FLUORINE IN HAMBERGITE[1]

GEORGE SWITZER, ROY S. CLARKE, JR., *U. S. National Museum, Washington, D. C.;* JOHN SINKANKAS, *Scripps Institute of Oceanography, University of California, La Jolla;* AND HELEN W. WORTHING, *U. S. Geological Survey, Washington, D. C.*

ABSTRACT

A chemical analysis of hambergite [$Be_2(OH, F)(BO_3)$] from the Little Three mine, near Ramona, San Diego County, California, disclosed that the mineral from this locality contains 6.0 per cent fluorine. Hambergite from a second California locality, the Himalaya mine near Mesa Grande, contains 0.2 per cent fluorine. Fluorine was not reported in analyses in the literature of hambergite from Madagascar, Norway, and Kashmir. New analyses of Madagascar and Norway hambergite gave 1.0 and 0.15 per cent fluorine, respectively. No material from Kashmir was available for study.

New data on hambergite from Anjanabanoana, Madagascar, and the Little Three mine, California, follow: Madagascar—BeO 53.6, B_2O_3 36.0, H_2O 8.8, F 1.0, less O≡F 0.4, sum 99.0 per cent; orthorhombic, $a=9.76\pm0.01$, $b=12.23\pm0.01$, $c=4.43\pm0.01$ Å. California—BeO 52.9, B_2O_3 36.6, H_2O 6.7, F 6.0, O≡F 2.5, sum 99.4 per cent; orthorhombic, $a=9.78\pm0.01$, $b=12.40\pm0.01$, $c=4.47\pm0.01$ Å; density 2.372 (obs.) gms/cm³; $\alpha=1.543$, $\beta=1.580$, $\gamma=1.617\pm0.001$, 2V=90°. Crystals from the Little Three mine show two new forms, {340} and {341}.

Substitution of F for OH in the Little Three material has caused the unit cell to expand in the b and c directions, while a remains essentially the same. This is because some hydrogen bonds lying in the bc plane are broken by replacing OH with F. Substitution of F for OH in the Little Three material has also substantially lowered the refractive indices and increased the density.

INTRODUCTION

Hambergite, $Be_2(OH)(BO_3)$, was first described from a nepheline syenite pegmatite on the island of Helgeråen, Langesundsfjord, southern Norway by Brögger (1890). The mineral has also been found in Madagascar and Kashmir, and more recently in California and Czechoslovakia.

A chemical analysis of hambergite from the Little Three mine, San Diego County, California, disclosed that the mineral from this locality contains 6.0 per cent fluorine, and that its formula should be written $Be_2(OH, F)(BO_3)$. Corresponding changes in refractive indices, density, and unit-cell dimensions were found to accompany the substitution of F for OH.

Because the literature contains only four hambergite analyses, in none of which was fluorine determined, it was decided to reinvestigate all

hambergite occurrences, as well as to describe those in California. The results of this investigation follow. No work was done on hambergite from Kashmir because material was unobtainable.

OCCURRENCE IN CALIFORNIA

The first discovery of hambergite in California was made by one of the authors (Sinkankas) at the Little Three mine, about four miles east of Ramona, San Diego County, in August 1956.

The Little Three pegmatite dike was discovered in May 1903. The original developers stripped off the exposed upper half of the dike to uncover a series of pockets containing large, deep olive-green tourmaline crystals, associated with quartz, morganite beryl and topaz. The dike averages about five feet in thickness over much of its length, and is about eight feet thick in the pocket area containing the hambergite crystals. The 20° S. dip of the dike conforms to the slope of the hillside.

Near the top of the open cut and about 25 feet east of the western limit of the workings, appears a pronounced central unit of large blocky feldspar euhedrons with interstitial granular gray quartz. The series of pockets which yielded the major production of minerals is said to have come from this unit. In the section of the dike in which hambergite was found, the floor of a small pocket was uncovered somewhat below the normal level, adjacent to this blocky feldspar-quartz unit, and resting on coarse granular feldspar, quartz and mica. Cleavelandite was common and formed typical rounded growths between light smoky quartz crystals which did not exceed two inches in length. The hambergite was found in small nests several inches in diameter, growing on quartz and cleavelandite. Massive material was noted in several places underlying an accumulation of euhedral crystals embedded in a reddish clay filling. Hundreds of hambergite crystals were found, ranging in size from very slender slivers less than five millimeters in length to blades more than 25 mm in length. Most of the detached crystals proved to be well-formed and doubly terminated except where broken or corroded. Several of the quartz crystals had either implanted or completely embedded hambergite crystals.

