A SECOND FIND OF EUHEDRAL BORNITE CRYSTALS ON BARITE

G. Kullerud and G. Donnay, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.*

AND

J. D. H. Donnay, *The Johns Hopkins University, Baltimore, Md.*

Abstract

Bornite crystals on barite have been found at the Coppercorp Mine in Ontario, Canada, the second locality for this association. The geology resembles that of the Upper Michigan copper area. The bornite cubes, truncated by octahedron faces, prove to be twinned edifices of two kinds, which simulate either cubic ($a = 21.94$ Å) or orthorhombic ($a = b = 21.90$, $c = 10.95$ Å) symmetry.

Introduction

Bornite, Cu_5FeS_4, although a common mineral in many copper-iron sulfide ore deposits, has rarely been reported in single crystals. Well developed, steel blue, euhedral crystals were found by one of us (G.K.) in August 1956 at the Coppercorp Limited Mine of the Mamainse Point copper area, Ontario, Canada. The hand specimen shows bornite crystals growing on barite (Fig. 2), an association previously reported only from the Cheshire locality in England.

General Geology

The Mamainse Point copper area is located on the east shore of Lake Superior in the district of Algoma and lies about 60 miles north of the city of Sault Ste. Marie,* The Keweenawan rocks of this area form the east end of the Lake Superior syncline, are the youngest in the Precambrian era, and are generally unaltered. Amygdaloidal lava flows predominate and are interbanded with a boulder conglomerate. The faults in the area are often well-defined tensional structures. Most of the copper-bearing zones are faulted and the apparent horizontal displacement varies from a few to more than 1000 feet. The faults are considered to be normal and generally dip in the direction opposite to the dip of the strata.

Since the geology of the Mamainse Point area is similar to that of the Michigan copper district, the occurrence of chalcocite and native copper on small fractures led to intensive explorations. These showed that, as to structure and mineralogy, the Mamainse copper deposits, which consist mostly of chalcocite on fissures and fractures, are quite different from the

---

* The areal geology and individual ore deposits of the Mamainse Point copper area have been described by Thomson (1954), who also presented an excellent geological map and thus provided invaluable data for the present report.

Michigan copper deposits, where native copper occurs in flow tops and conglomerates.

The main ore deposits are known as the C zone, the S zone, and the M zone (Fig. 1). The chief ore mineral is chalcocite. Native copper is found on a few localities. Chalcopyrite is much less common than chalcocite. A little massive bornite is found with chalcopyrite and chalcocite in several
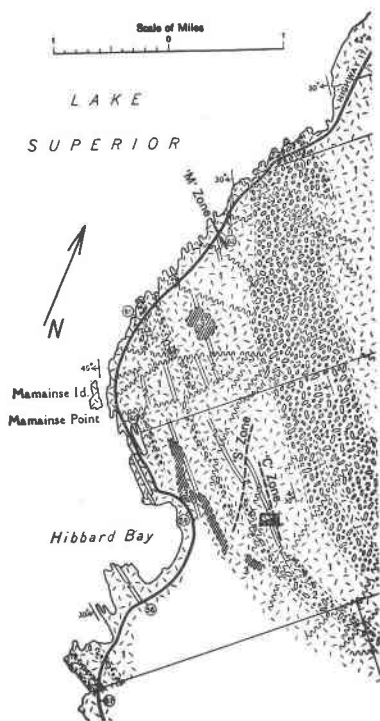

Fig. 1. Sketch map of Mamainse Point area. Numbers in circlets along highway 17 indicate mileage from Sault Ste. Marie. Black and white rectangle shows shaft of Coppercorp Mine.

localities and may be secondary. Chemical analyses have shown that a little silver occurs with the copper minerals; the silver values are highest where bornite is present (Thomson, 1954).

