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**WIDMANSTÄTTEN LAMELLAE IN
BORNITE-CHALCOPYRITE
INTERGROWTHS:
EXSOLUTION OR REPLACEMENT?**

S. MASTER

INFORMATION CIRCULAR No. 304

UNIVERSITY OF THE WITWATERSRAND
JOHANNESBURG

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by

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ABSTRACT

Widmanstätten-like intergrowths of chalcopyrite and bornite may form either by exsolution or by replacement. One of the most commonly used textural criteria for distinguishing between the two types of intergrowths, pinched or bundle-shaped lamellae, is shown to be invalid, and similar textures can be produced during both processes. This is illustrated by the presence of spindle-shaped crossing replacement lamellae of chalcopyrite in low-temperature bornite crystals from Mangula Mine, Zimbabwe, and other localities. The possible mechanisms for producing "exsolution-type" textures in replacement lamellae are discussed. It is concluded that previously regarded "exsolution" textures may be suspect, and the geothermometric deductions on orebodies based on such criteria may be invalid.

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INTRODUCTION

Widmanstätten-like lamellae oriented along crystallographic directions in bornite-chalcopyrite intergrowths (W lamellae of Durazzo & Taylor, 1982) have been interpreted to be of either exsolution or replacement origin (Graton & Murdoch, 1913; Schwartz, 1931a,b; Schouten, 1934; Brett, 1964; Brett & Yund, 1964; Superceanu, 1971; Ramdohr, 1980; Craig & Vaughan, 1981; Durazzo & Taylor, 1986). Criteria for distinguishing between W lamellae formed by exsolution from intermediate solid solutions during cooling, and lamellae formed by replacement of bornite by chalcopyrite, are given by Schwartz (1931b) and by Craig & Vaughan (1981). The main difference between the two types, these authors suggest, is that exsolution lamellae show a marked pinching where lamellae cross each other, whereas in replacement types there is a swelling where lamellae cross (Figure 1). The pinching of crossing exsolution lamellae is a consequence of the overlap of the sphere of influence or diffusion distance around each developing lamella where there is more depletion of the solute. Bornite-chalcopyrite W intergrowths have often been interpreted or assumed to be of exsolution origin, and then applied as geothermometers on ore suites (Viljoen, 1962; Brett, 1964; Superceanu, 1971; Fabricius, 1978, 1979). If the textures regarded as being diagnostic of exsolution origin (such as "bundle", "flame" and "basket-weave" textures of Brett, 1964) are shown to be formed also by replacement processes, then the geothermometric deductions based on these textures become suspect.

MANGULA BORNITES

Large euhedral bornite crystals growing on quartz, from Mangula Mine, Mhangura, Zimbabwe, are etched and replaced by an outer rim of chalcopyrite (Figure 2). In one of the seven bornite crystals studied, the chalcopyrite rim is further replaced by an intergrowth of pleochroic covellite and "blaubleibender" covellite, together with digenite. The bornites have varied morphologies, and are complexly intergrown and twinned. The presence of some cyclic-twinned pseudo-hexagonal crystals indicates that the bornites grew as the orthorhombic low-temperature modification which forms below 228°C (Koto & Morimoto, 1975), and are not pseudomorphic inversions of the unquenchable high-temperature cubic polymorph (Morimoto & Kullerud, 1961; Yund & Kullerud, 1966). The etched bornites are in turn covered by a layer of scalenohedral "dogstooth" calcite, chlorite (leuchtenbergite), and a second layer of dogstooth calcite and platy chalcopyrite. The bornite crystals were formed at low temperatures in open vugs (Jacobsen, 1965), and homogenisation data on single-phase