Aside from quartz the mineral most intimately associated with hambergite is cookeite. Other associated minerals are lepidolite and topaz. These associations point to a genesis for hambergite somewhat earlier than the pocket quartz, microcline perthite, and topaz, but later than cleavelandite, which was found penetrating hambergite crystals.

Hambergite was found distributed along a streak several inches wide and several feet long, following the dip of the pegmatite. Exploration in the immediate vicinity failed to uncover additional material, although further work clearing off debris from the top of the pegmatite, carried out

by the owner of the mine, uncovered more material. Of the total of several hundred crystals found only about a dozen exceeded 15 mm in length. The largest crystal found measured $55 \times 36 \times 11$ mm (U.S.N.M. R9930).

During mining operations conducted by Ralph Potter and associates at the Himalaya mine, Gem Hill, Mesa Grande, San Diego County, California, in the summer of 1958, a number of gem pockets were discovered in pegmatite a short distance above the main tunnel level and approximately 400 feet from the entrance. In at least three pockets numerous small crystals and crystal fragments of hambergite were recovered during washing of pocket debris. One pocket yielded a double handful of crystals and fragments, while the yield from all three pockets was estimated at about five pounds. The largest crystal did not exceed about 25 mm in length, the majority being considerably smaller. They were all nearly equant and commonly twinned.

All pocket debris was carefully washed because it contained corroded fragments of deep red-orange beryl. According to Elbert H. McMacken, hambergite was abundant in each beryl-bearing pocket and was absent, or at least escaped notice, in pockets in which beryl was absent. Other associated minerals in the hambergite pockets were pink apatite in simple prisms and the usual prismatic crystals of gem tourmaline for which this pegmatite is so well known.

All hambergite specimens at the Himalaya mine occurred as isolated crystals or fragments showing neither physical attachment to other minerals nor bearing impressions of other crystals. Their position in the sequence of crystallization is, therefore, not known.

Morphology

The crystallographic elements for hambergite given in Palache *et al.* (1951) are calculated from angles of Goldschmidt and Müller (1910) measured on crystals from Madagascar. The axial ratio thus obtained is in close agreement with that obtained from unit-cell dimensions by Zachariasen (1931), Zachariasen *et al.* (1963), and in the present work (Table 4).

None of the Little Three mine crystals were good enough for high quality goniometry. However, several were measured (U.S.N.M. R9952) which yielded data sufficiently good to permit identification of the following forms: {001}, {010}, {100}, {340}, {110}, {111}, {221}, {441}, {341}. Of these {340} and {341} are new and are prominent forms on many crystals. The measured range and calculated ϕ and ρ of the new forms measured on four crystals are compared in Table 1. The axial ratio of Goldschmidt and Müller (1910) was used in the calculation.

TABLE 1. MEASURED AND CALCULATED ANGLES FOR NEW FORMS ON HAMBERGITE

Form	Number of Measurements	Measured range		Calculated	
		ϕ	ρ	ϕ	ρ
340	3	42°20′–43°30′	89°55′–90°05′	43°04′	90°00′
341	5	42°50′–43°30′	61°17′–65°34′	43°04′	63°19′

The habit of typical Little Three mine hambergite crystals is shown in Fig. 1.

Four crystals of hambergite from the Himalaya mine were available for study (U.S.N.M. 116995). One of these is a single crystal with forms {110}, {001} and {341}, very similar to the Little Three mine crystal shown in Fig. 1a. The remaining three are twinned, with twin and composition plane {110}, as reported for Madagascar hambergite by Drugman and Goldschmidt (1912).

Several specimens of reticulated twinned hambergite were found at the Little Three mine, also with twin and composition plane {110}. A photograph of one of these (U.S.N.M. R12437) is shown in Fig. 2.

