
H···· O(4)e	2.14(5)	2.18(3)	2.45(4)	2.45(6)	2.30(6)
O(4)f-H···· O(4)e	155(4)	156(3)	140(4)	145(6)	146(5)
O(4)f-O(4)e	2.903(3)	2.931(2)	3.014(2)	3.042(2)	3.036(2)
O(1)-Be(1)-O(2)	110.8(2)	110.5(1)	110.4(1)	110.6(2)	110.7(1)
O(1)-Be(1)-O(1)a	109.7(2)	109.5(1)	109.3(1)	109.2(1)	109.2(1)
O(1)-Be(1)-O(4)b	111.0(2)	111.2(1)	110.8(1)	110.6(1)	110.5(1)
O(2)-Be(1)-O(1)a	106.0(2)	105.8(1)	106.4(1)	106.7(1)	106.7(1)
O(2)-Be(1)-O(4)b	115.0(2)	114.7(1)	112.9(1)	112.4(1)	112.4(1)
O(1)a-Be(1)-O(4)b	103.9(1)	104.8(1)	106.8(1)	107.2(1)	107.1(1)
<O-Be(1)-O>	109.4	109.4	109.4	109.4	109.4
O(2)-Be(2)-O(3)	107.5(2)	107.9(2)	108.4(2)	108.6(2)	108.6(2)
O(2)-Be(2)-O(4)	108.9(2)	108.5(2)	108.2(1)	108.0(2)	107.7(1)
O(2)-Be(2)-O(3)c	110.0(2)	110.2(2)	110.2(1)	110.2(2)	110.7(1)
O(3)-Be(2)-O(4)	109.6(2)	109.5(2)	109.1(2)	109.2(2)	108.7(1)
O(3)-Be(2)-O(3)c	110.3(2)	110.6(1)	110.9(1)	110.8(2)	111.2(1)
O(4)-Be(2)-O(3)c	110.5(2)	110.1(2)	110.0(2)	109.9(2)	109.9(2)
<O-Be(2)-O>	109.5	109.5	109.5	109.4	109.5
O(1)-B-O(3)	119.8(2)	119.6(2)	119.9(2)	119.7(2)	119.8(2)
O(1)-B-O(2)d	120.4(2)	120.5(2)	120.5(2)	120.7(2)	120.4(2)
O(3)-B-O(2)d	119.7(2)	119.8(2)	119.5(2)	119.6(2)	119.8(2)
<O-B-O>	120.0	120.0	120.0	120.0	120.0
Be(1)f-O(4)-Be(2)	133.3(2)	134.5(2)	138.1(2)	139.1(2)	138.9(1)

a = x, ½-y, z-½; b = x-½, y, -z+½; c = ½-x, -y, -½+z; d = x, y, z+1;
e = ½+x, ½-y, -z; f = x+½, y, ½-z

TABLE 4. FLUORINE CONTENT* OF HAMBERGITE DETERMINED BY EMPA AND SREF

	EMPA			SREF
	Points	At.% F	F apfu	F at OH(4)
HM1	12	0.14(1)	0.01(1)	0.06(5)
HM2	15	1.89(10)	0.09(1)	0.07(3)
HM3	0	-	-	0.30(4)
HM4	7	7.01(85)	0.35(4)	0.41(5)
HM5	0	-	-	0.48(3)

*σ given in brackets; - = not determined

(Table 1). The total number of unique observed reflections [$|F| \geq 5\sigma\,|F|$] ranged from 555 to 770 (Table 1).

Refinement of the crystal structures

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study; *R* indices are of the form given in Table 1 and are expressed as percentages.

