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SILVER - BEARING WITTICHENITE - CHALCOPYRITE - BORNITE INTERGROWTHS AND ASSOCIATED MINERALS IN THE MANGUALDE PEGMATITE, PORTUGAL

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ABSTRACT

Sulfide-rich samples from the Mangualde pegmatite, Viseu district, Portugal, contain intergrowths of wittichenite, chalcopyrite and bornite. The estimated compositions of these intergrowths plot in a Cu_2S-Bi_2S_3-$CuFeS_2$ diagram in a field extending from near the bornite composition point toward the wittichenite-chalcopyrite join. This composition field is presumably part of a wide bornite solid solution field, which exists at about 500°C in the Cu-Fe-Bi-S system. The textural development of the intergrowths shows (1) a stage of segregation of wittichenite and chalcopyrite from bornite solid solutions, (2) a stage of recrystallization and accumulation of the wittichenite segregations in larger blebs, veinlets and rims, commonly surrounding inclusions or earlier segregations of stannoidite, galena, a selenide of silver, a telluride and sulfide of silver, and native bismuth, and (3) a stage of recrystallization and accumulation of the chalcopyrite segregations in larger blebs, blades, veinlets and rims around the earlier accumulations of wittichenite. Microprobe analyses indicate about 0.2 wt. % Ag and 0.2 wt. % Bi in bornite and 0.2-1.1 wt. % Ag in wittichenite. The intergrowths were presumably formed by unmixing of high-temperature Ag-Bi-bearing bornite solid solutions subsequent to cooling below 271°C, i.e. the melting temperature of native bismuth. Grains of emplectite, matildite and Ag-bearing Bi-rich tennantite and tetrahedrite were formed by reaction of exsolved wittichenite with native bismuth, arsenopyrite, and loellingite.

SOMMAIRE

Des échantillons riches en sulfures provenant de la pegmatite de Mangualde, de la région de Viseu au Portugal, contiennent des enchevêtrements de wittichénite, de chalcopyrite et de bornite. Les compositions estimatives de ces enchevêtrements se placent, sur le diagramme Cu_2S-Bi_2S_3-$CuFeS_2$, dans un domaine qui s'étend du point figuratif de la bornite vers le joint wittichénite-chalcopyrite. On présume que ce domaine de composition fait partie d'un vaste domaine de solution solide de bornite qui existe vers 500°C dans le système Cu-Fe-Bi-S. Le développement textural des enchevêtrements indique: (1) un stade de ségrégation de wittichénite et chalcopyrite de la solution solide de bornite; (2) un stade de recristallisation et d'accumulation des ségrégations de la wittichénite dans de plus grandes plages, veinules et bordures, souvent entourant des inclusions ou des ségrégations antérieures de stannoïdite, de galène, d'un séléniure d'argent, d'un tellurure et sulfure d'argent, et de bismuth natif; (3) un stade de recristallisation et d'accumulation des ségrégations de chalcopyrite dans de plus grandes plages, lames, veinules et bordures autour des accumulations antérieures de wittichénite. Des analyses à la microsonde indiquent (en poids) environ 0.2% Ag et de 0.2% Bi dans la bornite et 0.2-1.1% Ag dans la wittichénite. On présume que les enchevêtrements ont été formés par démixtion des solutions solides de bornite de haute température, contenant Ag et Bi, après refroidissement à moins de 271°C, température de fusion du bismuth natif. Des grains d'emplectite, de mathildite et de tennantite riche en bismuth et à teneur d'argent, ainsi que de tétraédrite ont été formés par réaction de wittichénite avec bismuth natif, arsénopyrite et loellingite.

(Traduit par le journal)

INTRODUCTION

The Mangualde pegmatite, Viseu district, Portugal, is a beryl- and Li-phosphate-bearing pegmatite (De Jesus 1933). The pegmatitic masses of chiefly feldspars, quartz and micas contain small sulfide nests and impregnations, mostly consisting of chalcopyrite with minor Cu-Fe-Sn-sulfides, sphalerite, tennantite, bornite, wittichenite, arsenopyrite, loellingite, native bismuth, molybdenite, and other minerals (Oen 1959, 1970; Oen *et al.* 1973; Oen & Kieft 1976). There are also veinlets and nests of predominantly arsenopyrite and loellingite and, more rarely, of predominantly bornite. In these sulfide nests wittichenite is always intergrown or closely associated with bornite and chalcopyrite in two kinds of aggregates.

(a) *Bornite-rich aggregates consisting of wittichenite-chalcopyrite-bornite intergrowths associated with minor chalcopyrite.* Under the microscope the coarse, cm-size bornite grains or intergrowths commonly exhibit a zonal texture, showing core zones with estimated planimetric proportions of up to 3% wittichenite and up to 12% chalcopyrite intergrown as inclusions in the bornite, and rim zones with less than 1% wittichenite and chalcopyrite inclusions in the bornite. Assuming that for a rough approximation planimetric and volumetric percentages may be considered as roughly proportional and that the wittichenite, bornite and chalcopyrite have the compositions Cu_3BiS_3, Cu_5FeS_4, $CuFeS_2$ and approximate molar volumes of 110 cc, 97 cc and 44 cc, respectively, estimated molecular compositions of the intergrowths can be calculated and plotted in the Cu_2S-Bi_2S_3-$CuFeS_2$ diagram of Figure 1A. The Figure shows that the estimated compositions of the bornite intergrowths fall roughly in the area between *a* and the bornite composition point Cu_5FeS_4. The bornite aggregates contain interstitial masses and veinlets of chalcopyrite with Cu-Fe-Sn-sulfides (Oen 1970); often there is an interfingering of finer grained bornite and chalcopyrite, sometimes resulting in emulsion- or eutectic-like textures.