CHEMISTRY

The literature contains four chemical analyses of hambergite from Norway, Madagascar, Kashmir and Czechoslovakia. Those from the first three named localities would not be considered good by modern standards, and the analysis of the Czechoslovakian material was done on a 92 mg sample with F not determined.
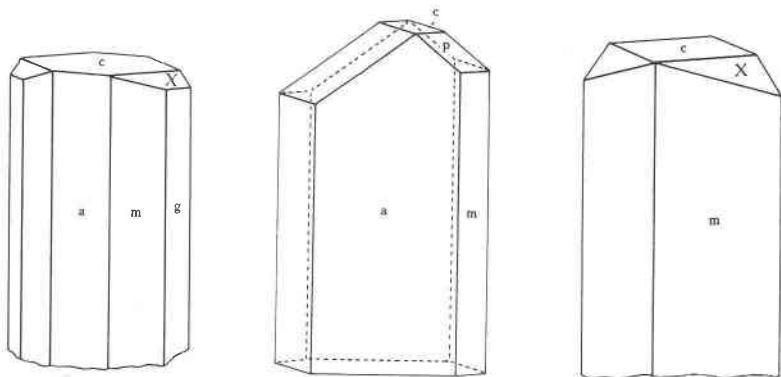

FIG. 1. Crystals of hambergite from the Little Three mine, San Diego County, California. Forms shown are: $a\{100\}$, $c\{001\}$, $m\{110\}$, p$\{221\}$, $g\{340\}$, X$\{341\}$.

It was decided, therefore, to analyze the hambergite from the Little Three mine. During the preliminary stages of the analysis it was noted that in a water determination the glass reaction tube became etched, indicating the presence of fluorine. The finished analysis showed 6.0 per cent F. A new analysis was then made of Madagascar hambergite that showed 1.0 per cent F, whereas none had been reported in the original
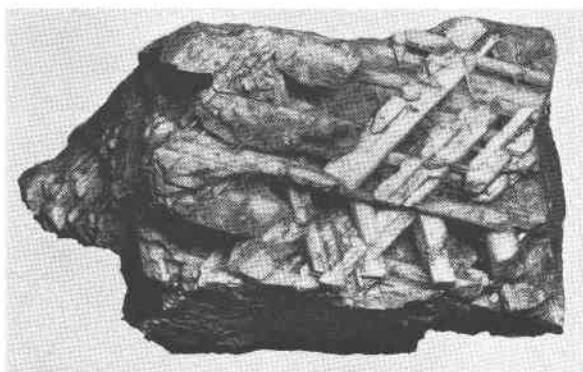

Fig. 2. Hambergite, Little Three mine, San Diego County, California, showing reticulated twinning. Twin and composition plane {110}.

analysis. Complete analyses were not made of hambergite from Norway and the Himalaya mine, but semiquantitative spectrographic analysis gave for these two localities F = 0.15 and 0.2 per cent, respectively.

A summary of the old analyses of hambergite is given in Palache *et al.* (1951).[1] The analysis of the Czechoslovakian material is given in Čech and Povandra (1961). The new analytical data are given in Tables 2 and 3.

Semiquantitative spectrographic analyses were performed on four samples of hambergite. The presence of major amounts of Be and B and smaller amounts of F was indicated. The figures in Table 3 indicate the level of contamination was probably less than 1 per cent. The following elements were looked for and found to be either below 0.02 per cent or below their limit of detectability: Ti, P, Mn, Ag, As, Au, Ba, Bi, Cd, Ce, Co, Cr, Cu, Ga, Ge, Hf, Hg, In, La, Li, Mo, Nb, Ni, Pb, Pd, Pt, Re, Sb, Sc, Sn, Sr, Ta, Te, Th, Tl, U, V, W, Y, Yb, Zn, Zr, Cs, Rb. The procedure employed was that described by Waring and Annell (1953).

Complete chemical analyses (Table 2) were performed on hambergite from Madagascar and Little Three mine, San Diego County, California. Beryllium was determined on approximately 125 mg samples making use

[1] The locality given for analysis 2 should read Norway.