GEOLOGY AND MINERALOGY OF THE COPPERCORP LIMITED MINE

The Coppercorp Limited mining operations explored the C zone ore deposit (Fig. 1). The mine shaft is situated about 1 mile east of Hibbard Bay of Lake Superior. The C zone strikes almost parallel to the strata (N 15° W), dips almost normal to them (55–68° E) and may be a strike

fault. Geologic information (Thomson, 1954) suggests that it is a normal fault with about 50 feet of vertical displacement. It does not outcrop but has been traced for 5400 feet along the strike by 34 drill holes. It has been estimated to average 8 feet in width. Testing to a depth of 400 feet and on a distance of 2275 feet showed its copper content to average 1.9 per cent. It is a fractured and brecciated zone in interbanded amygdaloidal basalt and conglomerate of the Keweenawan series. The wall rocks, to a depth of about 600 feet along the dip, are mostly lava flows from 20 to 100 feet thick; below this horizon the zone enters a thick conglomerate band. The C zone consists largely of vein breccia which contains massive chunks and sometimes stringers of erratically distributed chalcocite. Sometimes chalcocite also occurs in small fractures and amygdules in the adjacent lava. The breccia carries fragments of wall rocks, quartz, and calcite and is often vuggy (Thomson, 1954).

Bornite crystals growing most commonly on barite (Fig. 2), but also frequently on quartz, were found in vugs of the breccia. Bornite crystals occurring on barite appear with only few exceptions to have grown directly by deposition from a solution, while the bornite found on quartz without exception appears to have been formed by replacement of chalcopyrite (Fig. 3). In some cases some of the bornite which replaces chalcopyrite has in turn been replaced in part by chalcocite. Because of the presence of residual chalcopyrite and replacement chalcocite, it was not possible to obtain pure bornite in amounts sufficient for chemical analysis. The exact bornite composition, therefore, is unfortunately not known.

It was noted on crushing bornite crystals under acetone that fresh surfaces are tombac colored. However, on exposure to the atmosphere such surfaces change their color immediately and will after only a few seconds have acquired a pinkish cast. On continued exposure the pinkish color changes through brownish purple and purple to deep purple and finally an iridescent blue.

CRYSTALLOGRAPHY

Bornite crystals (at first presumed to be single crystals) were detached from the barite crystals found on the hand specimens. Examined under the binocular microscope they show the cube as their dominant form, modified by small faces of the octahedron. Their cube edge ranges in length from 0.2 to about 1.5 mm. The appearance of these edges constitutes the most striking morphological feature of the bornite crystals examined: every cube edge is replaced by a "staircase" of indentations, which consist of alternating octahedral faces, as could be established by a detailed study on the two-circle reflecting goniometer. For instance (Fig. 4) the three edges that meet at the cube corner truncated by (111) are re-
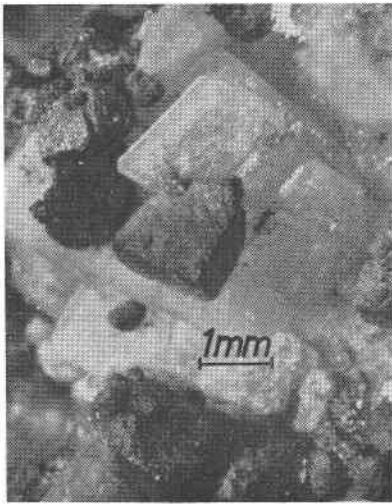
2
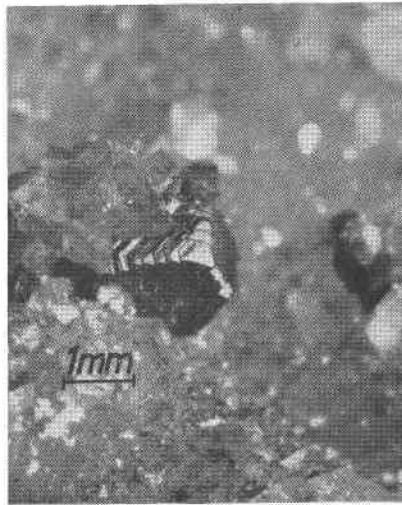
4
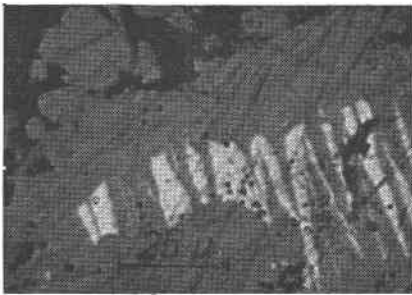
3(a)

3(b)

FIG. 2. Bornite cube on barite crystals. Hand specimen.

