SULFUR-RICH BORNITES

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ABSTRACT

Natural bornites in general remain homogeneous when heated and have cell edges close to that of stoichiometric Cu_5FeS_4(10.950 Å) before and after heating. Certain bornites exsolve chalcopyrite when heated at temperatures between 75° C. and 400° C. and have tetragonal cell edges less than 10.950 Å. Their cell edges after heating are close to 10.950 Å. The small initial cell edge and the induced exsolution can be correlated with a greater sulfur-to-metal ratio than is indicated by the stoichiometric formula Cu_5FeS_4. This conclusion is supported by studies on synthetic samples and heating experiments on natural samples. Exsolution rate studies indicate that natural sulfur-rich bornites were deposited below about 75° C. Therefore such bornites occurring in high-temperature type deposits must have formed by later, possibly supergene, processes.

INTRODUCTION

Natural bornites in general remain homogeneous when heated; however, certain bornites when heated at temperatures below 400° C. but above 75° C. exsolve up to 25 volume per cent chalcopyrite (Fig. 1), others exsolve both chalcopyrite and digenite. Recent studies (Brett, 1962a) have shown that exsolution of chalcopyrite from synthetic bornite is rapid even when the cooling rate is as low as 3° C. per day. Schwartz (1931) and others have shown that exsolution of chalcopyrite from natural bornites during cooling is also rapid. Therefore natural bornites which exsolve chalcopyrite on heating are anomalous because chalcopyrite-bornite solid solutions deposited at elevated temperatures would be expected to have exsolved chalcopyrite during the slow cooling that undoubtedly occurs in nature.

Unfortunately it is impossible to obtain precise chemical analyses of such bornites on account of the large number of sulfide inclusions which they invariably contain. Several suggestions have been proposed by previous workers to account for the chalcopyrite exsolution; some of these exhibit inconsistencies with the presently known facts, others do not completely explain the phenomenon. The present study was initiated to gain a better understanding of the exsolution.

PROPERTIES OF BORNITE

Composition. The composition of bornite is usually written as Cu_5FeS_4. However, Merwin and Lombard (1937) and later Yund and Kullerud

(1960) have shown that bornite has a considerable solid solution field in the system Cu-Fe-S. This field extends from chalcocite and digenite to a point on the join Cu_5FeS_4-$CuFeS_{2-x}$ at 700° C. (Fig. 2, after Yund and Kullerud, 1960). Kullerud (1960) showed that complete solid solution exists between Cu_5FeS_4 and Cu_9S_5 above 335° C. and that the solubility of Cu_9S_5 in Cu_5FeS_4 is less than 5 mole per cent below approximately 205° C. Brett (1963) showed that the solubility of $CuFeS_{2-x}$ in Cu_5FeS_4 and the solubility of Cu_2S in Cu_5FeS_4 are less than 5 mole per cent below about 200° C.

Available analyses of natural bornites (*e.g.* Zies and Merwin, 1955) indicate that they lie close to Cu_5FeS_4 in composition, in agreement with
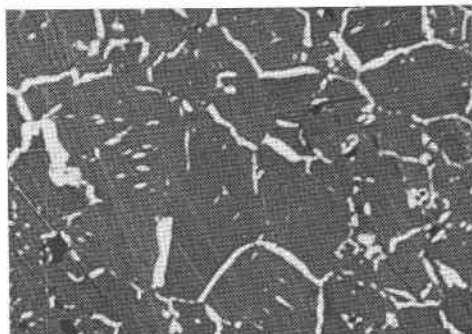

Fig. 1. Bornite (grey from an unknown New Mexico locality with chalcopyrite (white) which exsolved after heating at 250° C. for 1 hour. ($\times$600).

For similar photographs see Takeuchi and Nambu (1956), McCauley (1958, 1961) and Prouvost (1960).

the above experimental results. Cell-edge determinations on natural bornites (Brett, 1962a) support this conclusion.