TABLE 2. ANALYSES OF HAMBERGITE

	$Be_2(OH)(BO_3)$ Theoretical		Anjanabanoana, Madagascar, U.S.N.M. R10639		Little Three Mine, San Diego County, Calif. U.S.N.M. R9952	
	Wt. %	ratio	Wt. %	ratio	Wt. %	ratio
BeO	53.31	2.000	53.6	2.039	52.9	2.001
B_2O_3	37.09	0.500	36.0	.491	36.6	.498
H_2O	9.60	0.500	8.8	.465	6.7	.352
F			1.0	.053	6.0	.299
Total	100.00		99.4		102.2	
O≡F			.4		2.5	
Corr. Total			99.0		99.7	

Unit Cell	$8Be_2(OH)(BO_3)$	$8Be_{2.04}(OH, F)_{.98}(BO_3)_{.98}$	$8Be_{2.00}(OH, F)_{1.00}(BO_3)_{1.00}$

Content
  Number of ions on basis of $\Sigma Be + B + OH + F = 4.000$
  Roy S. Clarke, Jr., analyst

of a modification of the method of Dutta and Sen Gupta (1956). The sample was dissolved in HF, evaporated to dryness twice with HNO_3, and the residue taken up with a small volume of water and HNO_3. $BaBeF_4$ was precipitated by the addition of $BaCl_2$ to a boiling solution containing excess fluoride ion and boric acid and at a pH adjusted between 4 and 5. The precipitate was collected in a glass filtering crucible and washed until the filtrate was free of chloride. Considerable difficulty was encountered in washing the precipitate.

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF HAMBERGITE[1]

Little Three U.S.N.M. R9952		Himalaya Mine U.S.N.M. 116995	Madagascar U.S.N.M. R10639	Norway U.S.N.M. 116994
F	3.	.2	.7	.15
Si	.007	.15	.0015	.5
Al	.007	.01	.003	.007
Fe	.0015	.007	.003	.05
Mg	.003	.0015	.0015	.1
Ca	.0003	.002	.0003	.003
Na	0	.01	0	.1
K	0	.0015	0	.001

[1] Results are reported in per cent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc., which represent approximate midpoints of group data on a geometric scale. The assigned group of semiquantitative results will include the quantitative value about 30 per cent of the time.

Approximately 150 mg samples were taken for the determination of boron. A procedure similar to that described by Furman (1939) was used to separate F by precipitation as BaF_2, using $BaCO_3$ as precipitant. A 1/10 aliquot of this sample solution was taken for a microtitration of B. NaOH was the titrant and the course of the reaction was followed in detail potentiometrically. Mineral acid was first titrated, mannitol added, and then the B titrated. The equivalence points were determined graphically, based on work with known solutions of similar concentrations.

A 106 mg sample of Little Three mine and a 56 mg sample of Madagascar hambergite were used to determine H_2O. A modified microcombustion train of the type used to determine carbon and hydrogen in organic compounds was employed. The samples were ignited in the temperature range of 1000°–1100° C. in a stream of argon. This temperature was attained by use of a gas-oxygen torch and a fused silica ignition tube. The gases passed through a packing that removed fluorine.

Approximately 200 mg samples were used for the determination of F. The sample was fused in Na_2CO_3, distilled from a perchloric-phosphoric acid mixture and titrated with $Th(NO_3)_4$ (Grimaldi *et al.*, 1955).

Unit-Cell Dimensions

Unit-cell dimensions were determined from precession photographs for hambergite from the Little Three and Himalaya mines, San Diego County, California; Anjanabanoana, Madagascar; Sušice, Czechoslovakia; and Helgaråen, Langesundsfjord, Norway. The results are given in Table 4.