FIG. 3. (a) Residual chalcopyrite (white) replaced by bornite (dark gray). Polished section.

(b) Chalcopyrite (white) replaced by bornite (dark gray), in turn replaced by chalcocite (light gray). Polished section.

FIG. 4. Bornite "crystal" with cube truncated by octahedron. Cube edges show staircases due to alternation of octrahedral faces. Hand specimen.

placed by an alternation of (111) faces with ($\bar{1}$11), (1$\bar{1}$1), or (11$\bar{1}$), respectively, according as the edge is parallel to the a, b, or c axis. A survey of the available crystals shows that the height of the steps in the "staircase" ranges from 0.01 to 0.05 mm. These steps are visible on the figure, where they appear as small illuminated trapezia, between large and darker cube faces.

Several chips were studied by x-ray diffraction, on the rotation, Weis-

senberg, and precession cameras, using $MoK\alpha$ and $CoK\alpha$ radiations. Two types of crystalline edifices were observed.

One type appears cubic, as shown by rotation patterns taken about the three crystallographic axes. We find cell edge $a = 21.94 \pm 0.06$ Å, and diffraction aspect P***, provided weak reflections are taken into account.

The second type* is metrically tetragonal with $a = b = 21.90 \pm 0.06$, $c = 10.95 \pm 0.03$ Å, but the symmetry of the edifice, as determined from the relative intensities of the diffraction spots, is not higher than orthorhombic, with primitive lattice mode. Our observations agree with those reported by Frueh (1950) on low-temperature bornite from Bristol, Connecticut. Frueh gives the following cell dimensions, $a = b = 21.94$, $c = 10.97$ Å, and considers his material to be primitive orthorhombic and pseudotetragonal. He later informed us, however (priv. comm., July 28, 1958), that he had been dealing with a "multiple crystal." Quoting him: "the reason it was called orthorhombic was that the intensity of reflections did not show 4-fold symmetry. From the smaller fragment it appears to be truly tetragonal with $a = 10.97$ and $c = 21.94$ Å." Since then, Morimoto and Kullerud (1959) have established beyond doubt that the true symmetry is indeed tetragonal, with $a = b = 10.95$, $c = 21.90$ Å, space group $P\bar{4}2_1c$, and that the apparent symmetry results from the twinning (by 90° rotation about an a axis) of two crystals with *different* volumes. This tetragonal form has been found by Morimoto and Kullerud (1959) on synthetic samples and also on an annealed specimen from the Coppercorp locality. Our cubic type could likewise be explained as a trilling of the tetragonal form, in which the three mutually perpendicular crystals would have *equal* volumes.

A powder pattern of bornite of our "cubic" type was obtained on the Philips diffractometer. With very strong amplification one peak is observed, at $2\theta = 31.9°$ in $FeK\alpha$ radiation, that can be indexed only if the cell edge is 21.90 Å. Its symbol is 643. All other peaks could be indexed on the cell reported first by de Jong (1928) and later by Lundqvist and Westgren (1936): $a = 10.93$ Å, space group $Fd3m$. It is possible that these authors did not observe any weak reflection that would have required doubling the cell edge, or else they were dealing with a structural type that has not been confirmed for low-temperature bornite by later investigators. (A cubic cell with $a = 10.97$ Å and space group $Fm3m$, $F432$, or $F\bar{4}3m$ has been reported by Frueh, 1950, for high-temperature bornite.) For a bornite crystal from Cornwall, Tunell and Adams (1949) reported