Each refinement was done in the space group *Pbca*, with starting atomic coordinates taken from Zachariasen *et al.* (1963). The final cycles of refinement included atomic coordinates, anisotropic-displacement parameters, and site-scattering parameters for the O(4) site. The occupancy of the O(4) site was refined using the scattering factors for O, H and F with the constraint that O + F = 1, and H = O. The difference in the shapes of the scattering curves, as well as the height of the curves, was used in the determination. F is the heaviest element in hambergite, and absorption effects are not very significant. Therefore, we contend that the F contents derived from site-scattering refinements give a reasonable estimate of the F content of the hambergite crystals. An empirical isotropic-extinction correction and refinable structure-factor weighting scheme was tried for each refinement, but neither improved the results of the refinements. Final *R* indices (Table 1) range from 3.2% to 4.2%, and *wR* indices, from 3.3% to 5.4%. Refined positional parameters and equivalent isotropic-displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3, refined site-scattering values in Table 4, and a bond-valence analysis is given in Table 5. Anisotropic-displacement parameters and structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A OS2.

TABLE 5. BOND-VALENCE* ANALYSIS FOR HAMBERGITE (HM1)

	Be(1)	Be(2)	B	H	Σ
O(1)	0.536 0.455		0.995		1.986
O(2)	0.511	0.491	0.992		1.994
O(3)		0.495 0.540	0.989		2.024
OH(4)	0.517	0.512		0.8 0.2	2.029
Σ	2.019	2.038	2.976	1.0	

* parameters from Brown & Altermatt (1985)

Electron-microprobe analysis

The chemical composition of hambergite cannot be properly determined using an electron microprobe owing to the presence of light elements. However, in most cases, we did not have sufficient sample for other analytical techniques, and optical examination indicates that chemical heterogeneities occur within some larger crystals of hambergite. Therefore, despite its obvious inadequacies for this material, the electron microprobe was used to establish the F content of three of the hambergite crystals for which X-ray data were collected. The other two crystals were lost during the remounting and polishing process. The crystals were remounted, polished, carbon-coated and analyzed using a CAMECA SX–50 instrument in the wavelength-dispersion mode. Beam conditions were 15 kV, beam current 20 nA, and a spot diameter of 10 μm. Topaz was used as the standard for F; peak heights were used for the analyses. Peak scans for F-rich hambergite and the topaz standard gave very similar profile shapes, with ratios of peak area to peak height of 13.2 for the hambergite and 13.3 for the topaz. The matrix was assumed to be stoichiometric amounts of Be, B and O for purposes of data reduction. The results of the analyses, compared to the F contents derived from site-scattering refinements, are given in Table 4.

DESCRIPTION OF THE STRUCTURE

This work confirms the structure for hambergite reported by Zachariasen (1931) and refined by Zachariasen *et al.* (1963). In the structure description that follows, reference will be made only to hambergite HM1, which contains very little F. However, the structural connectivity of each of the hambergite crystals studied here is identical to that in crystal HM1; only minor changes in bond lengths occur with increasing F content.

$BeO_3(OH)$ and BO_3 polyhedra: The structure of hambergite contains two distinct Be positions, each of which is tetrahedrally coordinated by three O atoms and an OH group. The <Be-ϕ> (ϕ: O^{2-}, OH^-, F^-) distances, 1.634 and 1.631 Å, are within the range typically observed for $^{[4]}$Be–O, and both site-scattering refinement and the bond-valence analysis (Table 5) indicate that there is no significant substitution of another cation at either Be site. The structure contains a single B position, which is triangularly coordinated by three O atoms. The <B–O> distance is 1.374 Å, a value typical of $^{[3]}$B–O.

Structure connectivity: A projection of the structure of hambergite down [001] shows that it is a framework

