AN EXPERIMENTAL INVESTIGATION OF INTERGROWTH PHENOMENA IN BORNITE AND CHALCOPYRITE

by

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Abstract

Samples of bornite and chalcopyrite between the compositions Cu_5FeS_4 (Bo) and $CuFeS_{1.76}$ were heated in sealed, evacuated, silica glass capsules, then chilled in water and studied under a reflecting microscope.

The solvus curves delimiting the two phase region, join Bo_{80} at 500 °C to Bo_{65} at 800 °C and Bo_{10} at 500 °C to Bo_{25} at 800 °C. Lines extending from Bo_{35} at 800 °C through Bo_{28} and Bo_{45} at 500 °C bound a field of double exsolution. Chalcopyrite exsolves in bornite as lamellae up to 0.004 mm wide, boundary segregations and possibly rounded blebs; while bornite exsolves in chalcopyrite as irregular hair-like structures generally less than 0.001 mm wide. Chalcopyrite and bornite lamellae seem to be controlled by the low and high temperature forms of the respective host minerals.

Chalcopyrite lamellae grow more rapidly than bornite, and exsolution occurs faster in the pure system than in natural minerals (Schwartz, 1931), therefore these data are not directly applicable to geothermometry.

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Introduction

" Interpretation of textures will be possible only when laboratory experiments have examined the processes taking place in ore bodies."

G.Kullerud (1955, Pp. 99)

Chalcopyrite and bornite rank among the most important minerals in base metal deposits, excluding iron, and are known to occur, even if only in minor amounts, in a great variety of mineralised deposits. These two minerals commonly occur together, and their relationships and textures, particularly intergrowths, have puzzled geologists through the ages. Studies have prompted much speculation with regard to their origin and meaning, but there is no unanimity of opinion on the interpretation of such structures. Where conclusive evidence is lacking, controversy prevails regarding the importance of replacement, as opposed to exsolution processes, in forming these structures.

As yet, experimental investigation of this problem has lagged in favour of the pressing need for phase equilibrium studies in the common sulphide systems.

In the past ten years, great strides have been made in the study of sulphide systems in general, and the Cu-Fe-S system in particular. Chalcopyrite and bornite are isomorphous at temperatures above 550 °C, and because they have mutual cations (Cu and Fe), the chances of solid state diffusion are high. Rapid cooling however, should be capable of retarding reordering, and therefore ' freeze in ' intergrowth structures and crystal forms present at higher temperatures.

A study of the variation of intergrowth structures with temperature, time and mineral composition is applicable to the interpretation of conditions of formation of ore bodies in the following ways:

A study of the types of intergrowth textures would reveal those most likely to result from exsolution in contrast to similar types formed by replacement processes. Such a distinction must affect the interpretation of the paragenesis of the minerals concerned.

A determination of the sub-solidus relations of chalcopyrite and bornite may reveal information on the conditions of formation of the minerals. Kullerud (1955) regards pressure in the earth's crust as being of minor importance. On this assumption, a sub-solidus temperature - composition diagram could be used to evaluate the approximate temperature range of formation. By determining the bulk composition of the natural sample, the amount of material exsolved could be correlated with equivalent amounts indicated on the sub-solidus diagram in order to reveal the temperature corresponding to that amount.

Schwartz (1931) and Sugaki (1955) have demonstrated that time has an important effect on the amount of material exsolved below 400 °C in natural bornite-chalcopyrite samples. Investigations of time and cooling effects on controlled synthetic systems may therefore reveal information on the nature and rate of exsolution processes involved and indicate the relative importance of these processes under natural conditions of ore formation.

Synthetic systems, under controlled physico-chemical conditions, form a justifiable basis for investigating and interpreting the varied, and often apparently complex processes involved in ore genesis. In

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solid diffusion processes in sulphides, the effects of impurities usually constitute a problem about which relatively little is known. In the Cu-Fe-S system, Cu⁺⁺ and Fe⁺⁺ are the main cations involved in solid diffusion, but it is possible that bivalent ions of similar size (Co, Ni, Zn, Mn) may substitute for these atoms with varied effects.

The main experimental work to date on bornite-chalcopyrite intergrowth textures has been confined to studying natural samples. To the writer's knowledge, no work has been done on the variation of intergrowth textures with temperature and time in synthetic bornite-chalcopyrite systems.

The writer has conducted a series of experiments on bornitechalcopyrite relations within a specific composition range in an attempt to solve some of the problems concerning the types and distribution of intergrowth textures. The experiments and results are discussed in pages to follow.

Previous Work

Evidence from natural examples.

The early observers of bornite and chalcopyrite intergrowths explained the textures as the result of either replacement or eutectic crystallisation processes. Replacement intergrowths were regarded as the most important in view of the greater number of examples cited with "indisputable" evidence in their favour. "Eutectic" and "eutectoid" structures were of theoretical interest.

Overbeck (1916) was one of the first to describe intergrowth textures typical of exsolution processes, however, he interpreted them as the result of replacement, despite the distinct evidence of pinching intersections of the intergrowths. These were regarded as anomalous. Rogers (1915) recognised the true nature of exsolution textures, and was a leading figure in promoting this explanation. Nevertheless, these new ideas met with stiff opposition.

Schneiderhohn's excellent treatment of the subject of exsolution textures in 1922 had considerable influence on the controversy. Reports of exsolution intergrowths multiplied in Europe. Schneiderhöhn emphasised the need for experimental research to verify structures due to unmixing* as distinct from those resulting from replacement processes.