---

* In a preliminary report (Carnegie Institution of Washington Year Book 57, 1957–58, p. 248) the limits of error on the value of a and b are misprinted as ± 0.006.
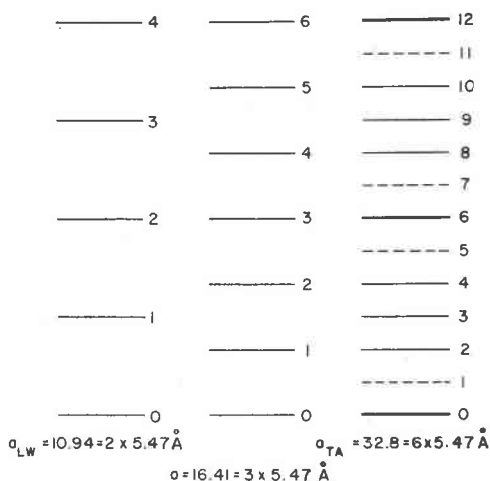
FIG. 5. Schematic explanation of bornite rotation pattern (observed by Tunell and Adams). The proposed intergrowth of two cubic forms, one with $a = 2 \times 5.47$ Å (found by Lundqvist and Westgren) and a second one with $a = 3 \times 5.47$ Å (not yet reported in the literature) accounts for the observed absence of first, fifth, seventh, and eleventh layer lines.

a metrically cubic type with cell edge 32.8 Å, but with non-isometric symmetry. They made the intriguing observation that a rotation photograph, which they obtained from a crystal rotating about a "cube" edge and which gave them their value of a, does not show the first, fifth, seventh, and eleventh layer lines.

We have attempted to find an explanation for the Tunell-Adams observation. The large cell content of a cube with $a = 32.8$ Å—1080 copper atoms, 216 iron atoms, and 864 sulfur atoms—makes us suspect that we are dealing with a complex edifice, either a twin as in digenite (Donnay, Donnay, and Kullerud, 1958) or a syntaxic intergrowth of two distinct phases as with andorite IV and andorite VI (Donnay and Donnay, 1954). Either hypothesis provides an interpretation of the Tunell-Adams rotation pattern. The missing layer lines could be missing as a result of the intergrowth of two phases, one rotating about an edge* of $10.94 = 2 \times 5.47$ Å, the other about an edge of $16.41 = 3 \times 5.47$ Å, as is shown in Fig. 5. The repeat of 10.94 Å is available in the cubic type of Lundqvist and Westgren, as the c length of our "orthorhombic" form, or as the a length of the tetragonal form. The 16.41 Å repeat has recently been found (Morimoto and Kullerud, in preparation) on synthetic material.

* In the preliminary report (C.I.W. Year Book 57, p. 249) two cubic forms had been suggested; their a values were misprinted in the legend of Fig. 46 as 2.547 and 3.547 Å, instead of 2×5.47 and 3×5.47 Å.

REFERENCES

DONNAY, G., DONNAY, J. D. H., and KULLERUD, G. (1958), Crystal and twin structure of digenite, Cu_9S_5: *Am. Mineral.*, **43,** 228–242.

DONNAY, J. D. H., AND DONNAY, G. (1954), Syntaxic intergrowths in the andorite series: *Am. Mineral.*, **39,** 161–171.

FRUEH, A. J., JR., (1950), Disorder in the mineral bornite, Cu_5FeS_4: *Am. Mineral.*, **35,** 185–192.

DE JONG, W. (1928), Doctoral dissertation, Delft.

LUNDQVIST, D., AND WESTGREN, A. (1936), On the crystal structure of bornite, Cu_5FeS_4: *Arkiv. f. Kemi, Mineral. och Geologi*, **12B,** (23), 1–6.

MORIMOTO, N., AND KULLERUD, G. (1959), Single-crystal studies of Cu_9S_5-Cu_5FeS_4 solid solutions: *Carnegie Inst. Wash. Year Book*, **58,** 1958–59, 201–203.

THOMSON, J. E. (1954), Geology of the Mamainse Point copper area: *Annual Report of the Ontario Department of Mines*, **62,** pt. 4, 25 pp.

TUNNELL, G., AND ADAMS, C. E. (1949), On the symmetry and crystal structure of bornite: *Am. Mineral.*, **34,** 824–829.

Manuscript received February 6, 1960.