Substitution of F for OH in the Little Three material has caused the unit cell to expand in the *b* and *c* directions, while *a* remains essentially the same. A structural explanation for this may be found in the crystal

TABLE 4. UNIT CELL DIMENSIONS OF HAMBERGITE

	Little Three Mine, San Diego Co., Calif. U.S.N.M. R9952	Himalaya Mine, San Diego Co., Calif. U.S.N.M. 116995	Anjana-banoana, Madagascar U.S.N.M. R10639	Anjana-banoana, Madagascar (Zachariasen *et al.*, 1963)	Sušice, Czecho-slovakia U.S.N.M. 115663	Helgaråen, Langesunds-fjord, Norway U.S.N.M. 116994
a	9.78 Å	9.77 Å	9.76 Å	9.755 Å	9.75 Å	9.76 Å
b	12.40	12.21	12.23	12.201	12.23	12.20
c	4.47	4.43	4.43	4.426	4.43	4.43

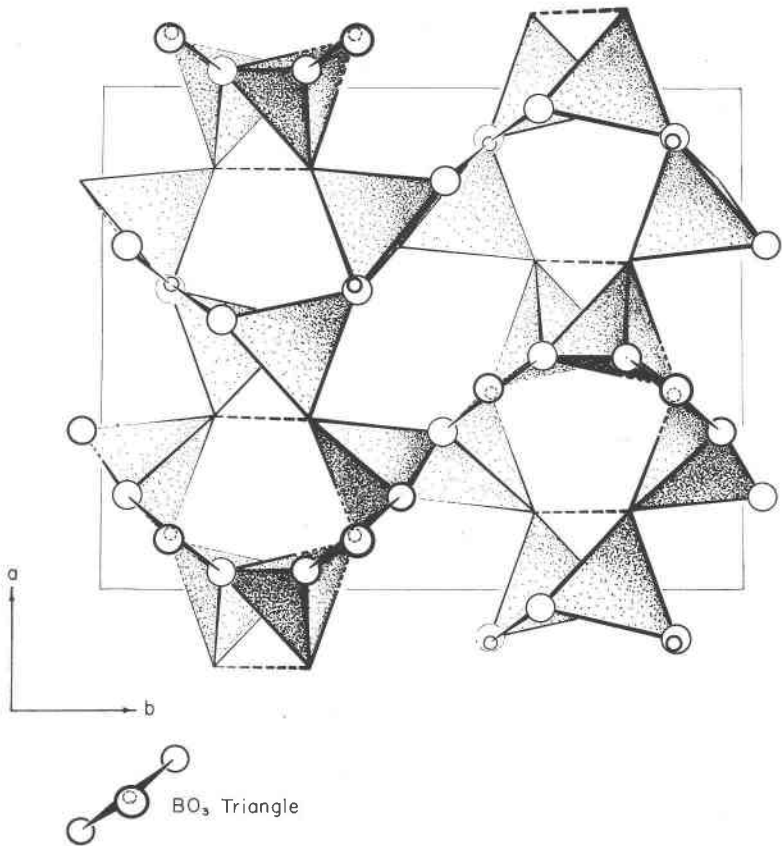All values ±0.01 except for those of Zachariasen *et al.* (1963), which are ±0.001.

FIG. 3. A portion of the hambergite structure projected on (001). The $BeO_3(OH)$ groups are shown as shaded polyhedra (from Ross, 1964).

structure as determined by Zachariasen (1931), refined by Zachariasen et al. (1963).

The structure of hambergite is described by Ross (1964) as follows: The beryllium atoms are coordinated tetrahedrally by three oxygen atoms and one (OH) group. Each oxygen atom of the $BeO_3(OH)$ tetrahedra is shared with another $BeO_3(OH)$ group and a BO_3 triangle. The (OH) group is shared between two $BeO_3(OH)$ tetrahedra. The boron atoms are in triangular coordination by three oxygens. Each of these oxygens is also shared with two $BeO_3(OH)$ tetrahedra. The triangles lie in a plane parallel to the c axis.

A portion of the hambergite structure projected on (001) is shown in Ross (1964), reproduced here in Fig. 3. The $BeO_3(OH)$ groups are shown

as shaded polyhedra. Ross points out that the structure is a three-dimensional one formed by the linking of tetrahedra in infinite spirals parallel to c. Zachariasen *et al.* (1963) find a hydrogen bond of 2.905 Å between (OH) groups. These hydrogen bonds are shown by dashed lines in Fig. 3.

The hydrogen bonds lie in the bc plane, inclined to the plane of the projection (001) and, therefore, having components only in the b and c directions. Their presence is substantiated by the greater b and c unit-cell dimensions of fluorine-containing hambergite, for some of these hydrogen bonds would be broken by replacing (OH) with F.