Numerous types of microtextures have been observed and several classifications, both descriptive and genetic have been suggested. Schneiderh ohn (1922) proposed the following classification of segregation textures.

Lemulsion structures - those due to the segregation of submicros * 'Unmixing' was used originally by the metallurgists whereas 'exsolution' has been adapted more to geological processes. Both terms are synonymous.

copic to microscopic globules from the parent crystal.

2. Cell, net or mesh structures- those due to the migration to, and accumulation at, the boundaries of the crystalline grains.

3. Lamellar or Widmanstatten structures - plate and needle-like segregations controlled by the structural planes of the parent crystal.

4. Eutectic structures - those comprising an intimate granular or lamellar intergrowth of two or more kinds of crystals.

Schwartz (1931; p.742) was very careful to distinguish between the origins of the textures, and proposed the following classification with criteria for identifying the main groups.

1. Graphic intergrowths - eutectic and eutectoid;

contemporaneous deposition;

replacement;

recrystallisation;

2. Unmixing textures.

3. Irregular rounded structures.

There is still much controversy on the matter, and for further considerations the reader is referred to works by Schneiderhohn (1922); Schwartz (1931, 1939, 1942); Sugaki (1951) and Edwards (1954).

Schwartz produced a classic paper in 1931 describing the results of some experimental investigations. Using natural samples, sealed in evacuated pyrex or silica tubes, he showed that intergrowths of chalcopyrite could be absorbed in solid solution with bornite when heated for one week at temperatures above 475 °C. Chilling in cold water was sufficient t o quench the solid solution, but slower cooling rates enabled the chalcopyrite to exsolve as intergrowths or, if slow enough, as completely segregated masses. The cooling rate and bulk composition were considered to be critical factors in controlling the type of intergrowth; however, reference was only made to composition where the host phase was distinctly in excess of the exsolved phase. Schwartz concluded that exsolution textures were uncommon in nature owing to the rapid rate of exsolution and the fact that most bornite mineralisation was mesothermal - approximately $175 \, {}^{\circ}C$ to $300 \, {}^{\circ}C$ (Emmons; 1940) - thus forming below the region of extensive bornite-chalcopyrite solid solution. Similar textures have been observed between bornite and chalcocite, and solid solution here extends well down into the mesothermal range.

Schouten (1934) extended the controversy by producing lattice intergrowths through metasomatic processes involving the immersion of bornite and chalcopyrite samples in a variety of solutions at 120 °C. He concluded that replacement and solid diffusion were not necessarily exclusive, but could be intimately associated as a complex process involving solid solution at higher temperatures. Ray (1930) had demonstrated however, that bornite was very unstable in an aqueous environment involving distilled water, copper sulphate solution, ferrous sulphate solution or a combination of these and decomposed readily to form chalcopyrite which replaced the bornite progressively along specific directions.

Sugaki (1951) conducted a series of experiments using natural intergrowths of bornite and chalcopyrite from the Akayama Mine, Japan. He was able to form solid solutions of bornite and chalcopyrite at temperatures appreciably below those demonstrated by Schwartz. At lower temperatures greater lengths of time were required for solid solution to occur, and at 300 °C solid solution only occurred after 175 hours. Sugaki produced

a variety of exsolution patterns, many of which had not been described before. Typical lattice intergrowths, with chalcopyrite as the exsolved phase, were abundant with forms resembling wedges, drops, lenses, dendritic and thread-like structures, cells and fine granular clusters or chains. Sugaki (1955) followed up this research with a quantitative study of the variation of chalcopyrite intergrowths in bornite. By heating natural samples at specific temperatures for different lengths of time, he was able to show that the variation of thickness of the lamellae was dependent basically on time (fig. 1). Increased time caused a slight increase in the amount and width of the exsolving chalcopyrite body (figs. 1 and 2). These experiments were conducted in air, and it is significant that a differential thermal analysis (D.T.A.), also in air (Frueh; 1950) reveals an exothermic peak between 300 °C and 400 °C (fig 4). This represents the dissociation and oxidation of bornite, and is accompanied by the release of SO₂ gas.

In subsequent experiments on the diffusion of copper through pyrite and chalcopyrite blocks, Sugaki (1956) was able to form mineral zones decreasing in copper content away from the copper plate source. The contact between the bornite and chalcopyrite zones was indistinct and invariably marked by a pinkish colouration. On cooling, lattice intergrowths of chalcopyrite exsolved from the bornite, and fine blades of bornite exsolved from the pink zones. No further details are given on the specific form and variation of intergrowth structures across the zone.

Evidence from synthetic systems.

In 1937, Merwin and Lombard published the results of their investigation of the Cu-Fe-S system at a sulphur vapour pressure of 455 mms. They





(after Sugaki; 1955)



Time in hours.



time. (after Sugaki; 1955)

- I. No change in chalcopyrite lamellas.
- II. Chalcopyrite lamellae grow thicker than before heating.
- III. Chalcopyrite lamellae become narrower than before heating, or partly disappear.
- IV. Chalcopyrite lamellae disappear entirely.

delimited the equilibrium and solid solution fields of the various binary and ternary minerals, and demonstrated that the sulphur pressure over bornite and chalcopyrite was extremely low, even at temperatures of 1000 °C. In a closed system with restricted vapour space, the loss of sulphur and metal atoms to the vapour would be very small, probably less than 0.1 wt %.