(b) *Chalcopyrite-rich aggregates consisting of chalcopyrite with minor, interstitial intergrowths of bornite, wittichenite and chalcopyrite.* The compositions of the intergrowths range roughly between those of some chalcopyrite-wittichenite-bornite intergrowths with planimetric proportions of less than 1% chalcopyrite, less than 5% wittichenite and more than 94% bornite, and those of some wittichenite-bornite-chalcopyrite intergrowths with planimetric proportions of up to 25% wittichenite, up to 25% bornite and up to somewhat more than 50% chalcopyrite. Recalculated in molecular percentages the estimated compositions of the intergrowths fall roughly in the area between *b* and *c* in Figure 1A.

The chalcopyrite-bornite-wittichenite relations are discussed in the following with reference to phase relations in the Cu_2S-Bi_2S_3-$CuFeS_2$ system (Fig. 1). However, inclusions of Pb-, Ag-, Se-, Te-, Sn- and Zn-bearing minerals in the intergrowths, the presence of Ag in more than trace amounts in wittichenite and bornite, and the association with sphalerite, stannoidite and mawsonite, arsenopyrite, loellingite and native bismuth, indicate crystallization from complex Pb-Zn-Sn-Ag-Te-Se-As-Sb-bearing Cu-Fe-Bi-S-rich solutions.

PHASE RELATIONS IN THE Cu_2S-Bi_2S_3-$CuFeS_2$ SYSTEM

Schematic phase relations in the Cu_2S-Bi_2S_3-$CuFeS_2$ system at about 500° and 200°C (Figs. 1A & 1B) were deduced from the available experimental and paragenetic data summarized below.

In the Cu_2S-$CuFeS_2$ system at 500°C there are two solid solution fields: digenite-bornite *ss*, extending from compositions comprising Cu_2S and $Cu_{1.8}S$ to beyond the bornite composition Cu_5FeS_4, and chalcopyrite *ss*. The solid solution limits decrease with temperature and below 290°C the digenite-bornite *ss* field is disintegrated into a narrow bornite and broader chalcocite (Cu_2S) and digenite ($Cu_{1.8}S$) *ss* fields (Yund & Kullerud 1966).

In the Cu_2S-Bi_2S_3 system there are six stable phases at 500°C: Cu_2S *ss*, Cu_9BiS_6 *ss*, Cu_3BiS_3 *ss* (wittichenite), $Cu_3Bi_5S_9$ *ss*, $CuBi_3S_5$ and Bi_2S_3 (bismuthinite) (Buhlmann 1971; Sugaki & Shima 1972). Below about 400°C, Cu_9BiS_6 *ss* breaks down to form Cu_2S *ss* and wittichenite, and $Cu_3Bi_5S_9$ decomposes into cuprobismutite ($Cu_{24}Bi_{26}S_{51}$) and $CuBi_3S_5$. At still lower temperatures cuprobismutite is replaced by emplectite, which has about the same composition as cuprobismutite. The stable phases at 200°C are chalcocite (and digenite), wittichenite, emplectite, $CuBi_3S_5$ and bismuthinite.

Sugaki & Shima (1971) have found that in the Cu-Fe-Bi-S system at 500°C a wide bornite *ss* area intervenes between wittichenite and chalcopyrite. Stable two-phase assemblages at this temperature include Cu_9BiS_6 *ss*-bornite *ss*, wittichenite *ss*-bornite *ss*, $Cu_3Bi_5S_9$ *ss*-bornite *ss*, $Cu_3Bi_5S_9$ *ss*-chalcopyrite *ss*, $CuBi_3S_5$-chalcopyrite, bismuthinite-chalcopyrite, and bornite *ss*-chalcopyrite *ss*. In Figure 1A the wide extension of the Bi-bearing bornite *ss* field toward chalcopyrite is speculative and based on the estimated compositions of the wittichenite-bornite-chalcopyrite intergrowths as described above. The lower temperature phase relations in the Cu_2S-Bi_2S_3-$CuFeS_2$ system were inferred from paragenetic data. The paragenesis bornite-wittichenite-chalcopyrite described in this paper suggests that with falling temperature and shrinking of the bornite *ss* area a wittichenite-chalcopyrite tie line is established.

An emplectite-chalcopyrite tie line is suggested by the occurrence of emplectite in some chalcopyrite-wittichenite veinlets described later in this paper. The relations of hodrushite, a mineral found in ores containing chalcopyrite and possibly wittichenite (Koděra *et al.* 1970) are uncertain; hodrushite has a composition similar to, but optical and X-ray properties different from, those of the synthetic phase $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$, which is stable below 500°C (Sugaki *et al.* 1972).

Phase relations in the Cu_2S-Bi_2S_3-$CuFeS_2$ system as shown in Figure 1 indicate the possibility of formation of high-temperature Bi-bearing bornite solid solutions, which on cooling will unmix to form bornite, wittichenite and chalcopyrite. These minerals in the Mangualde pegmatite show textural relationships consistent with such an origin.

TEXTURAL RELATIONSHIPS

(a) *Bornite-rich aggregates*

The wittichenite-chalcopyrite-bornite intergrowths in the bornite-rich aggregates consist of bornite with microscopic inclusions of wittichenite and chalcopyrite.