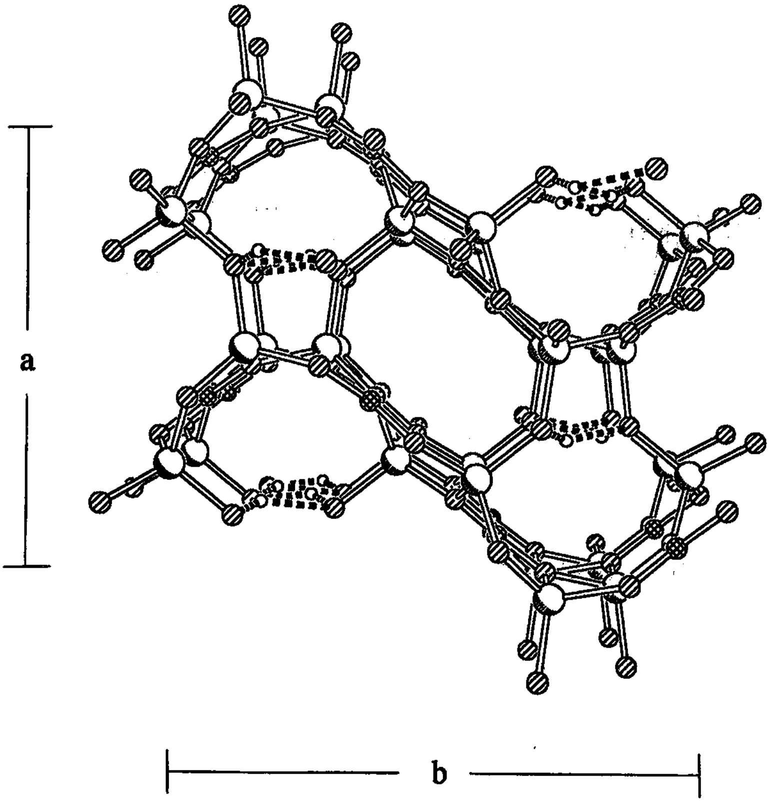

FIG. 1. The structure of hambergite projected down [001]. B atoms are shown as cross-hatched circles, Be atoms as open circles with shading in the lower left, O atoms as circles shaded with parallel lines, H atoms are shown as small open circles. Hydrogen bonds are shown as broken heavy lines.

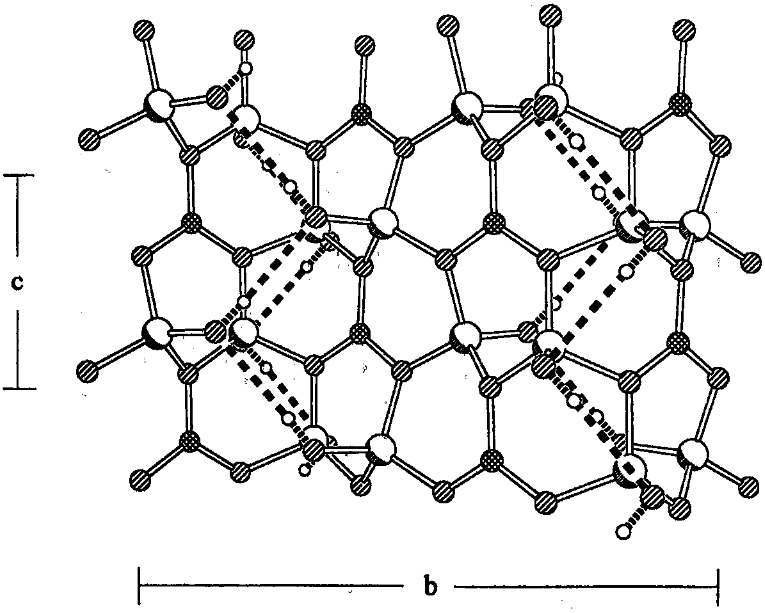

FIG. 2. The structure of hambergite projected down [100]. Legend as in Figure 1.

structure (Fig. 1); the Beϕ_4 tetrahedra and BO_3 triangles share corners to form modulated sheets parallel to (100). The details of one of these sheets are shown in Figure 2. Each O atom bonds to one B atom and two Be atoms, resulting in a highly connected sheet. Each Be atom also bonds to one OH group located either above of below the sheet (Fig. 1). Adjacent sheets are connected through these OH groups, which bond to two Be atoms, one in each adjacent sheet (Fig. 1).