Yund and Kullerud extended the research, and in 1960 published the preliminary results of their investigation of the Cu-Fe-S system at 700 $^{\circ}$ C. (fig. 3). They accurately delimited the various solid solution fields, and observed that in the bornite-chalcopyrite relationship, bornite solid solution, with less than 57 wt. % Cu, and greater than 12.2 wt. % Fe, was unquenchable and exsolved chalcopyrite when chilled in water. Solid solutions of both chalcopyrite and bornite exsolved the minor constituent, but the exsolved bornite was present as fine lattice intergrowths in contrast to the coarser blades of exsolved chalcopyrite. Furthermore, the chalcopyrite present with exsolved bornite was richer in copper than the chalcopyrite in bornite-free samples.

Crystallography of bornite and chalcopyrite.

Both bornite and chalcopyrite have high and low temperature polymorphs with transformations of the order-disorder type.

<u>Bornite</u> - is face-centred cubic at high temperatures ($a = 5.50 \pm 0.01$ Å) (Morimoto and Kullerud; 1961) and probably has an antifluorite structure. It is unquenchable and inverts below 228 \pm 5 °C., to the low temperature form. Frueh (1950) notes that the transformation, as indicated by D.T.A. (fig.4) and resistivity measurements, occurs over a range of temperature, between 220 °C and 170 °C. With rapid cooling, Morimoto and Kullerud observe that the high temperature form inverts to a metastable form which is face centred cubic ($a = 10.94 \pm 0.02$ Å) and space group Fd3m or



Fig. 3 - Phase relations in the Cu-Fe-S System (Yund and Kullerud; 1960)

Stability Fields.

	Bo = Bornite;	Cp = Chalcopyrite; Po =	Pyrrhotite.
1.	Bo-Iiq-Vap.	5. Cp-Py-Po-Vap.	10. Bo-Po-Vap.
2.	Bo-Cp-Liq-Vap.	6. Py-Po-Vap.	11. Bo-Po-Fe-Vap.
3.	Cp-Liq-Vap.	7. Cp-Po-Vap.	12. Bo-Fe-Cu-Vap.
4.	Cp-Py-Liq-Vap.	8. Bo-Cp-Vap.	13. Bo-Cu-Vap.
		9. BoCp-Po-Vap.	

(Phase relations at 700 °C and vapour pressure of the system) The delimited area is enlarged in fig. 11 to show details applicable to the present research.

Shaded areas denote fields of solid solution.

F43m. This changes slowly at room temperature to the stable low temperature form which has a primitive tetragonal pseudo-body-centred structure $(a = 10.94 \pm 0.02 \text{ Å}; c = 21.88 \pm 0.04 \text{ Å})$ with a space group P42d pseudo I42d.

<u>Chalcopyrite</u> - is face-centred cubic at high temperatures (a = 5.29 ± 0.02 Å - Fruch; 1958) and is isostructural with the high temperature form of bornite. The high temperature form is quenchable but inverts slowly - within a year (Fruch) - to the stable low temperature form. The inversion temperature is 547 ± 5 °C (Yund and Kullerud; 1961), and a D.T.A. of natural chalcopyrite by Sugaki (1956) reveals a corresponding endothermic peak at 550 °C (fig. 4). The low temperature form of



Fig. 4 - Differential thermal analysis of bornite and chalcopyrite.

Bornite measurements were made in air with a thermal rise of 12 °C per min. (Fruch; 1950)

Chalcopyrite measurements were made in a nitrogen atmosphere with a thermal rise of 5 °C per min. (Sugaki; 1955)

Endothermic peaks in both minerals represent energy changes resulting from polymorphic transformations whereas the exothermic peak in bornite represents dissociation and oxidation with the release of sulphur dioxide gas. chalcopyrite is tetragonal (a = 5.24 Å; c = 10.30 Å) (Fruch; 1958). The order-disorder transformation from high to low temperature forms involves a slight shrinkage of the lattice as is indicated by the relation : c is less than 2a. This means that the ordered domains no longer have an orthogonal relationship but show a slight angular discrepancy in domain boundaries - a fact that may well affect the structural control of intergrowths.

Studies of chalcopyrite, using neutron diffraction techniques to determine the magnetic space lattice, have indicated that chalcopyrite conforms more closely to $Cu+Fe^{+++}S_2$ than $Cu^{++}Fe^{++}S_2$. This is an important consideration where atoms with magnetic moments - Fe = 3.8 Bohr magnetons (Donnay et. al; 1958) - are concerned, as it places a restriction on the ease of diffusion of such atoms or ions.

Processes involved in exsolution phenomena.

Exsolution, or the separation of phases in a crystal, will occur along planes common to both phases in order to approach a lower energy state. Low temperature bornite and chalcopyrite have mutual sulphur and copper planes parallel to (111), (Edwards; 1954), but in view of the orderdisorder relations of the metal atoms with temperature changes, it is the sulphur planes that are most likely to constitute the common contact plane on which exsolution occurs. No intergrowths have been observed parallel to the cubic (100) and pentagonal dodecahedral (112) planes.

In bornite, the (111) plane is represented by a well-developed cleavage and twin plane, and in chalcopyrite it forms a very good parting.