Polymorphic changes. The structures of the three polymorphs of Cu_5FeS_4 have been determined by Morimoto and Kullerud (1961). A non-quenchable face-centered cubic form is stable above $228\pm5°$ C. A metastable cubic form ($Fd3m$ or $F\bar{4}3m$) appears on rapid cooling from above this temperature, but inverts to the stable low temperature tetragonal polymorph within days.

Previous Work

Wandke (1926) heated bornite from five localities at 160° C. Chalcopyrite formed in some of these, but because the experiments were not performed in a controlled atmosphere, little may be derived from the results. Merwin and Lombard (1937) heated a natural bornite containing

about 2 per cent of fine grains of chalcocite (or digenite). At 200° C. they obtained chalcopyrite in addition to the original bornite and chalcocite, and at 300° C. the chalcocite disappeared.

Sugaki (1949, 1955) reported that a specimen containing bornite with a little chalcopyrite from the Jinmu Mine, Japan, a skarn deposit, exsolved additional chalcopyrite when heated in sealed non-evacuated glass tubes at temperatures between 200° C. and 380° C. Sugaki (1949) suggested that the bornite contained chalcopyrite in metastable solid solution, which exsolved on heating.
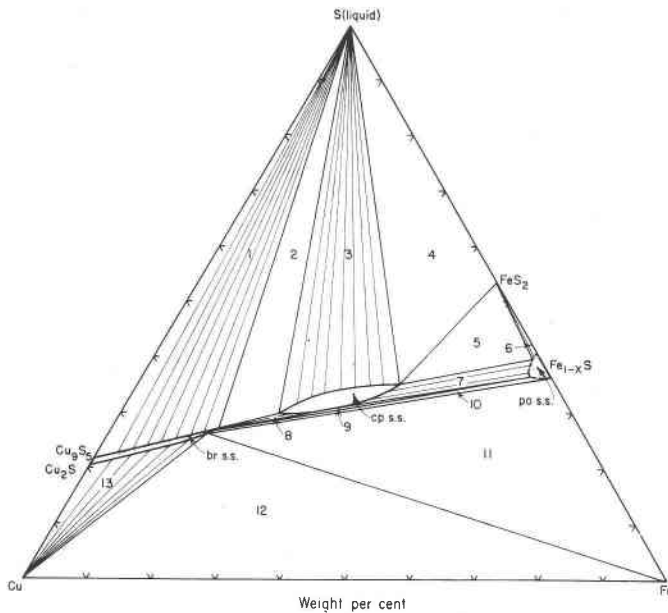

FIG. 2. The system Cu-Fe-S at 700° C. (*Carnegie Inst. Wash. Year Book* 59, Fig. 43, after Yund and Kullerud, 1960.)

Takeuchi and Nambu (1956) heated bornites from four Japanese localities in sealed tubes at temperatures ranging from 100° C. to above 450° C. They suggested that the exsolution of chalcopyrite was due to coalescence of submicroscopic particles in the bornite. Although they analyzed each of the bornites (Table 1), the analyses are not reliable because the specimens contained inclusions. A description of their analytical method is not given.

Gaucher (1959) concluded that bornites which exsolve chalcopyrite on heating never attained elevated temperatures during their formation or later, because chalcopyrite would have exsolved in nature even at moder-

ate temperatures. Prouvost (1960) observed the exsolution of chalcopyrite, with subordinate amounts of a blue sulfide, on heating bornite from Funambana, Madagascar, at 350° C. in a nitrogen atmosphere. He suggested that the bornite was stoichiometric initially, and decomposed to chalcopyrite and chalcocite on heating. The analysis of his material is given in Table 1.

Morimoto *et al.* (1960) heated bornite from the Carn Brea Mine, Cornwall, a hypothermal deposit, at 175° C. in evacuated silica glass tubes. Part of the bornite, which was lighter in color than the main mass prior to heating, exsolved fine lamellae of chalcopyrite.