Hydrogen bonding: There is one H position in the structure of hambergite. The O(4) atom is the donor anion, and both the refined H position and the bond-valence analysis indicate that O(4) also accepts the hydrogen bond. The O(4)f–H...O(4)e bond has donor and acceptor distances of 0.81(5) and 2.14(5) Å, respectively, with a bond angle of 155(4)°. These distances indicate that it is a moderately strong hydrogen bond. As each O(4) atom donates and accepts a hydrogen bond, there is a zig-zag chain of hydrogen bonds along [001] both above and below the sheets of Beϕ_4 tetrahedra and BO_3 triangles (Fig. 2).

F↔OH SUBSTITUTION

Variation of unit-cell dimensions with F↔OH substitution

Switzer *et al.* (1965) reported unit-cell dimensions for several crystals of hambergite, including samples that contain significant amounts of F. Their data indicate that F↔OH substitution in the structure of hambergite causes the unit cell to expand in both the *b* and *c* directions, whereas the *a* dimension remains essentially constant. Switzer *et al.* (1965) concluded that the observed variation of unit-cell dimensions occurs because the hydrogen bonds in the structure lie within the *bc* plane, and do not have a component in the *a* direction; thus, removal of hydroxyl groups presumably causes unit-cell expansion only in the *b* and *c* directions.

Figure 3 shows the variation of unit-cell dimensions with extent of F↔OH substitution as obtained by site-scattering refinement of the X-ray data for the five crystals studied here. Both the *a* and *b* dimensions vary linearly (r = 0.977 and 0.965, respectively) with increasing F content (Fig. 3); there is a significant decrease (0.12 Å) in the *a* dimension, and a significant expansion (0.17 Å) of the *b* dimension with increasing F (Fig. 3). The *c* dimension increases slightly (0.01 Å) with increasing F (Fig. 3). These trends are in contrast to those reported by Switzer *et al.* (1965), who stated that the *a* dimension is essentially unaffected by F↔OH substitution.

Examination of the structure of hambergite (Figs. 1, 2) shows that all the hydrogen bonds are in the *bc* plane. As F replaces the hydroxyl group, hydrogen bonds are lost. The largest component of the hydrogen bond is along *c*, with a somewhat lesser component along *b*. However, in the crystals studied, the increase in proportion of F has caused the *c* dimension to increase by only 0.2%, whereas the *b* dimension has increased by 1.4%. As hydrogen