The wittichenite inclusions occur in the bornite as very small blebs, commonly arranged in rows and coalesced to fine spindles or lenticles parallel to the bornite {111} directions, as larger blebs, as veinlets along crystallographic directions and recrystallization grain boundaries, and as rims along bornite-chalcopyrite grain boundaries (Fig. 2A-H). The coarser bornite grains usually have a rim zone with only few small blebs and lenticles of wittichenite; the central zone is characterized by the alternation of areas relatively rich in fine wittichenite blebs and lenticles and areas where these fine blebs and lenticles have apparently accumulated in larger bleb- and vein-like aggregates of fine-grained wittichenite showing radiating and columnar textures (Fig. 2C).

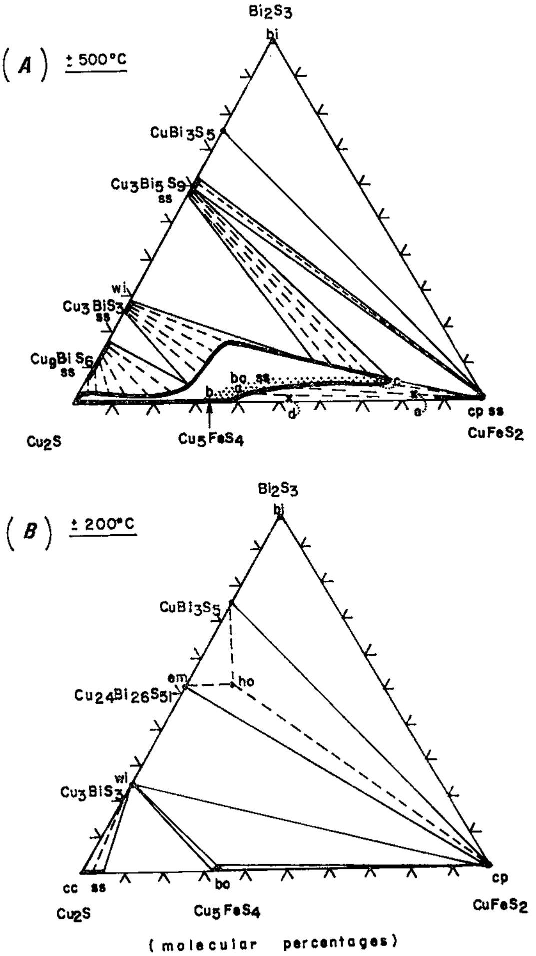

FIG. 1. Schematic phase relations in the Cu_2S-Bi_2S_3-$CuFeS_2$ system at about 500° and 200°C. The stippled area *b-a-c* in the bornite *ss* field in Fig. 1A represents estimated compositions of the intergrowths of wittichenite (*wi*), chalcopyrite (*cp*) and bornite (*bo*); bornite-rich assemblages may crystallize from solution *d*, chalcopyrite-rich assemblages from solution *e; bi* bismuthinite, *em* emplectite, *cc* chalcocite, *ho* hodrushite, *ss* solid solution.

The bornite and wittichenite often contain very small granular inclusions of galena, of an Ag-selenide which is possibly naumannite, of fine intergrowth of an Ag-telluride and an Ag-sulfide which are possibly hessite and acanthite, and of native bismuth (see analyses given in a later section of this paper). The polished sections have many holes, which may be due in part to the polishing away of these granular inclusions of not more than a few micron in size. However, the minerals constituting these inclusions commonly show a selective replacement by covellite and chalcocite (Fig. 2G) and possibly late-stage leaching and replacement may also have caused holes. Most granular inclusions and their holes are in the centre of wittichenite blebs with radiating textures, or occur as rows of granules and holes enclosed in wittichenite lenticles and veinlets (Fig. 2B, C, F, G). The granules have apparently acted as nuclei around which wittichenite segregations have accumulated. Disseminated granules in bornite and granules of native bismuth which form a fringe along a bornite grain boundary have also been observed. The granules of galena, Ag-selenide, Ag-telluride and Ag-sulfide, and native bismuth may have originated either as early segregations of the bornite