TABLE 1. ANALYSES OF BORNITES BY PREVIOUS WORKERS

Locality	Type of Deposit	Cu	Fe	S
Cu_5FeS_4		63.33	11.12	25.55
Sakurago Mine, Japan	Contact metasomatic in limestone	63.65	11.66	24.69[1]
Sangasho Mine, Japan	meso-hypothermal vein	62.57	11.51	25.92[1]
Kotzu Mine, Japan	Kieslager	64.03	10.83	25.14[1]
Yakuwa Mine, Japan	meso-hypothermal vein	66.44	8.82	24.74[1]
Funambana, Madagascar		63.06	11.34	25.60[2]

[1] Analysis by Takeuchi and Nambu (1956) recalculated to 100%, silica subtracted and analysis again recalculated to 100% by the present authors.

[2] Analysis by Prouvost (1960), recalculated to 100%.

Phillips (1960) reported the exsolution of chalcopyrite from bornite from a red bed deposit in Utah during the preparation of a polished thin section which was not heated above 120° C. He concluded that iron was removed from the bornite by acid leaching so that later heating caused exsolution of chalcopyrite.

McCauley (1958, 1961) obtained exsolution of chalcopyrite in bornite from red-bed type deposits in Pennsylvania after heating the specimens in sealed tubes at temperatures ranging from 75° C. to 300° C. He suggested that the chalcopyrite may be in metastable solid solution in the bornite, or alternatively that bornite breaks down to chalcopyrite and a copper-rich phase on heating.

Digenite has been observed with chalcopyrite as a product of heating experiments on natural bornites (J. W. Greig, pers. comm., 1962; J. Prouvost, pers. comm., 1962).

Experimental Methods

Experiments were performed in evacuated silica glass tubes under the pressure of the system and in gold tubes under fixed confining pressures. The phases were identified by the standard techniques of reflected light microscopy and x-ray powder diffraction.

Determinations of the bornite cell edges were made using a Norelco x-ray diffractometer with CuKα radiation. Oscillations were made about the (440) peak; both Lake Toxaway quartz ($d_{112} = 1.8177$ Å) and silicon ($d_{220} = 1.9200$ Å) were used as standards. At least six oscillations at one-half degree per minute were made for each determination.

Natural bornite was used as starting material in most experiments. Elemental copper, iron and sulfur of high purity (>99.97 weight per cent) were used in the synthetic studies.

Exsolution of Chalcopyrite from Natural Bornite

Results of heating experiments. Bornites from nine localities were heated at temperatures between 75° and 800° C. Each bornite specimen was examined microscopically prior to heating in order to establish its homogeneity. Phases other than bornite were present in many samples (Table 2). The heating results (Table 2) indicate that only those bornites from Similkameen, B. C.; Beaverdell, B. C.; and red bed copper localities in Utah and New Mexico exsolved chalcopyrite (Fig. 1).

The upper and lower limits at which the exsolution occurred are approximately 400° C. and 75° C., respectively. The reaction is rapid: chalcopyrite was completely exsolved at 200° C. within 3 minutes. The bornite color before heating is tombac; after heating it is bluer.

Digenite was not detected as an exsolution product in the heating experiments in the present study.

All bornites gave typical tetragonal bornite x-ray patterns both before and after heating[1] except for those heated above 228° C., which gave a cubic pattern after heating and chilling. The cubic polymorph inverted to the low-temperature tetragonal polymorph after a few days at room temperature. Some of the red bed bornites from Utah showed faint chalcopyrite reflections before heating; less than 2 per cent chalcopyrite was visible microscopically in these specimens. The chalcopyrite which formed during the heating process was identified both from its optical properties and by the appearance of the three principal tetragonal chalcopyrite reflections (112, 024, and 132) in x-ray powder diffraction patterns.

Unheated bornite specimens from the Utah localities (Table 2) were

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[1] See footnote, p. 1096.