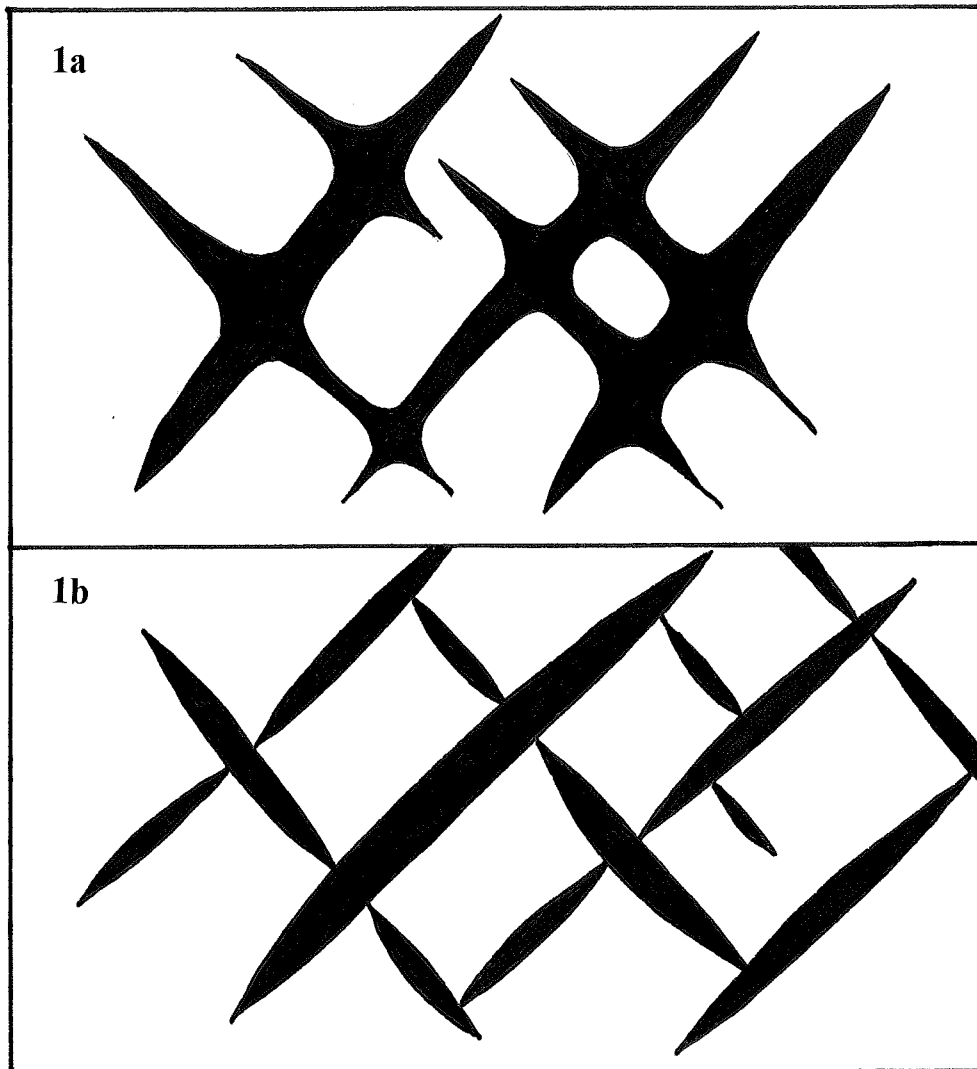


Figure 1: Schematic representation of suggested criteria for distinguishing between Widmanstätten lamellae formed by replacement (1a) and exsolution (1b), after Schwartz (1931a) and Craig & Vaughan (1981). 1a: In replacement lamellae, there is a swelling at the intersection of crossing lamellae. 1b: In exsolution lamellae, crossing lamellae are pinched at intersections.

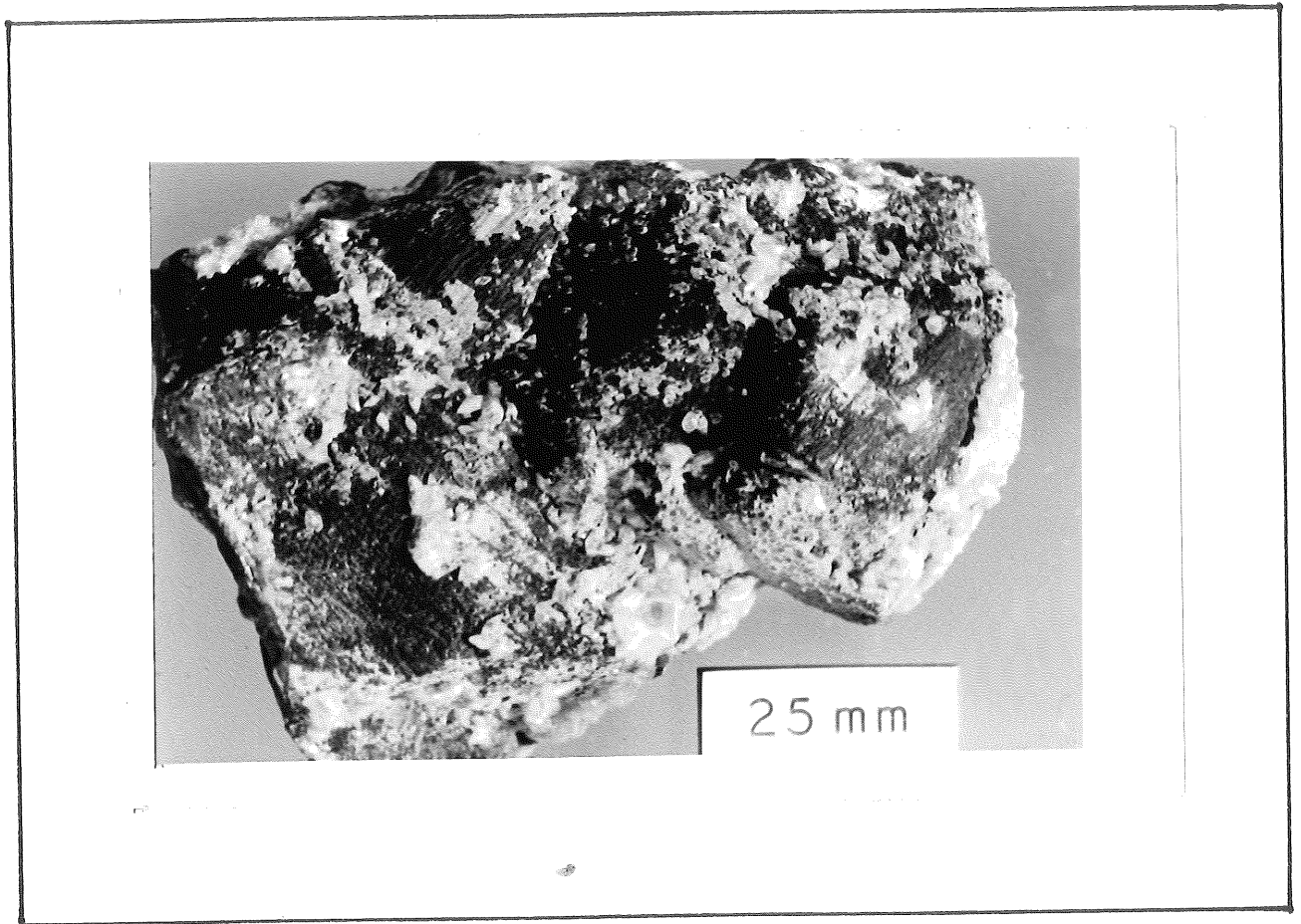


Figure 2: Bornite crystal from Mangula Mine, Zimbabwe, showing outer chalcopyrite replacement rim in which etched chalcopyrite W lamellae stand out in relief. The crystal is partly covered by calcite and chlorite.