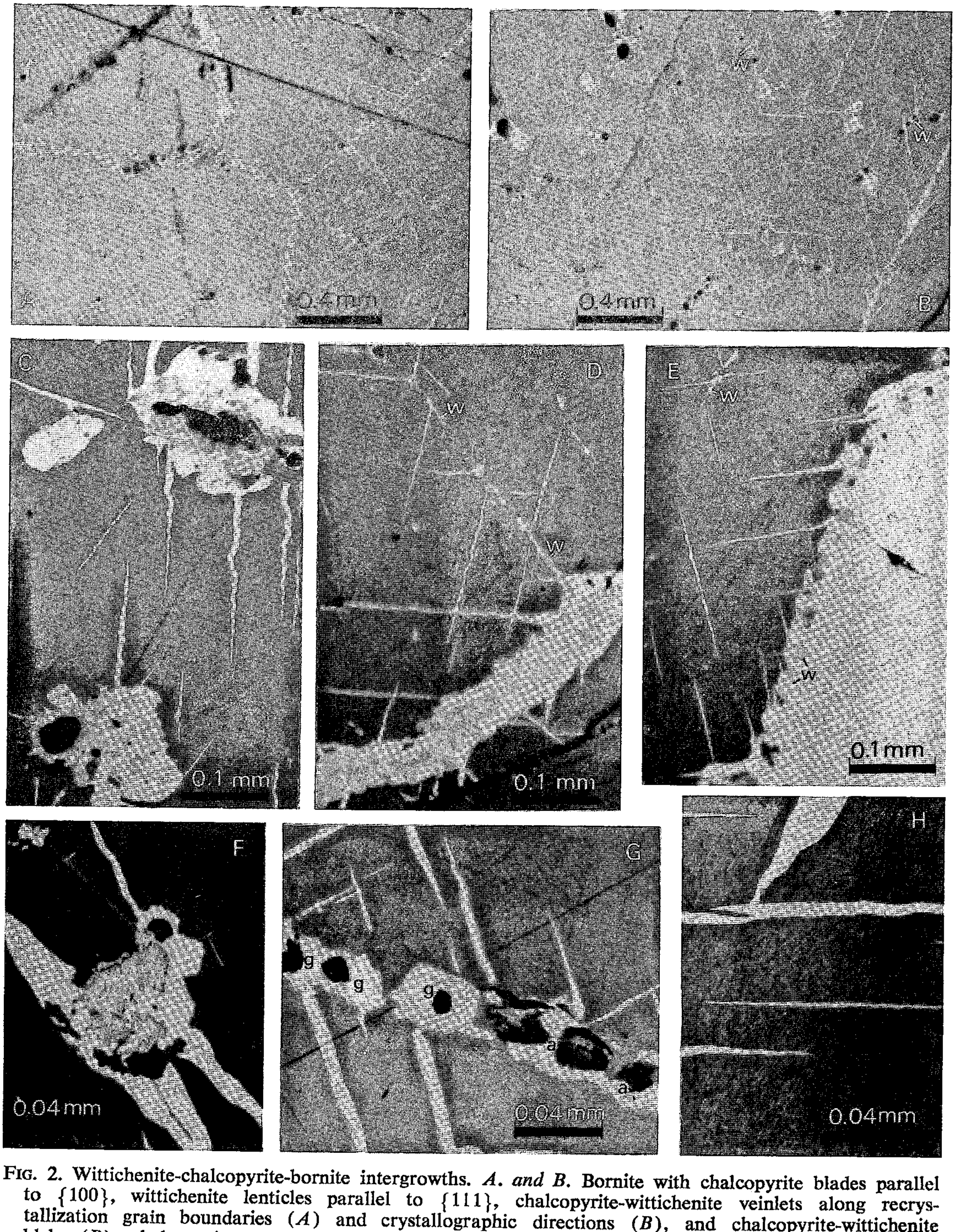

FIG. 2. Wittichenite-chalcopyrite-bornite intergrowths. *A. and B.* Bornite with chalcopyrite blades parallel to {100}, wittichenite lenticles parallel to {111}, chalcopyrite-wittichenite veinlets along recrystallization grain boundaries (*A*) and crystallographic directions (*B*), and chalcopyrite-wittichenite blebs (*B*); chalcopyrite and wittichenite appear in same shade of light grey; wittichenite (*w*) lenticles commonly show a row of holes. *C.* Chalcopyrite-wittichenite blebs in bornite; wittichenite shows columnar and radial textures around holes (black); wedge-shaped chalcopyrite blades open toward where they coalesce with larger chalcopyrite blebs surrounding the wittichenite. *D.* Wittichenite veinlet with chalcopyrite rims; row of wittichenite (*w*) blebs and lenticles in bornite. *E.* Bornite-chalcopyrite grain boundary with the bornite showing an outer rim of wittichenite (*w*) blebs and an inner rim of chalcopyrite. *F.* Intergrowth of Ag-telluride, Ag- and Cu-Ag-sulfides enclosed in a wittichenite bleb (light grey) surrounded by chalcopyrite blades in bornite. *G.* Bornite with chalcopyrite blades and a row of wittichenite blebs (light grey) enclosing granules of galena (*g*) and a Ag-selenide (*a*); replacement by covellite and chalcopyrite (dark grey); black are holes. *H.* Bornite with chalcopyrite blades and a very fine network of chalcopyrite lamellae parallel to {100}.

ss or as early crystallites or drops of liquid, which during crystallization of the bornite *ss* became attached to growth faces of the latter mineral and were eventually entrapped as inclusions. Wittichenite segregations also occur around inclusions of stannoidite.

Chalcopyrite in the bornite forms a relatively coarse network of lenticular and wedge-shaped blades parallel to $\{100\}$ of the bornite; the blades are enlarged where they coalesce with larger chalcopyrite blebs, veinlets and rims (Fig. 2A-H). Under crossed nicols the chalcopyrite blades extinguish parallel to their elongation, i.e. to the traces of $\{100\}$ of the bornite; apparently the chalcopyrite blades and their bornite host have parallel axes and the three sets of chalcopyrite blades show twin relationships with c-axes making angles of 90°. Some chalcopyrite blebs and veinlets in the bornite show sector twinning with twin individuals extinguishing in the same directions as the chalcopyrite blades; more commonly, however, there is complex, often poly-synthetic twinning in several directions. The frequent twinning of chalcopyrite in the intergrowths contrasts with the relatively rare twinning in chalcopyrite outside the intergrowths. Many bornite grains show patches with, besides the coarser chalcopyrite blades, another generation of extremely fine chalcopyrite lamellae which forms a dense network parallel to $\{100\}$ of the bornite (Fig. 2H).

The chalcopyrite blades, blebs, veinlets and rims commonly surround earlier accumulations of wittichenite. Thus, some chalcopyrite blades have developed around wittichenite lenticles parallel to $\{111\}$, chalcopyrite blebs and veinlets mostly enclose a wittichenite bleb or veinlet, and chalcopyrite rims usually adjoin an outer and earlier wittichenite rim (Fig. 2A-H). On the other hand, wittichenite blebs enclosing very fine chalcopyrite lamellae are rare.