The mechanism of intergrowth formation is imperfectly understood

but is clearly associated with solid diffusion within the crystal lattice. Several types of solid diffusion are known (Smoluchowski; 1951), but Ross (1954) favours the diffusion of ions in both directions with a probable flow of electrons in opposite directions to maintain electric neutrality. The exsolution of material is closely associated with phase interface reactions, and these seem to be controlled directly by the ionic stability at the interface and activation energy of the intermediate or exsolving phase, and indirectly by the individual ion or atom mobilities.

Exsolved phases are usually present as intergrowths or similar structurally related bodies and are metastable, changing in time to form larger bodies with lower surface energies. During chilling, the exsolved phase grows in a manner favouring minimum energy on the surface of separation. Commonly this growth is coherent with the matrix structure, but differences in the nature of the host and exsolving material may induce strains in both crystals (Smoluchowski; 1951). When the crystal growth reaches a stage where the strain energy exceeds the activation energy required to initiate exsolution, the exsolved phase changes slowly from the transient form to the stable, lower energy structure.

In considering exsolution phenomena, it is necessary to distinguish phases stable at the temperature of the run from those resulting from exsolution during chilling. Commonly, stable phases are present as distinct bodies with forms that bear little or no structural relationship to other phases. The stable phase is one with minimum free energy, and therefore is one in which the surface energy is minimised by the growth of larger crystals. It is highly probable however, that exsolution may contribute material to the stable phase without noticeably altering the shape of that phase.

Experimental Work

In the study of bornite and chalcopyrite intergrowth textures, 33 runs were conducted, each one comprising a maximum of 5 samples. All samples were sealed in evacuated silica glass capsules, and the free space within the capsule was reduced to a minimum. Stock samples of 1.0 gm. were synthesised from pure elements and checked by X-ray diffraction techniques to ensure that no other minerals, especially pyrrhotite, were present. 0.02 gm. portions were heated in a furnace at a given temperature for a specific length of time and then quenched in either cold water, air or liquid air.

The sample was then mounted in a plastic pellet, glued to a slide, polished and studied with the aid of a reflecting microscope (Clark, 1959). Materials and Equipment

Element Materials

The same reagents were used throughout for the synthesis of samples.

Iron powder, consisting of irregular grains averaging 0.007 mms. diameter, was purchased from Johnson Matthey & Co., England. Of the 50 elements sought as impurities, 42 were not detected by standard spectroscopic methods; Ag, Mg and Cu showed less than 1 ppm. each; Na, Si and Ni registered 1 ppm. each; and Mn showed 3 ppm.

Copper powder, from the same source, consisted of irregular grains averaging 0.012 mms. diameter. The powder had been reduced from high purity cupric oxide in which Fe was present as 2 ppm; Na, Ag, Si, Mg, Li, Ca, Cd and B showed less than 1 ppm. each; and 41 other elements were not detected by standard spectrographic methods.

Spectroscopically pure crystalline sulphur was obtained from the American Smelting & Refining Co., New Jersey. A chemical analysis showed only traces of Na and Cl.

Transparent and translucent quartz glass tubing and rods (Vitreosil brand) were obtained from Fisher Scientific Co. Ltd., Montreal. Tubing of 5mm. bore and 1.5 mm. wall thickness and rods 5 mm. in diameter were used for all the experiments. The silica glass was ideal for the experimental work owing to its high melting point, extremely low thermal coefficient of expansion and chemical inertness.

Furnaces

Two furnaces were used in the course of the experimental work.

The first furnace (fig. 7), a Hevi-Duty furnace, was adapted for the experimental work. Single circular marialite plates with central openings, sealed by bevelled trap-doors, were fastened to each end of the furnace. A quartz tube, 2" I.D. and 0.25" wall thickness, was installed as the furnace chamber between the marialite ends. The furnace was used for some initial synthesis runs, but owing to its small size (6" x 8.5"), very poor insulation and consequently undesirable temperature gradient (fig. 6), it was abandoned for the major part of the experimental work in favour of a second furnace of more suitable design.

The second furnace (fig. 8), which was based on a design by Dr. G. Kullerud of the Geophysical Laboratory, Washington, was built by the writer. It consisted of a metal shell, 18" long, that was sealed by transite ends and filled with magnesia powder (fig. 9). The core comprised two concentric alundum tubes separated in the centre by a concentric nickel tube which distributed the heat more uniformly. The outer alundum tube was wound with No. 18 nichrome wire and cemented in place with a zirconia refractory cement. The total resistance was approximately 29 ohms at room temperature.

The furnace was adapted for use in the vertical position to ensure rapid chilling, and the following modifications were made. Bevelled trap-doors were affixed to both ends of the furnace to reduce internal convection to a minimum (fig. 5). An electrical release circuit was built into the upper trap-door so that the capsule tray could be released while the trapdoor remained clamped in place. The lower trap-door could be swung out of position momentarily to enable quenching with no observable effect on the furnace temperature. The wiring of the heating element comprised a central 8.5^{m} zone with 6 turns per inch flanked below and above by 5^{m} and 3^{m} zones respectively, each with 10 turns per inch. The central hot zone was displaced slightly upwards with respect to the centre of the furnace but was very uniform over a distance of 4^{m} with a range of $1.5 \,^{\circ}\text{C}$ at $400 \,^{\circ}\text{C}$ and $3 \,^{\circ}\text{C}$ at $600 \,^{\circ}\text{C}$. To facilitate loading and quenching oper-

Fig. 5 - Diagram illustrating the bevelled trap-door seal and thermocouple inlets.