TABLE 2. HEATING EXPERIMENTS ON NATURAL BORNITE

Locality	Temperature °C	Time	Impurities before heating (vol. per cent)	Results
Moonta, Sth. Australia	270	2 hrs.	10% chalcopyrite	unchanged
Messina, South Africa	270	2 hrs.	none	unchanged
Magma, Arizona	250	2 hrs.	none	unchanged
Magma, Arizona	300	24 hrs.	none	unchanged
Bristol, Conn.	250	2 hrs.	none	unchanged
Similkameen, B. C.	265	1 hr.	20% gangue	blebs and coalescing laths of chalcopyrite from 5–25% by volume
Beaverdell, B. C.	100	3 days	20% chalcopyrite, 10% gangue	unchanged
Beaverdell, B. C.	250	3 hrs. (cooled in 10 hrs.)	20% chalcopyrite, 10% gangue	chalcopyrite in irregular blebs up to 15% in addition to original chalcopyrite
Beaverdell, B. C.	270	2 hrs.	20% chalcopyrite, 10% gangue	chalcopyrite lamellae and chalcopyrite at grain boundaries of bornite; 15% additional chalcopyrite present
Red bed bornite, Utah	75	8 days	5% chalcocite or digenite	no change
Red bed bornite, Utah	75	10 days	5% chalcocite or digenite	chalcopyrite in irregular blebs and masses up to 5%
Red bed bornite, Utah	90	4 hrs.	5% chalcocite or digenite	no change
Red bed bornite, Utah	100	4 hrs.	5% chalcocite or digenite	up to 15% chalcopyrite in laths
Red bed bornite, Utah	250	3 min.	5% chalcocite or digenite	laths and lamellae of chalcopyrite up to 15%
Red bed bornite, Utah	250	1 hr.	5% chalcocite or digenite	laths and lamellae of chalcopyrite up to 15%
Red bed bornite, Utah	300	1 hr.	5% chalcocite or digenite	chalcopyrite exsolved in irregular grains and pods exhibiting caries texture; up to 12%
Red bed bornite, Utah	350	1 hr.	5% chalcocite or digenite	chalcopyrite exsolved in blebs and laths; up to 12%
Red bed bornite, Utah	400	1½ hrs.	5% chalcocite or digenite	local formation of irregular blebs or laths up to 2%
Red bed bornite, Utah	600	1 hr.	5% chalcocite or digenite	unchanged

TABLE 2—(Continued)

Locality	Tem-pera-ture °C	Time	Impurities before heating (vol. per cent)	Results
Red bed bornite, Utah	800	1 hr.	5% chalcocite or digenite	cc or dg dissolved; particles of grey blue phase remain
Red bed bornite, Utah	800	1 week	5% chalcocite or digenite	cc or dg dissolved; particles of grey blue phase remain
Red bed bornite, Utah (2nd locality)	200	1½ hrs.	5% chalcocite or digenite	irregular crossing laths, vein-like laths of chalcopyrite up to 15%
Red bed bornite, New Mexico	200	1 hr.	10% chalcopyrite, 5% chalcocite or digenite	formation of chalcopyrite at grain boundaries up to 10%
Synthetic Cu_5FeS_4	200	1 hr.	—	no change
Synthetic Cu_5FeS_4	200	10 days	—	no change

studied by means of an electron microscope, using the palladium-carbon negative replica technique. This study was made in order to determine whether the chalcopyrite was present in the bornite as a submicroscopic phase as suggested by Takeuchi and Nambu (1956). No phase other than bornite was observed in the electron micrographs which were made at magnifications up to 10,000 times.

Effect of pressure. In order to observe the effect of pressure on the reaction induced by heating sulfur-rich bornites, Utah bornite was heated for 24 hours in a welded gold tube under approximately 2000 bars hydrothermal pressure at 200° C. in a cold-seal bomb. Approximately the same amount of chalcopyrite exsolved as in the silica glass tube experiments at 200° C.

Chemical analysis. Bornite usually cannot be accurately analyzed by chemical methods because of the presence of included sulfides. This is unfortunate as a slight deviation from stoichiometry could be critical in determining the behavior of a bornite on heating. Because of separation difficulties, no analyses of bornite were made in the present study.

Effects of oxidation. The possibility that oxidation could be responsible for the formation of chalcopyrite in some heated bornites was investigated. The Bristol, Connecticut, bornite was chosen because of its purity and because the unoxidized specimen did not exsolve chalcopyrite on heating.