Na-K-Cl fluid inclusions from the paragenetically earlier euhedral quartz crystals indicate maximum temperatures of formation of around 161°C (Master, 1991). Digenite, covellite and "blaubleibender" covellite can coexist at 157°C (Barnes, 1990), and this would indicate the approximate temperature of the replacement event. The outer chalcopyrite replacement rim is continuous around the perimeter and is about 0.5 mm thick. Projecting inwards from this rim are two to three intersecting sets of crystallographically oriented wedge-shaped Widmanstätten lamellae of chalcopyrite (Figure 3). The interior of the crystals consists of bornite only, clearly indicating the replacement origin of the chalcopyrite rim and lamellae. Where Widmanstätten lamellae intersect the outer continuous chalcopyrite rim, there is a flaring of the lamellae, as is typical for replacement textures (cf Figure 1a). Such flaring is also evident where some intersecting Widmanstätten lamellae cross (Figures 3 & 4). However, the intersections of many sets of lamellae are characterised by pinching similar to that considered diagnostic for exsolution lamellae (Figures 3 & 4, cf. Figure 1b). Similar pinching of crossing W lamellae in bornite-chalcopyrite intergrowths of replacement origin is observed in chalcopyrite-rimmed bornite from fault zones at Klein Aub Mine, Namibia (Figure 5, after Borg, 1987) and from Botswana (Figure 6, after Ramdohr, 1980). Such textures have also been produced during experimental replacement of chalcopyrite by bornite (Amcoff, 1987, 1988).

DISCUSSION

Three processes may account for the presence of "pinch"-, "bundle"- or "flame"-textured W lamellae in bornite-chalcopyrite intergrowths that are known to be of replacement origin using other criteria such as rimming, viz. modification of replacement lamellae by metamorphism, modification by sub-solidus diffusion at low temperatures, and primary formation of pinch textures due to diffusion effects during the replacement event.

It is possible that pinched W lamellae may have formed by true exsolution processes after a composite grain of bornite replaced by a chalcopyrite rim had been heated up during metamorphism and then cooled, resulting in a hybrid texture indicative of both replacement and exsolution (MacDougall et al., 1961). An example of W lamellae of chalcopyrite in bornite formed by thermal metamorphism is given by Filiminova (1959). Such an origin may be argued for similar textures in the metamorphosed ores of the Zambian Copperbelt (Schwartz, 1931b; Mendelsohn, 1961). A similar origin may be discounted, however, for the example from Klein Aub Mine, since the timing of the chalcopyrite replacement was later than the greenschist facies metamorphism of the host rocks (Borg, 1987).

In the case of the Mangula bornites, it is quite clear that a metamorphic temperature-induced exsolution origin for the W lamellae must be ruled out because of the low temperature mineral associations. For these bornites, sub-solidus diffusion processes may have produced the bundle-shaped pinched W lamellae through modification of replacement lamellae. The surface of the bornites has been etched, and the replacement