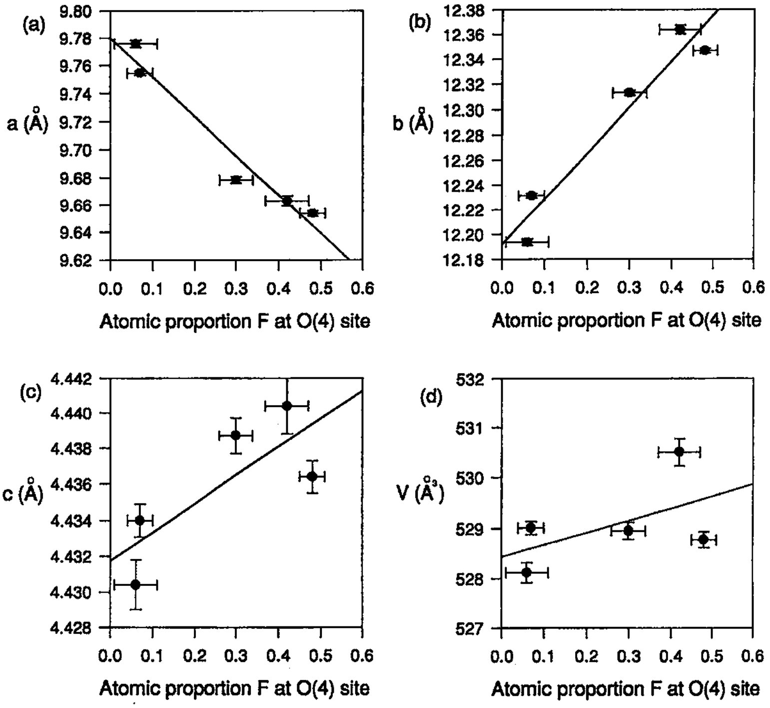

FIG. 3. The effect of F↔OH substitution upon the unit-cell dimensions of hambergite. (a) the a unit-cell dimension, the best-fit line is $a = -0.2813\mathrm{F} + 9.7798$, $r = 0.977$; (b) the b unit-cell dimension, the best-fit line is $b = 0.3669\mathrm{F} + 12.1921$, $r = 0.965$; (c) the c unit-cell dimension, the best-fit line is $c = 0.0158\mathrm{F} + 4.4318$, $r = 0.782$; (d) the unit-cell volume, the best-fit line is $V = 2.37\mathrm{F} + 528.44$, $r = 0.528$. Units: a, b and c in Å, V in Å^3.

bonds are removed, the sheets of Beϕ_4 tetrahedra and BO_3 triangles tend to flatten somewhat, causing a larger expansion along the b direction.

The increase of F substitution for OH causes a significant decrease in the a dimension; in the crystals studied, the reduction is 1.2%. As the hydrogen bonds are in the bc plane, another factor must affect the a dimension. The sheets of Beϕ_4 tetrahedra and BO_3 triangles in the structure of hambergite link through the OH group (Fig. 1), and there are four Be–O(4) bonds along the a direction per unit cell. The ionic radii of $^{[2]}\mathrm{F}^-$ and $^{[3]}\mathrm{O}^{2-}$ are 1.285 and 1.36 Å, respectively (Shannon 1976); thus the reduction of the a dimension that occurs with increasing F may be attributed to the smaller size of the F^- anion. Assuming 50% of the O(4) anions have been replaced by F, anion size alone could account for a shortening of the a dimension of ~0.15 Å, comparable with the maximum shortening of 0.12 Å that is observed (Fig. 3).

Bond-length variations with F↔OH substitution

Each (OH, F) anion bonds to one Be(1) and one Be(2) atom, and substitution of F at the O(4) site will be reflected by a decrease in the Be–O(4) bond lengths. The values of <Be–O(4)> for each crystal studied are plotted as a function of F/(F + OH) in Figure 4. The <Be–O(4)> distance decreases with increasing F in a linear fashion ($r = 0.934$).

Sums of ionic radii for $^{[4]}\mathrm{Be}^{2+}$, $^{[2]}\mathrm{F}^-$ and $^{[3]}\mathrm{O}^{2-}$ from Shannon (1976) give expected Be–OH and Be–F bond lengths of 1.63 and 1.555 Å, respectively. The sum of the constituent ionic radii is shown as a broken line in Figure 4; this is the hard-sphere model for bond-length variations in crystals. The best-fit line for the data is parallel to the hard-sphere model (Fig. 4), although is it displaced to lower bond-lengths by about 0.003 Å. The best-fit line gives a Be–OH bond length of 1.627 Å, and extrapolating the line gives a Be–F bond length of 1.550 Å, values in good agreement with the expected values from sums of ionic radii. Notably, the agreement between expected and observed trends of <Be–O(4)> distances with F↔OH substitution (Fig. 4) provides independent evidence that the F contents obtained by site-scattering refinement of the X-ray data are correct.