The above observations suggest the following partly overlapping sequence:

(1) annealing recrystallization of the bornite *ss*, segregation of small wittichenite blebs and lenticles along grain boundaries and the $\{111\}$ directions in bornite, and segregation of very fine chalcopyrite lamellae along $\{100\}$ in the bornite (Fig. 4A);

(2) accumulation and recrystallization of the segregated wittichenite in columnar and radiating aggregates forming larger blebs, veinlets and rims often enclosing granules of galena, Ag-selenide, Ag-telluride and Ag-sulfide, Bi, and stannoidite (Fig. 4B);

(3) accumulation and recrystallization of the segregated chalcopyrite in coarser blades, larger blebs, and wider veinlets and rims, generally

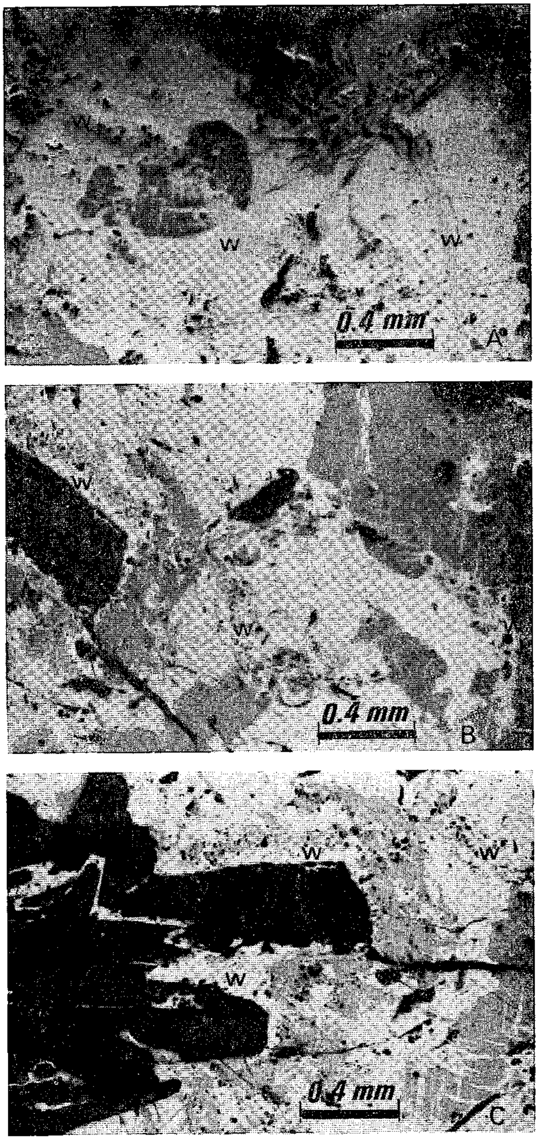

FIG. 3. Wittichenite-bornite-chalcopyrite intergrowths. Bornite dark grey; wittichenite and chalcopyrite grey to white; black is mica. *A*. Wittichenite (*w*) veinlets and aggregates in chalcopyrite and bornite; bornite patches in chalcopyrite have palimpsest appearance. *B*. Right side has a large patch of bornite with wittichenite (*w*) blebs and chalcopyrite blades; left side shows mainly chalcopyrite with wittichenite (*w*) veinlets and smaller bornite patches and blades of palimpsest appearance; the mica flake at the left is surrounded by columnar aggregates of wittichenite. *C*. Mica flake in the centre is the same as that shown in Fig. 3B; note wittichenite (*w*) aggregates surrounding the micas and remobilized wittichenite veinlets traversing the micas; at lower right is a bornite patch rich in chalcopyrite blades.