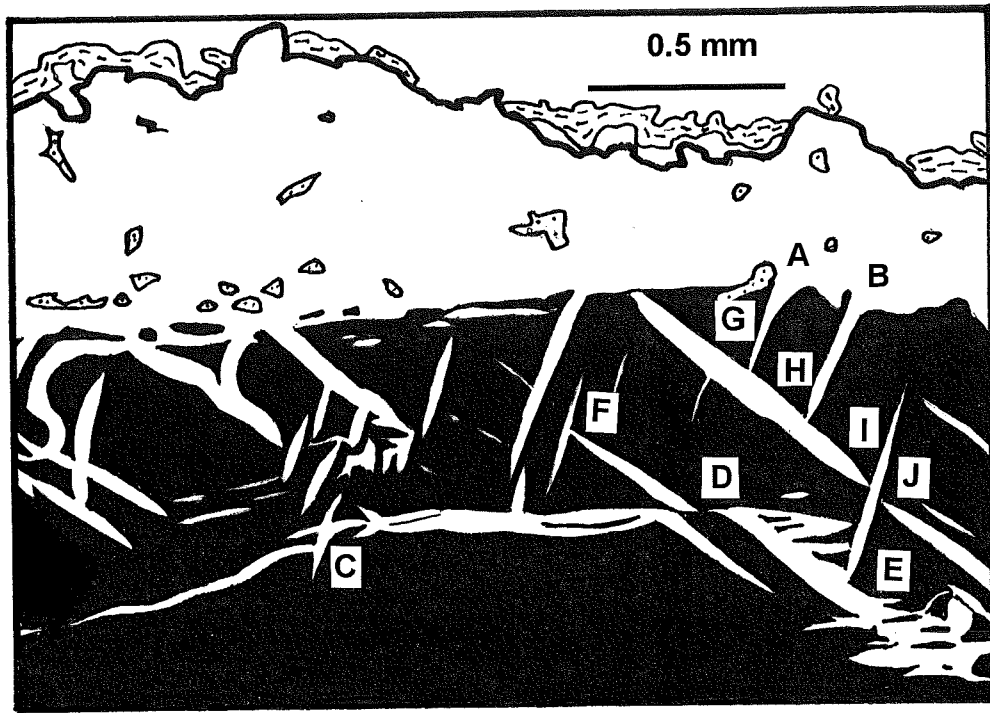


Figure 3: Section through Mangula bornite crystal, showing outer replacement rim of chalcopyrite (white), from which replacement Widmanstätten lamellae extend into bornite (black). Swelling of W lamellae is evident where they intersect the outer continuous chalcopyrite rim (A, B), and where they cross other lamellae (C, D, E). Pinching of crossing W lamellae is seen in many places, eg. F, G, H, I & J. Voids are indicated by stippling, while dashed ornament represents chlorite (leuchtenbergite) covering the outer chalcopyrite rim. Redrawn from photomicrograph.

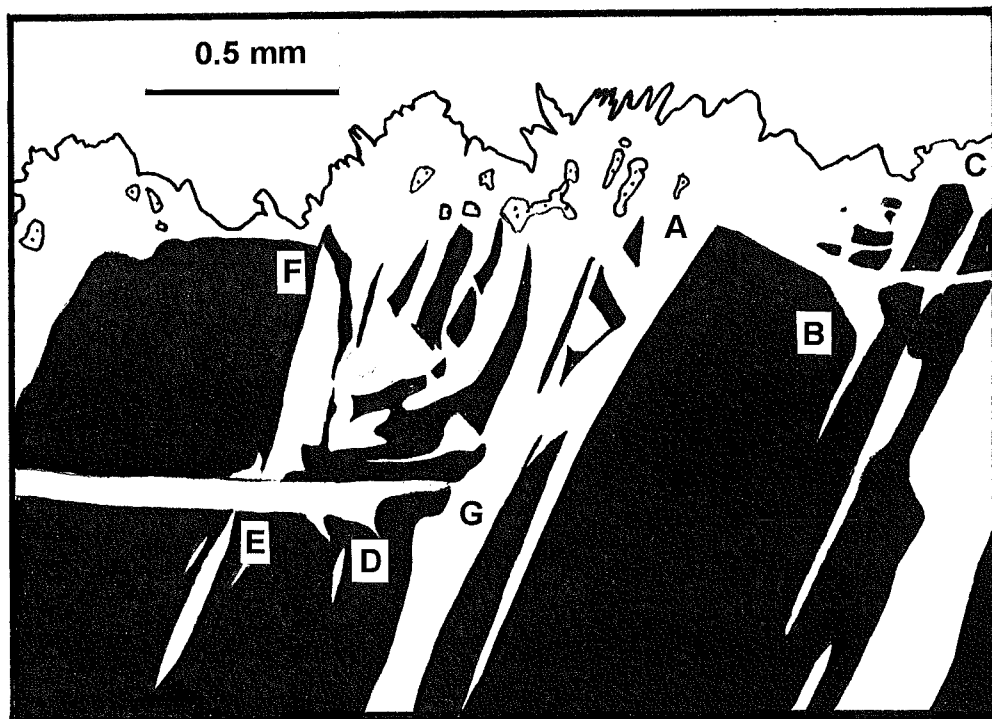


Figure 4: Close-up of etched chalcopyrite (white) replacement rim and W lamellae in Mangula bornite crystal (black), showing both swelling (A, B, C, D) and pinching (E, F, G) at intersections of crossing lamellae. Voids are indicated by stippling. Redrawn from photomicrograph.

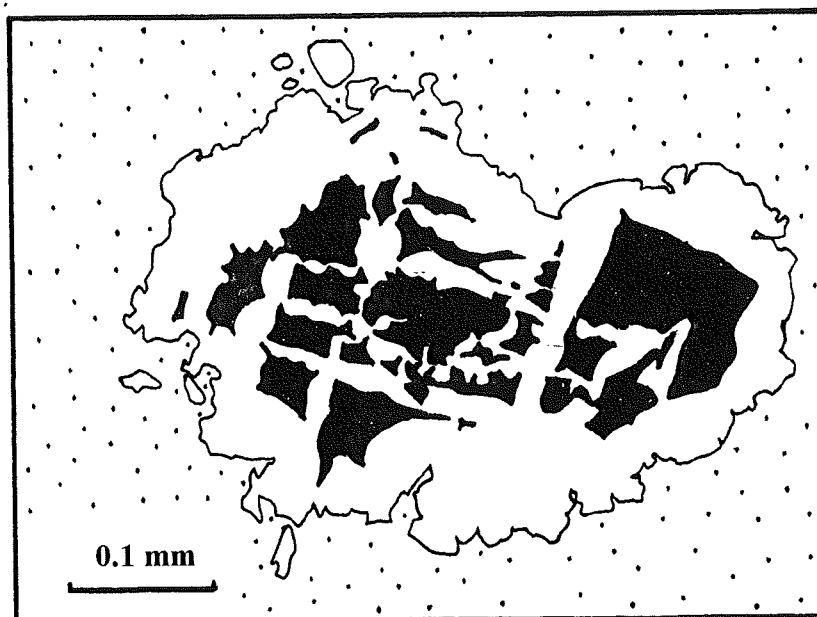


Figure 5: Bornite grain (black) with replacement rim and W lamellae of chalcopyrite (white), from Klein Aub Mine, Namibia (after Borg, 1987). Silicate gangue is stippled. Note pinching of crossing replacement W lamellae.