The copper wire for releasing the capsule tray is connected to the two screws in the trap-door base.





-O-- Measurements in the second furnace made with a recording potentiometer. Measurements in the second furnace made with a portable potentiometer.



Fig. 7 - First furnace prepared for calibration of temperature gradients.

In the foreground is the Leeds and Northrup potentiometer and relay switch used for controlling the temperature in the furnace.

Fig. 8 - Second furnace mounted in the travelling cage.

> The Honeywell Pyr-O-vane controller used for regulating the temperature is mounted on the wall.

The desiccator used for storing pure materials a nd synthetic stock samples is shown at the base of the furnace stand.





Fig. 9 - Structural details of the second furnace.

ations, the furnace has been mounted in a cage which travels on bearings between vertical runners.

Temperature control Instruments

Two types of temperature control mechanism's were used with the first and second furnaces respectively. The first furnace was connected via a relay switch to a Leeds and Northrup recording potentiometer capable of controlling the temperature to ± 10 °C. Regulated current was fed to the second furnace element through a Honeywell Pyr-O-Vane controller equipped with a burn-out protection device. An adjustable on-off type control circuit provided temperature control within ± 3 °C, and the instrument had a measuring sensitivity of 0.15% of scale span.

Furnace temperatures were measured with chromel-alumel thermocouples calibrated at $100^{\circ}C$ (manufacturer's tolerances 0.75% max. from 277 °C to 871 °C). Chromel-alumel leads completed the measuring-control circuit to the second furnace, and all temperatures were read to the nearest degree off the Pyr-O-Vane scale panel. For more sensitive temperature measurements a Leeds and Northrup portable potentiometer was used.

Apparatus for analysing products

a) <u>X-ray Diffraction</u> - Two methods were used to test for undesirable minerals in the synthesis of stock material.

(i) A small portion of material was finely ground under acetone in a mullite mortar and pestle and then smeared on a glass slide with an acetone-glue mixture. The mount was rotated from $20 = 25^{\circ}$ to 80° on a General Electric XRD-3 X-ray diffractometer using iron radiation. Crystalline phases giving reflections sufficiently distinctive from the background intensity were then identified from the diffraction peak pattern.



Fig. 10 Nonius Guinier focussing camera used for analysing the synthetic stock samples for the presence of minerals other than bornite and chalcopyrite.

(ii) A check was made on another portion of sample using a more sensitive Nonius Guinier focussing X-ray diffraction camera and Co K_c radiation (Fig. 10). The material was finely ground and then transferred to the sticky surface of mylar pressure sensitive tape pasted across the windows of mount to form a layer of uniform thickness. The sample was then exposed for eight hours. The interplanar spacings were measured and correlated with mineral patterns.

b) <u>Reflecting Microscope</u> - A Cooke Troughton and Simms reflecting microscope was used solely for the identification and analysis of polished mineral and intergrowth textures. It provided yet a third check on the purity of the mineral compositions. Low power ($l\mu$ X) was suitable for general microchemical tests, but for an analysis of the intergrowth textures and phase relations oil immersion techniques with a magnification of 380 X were necessary. Graduated and grid oculars were used for the statistical analyses.

General

All pure elements and synthesised materials were kept in a desiccator to prevent oxidation and contamination of the products.

A Zeiss reflex camera positioned above the microscope with the aid of a retort ring or lens adaptor, was used for recording all the figures. Experimental Procedure

The relative quantities of Cu, Fe and S required to form the desired minerals were computed from data given in the Cu-Fe-S phase equilibrium diagram of Yund and Kullerud (1960). Sample proportions were calculated for 10% intervals along a line between stoichiometric bornite and a selected value of chalcopyrite (Cu Fe $S_{1.761}$) in the centre of the chalcopyrite solid solution field at 700°C (Fig. 11). This line passes through the fields of bornite solid solution, bornite-chalcopyrite two- phase region and chalcopyrite solid solution. It just avoids the bornite-chalcopyrite-pyrrhotite equilibrium field in the same diagram.

Weighing Procedures - Two methods were used in charging the capsule tubes - silica tubes sealed at one end.

Initially the elements were weighed out individually in a specially moulded pyrex glass tray and transferred to the tube via a glass funnel. In each step the material adhering to the walls of the tray, funnel and tube was tapped free, and the walls of the tube were cleaned with an acetone tainted pipe cleaner. The weight of material in the tube was recorded. The quantities of subsequent elements added were corrected and recorrected for losses during transfer so that the final quantity of material in the tube





Circled dots represent the compositions synthesised for experimental investigations. Dashed line demarks the estimated compositions following the loss of sulphur.

(After Yund & Kullerud, 1960)

was in the desired proportions correct to 0.2 mgms. for approximately 1 gm. samples. In transferring the material, Cu and Fe suffered moderate though comparable losses whereas the loss of S was negligible. On heating the material, the layers of Fe and Cu formed layers of pyrite and chalcocite respectively. Regrinding the material for subsequent runs was greatly hampered by the markedly contrasting hardnesses of the two minerals and occasionally resulted in the loss of material by spattering. Accordingly, a method was adopted whereby the correct proportions of Cu and Fe were weighed into the glass tray and then carefully mixed using a stainless steel spatula. The mixture was then transferred to the capsule tube as before, the differential loss of Cu and Fe being regarded as negligible. Sulphur was added to give the desired metal to sulphur proportion. <u>Preparing capsules</u> - A 1.5 cm. length of silica rod^{*} was placed on top of the charge to reduce vapour volume.