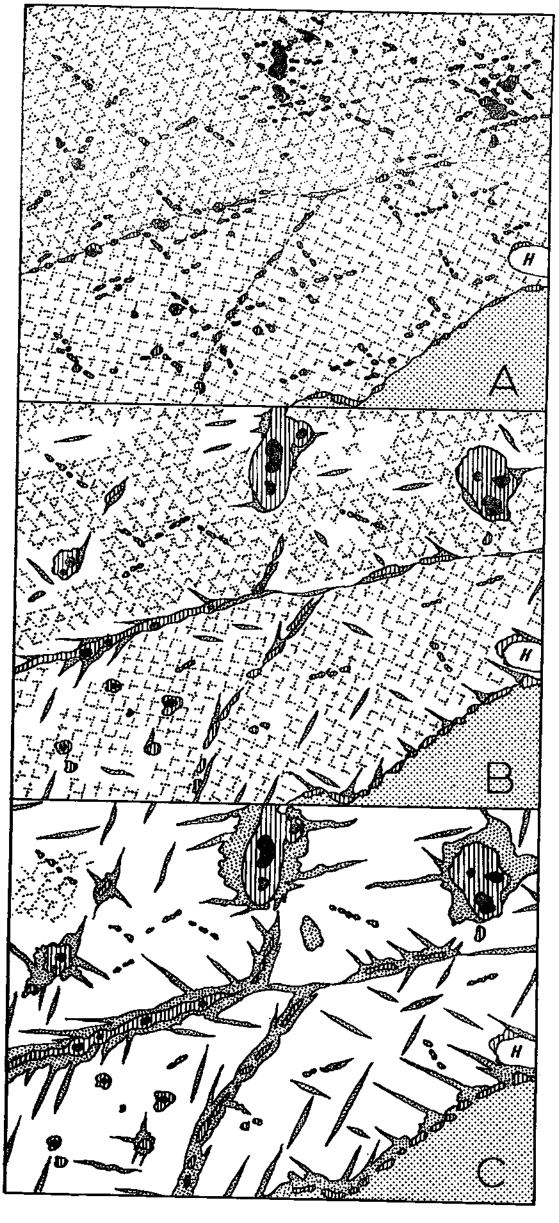

FIG. 4. Schematic representation (not to scale) of the textural development of the wittichenite-chalcopyrite-bornite intergrowths. Wittichenite vertically striated, chalcopyrite stippled, and bornite without special notation. *A*. Step 1: annealing recrystallization of bornite; segregation of wittichenite in small blebs and lenticles parallel to {111} and along recrystallization and grain boundaries in the bornite; segregation of chalcopyrite mainly in a fine network of lamellae parallel to {100} in the bornite; black areas are inclusions of galena, Ag-selenide, Ag-telluride, and Ag-sulfide; H is hexastannite. *B*. Step 2: accumulation and recrystallization of the segregated wittichenite in larger blebs, veinlets and rims. *C*. Step 3: accumulation and recrystallization of the segregated chalcopyrite in coarser blades, blebs and veinlets surrounding the wittichenite aggregates corresponds to the present appearance of the intergrowths.

surrounding the earlier accumulations of wittichenite and crystallographically intergrown with the bornite (Fig. 4C).

(b) Chalcopyrite-rich aggregates

The chalcopyrite-rich aggregates contain bornite-rich and chalcopyrite-rich intergrowths; the bornite-rich intergrowths show textures similar to those of the wittichenite-chalcopyrite-bornite intergrowths described above; the textures in chalcopyrite-rich wittichenite-bornite-chalcopyrite intergrowths are described below.

The wittichenite-bornite-chalcopyrite intergrowths generally show patches of bornite with few inclusions of wittichenite and chalcopyrite, passing laterally into patches of bornite with an increased amount of chalcopyrite blades and patches of chalcopyrite enclosing appreciable amounts of wittichenite and bornite of palimpsest appearance (Fig. 3A-C). The chalcopyrite and bornite often appear intergrown with parallel crystallographic axes in the same fashion as described in the previous section; simple and polysynthetic twinning in the chalcopyrite are frequent. Wittichenite accumulations occur in relatively coarse bleb-, vein- and rim-like aggregates of fine-grained columnar, otfen radiating crystals; these aggregates are sometimes enclosed in bornite, but more often they appear completely surrounded by chalcopyrite. Inclusions of native bismuth, Ag-selenide and Ag-telluride are extremely rare.

The bornite-rich and chalcopyrite-rich intergrowths show essentially similar textural characteristics and a similar sequence of steps in their development, but they differ in appearance because the proportions of the minerals in the intergrowths differ (Figs. 4, 5). The chalcopyrite-rich intergrowths were formed from $CuFeS_2$-Bi_2S_3-richer bornite solid solutions and apparently, the higher the proportions of segregated wittichenite and chalcopyrite, the more rapid these minerals gather in larger blebs, veinlets and grains. Therefore, step 1 in the sequence described in Figure 5 is very rarely preserved, but steps 2 and 3 are clearly shown by wittichenite aggregates enclosed in chalcopyrite rather than in bornite. Compared to the bornite-rich intergrowths, the formation of chalcopyrite-rich intergrowths involved a higher degree of unmixing

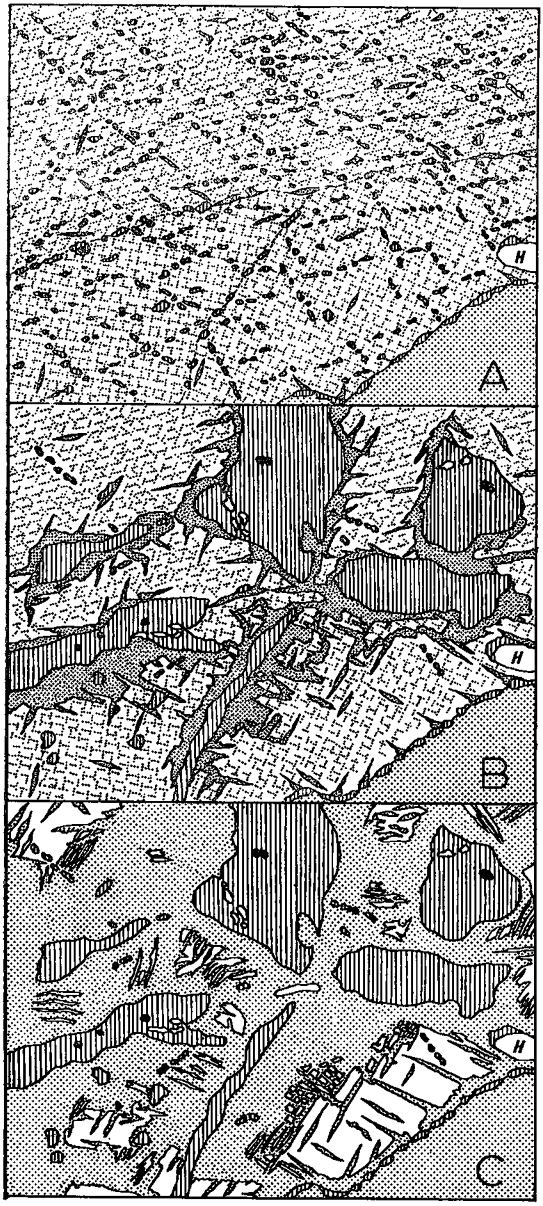

FIG. 5. Schematic representation (not to scale) of the textural development of the wittichenite-bornite-chalcopyrite intergrowths. Notations are the same as in Fig. 4. *A*. Step 1: same as in Fig. 4A, but the amounts of segregated wittichenite and chalcopyrite are considerably higher. *B*. Step 2: same as in Fig. 4B, but with the wittichenite accumulations attaining larger size and the accumulation of chalcopyrite around the wittichenite aggregates taking place at an accelerated rate. *C*. Step 3: same as in Fig. 4C, but with considerably more chalcopyrite involved. The sequence of steps is the same as in Fig. 4, but the resulting textures appear different (compare also Figs. 2, 3). Fig. 5C corresponds to the present appearance of the intergrowths, which consist essentially of wittichenite aggregates and bornite patches of palimpsest appearance enclosed in chalcopyrite.