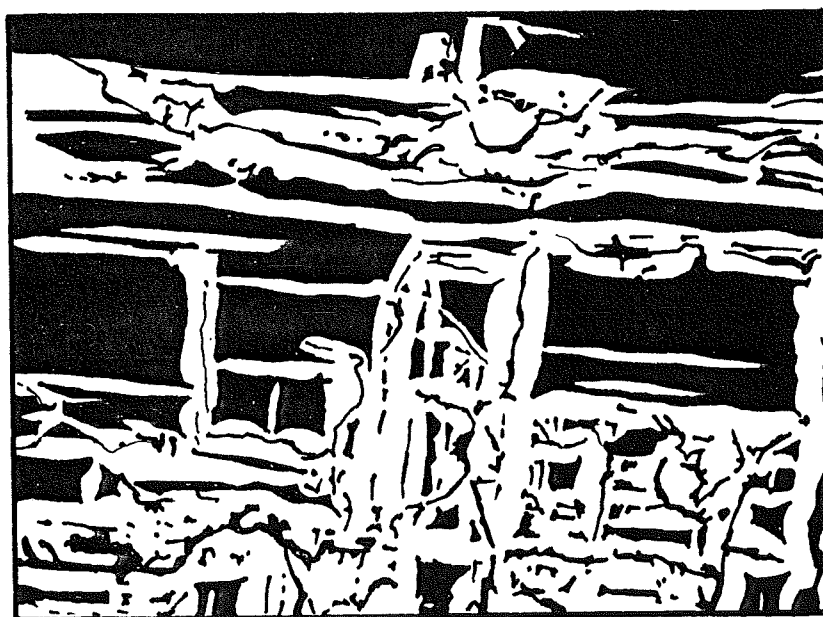
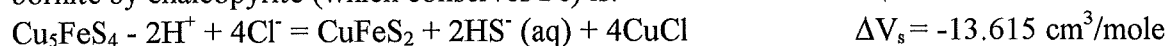


Figure 6: "Replacement lamellae" of chalcopyrite (white) in bornite (black) from Botswana (after Ramdohr, 1980). Pinching of crossing W is clearly evident.

chalcopyrite lamellae stand out in relief (Figure 2), indicating the dissolution and removal of some of the bornite. The chalcopyrite (with a molar volume of 44.11 cm³/mol) has formed by replacement of bornite (with a molar volume of 98.57 cm³/mol) through interaction with a solute (Roberts, 1963; Dutrizac et al., 1970), resulting in a volume loss.

Kopylov & Orlov (1963) investigated the dissolution of bornite in ferric sulphate solutions and noted that the reaction produced a layer of chalcopyrite on the surface of the bornite. According to Dutrizac and MacDonald (1974), the bornite dissolved according to the reactions: $\text{Cu}_5\text{FeS}_4 + 8\text{Fe}^{3+} \rightarrow \text{CuFeS}_2 + 4\text{Cu}^{2+} + 8\text{Fe}^{2+} + 2\text{S}^0$ (1) and $\text{CuFeS}_2 + 4\text{Fe}^{2+} \rightarrow \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$ (2). Dutrizac et al. (1970) noted that the formation of chalcopyrite in (1) may proceed via the intermediate formation of a copper-poor non-stoichiometric bornite phase, $\text{Cu}_{5-x}\text{FeS}_4$.

Assuming that the fluids responsible for the replacement of the Mangula bornites were chloride-rich (ie., similar to the fluids that deposited the paragenetically earlier quartz), the most important Cu complex would have been CuCl (Barton and Skinner, 1979). According to Lonker (pers. comm. 1994), a possible reaction for the replacement of bornite by chalcopyrite (which conserves Fe) is:



In the Mangula bornites, the reaction sequence of bornite \rightarrow chalcopyrite \rightarrow covellite + "blaubleibender" covellite + digenite indicates that in the reacting fluids, the copper ion activity decreased initially, followed by a decrease in the activity of iron (otherwise pyrite would have formed instead of covellite). The schematic $\log(a_{\text{Fe}^{2+}}/a_{\text{H}^+}^2)$ vs. $\log(a_{\text{Cu}^+}/a_{\text{H}^+})$ diagram of Figure 7, constructed for 150°C, shows how the replacement sequence chalcopyrite \rightarrow covellite \rightarrow digenite can form under isothermal conditions by a decrease in $\log(a_{\text{Fe}^{2+}}/a_{\text{H}^+}^2)$ and an increase in $\log(a_{\text{Cu}^+}/a_{\text{H}^+})$. The boundaries for the digenite field are qualitative due to the absence of thermochemical data for digenite, but the slopes of the boundary curves are correct (S. Lonker, pers. comm., 1994). Also note that with decreasing $a_{\text{H}_2\text{S}}$ (or decreasing ΣS^{2-}), decreasing $\log(a_{\text{Cu}^+}/a_{\text{H}^+})$, or both, fluid composition in the bornite field will be shifted into the chalcopyrite field. This could also explain the resorption and replacement of bornite. It should be noted that the replacement texture could also have formed with changing temperature, as well as changing concentrations of CuCl, FeCl⁺, and ΣS^{2-} , if the assemblage digenite, covellite and "blaubleibender" covellite did not form at the same temperature conditions.