Keeping the sample end of the tube wrapped in a wet cloth to prevent heating and oxidation of the sample, the tube was necked down to capillary size just above the rod using an oxy-acetylene torch (Fig. 12). The tube was then evacuated with a Cenco hyvac pump capable of producing a vacuum of 0.2mm. Hg. After approximately 5 minutes, the capillary was sealed, and the tube was collapsed onto the rod to further reduce vapout space.

An attempt was made to increase the rate of quenching of the sample by preparing an evacuated pyrex capsule as above and enclosing it in a silica tube necked down but open at both ends. The generation of steam destroyed both tubes, and further investigations were abandoned.

<u>Synthesis runs</u> - Samples were kept at 800°C for a period of approximately *5 mm. diameter rod was 'etched' in hydrofluoric acid to give a

tight sliding fit.

48 hours and then quenched. The material was then ground to a fine powder (-325 mesh) with a mullite mortar and pestle, initially under acetone but later dry owing to complications and material losses, and sealed in a new capsule. Oxidation of the material appeared to be of minor importance, and no oxides were detected in the final products. The process was repeated until the sample appeared to be homogeneous. Experimental runs - 0.2 gm. portions of the sample were sealed in capsules in which powdered silica glass (-150 +200 mesh) had been packed to reduce the vapour space in the bowl of the tube between the sample and the rod. The samples were heated at 500, 600, 700 or 800 °C for a specific length of time and then dropped onto a fibre-glass mat or into a can containing cold water (approximately 10°C) or liquid air (-193 °C).



Fig. 12 - Apparatus for preparing capsules.

The vacuum pump is connected via a control stop-cock to a necked down, partly completed capsule. The bar above the oxy-acetylene torch serves as a hand rest to facilitate necking, sealing and shrinking operations.

Fig. 13 PELLET MAKING









Mounting the sample for analysis - Sample particles were separated from the crushed glass packing by handpicking under a binocular microscope with the aid of a simple water diffusion suction pump and several glass nozz]es with different sized openings. The sample was then placed in a steel pellet press (fig. 13) with some dental plastic and compressed for 5 minutes to harden. The resultant pellet was oriented and mounted in vinylite glue on a glass slide, and a second slide was used to align the bevelled pellet surface with the farthest edge of the glass slide mount (fig. 13 bottom diagram, and fig. 14). The mounted section was then polished dry on thin cardboard sheets covered with progressively finer abrasives and mounted on a putty cone, using a sample press in contact with the pellet-glass slide alignment plane, for examination under the reflecting microscope.



Fig. 14 - Sealed capsules, pellet press and mounted samples illustrate three stages involved in the preparation of samples for analysis under the reflecting microscope.

<u>Analysis of the products</u> - In addition to the X-ray and microscope identification apparatus already discussed, the reflecting microscope was used solely in the following analyses and studies.

a. <u>Intergrowth and phase patterns</u> - Oil immersion with a magnification of 380x was used for the majority of descriptions and identifications of chalcopyrite-bornite phase relations and intergrowth patterns. Without oil immersion, the intergrowths of bornite in chalcopyrite were barely visible, even with high power magnification. For quantitative determinations of intergrowth widths and lengths, a calibrated graduated ocular was used (fig.15). Volume determinations were made applying Delesse's area/volume principles to quadrant estimates (Chayes; 1956) or if greater accuracy was required a point-counting technique described in the next section was used.

b. <u>Relative proportions of phases and structures present</u> - A determination of the proportions of phases and textures present necessitated a statistical analysis of the features. Owing to the high magnification, mechanical and integrating stage techniques proved hopelessly insensitive and were abandoned in favour of the following 2 methods similar to those described by Chayes (1956).

A Rosiwal 's analysis, used in initial determinations, was found to have insufficient reproducibility. The technique was abandoned in favour of the Chayes analysis, in which a grid ocular was used in place of the mechanical stage to position the intercepts (Fig. 16). The grid was oriented at 45° to the intergrowth direction, and phases and/or specific textures falling beneath each grid intercept were recorded on a point counter. Complications of orienting the intergrowth directions, especially the triangular lattices, with relation to the grid system were not eliminated, but the results were favourably reproducible. Investigations using the correct


Fig. 15 - Graduated ocular used in the Rosiwal 's analysis and in the measurement of the thicknesses of intergrowths.(Sample run E_{50a})*

0.0	0.05	0.1 mm
<u> </u>		L. L.
	Scale	



Fig. 16 - Grid ocular used for the Chayes analysis. Lattice intergrowths or segregations of chalcopyrite (light grey) in a single bornite crystal (outlined) are analysed by recording the phase and structure beneath each cross-hair. (Sample run E50a)*



orientation with respect to each intergrowth direction of a single crystal and then averaging the results demonstrated that where one intergrowth direction was dominant, a single analysis orienting the grid system at 45° to the dominant intergrowth gave results comparable with the average figure. As far as possible, only crystals showing good orthogonal lattices or triangular lattices with a dominant direction were used in the analysis.