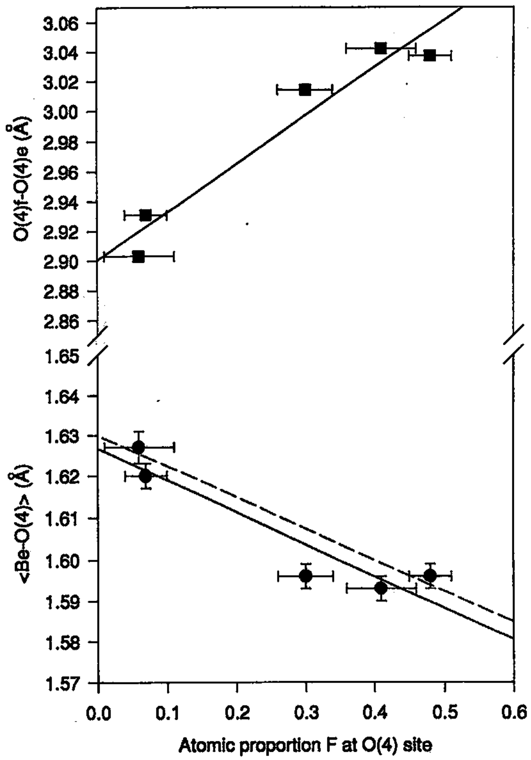

FIG. 4. The effect of F↔OH substitution upon the <Be–O(4)> and O(4)f–O(4)e separations. The best fit line for <Be–O(4)> *versus* F is <Be–O(4)> = –0.077F + 1.627, r = 0.934, and for O(4)f–O(4)e *versus* F, it is O(4)f–O(4)e = 0.322F + 2.900, r = 0.968. The broken line represents the expected variation of <Be–O(4)> obtained from sums of ionic radii.

Substitution of F at the O(4) site results in the loss of O(4)f–H...O(4)e bonds. It was indicated above that this leads to a flattening of the sheets of Beϕ_4 tetrahedra and BO$_3$ triangles, resulting in a significant increase of the b dimension. Figure 4 shows that the donor–acceptor separation does increase linearly with increasing F proportion (r = 0.968), confirming that the amplitude of the modulations of the sheets is reduced by the entry of F at the O(4) site.

Possible factors that may limit the extent of F↔OH substitution in hambergite

To the best of our knowledge, the hambergite crystals from Kracovice (HM4 and HM5) have the highest F content yet reported. Electron-microprobe analysis indicates an F content of 7.0 wt% for HM4, corresponding to 0.35 atoms per formula unit (*apfu*), and site-scattering refinement gives an F content of 9.6 wt% for HM5; the latter corresponds to a composition Be$_2$(BO$_3$)(OH)$_{0.52}$F$_{0.48}$. Can one expect a complete range of F↔OH substitution in hambergite?

A mineral with composition Be$_2$(BO$_3$)F has not been described, but Baidina *et al.* (1978) have synthesized crystals of Be$_2$(BO$_3$)F by reaction at 600°C. Their structure analysis for Be$_2$(BO$_3$)F shows that it is monoclinic, space group $C2$, a 7.687(4), b 4.439(3), c 8.669(4) Å, β 107.08°.

The structure of Be$_2$(BO$_3$)F is shown projected down [010] in Figure 5. Be$_2$(BO$_3$)F has a framework structure, and, as in the structure of hambergite, the Beϕ_4 and BO$_3$ polyhedra occur in sheets, in this case parallel to (001). These sheets are connected into a framework through the F position; each F atom bonds to a Be atom in each adjacent sheet (Fig. 5). Comparison of the structure of hambergite (Fig. 1) and Be$_2$(BO$_3$)F (Fig. 5) shows that the structures have