Short & Ettlinger (1926), Ray (1930), Schouten (1934) and Amcoff (1988) have shown experimentally that "exsolution-type" lattices, lenses and lamellae can be produced in sulphides by replacement from solution. Nabarro (1940) showed that the elastic strain energy is much less for an exsolved particle in the form of a plate than for a sphere of equal volume. The exsolving phase is oriented in crystallographic directions in which the interatomic distances are similar. This may also apply in the case of replacement, and together with the effect of crystallographic anisotropy (Bosze & Trivedi, 1975), would

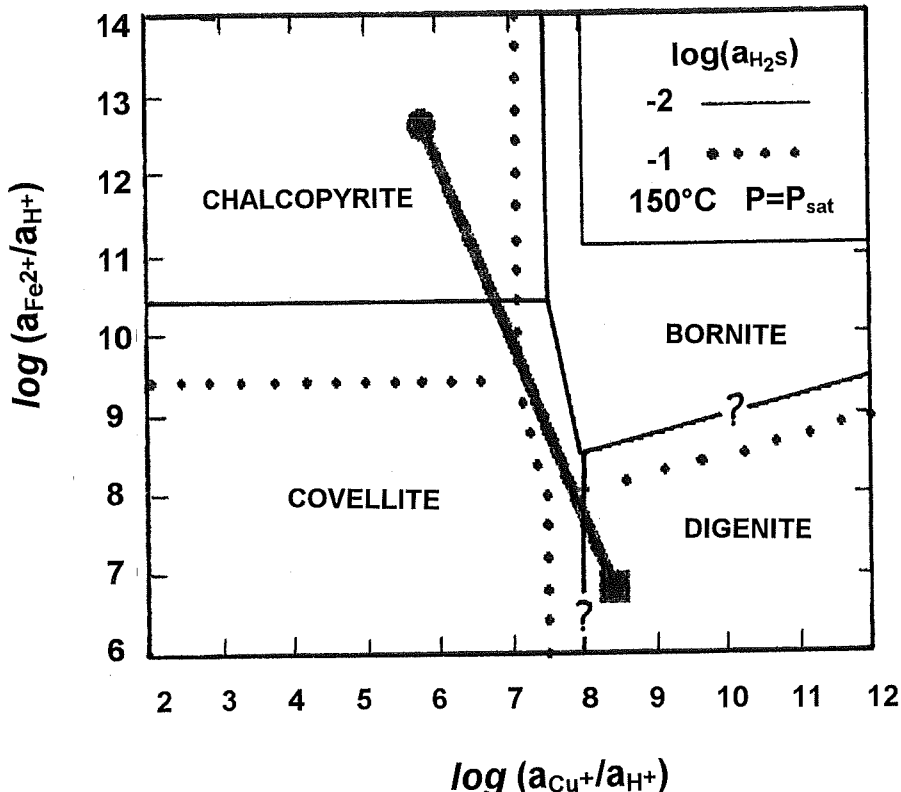
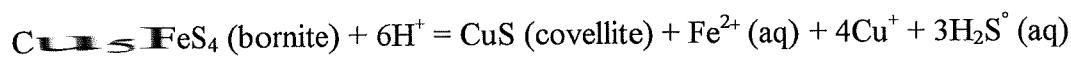
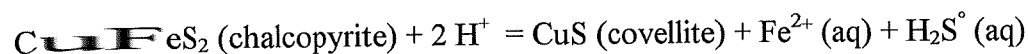


Figure 7: Stability field of bornite, chalcopyrite, covellite and “blaubleibender” covellite, constructed using SUPCRT92 (Johnson et al., 1991), utilising data from Pankratz and King (1970), and Barnes (1979). The following reactions were used to construct the activity diagram:



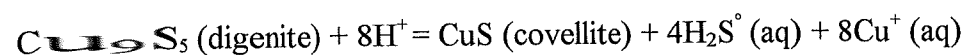
$$\log (a_{\text{Cu}^{+}}/a_{\text{H}^{+}}) = 1/4(\log K - \log(a_{\text{Fe}^{2+}}/a_{\text{H}^{+}}) - 3\log a_{\text{H}_2\text{S}})$$

$$\log K_{150^{\circ}\text{C}} = 34.623 \text{ (Johnson et al., 1991)}$$

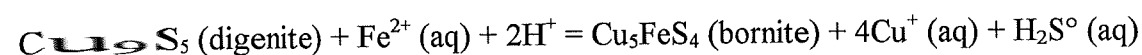


$$\log(a_{\text{Fe}^{2+}}/a_{\text{H}^+}) = \log K - \log a_{\text{H}_2\text{S}}$$