The unit-cell data summarized in Table 4 indicate that there is little or no fluorine in the hambergite from Sušice, Czechoslovakia.

Physical Properties

The optical properties and density of hambergite from various localities are given in Table 5.

TABLE 5. Optical Properties and Density of Hambergite

	1	2	3	4	5
α	1.543	1.552	1.5536	1.556	1.5595
β	1.580	1.588	1.5873	1.588	1.5908
γ	1.617	1.628	1.6278	1.630	1.6311
2V	90°	90°	87° 1′	84°	87° 7′
Dgms/cm³	2.372		2.36		2.347

$X = a$, $Y = b$, $Z = c$

1. Little Three mine, San Diego County, California. Refractive indices by immersion method, ±0.001. Density by pycnometer. U.S.N.M. R9952.

2. Himalaya mine, San Diego County, California. Refractive indices by immersion method, ±0.001.

3. Anjanabanoana, Madagascar. Optics from Goldschmidt and Müller (1910). Density from Lacroix (1909).

4. Sušice, Czechoslovakia, from Cěch and Povandra (1961).

5. Helgaråen, Norway, from Brögger (1890).

Substitution of F for OH in the Little Three material has substantially lowered the refractive indices. A similar decrease in refractive index with increasing F/OH ratio is shown by fluoborite, herderite, amblygonite, apatite and other minerals where F and OH substitute isomorphously.

The striking hemihedral development of many of the Little Three mine hambergite crystals suggests that the mineral might be noncentrosymmetric. Dr. J. W. Davisson of the U. S. Naval Research Laboratory very kindly checked one crystal, and reported that the results of both a

TABLE 6. X-RAY DIFFRACTION POWDER DATA FOR HAMBERGITE

Cu Kα=1.5418 Å   Camera diameter 114.59 mm.

Little Three mine, San Diego Co., Calif. U.S.N.M. R9952		Anjanabanoana, Madagascar U.S.N.M. R10639		Calculated	
I	d	I	d	d	hkl
8	4.53	8	4.53	4.527	210
10	3.82	10	3.81	3.822	111
4	3.62	5	3.60	3.578	021
6	3.18	8	3.19	3.162	211
9	3.13	9	3.13	3.121	230
5	3.08	5	3.06	3.048	040
4	2.89	4	2.89	2.885	221
2	2.59	2	2.58	2.584	240
4	2.56	5	2.55	2.560	311
6	2.38	7	2.40	2.390	410
2	2.24	2	2.23	2.231	241
7	2.20	7	2.21	2.210	002
1	2.16	2	2.17	2.181	250
5	2.13	7	2.13	2.122	112
7	2.10	7	2.09	2.090	430
2	2.04	4	2.04	2.032	122
4	1.99	6	1.99	1.986	341
3	1.96	4	1.96	1.956	251
3	1.90	3	1.91	1.911	222
4	1.82	5	1.82	1.828	302
4	1.76	3	1.77	1.765	511
4	1.73	4	1.73	1.726	261
2	1.67	2	1.67	1.667	332
2	1.65	2	1.65	1.640	270
1	1.61	2	1.62	1.625	600
1	1.57	2	1.56	1.570	620
2	1.54	1	1.54	1.540	541
1	1.50	2	1.53	1.524	080
2	1.44	1	1.47	1.472	461
1	1.42	2	1.43	1.430	262
3	1.36	2	1.37	1.371	133

Giebe-Schiebe and pyroelectric test were negative, suggesting but not proving that hambergite is centrosymmetric. Zachariasen *et al.* (1963) definitely found the structure to be centrosymmetric.

X-RAY DIFFRACTION POWDER DATA

The *x*-ray powder data are given in Table 6 for hambergite from the Little Three mine, San Diego County, California, and Anjanabanoana,

Madagascar. d spacings were calculated from the following unit cell dimensions determined on Madagascar material: $a = 9.76$ Å, $b = 12.23$, $c = 4.43$. Calculated spacings are listed only if indexed to an observed reflection. Intensities were estimated visually.

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