recrystallization or rearrangement of grains within the intergrowths; chalcopyrite and wittichenite are concentrated in certain sectors of the intergrowths and further recrystallization is commonly manifested in a tendency of the intergrowths to disintegrate in separate aggregates of chalcopyrite, wittichenite, and bornite (Figs. 3A-C, 5). Some apparently remobilized wittichenite and chalcopyrite occur in cracks and along cleavages in adjacent crystals of arsenopyrite, loellingite and mica (Fig. 3C); emplectite, matildite, Bi-rich tennantite and tetrahedrite were formed in small grains by reaction with the arsenopyrite, loellingite and inclusions of native bismuth (Oen & Kieft 1976).

CHEMISTRY

Analyses were obtained with a Cambridge Geoscan microprobe operated under the following conditions: acceleration potentials 20 kV and 25 kV; counting times 50 sec; $K\alpha$ lines were used for Cu, Fe, Zn, S, Se and $L\alpha$ lines for Bi, Ag, Sn, Te; background corrections were based on measurements at either side of the analytical lines used. Standards were pure metals for Bi, Cu, Ag, Fe and Zn, analyzed pyrite for S, synthetic SnS for Sn, synthetic Cu_7Te_5 for Te and synthetic Ag_2Se for Se. Raw data were corrected using a computer program adapted from Springer (1967).

Table 1 gives average compositions and ranges of analytical values of the chalcopyrite, wittichenite and bornite in the bornite-rich and the chalcopyrite-rich intergrowths. The minerals show homogeneous compositions and no significant deviations from their theoretical formulae. The chalcopyrites and the bornites in the bornite-rich and in the chalcopyrite-rich intergrowths are similar in composition: the chalcopyrites have trace amounts of Ag and Bi, whereas the bornites are characterized by about 0.2 wt. % Ag and 0.2 wt. % Bi. The wittichenites in the bornite-rich intergrowths are commonly Fe-bearing and characterized by about 0.8 wt. % Ag, whereas those in the chalcopyrite-rich intergrowths are Fe-free and characterized by about 0.4 wt. % Ag. There is apparently a regular partition of Ag, Bi and other accessory elements in the minerals of the intergrowths. This agrees with the presumption that the intergrowths were formed by unmixing or decomposition of high-

TABLE 1. MICROPROBE ANALYSES OF CHALCOPYRITE, Ag-BEARING WITTICHENITE AND Ag-Bi-BEARING BORNITE; AVERAGE COMPOSITION AND RANGES OF ANALYTICAL DATA IN WEIGHT PERCENTAGES

	chalcopyrite		wittichenite		bornite	
	1	2	3	4	5	6
Cu	34.9 ±0.2	34.7 ±0.3	36.7 ±0.6	37.2 ±0.3	62.8 ±0.5	63.1 ±0.4
Fe	30.5 ±0.4	30.8 ±0.6	0.4 ±0.4	-	11.2 ±0.2	11.1 ±0.4
Zn	0.0-0.05	0.0-0.05	-	-	-	0.0-0.05
Sn	0.0-0.15	0.0-0.05	-	-	-	-
Ag	0.0-0.05	0.0-0.05	0.8 ±0.3	0.4 ±0.2	0.2 ±0.1	0.2 ±0.1
Bi	0.0-0.05	0.0-0.05	43.3 ±0.3	43.8 ±0.3	0.2 ±0.1	0.2 ±0.1
Se	0.0-0.01	-	-	-	0.0-0.03	-
Te	-	-	-	-	-	-
S	35.1 ±0.2	34.5 ±0.4	19.2 ±0.3	18.9 ±0.3	26.0 ±0.1	25.5 ±0.4
	100.5	100.0	100.4	100.3	100.4	100.1

bornite-rich intergrowths:
1. chalcopyrite $Cu_{1.00}Fe_{1.00}S_{2.00}$
3. wittichenite $Cu_{2.89}Fe_{0.03}Ag_{0.04}Bi_{1.04}S_{3.00}$
5. bornite $Cu_{4.93}Fe_{1.00}Ag_{0.01}Bi_{0.00(5)}S_{4.05(5)}$

chalcopyrite-rich intergrowths
2. chalcopyrite $Cu_{1.00}Fe_{1.00}Fe_{1.01}S_{1.99}$
4. wittichenite $Cu_{2.94}Ag_{0.02}Bi_{1.06}S_{2.98}$
6. bornite $Cu_{5.00}Fe_{1.00}Ag_{0.01}Bi_{0.00(5)}S_{3.98(5)}$

temperature solid solutions and not by metasomatic replacement involving disequilibrium relations among the minerals in the intergrowths. The homogeneous compositions of the minerals indicate rapid reaction rates and attainment of equilibrium, suggesting that the high-temperature Ag-Bi-bearing bornite solid solutions may represent an unquenchable phase, at least under geological conditions. The compositions of the chalcopyrite, bornite and wittichenite also suggest that unmixing occurred at rather low temperature, precluding appreciable solid solution in these minerals.