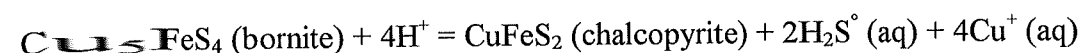
$$\log K_{150^{\circ}\text{C}} = 8.406 \text{ (Johnson et al., 1991)}$$



$$\log(a_{\text{Cu}^{+}}/a_{\text{H}^{+}}) = 1/8(\log K - 4\log a_{\text{H}_2\text{S}})$$



$$\log(a_{\text{Cu}^{+}}/a_{\text{H}^{+}}) = 1/4(\log K + \log(a_{\text{Fe}^{2+}}/a_{\text{H}^{+}}) - \log a_{\text{H}_2\text{S}})$$



$$\log (a_{\text{Cu}^{+}}/a_{\text{H}^{+}}) = 1/4(\log K - 2\log a_{\text{H}_2\text{S}})$$

$$\log K_{150^{\circ}\text{C}} = 26.217 \text{ (Johnson et al., 1991)}$$

account for the crystallographic control of replacement lamellae. The structural control of the replacement process is facilitated by the interdiffusion and reorganization of copper and iron atoms through an intact sulphur framework (Condit et al., 1974; Birchenall, 1974; Grace & Putnis, 1976). Amcoff (1988) has suggested that such textures may also be produced via the formation of an intermediary, metastable solid solution, structurally resembling the host, rather than the exsolved phase. Brett (1964) has demonstrated the variety of morphological changes that can occur in exsolution textures due to the influence of different degrees of supersaturation, temperature gradients, rates and mechanisms of exsolution, and time-dependent diffusion and annealing. Changes in the shape of exsolution lamellae due to kinetic effects are discussed by Yund & McCallister (1970) and Putnis & McConnell (1980). In tetrahedrally coordinated covalent solids, like bornite (Manning, 1967; Vaughan et al., 1987), saturation of bonds is probably a major factor controlling grain boundary energy (Sutton & Balluffi, 1987). Along bornite-chalcopyrite interfaces, kinetic effects, such as decrease in interfacial energy (Craig & Vaughan, 1981), and segregation kinetics (Militzer & Wieting, 1987), may cause changes in the shape of replacement lamellae through diffusive re-equilibration. This could effectively produce lamellae shapes that are indistinguishable from those produced by exsolution.

A third possibility is that pinched replacement lamellae may be primary features produced during the replacement process. This is supported by the presence, in experimentally replaced chalcopyrite, of pinched crossing bornite lamellae which have undergone rapid quenching in air (Amcoff, 1987). The reason for such textures developing in replacement lamellae may be similar to that for exsolution lamellae, viz. depletion in a component due to overlap of the sphere of diffusion influence around the crossing lamellae. In the case of chalcopyrite replacement of bornite, a saline fluid might be reacting with the bornite along crystallographic cleavage planes. The bornite component in this reaction would be used up faster at cleavage intersections, so that further growth of the replacement lamellae is retarded at crossover points, while the central parts of lamellae continue to grow, resulting in pinched shapes similar to those produced by exsolution processes. This mechanism has the opposite effect of, and competes with, the nucleation mechanism for replacement chalcopyrite lamellae in the bornite host, which is controlled by the free energy difference between matrix phase and nucleating phase, and supersaturated matrix phase (Amcoff, 1988).

In the Cu-Fe-S system, there is a limited field of bornite solid solution, trending towards the chalcopyrite end-member, which shrinks with decrease in temperature from 600°C to 300°C (Barton, 1973; Cabri, 1973; Craig & Scott, 1974; Sugaki et al., 1975). The degree of supersaturation of the chalcopyrite component in bornite will strongly influence the free energy difference between the exsolved components and the matrix phase. During chalcopyrite replacement of bornite, the saturation level of chalcopyrite in bornite is rapidly approached near the advancing chalcopyrite "front", resulting in a corresponding increasing probability of chalcopyrite "embryo" or "subcritical nucleus" formation in bornite (Amcoff, 1988). Around each embryo, the bornite matrix will become depleted in the chalcopyrite component. The steepness of this gradient, which determines if the critical nucleus size will be reached, depends on the degree of

supersaturation. The driving force for nucleation, the free energy difference, decreases when the composition gradient around the embryos decreases in steepness (Yund & McCallister, 1970). Thus, in crystallographically controlled replacement, if the reacting fluids are diffusing equally along several crystallographic planes, then the intersections of these planes will be characterised by the greatest amount of depletion in the chalcopryite component of the host bornite, resulting in greater free energy gradients between the chalcopryite replacement lamellae and the bornite host, and in a greater probability of new chalcopryite grains nucleating. Hence, according to this consideration, there should be a greater amount of chalcopryite where replacement lamellae cross, resulting in textures similar to those given in Figure 1a. However, if the reacting fluids are diffusing primarily along one set of crystallographic planes, then the amount of fluid will be dispersed at cleavage intersections, and the degree of supersaturation between chalcopryite lamellae and bornite host will be reduced, resulting in shallower concentration gradients and lower free energy differences. In this case, there will be a lower probability for nucleation of chalcopryite, and this will result in pinched textures of crossing lamellae.