Two samples were finely ground and exposed to the air for 5 days and 4 months, respectively. The originally tombac colored bornite changed color to a bluish purple in both experiments (see Kullerud *et al.*, 1960) so that some oxidation was assumed to have taken place. There was no detectable change in weight on oxidation. After heating both samples of the oxidized bornite at 270° C. for 15 minutes, approximately 2 vol. per cent of a phase resembling chalcopyrite in optical properties was found as irregular blebs only around the grain boundaries of the bornite. No further chalcopyrite was developed upon heating for 4 hours. The oxidized bornite, annealed at 100° C. for 2 weeks, remained unchanged. Oxidized

TABLE 3. CELL DIMENSION (a) OF NATURAL BORNITES BEFORE AND AFTER
HEATING AT 250° C. FOR 1 HOUR

Locality	a (prior to heating) $\pm .005$ Å	a (after heating) $\pm .005$ Å[1]
Magma, Ariz.	10.950	10.950
Bristol, Conn.	10.945	10.945
Messina, South Africa	10.956	10.956
Red bed bornite, Utah[2]	10.932	10.950
Red bed bornite, Utah[2]	10.928	10.950
Red bed bornite, second Utah locality[2]	10.906	10.950
Oxidized Bristol bornite[2]	10.958	10.950
Synthetic Cu_5FeS_4	10.950	10.950

[1] Uncertainty represents standard deviation from the mean of cell edges calculated from seven oscillations.

[2] Bornite exsolves chalcopyrite on heating.

synthetic stoichiometric bornite treated the same way as the Bristol bornite produced a small amount (less than 1 vol. per cent) of chalcopyrite, upon heating at 300° C. for 1 hour. Exsolution of chalcopyrite from bornite can therefore be caused by heating oxidized bornite.

Effect of annealing on cell edge. The a cell dimension of some bornites was measured before and after heating (Table 3). Table 3 shows that the cell edge of natural bornite which does not exsolve chalcopyrite is almost identical to that of stoichiometric bornite, whereas those bornites which exsolve chalcopyrite have significantly smaller cell edges. If the latter bornites contain only Cu, Fe, and S, a cell dimension smaller than that of stoichiometric bornite (10.950 ± .005 Å) may be due to either a change in composition towards $CuFeS_2$ relative to Cu_5FeS_4 (Brett, 1962b) or higher sulfur content (see next section), or both. Upon heating, each cell dimension reverts to 10.950 Å. The small dimension cannot be ascribed to

oxidation because the oxidized Bristol bornite, prior to heating, had a greater cell edge than the unoxidized bornite.

STUDIES ON SYNTHETIC BORNITE

Synthesis of sulfur-rich bornite and relation of cell edge to composition. Bornite compositions from Cu_5FeS_4 to $Cu_5FeS_{4.12}$[1] were synthesized at 700° C. and 600° C. and rapidly cooled (Table 4). Bornite of accurately known composition could not be synthesized in runs in which the sulfur

TABLE 4. RESULTS OF EXPERIMENTS USED TO OBTAIN FIG. 4

Composition			Tempera-ture, °C	Time, Days	Products	a of bornite ($\pm$ .005 Å)
Cu	Fe	S				
63.33	11.12	25.55	700	14	bn	10.950
63.23	11.12	25.65	600	15	bn	10.942
63.06	11.09	25.85	600	15	bn	10.924
62.81	11.04	26.15	600	15	bn+S[1]	10.909
62.11	11.94	25.95	600	75	bn	10.932
62.15	12.45	25.40	700	15	bn	10.957
62.85	11.44	25.71	700	15	bn	10.939
62.73	12.06	25.20	910	3	bn	10.958
61.48	12.90	25.62	900	32	bn	10.940
60.87	12.77	26.36	700	21	bn	10.915
59.60	13.62	26.76	700	90	bn[2]	10.905
63.97	11.23	24.80	700	21	bn	10.965
61.89	12.28	25.83	500	21	bn	10.934
60.55	13.25	26.20	700	15	bn	10.915

[1] Sulfur condensed from vapor during cooling.