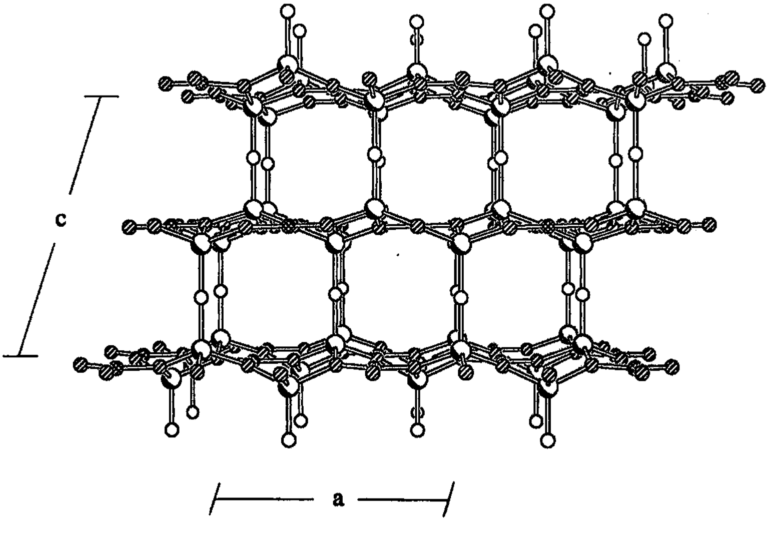

FIG. 5. The structure of Be$_2$(BO$_3$)F projected down [010]. B atoms are shown as cross-hatched circles, Be atoms as open circles with shading in the lower left, O atoms as circles shaded with parallel lines, and F atoms are shown as open circles.

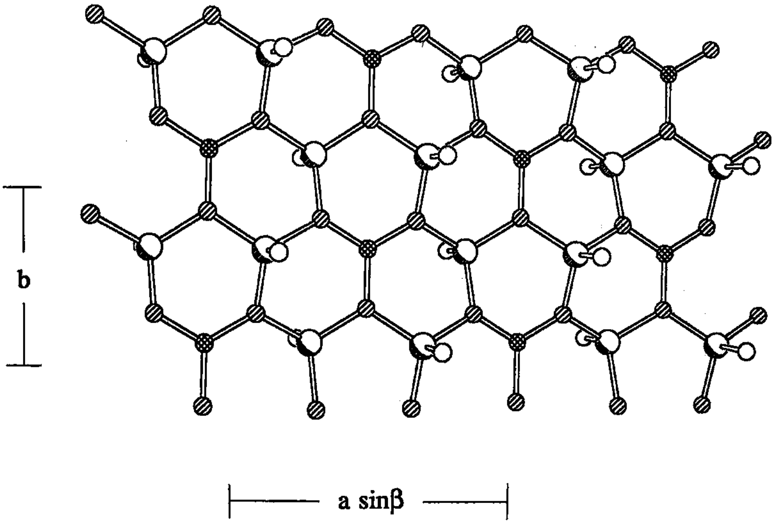

FIG. 6. The structure of $Be_2(BO_3)F$ projected down [001]. Legend as in Figure 5.

similar connectivities. However, in $Be_2(BO_3)F$ the sheets are flat, whereas in hambergite the sheets are modulated.

In the sheet of the $Be_2(BO_3)F$ structure (Fig. 6), each O atom bonds to one B atom and two Be atoms, and the connectivity of the sheets is the same as in hambergite (Fig. 2). However, the orientation of the $Be\phi_4$ tetrahedra is not the same in $Be_2(BO_3)F$ and hambergite. In $Be_2(BO_3)F$, the apical F positions of the $Be\phi_4$ tetrahedra point up (U) and down (D) with the sequence UDUDUD along the sheets in both the *b* and *a sin*β directions (Fig. 6). In hambergite, the apical OH positions of the $Be\phi_4$ tetrahedra point up and down with the sequence DUUDUDDU, as can be seen in Figures 1 and 2. Thus, the connections between the sheets of $Be\phi_4$ tetrahedra and BO_3 triangles are ordered differently in the structures of $Be_2(BO_3)F$ and hambergite (Figs. 1, 5).