The size of the crystal was found to be a critical factor. Small host crystals (less than 0.07 mm. diameter) showed a marked segregation of the minor constituent to the boundary (fig. 17). It was necessary therefore to confine the above investigation to crystals of comparable sizes larger than approximately 0.07 mm. diameter.



Fig. 17 - The effect of crystal size on the exsolution relations between bornite (dark grey) and chalcopyrite (light grey) is revealed by the marked segregation of the latter to the boundaries of smaller crystals. (Sample run F70a)*

0.05 mm 0.0 Scale

Results

General Observations.

When the capsules were opened after heating there was an unmistakable odour of hydrogen sulphide. No condensation of sulphur on the walls of the capsules was detected with a binocular microscope. Sulphur losses from 0.02 gm. samples of bornite and chalcopyrite were calculated for a temperature of 700 $^{\circ}$ C and sulphur vapour pressure of 60 mm. and found to be 0.08 and 0.06 weight percent respectively. A line joining these values (fig. 11) intersected the bornite-chalcopyrite-pyrrhotite stability field. However, a careful study of samples C, D and E failed to reveal the presence of pyrrhotite. It was concluded therefore that the sulphur vapour pressure over bornite and chalcopyrite was extremely low, in the order of 30 mm. at 700 $^{\circ}$ C, and resulted in a loss of sulphur to the vapour phase in the confined system of less than 0.01 weight percent.

In most of the runs the sulphides were observed to cement silica fragments together (fig. 18) thus demonstrating rapid solid diffusion and recrystallisation at high temperatures. This was further exemplified by the growth of euhedral crystals (fig. 19).

Types of Textures.

<u>Solid solution</u> - The regions of bornite and chalcopyrite solid solution deviate from the homogeneous phase only in the vicinity of the solvus curve. Bornite frequently becomes yellowish in colour and often noticeable, though indistinct, irregular yellow patches are discernable in it (fig. 20). Occasionally fine chalcopyrite intergrowths form within these areas.

Chalcopyrite becomes pinkish in colour with an intensity that





Fig. 18 - Sulphides (S) cementing silica fragments (Q) used to reduce vapour space in the capsule. (Sample run J80a)* 2 mm 0 l



Fig. 19 - Sulphide crystals grown at 800 °C over a period of 164 hours. (Sample run D80d)*

1 2 mm Scale



Fig. 20 - Irregular yellow patches of chalcopyritie material formed in darker bornite with a composition on the solid solution margin of the bornite solvus curve. The bornite is lighter in colour than samples nearer Cu5FeSL at the same température. (Sample run C50a)*

0.0 0.05 mm Scale

Fig. 21 - Sample composition in the twophase region near the chalcopyrite solvus curve showing fine bornite structures in the lighter coloured chalcopyrite. These are best illustrated in the upper right corner.(Sample run 180b)*

0.0 0.05 mm Scale



frequently varies slightly between adjacent crystals. Fine lamellae of exsolved bornite have been detected in some crystals but usually only with difficulty (fig. 21).

The change in mineral appearance in compositions near the solvus curve seems to represent an increasing instability of the host material with respect to the minor phase. The colour change probably indicates a metastable, supersaturated condition that has been quenched in by rapid cooling, only limited exsolution having occurred in those areas where intergrowths are present. The yellowish patches in the bornite may represent quenched zones of transient, disordered, differentiated material analogous to the Preston-Guinier zones observed by Smoluchowski (1951) in alloys. <u>Exsolution textures</u> - In contrast to the variety of structures noted by Sugaki (1951) at low temperatures, only four types of textures have been observed in the present series of experiments. Of these, the first three mentioned refer to the exsolution of chalcopyrite from bornite.

a) Lattice intergrowth textures - These constitute the most important group and occur in all samples, except a few chalcopyrite-rich varieties, showing exsolution textures (figs. 22 & 23). In form, the chalcopyrite segregations are elongated, lens-shaped bodies which occur as separate forms or else as a network with pinching intersections. The intergrowths conform to two main patterns: i) Orthogonal - the most common type in which the exsolved bodies are roughly perpendicular to each other but rarely intersect. ii) Triangular - in this type, the intergrowths intersect at angles ranging from 40° to 75 ° with an average of approximately 60°.

The individual intergrowths vary in size and distribution from uniform examples to those where one or two directions predominate. There



Fig. 22 - Well developed triangular lattice intergrowths of chalcopyrite formed in the darker coloured bornite in a sample from the sub-solvus two-phase region near the bornite solvus curve. (Sample run D60a)*



1

Scale



Fig. 23 - Lattice intergrowths chalcopyrite in the darker coloured bornite showing the different orientations of exsolution lamellae in adjacent crystals (outlined) of the same bornite mass. (Sample run D50a)* 0.0 0.05 mm

does not seem to be any consistency in this relationship and often one intergrowth direction is completely absent.

No single crystal has been observed to contain both orthogonal and triangular intergrowths. Apparent contradictions have been found, on closer examination, to represent separate adjacent crystals (fig. 23).