The above discussion shows that it may be impossible to distinguish, on the basis of morphology alone, between Widmanstätten lamellae of chalcopryite in bornite that have formed by exsolution processes, and those that have formed by replacement. It is thus pertinent to examine what other textural criteria can be used to effectively distinguish between exsolution and replacement textures. Some of the more critical criteria would be those that can show a replacement origin for the W lamellae. Outer rims of chalcopryite around bornite grains and crystals (Figures 2, 3, 4 & 5) are quite diagnostic of replacement, and W lamellae extending into the grains from such replacement rims must be considered to be of replacement origin. Another important criterion is the presence of cracks and fractures in the host grains, around which chalcopryite W lamellae may be preferentially developed (e.g. Figure 6). In the ores of Sasca Montana, George Valley, Rumania, chalcopryite W lamellae spatially associated with fractures in the host bornite (Figure 8) have been called "exsolution lamellae" by Superceanu (1971). The textures illustrated in Figure 8 were most likely produced by replacement from the fractures, and the spindle-shaped morphology of the chalcopryite lamellae can no longer be used to argue for an exsolution origin. It is of interest to note that spindle-shaped chalcopryite lamellae in bornite from Maryland were assigned to a replacement origin by Overbeck (1916). Schwartz (1931b) interpreted the textures to indicate an exsolution origin, since the "bands became narrow where two bands cross, instead of broadening out as would be expected if they were formed by replacement". The inapplicability of morphological criteria for the origin of W lamellae, as shown above, means that Overbeck's (1916) interpretation may have been the correct one, after all. Diagnostic criteria for the unequivocal recognition of exsolution lamellae in chalcopryite-bornite W intergrowths may include the presence of "cell", "patch", "worm" and "emulsion" exsolution textures that have been produced experimentally by Durazzo & Taylor (1982, 1986).

These considerations cast doubt on previous geothermometric deductions on orebodies based on presumed "exsolution" textures in bornite-chalcopryite intergrowths. For example, at the Umkondo Mine, Zimbabwe, Viljoen (1962) used the presence of spindle-

shaped chalcopyrite W lamellae in bornite pseudomorphing pyrite (Figure 9) to infer that the texture was produced by exsolution through cooling from high temperatures (above 475°C). Because pinched textures of W lamellae are no longer considered diagnostic of an exsolution origin, the grain illustrated in Figure 9 could have been the result of low-temperature replacement of pyrite by bornite, with a resultant goethite fringe, and later replacement of bornite by crystallographically oriented chalcopyrite lamellae. This is considered the more likely possibility, since the host rocks at Umkondo Mine have suffered only very low grade metamorphism (Tyrwhitt, 1966). In the Repparfjord copper deposits, Norway, Fabricius (1978, 1979) interpreted pinched W intergrowths of bornite, chalcopyrite and neodigenite as having formed by exsolution, and used these textures as a geothermometer which indicated a formation temperature of 335°C. Stribrny (1985) interpreted these textures as being due to two generations of chalcopyrite exsolution in bornite (formed during regional metamorphism), with later replacement by neodigenite and chalcocite. Since W lamellae are no longer diagnostic of an exsolution origin, an alternative (and simpler) explanation that can account for these textures is one involving the sequential replacement of bornite by chalcopyrite W lamellae, neodigenite, and chalcocite. Textures produced through the latter (replacement) mechanism cannot be used as geothermometers.

CONCLUSIONS

It has been previously shown that the shape of exsolution lamellae may be influenced by such factors as supersaturation, reaction rate, reaction kinetics and subsolidus diffusion. It is argued here that similar factors, as well as subsequent geologic (especially geothermal) history, can modify the shapes of replacement lamellae through subsolidus diffusion to make them look identical to exsolution lamellae. In particular, the pinching of crossing Widmanstätten lamellae at their intersections can no longer be considered diagnostic of an origin by exsolution. It is concluded that caution must be exercised when interpreting Widmanstätten intergrowths of bornite and chalcopyrite, as similar textures (previously diagnostic of one mechanism of formation) may be formed by different or multiple processes. Previously regarded "exsolution" textures may be suspect, and the geothermometric deductions on orebodies based on such criteria may be invalid.

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Figure 8: Chalcopyrite lamellae (white) associated with fractures in bornite (black), from Sasca Montana, George Valley, Rumania (after Superceanu, 1971). See text for discussion.

0.5 mm

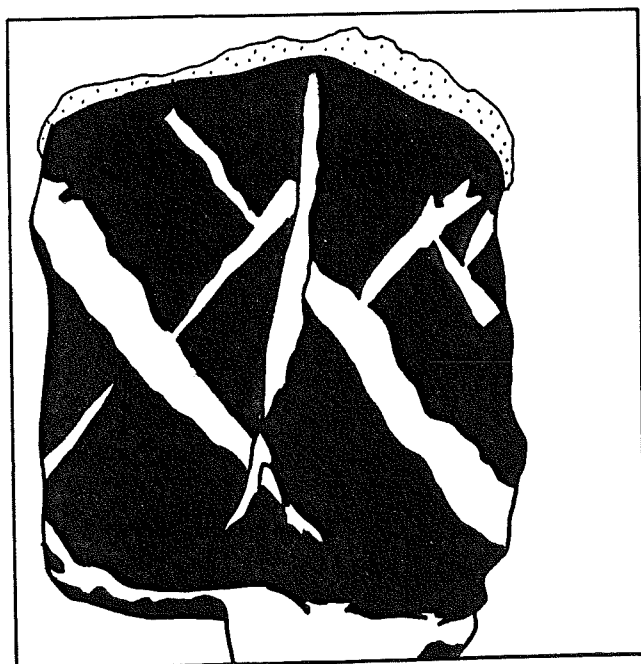


Figure 9: Chalcopyrite W lamellae (white) in bornite (black) pseudomorph after euhedral pyrite, fringed by goethite (stippled), Umkondo Mine, Zimbabwe (after Viljoen, 1962). See text for discussion.

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