[2] Plus 0.5 vol. per cent chalcopyrite as quench product.

content was greater than that of $Cu_5FeS_{4.06}$ because sulfur which had condensed from the vapor was always a product in addition to homogeneous bornite. Sulfur-rich bornites therefore have a considerably higher sulfur vapor pressure than Cu_5FeS_4. Attempts to synthesize the more sulfur-rich compositions in gold tubes under 500 bars confining pressure, to eliminate the vapor phase, were unsuccessful because chalcopyrite exsolved from these preparations even during the most rapid cooling (about 30 sec.) of the cold-seal pressure vessel.

The maximum sulfur content of synthetic bornite at 600° C. is greater than 26.02 weight per cent (Fig. 3), but it could not be accurately deter-

[1] The above formula correctly indicates chemical composition, it may or may not be structurally correct.

mined. The relation of the a cell dimension to the composition of sulfur-rich bornite is shown in Fig. 3. The cell edge appears to decrease linearly with increasing sulfur content.

Solid solution of $CuFeS_{2-x}$ in stoichiometric Cu_5FeS_4 also causes a decrease in the cell edge (Brett, 1962b), and a solid solution of Cu_9S_5 increases the cell edge of bornite (Kullerud, 1960). Figure 4 shows a contoured plot of a cell dimensions obtained for homogeneous compositions close to Cu_5FeS_4 in the bornite solid solution field (Table 4). Although the
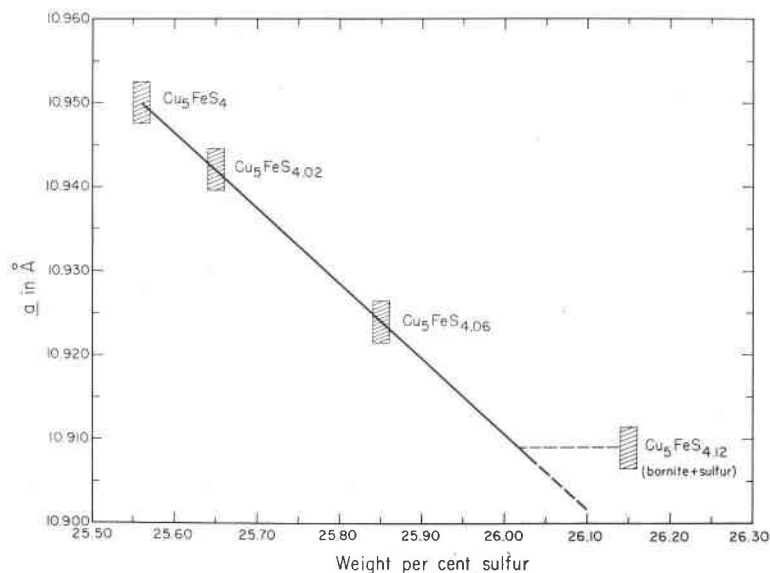

FIG. 3. Variation in the cell edge of synthetic bornite as a function of its sulfur content.

diagram covers only a narrow range of compositions, the change in cell dimension is quite appreciable (from 10.905 Å to 10.965 Å). Owing to the relatively small number of determinations Figure 4 is semiquantitative only. The contour interval (0.015 Å) is only triple the standard deviation of any single cell edge determination, hence the change in cell dimension with composition may be linear.

Exsolution of chalcopyrite and digenite. A bornite of $Cu_5FeS_{4.09}$ composition ($a = 10.909$ Å), synthesized at 600° C. was annealed at low temperatures. This synthetic bornite exsolved chalcopyrite in lamellae when heated at 400° C., 300° C. and 250° C. (Table 5). The cell edge after heating was larger than originally (Table 5). At 300° C. and 250° C. the cell edge was larger than that of stoichiometric Cu_5FeS_4. The data in Fig. 4 in-

Fig. 4. Contoured plot of cell edges obtained for homogeneous compositions close to bornite in the bornite solid solution field. Dots indicate bornite compositions synthesized.

dicate that the copper-to-iron ratio of the remaining bornite increased as would be expected after exsolution of chalcopyrite.