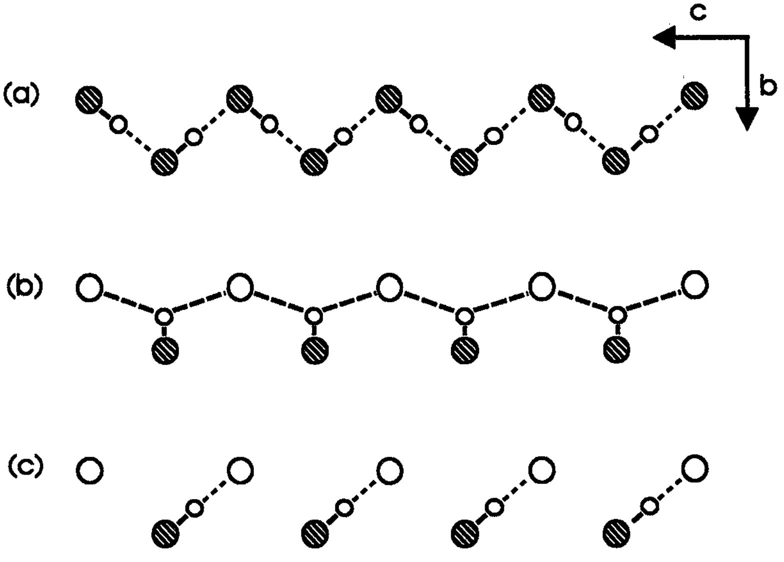

FIG. 7. Possible local F–OH arrangements along the hydrogen-bonded strips in hambergite. (a) All sites are occupied by OH, (b) one half the sites are occupied by F, the OH(4)f–H bond is parallel to the *b* direction, and the H atom forms a bifurcated hydrogen bond with adjacent F atoms; (c) one half the sites are occupied by F with the occurrence of hydrogen-bonded OH–F pairs. O atoms are shown as circles shaded with parallel lines, F atoms are large open circles, and H atoms are shown as small open circles.

In hambergite, the hydrogen bonds occur between vertices of adjacent Beϕ_4 tetrahedra that point in the same direction, with a donor–acceptor distance of about 2.9 Å. Inspection of Figure 1 shows that the sheets in hambergite are modulated extremely strongly in the *b* direction. This modulation is induced to a considerable extent by the hydrogen bonding between rows of O(4) anions along the *c* direction (Fig. 1). If this interaction were removed, the sheets would have less impetus to modulate. Examination of Figure 1 shows that, in doing this, the structure would not remain stable. Consider the row of hydrogen bonding in the top left-hand part of Figure 1. If the attractive interaction between the two rows of O(4) anions were removed, the upper sheet would tend to flatten and expand in this particular region, whereas the lower sheet would tend to contract in the same region; these two opposing tendencies would destroy the connectivity between adjacent sheets. Thus we may conclude that there must be an interaction involving attraction between adjacent O(4) anions in the hambergite structure.

Consider next the interaction between adjacent O(4) anions along a hydrogen-bonded strip parallel to the *c* direction (Figs. 2, 7a); each row of O(4) anions is bonded to the adjacent row. Suppose one half of the OH groups are replaced by F atoms. There are two possible arrangements, both involving a locally ordered alternation of F and OH along a particular chain: (1) the O(4)f–H bond is oriented parallel to the *b* direction, and the H atom forms a bifurcated hydrogen bond with the adjacent F atoms (Fig. 7b); (2) there are hydrogen-bonded OH–F pairs (Fig. 7c). To investigate which arrangement occurs in the crystals studied, difference-Fourier maps were calculated with the H position vacant for each data set. In all cases, the electron density attributable to the H atom is centered near the O(4)f – O(4)e join, indicating that the arrangement shown in Figure 7c is the one that occurs. In either case, there is significant interaction between anions belonging to adjacent rows. However, this cooperative attraction is destroyed if the amount of F significantly exceeds 50%, as there is no longer any hydrogen bonding possible when F atoms are adjacent, and hence the linkage becomes unstable.

We examined the diffraction characteristics of the HM5 hambergite to see if we could find any indication of a change in space group or the occurrence of a supercell at this half-way composition. The X-ray data did not contain any violations of the space group *Pbca*, and electron-diffraction patterns collected for several zone axes did not contain any supercell reflections. Consequently, we may conclude that any ordering within these rows of the OH(4) anions is not correlated with regard to translationally equivalent rows. Thus the limit of about 50% F substitution for OH in hambergite is structurally dictated, but in a locally ordered one-dimensional fashion that does not lead to any change in long-range symmetry.

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