Investigations in the Ag_2S-Cu_2S-Bi_2S_3 system (Chen & Chang 1974) show that Ag_2S solid solution in wittichenite ranges up to $(Cu_{0.8}Ag_{0.2})_3BiS_3$ at 454°C. The association of wittichenite and Cu-rich matildite with about 28 mole % Cu_2S is stable near 454°C, but the association of Ag-poor wittichenite, Cu_3BiS_3, and Cu-free matildite, $AgBiS_2$, is apparently indicative of lower temperatures. In the Mangualde pegmatite, veinlets of remobilized chalcopyrite and wittichenite (about 0.4 wt. % Ag), derived from chalcopyrite-rich intergrowths, occur in crystals of arsenopyrite and loellingite and by reaction with inclusions of native bismuth have given rise to the formation of grains of matildite (approx. composition: Ag 27.7, Bi 55.4, S 16.6 wt. %). This association of Ag-poor wittichenite and Cu-free matildite must have been formed at temperatures below 271°C, the melting temperature of native bismuth. Also associated with the chalcopyrite-wittichenite veinlets are grains of emplectite (approx. composition: Cu 17.6, Bi 64.0, S 19.1 wt. %) and Ag-bearing Bi-rich tennantite and tetrahedrite with about 0.3 wt. % Ag and 9.0-19.0 wt. % Bi (Oen & Kieft 1976). In the arsenopyrite, loellingite and native bismuth, Ag was not detected with the microprobe. In the Mangualde pegmatite, silver is apparently a rare element, which was primarily concentrated in high-temperature Ag-Bi-bearing bornite solid solutions and associated inclusions of accessory Ag-minerals; the silver is now found in the decomposition and reaction products of the bornite solid solutions and in their inclusions.

The granular inclusions of galena, Ag-selenide, Ag-telluride and Ag-sulfide, and native bismuth in the intergrowths are generally less than 5 microns in size, too small for accurate microprobe analysis. An average of about 0.3 wt. % Ag and 1.5 ± 0.3 wt. % Se is indicated in the granules of galena. The galena is often associated with granules of a mineral (Fig. 2G) of approximate composition: Ag 70.0, Se 20.5, Cu 5.5, and S 3.0 wt. %. It is suspected that the Cu and S values may be due to the surrounding Cu-sulfides or to submicroscopic intergrowths with Ag-Cu-sulfides; with this in mind the observed chemistry and optical properties of the mineral are consistent with those of naumannite, Ag_2Se. Another type of granule is optically heterogeneous (Fig. 2F); under the microscope an acanthite-like phase can be distinguished, very finely intergrown with a somewhat darker phase and fine needles of a covellite- or stromeyerite-like mineral. Microprobe analysis indicates an approximate composition of these intergrowths of Ag 65.0, Te 21.2, Cu 7.0, and S 5.3 wt. %. The intergrowths, which probably consist of acanthite Ag_2S, hessite Ag_2Te, and a Cu- or Cu-Ag-sulfide, may represent the decomposition product of an unknown Cu-Ag-sulfotelluride. Traces of Ag are sometimes found in granules of native bismuth and traces of Se occur in the bornite of the bornite-rich intergrowths.

Sn and Zn in the intergrowths occur in inclusions of stannoidite (approx. composition: Cu 38.5, Fe 9.6, Zn 3.8, Sn 18.4, and S 29.1 wt. %) and in the chalcopyrite, which shows a sympathetic variation in its trace amounts of Sn and Zn.

CONCLUSIONS

Chemical and textural relationships in intergrowths of Ag-Bi-bearing bornite, Ag-bearing wittichenite, and chalcopyrite are consistent with an interpretation presuming, in accordance with available data in the Cu_2S-Bi_2S_3-$CuFeS_2$ system, that these intergrowths were formed by unmixing of high-temperature Ag-Bi-bearing bornite solid solutions. At temperatures of about 500°C, sulfide solutions of compositions *d-e* in Figure 1A will crystallize in a two-phase assemblage of bornite *ss* and, depending on composition or sulfur fugacity of the solutions, a minor, equal or major proportion of chalcopyrite. The bornite *ss* may have a range of compositions corresponding roughly to the stippled area in Figure 1A; bornite-rich assemblages will in general contain bornite-rich *ss,* chalcopyrite-rich assemblages may also contain chalcopyrite-rich bornite *ss*. Unmixing of these solid solutions will result in intergrowths showing different proportions of bornite, wittichenite, and chalcopyrite. From Figure 1A, progressive unmixing during cooling of the solid solutions considered will presumably involve segregation of chalcopyrite, followed by simultaneous segregation of chalcopyrite and wittichenite along a cotectic curve of unmixing. However, in the present case of unmixing under conditions of undercooling below 271°C and oversaturation with both chalcopyrite and wittichenite, the two minerals were apparently segregated at the same time. Accumulation of wittichenite in larger blebs, veinlets, and rims occurred at a faster rate than that of chalcopyrite and this has resulted in textural relations with the chalcopyrite surrounding the wittichenite. In chalcopyrite-rich intergrowths the high proportion of chalcopyrite and wittichenite veinlets and rims often suggests replacement textures (Figs. 3A-C & 5), but such an interpretation is inconsistent with the observation that the wittichenite and chalcopyrite veinlets and rims never intersect.

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