When the synthetic bornite of $Cu_5FeS_{4.09}$ composition was heated at 200° C. and 150° C. digenite exsolved in addition to chalcopyrite (Fig. 5). Digenite was identified both optically and by x-ray diffraction. The cell edge of the bornite in these preparations was less than that of bornite heated at 400°, 300°, and 250° C. From Fig. 4 it appears that the bornite

TABLE 5. ANNEALING OF SULFUR-RICH SYNTHETIC BORNITE

Composition	Temperature, °C	Time, Days	Products	a of bornite $\pm .005$ Å[1]
$Cu_5FeS_{4.09}$	400	5	bornite+chalcopyrite	10.930
$Cu_5FeS_{4.09}$	300	112	bornite+chalcopyrite	10.974
$Vu_5FeS_{4.09}$	250	112	bornite+chalcopyrite	10.981
$Cu_5FeS_{4.09}$	200	112	bornite+chalcopyrite+digenite	10.967
$Cu_5FeS_{4.09}$	150	3	bornite+chalcopyrite+digenite	—
$Cu_5FeS_{4.09}$	150	40	bornite+chalcopyrite+digenite	10.949
$Cu_5FeS_{4.09}$	100	14	bornite[2]	
$Cu_5FeS_{4.07}$	100	12	bornite[2]	

[1] Uncertainty represents standard deviation from the means of cell edges calculated from eight oscillations.

[2] Does not give normal low-temperature bornite X-ray pattern (see text).

heated below 250° C. was nearer Cu_5FeS_4 in composition than the bornite heated from 250° C. to 400° C. which did not exsolve digenite.

The results of these experiments as well as other data on the phase relations in the system Cu-Fe-S, which is currently being investigated by one of us (R.A.Y.), indicate that an assemblage consisting of digenite, bornite and chalcopyrite is stable at 200° C., and below. This assemblage occurs in nature and has been discussed by Bartholomé (1958) and McKinstry
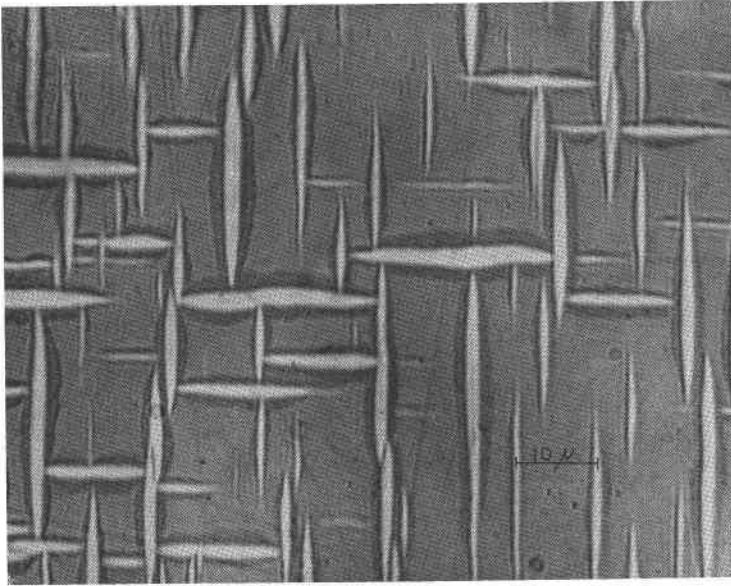

FIG. 5. Exsolution in an originally homogeneous synthetic bornite of $Cu_5FeS_{4.09}$ composition after annealing at 150° C. for 3 days. Bornite (light gray) with chalcopyrite lamellae (white) which are rimmed by digenite (dark gray).

(1959). Sulfur-saturated synthetic bornite synthesized at 600° C. exsolves chalcopyrite at 400° C., 300° C. and 250° C. and chalcopyrite plus a digenite-rich phase at 200° C. and 150° C. because of the decreased solubility of sulfur in bornite at these temperatures. Only chalcopyrite exsolves above *ca.* 200° C. because the composition of the sulfur-rich bornite lies in the two-phase field chalcopyrite and bornite-digenite solid solution.

It should be emphasized that the exsolved phase referred to here as chalcopyrite is probably not stoichiometric $CuFeS_2$. A large chalcopyrite solid solution field exists above 500° C. (Merwin and Lombard, 1937; Yund and Kullerud, 1960) and the solid solution field is undoubtedly extensive at lower temperatures.

Synthetic bornites of $Cu_5FeS_{4.09}$ and $Cu_5FeS_{4.07}$ compositions were annealed at 100° C. for 14 and 12 days, respectively (Table 5). Exsolution was not observed in these bornites; however, the x-ray powder diffraction pattern after annealing is significantly different from that of low-temperature tetragonal bornite. Details of this phase will be published elsewhere.[1]

CONCLUSIONS

1. The bornite solid solution field at 600° C. extends to approximately 0.5 weight per cent more sulfur than stoichiometric Cu_5FeS_4. At 200° C., which is below the crest of the digenite-bornite solvus, a tie line exists between digenite and chalcopyrite. The univariant assemblage bornite +chalcopyrite+digenite+vapor is therefore stable at 200° C. and below.

2. All natural bornites which exsolve chalcopyrite on heating are characterized by a relatively high sulfur-to-metal ratio as compared to stoichiometric Cu_5FeS_4. The similarity in properties between synthetic sulfur-rich bornite and the natural bornites is evidence for the conclusion. These properties include cell edge, color and behavior on heating.

In addition to their high sulfur content some of these natural bornites contain iron in excess of stoichiometric Cu_5FeS_4. This is indicated by the failure of some sulfur-rich bornites to exsolve digenite below *ca.* 200° C., or at least as much digenite as a synthetic sulfur-rich bornite with a Cu/Fe ratio of 5:1. A bornite which is both sulfur and iron rich would exsolve only chalcopyrite.

3. A natural bornite which does not exsolve chalcopyrite on heating will do so when oxidized and heated. The color and *a* cell dimension of oxidized bornite is different from that of sulfur-rich bornite.

4. There is no evidence supporting the suggestion that chalcopyrite necessarily occurs as a submicroscopic phase in bornites which exsolve chalcopyrite on heating.

5. Sulfur-rich bornites are especially common in red bed copper deposits; so far all samples from these deposits investigated by the writers exsolved chalcopyrite on heating. In addition, both McCauley (1958, 1961) and Phillips (1960) reported chalcopyrite exsolution in bornites from red bed copper deposits.

6. The results of the present study suggest that the maximum temperature of formation of sulfur-rich bornites is less than 75° C., in agreement with Gaucher's (1959) conclusion that bornites which exsolve chalcopy-

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[1] *Note added in proof:* Further examination of diffraction patterns of natural bornites which exsolve chalcopyrite from several localities discloses that they are a mixture of tetragonal bornite and the new phase.

rite on heating never attained elevated temperatures. It would therefore appear that sulfur-rich bornite occurring in deposits formed at higher temperature was deposited by later, possibly supergene, processes below about 75° C.

7. The writers have not explained why bornite formed in nature below 75° C. can contain more sulfur than bornite formed between 75° C. and 400° C. We have found, however, that $Cu_5FeS_{4.09}$ synthesized at 600° C. is stable at 100° C. but decomposes to bornite (apparently Cu_5FeS_4), chalcopyrite, and digenite at 150° C. Sulfur-rich bornites may therefore be stable at both elevated temperatures and temperatures below about 100° C. to 75° C., depending on their composition.

8. The experimental results obtained by previous workers may be satisfactorily explained in the light of the present results. Most of the bornite analyses of Takeuchi and Nambu (1956) and Prouvost (1960) do not plot in the sulfur-rich portion of the bornite field. However, an error of 0.3 wt. per cent would be critical in determining whether a bornite is sulfur rich or not as may be seen from Fig. 4. Since sulfur analyses at best are precise to only ± 0.2 wt. per cent for sulfides free of inclusions (Kullerud and Yoder, 1959), the writers consider that the previous analytical results do not contradict their conclusions.

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