The widths of the intergrowths vary from sample to sample and even within each sample but with no apparent consistency. Frequently noticeably thick (0.004 mm.) and thin (0.001 mm.) lamellae occur within the same crystal, and often they are parallel to each other. In other crystals, more noticeably in the central part of the two-phase region (fig. 31), there is a complete gradation from fine to coarse lattice intergrowths. In yet other examples, fine intergrowths are missing altogether. b) <u>Emulsion textures or blebs</u> -(Schneiderhohn; 1922)- Blebs of chalcopyrite with smooth lensoid to irregular outlines have been observed in



Fig. 24 - Lattice intergrowths and elongated emulsion blebs of chalcopyrite in a darker bornite matrix. (Sample run D50a)*



most samples (fig. 24). Their prominence is more noticeable in samples from the central part of the two-phase region. The blebs may occur in the centres of the bornite crystals or else adjacent to the margins where they merge with segregation textures. Frequently the blebs taper off into lattice-like structures, but in these cases they are rarely associated with more than one direction (fig. 29).

c) <u>Segregation textures</u> - In most samples with bornite as the major phase there is a rim or partial rim of chalcopyrite around the individual crystal margins (figs. 17 and 25). In mineral masses these rims generally demark the contact between adjacent crystals (fig. 26), and the amount of segregated material varies with the size of the individual crystals. In crystals of similar size, greater than approximately 0.07 mm. diameter, comparable amounts of segregated material occur in addition to the intergrown chalcopyrite. As the size of the bornite crystal decreases proportionally greater amounts of chalcopyrite segregate to the margin at the expense of the intergrowth material, and the ratio of chalcopyrite to bornite becomes exceedingly erratic (fig. 17).

d) Exsolved bornite textures - The exsolution of bornite from chalcopyrite is manifested mainly as a maze of fine, irregular to sub-parallel lattice intergrowths less than 0.001 mm. thick (fig. 27). Rudimentary orthogonal and triangular textures are present, but there is poor consistency in the form and distribution of these arrangements. Textures involving exsolution of bornite from chalcopyrite are confined to a limited composition and temperature range (fig. 31) and occur mainly in massive chalcopyrite host material. Several examples of double exsolution have been observed (fig. 28) where chalcopyrite lamellae exsolved from bornite have reexsolved fine intergrowths of bornite on reaching a state of supersaturation



Fig. 25 - Bornite crystal containing coarse lenticular lamellae of lighter coloured chalcopyrite and displaying moderate segregation of chalcopyrite at the crystal boundary. (Sample run E60b)*

0.0	0.05 mm
<u> </u>	- I - I
Scale	



Fig. 26 - Bornite mass showing the formation of lattice intergrowths within crystals and the exsolution of segregation textures along the crystal margins. (Sample run E70b)*

* See appendix.

0.0 0.05 mm Scale



Fig. 27 - Chalcopyrite crystal containing numerous oriented to irregular hairlike intergrowths of darker bornite. (Sample run H60a)*

0.0 0.05 mm Scale

Fig. 28 - Double exsolution texture showing the initial exsolution of chalcopyrite from the darker bornite and the subsequent exsolution of fine bornite intergrowths in the chalcopyrite lamellae (See arrow). (Sample run H50b)*

0.0 0.05 mm Luni Scale





Fig. 29 - Mixed textures showing lighter coloured chalcopyrite as separate masses (A) and as bleb (B) and lattice-like extensions (C) exsolved from the darker bornite. (Sample run G60a)*

0.0 0.05 mm Scale

at lower temperatures. The approximate limits of this field are shown in figure 31.

<u>Discussion</u> - In considering the various intergrowth textures mentioned, it is necessary to keep the following points in mind : (a) the relative rates of exsolution of the respective phases, (b) the change in exsolution textures with decreasing temperature and (c) the polymorphic transformations of the minerals concerned with decreasing temperature.

Schwartz (1931) noted that in natural samples, the rate of exsolution of chalcopyrite from bornite was approximately twenty-four times faster than the exsolution of bornite from chalcopyrite. When cooled from 600 °C to room temperature in 24 hours, chalcopyrite was still present as coarse lattice intergrowths and in some cases had partly segregated to the boundaries of the respective bornite crystals. The writer obtained segregation of chalcopyrite to crystal margins in 15 minutes with a synthetic sample cooled in air from 800 °C to room temperature. Even allowing for a slight difference in temperature conditions, a comparison of the results appears to demonstrate that exsolution and solid diffusion are far more rapid in this synthetic system than in the equivalent natural minerals - approximately ninety-five times more rapid. A possible explanation for this discrepancy is that impurities in natural samples inhibit the diffusion of copper and iron atoms by reducing the relative number of vacancies required to promote atomic, or conversely "vacancy," diffusion (Smoluchowski, 1951).

The effects of decreasing temperature on exsolution processes may be referred to figure 30 which is based on the writer's research. MO and NP represent the solvus curves separating a central two-phase field from solid solution fields of bornite and chalcopyrite on either side. It is



Fig. 30 - Subsolidus relations of bornite and chalcopyrite.

assumed that sufficient time is available for the system to achieve equilibrium as the temperature falls.

A bornite solid solution sample cooled along AC will begin to exsolve chalcopyrite of composition Q when the temperature reaches R. With decreasing temperature the compositions of the bornite and chalcopyrite phases change along RO and QP respectively. The proportion of exsolving chalcopyrite with respect to the bornite host is given by the ratio x : y.

Chilling the sample decreases the time available for solid diffusion and therefore tends to reduce the extent of exsolution, depending on the rate of exsolution of the phase concerned. This restriction becomes increasingly important as the temperature falls and tends to inhibit the diffusion of the exsolving phase to the margin of the host mineral. Exsolved bodies therefore occur within the host material in forms that are usually controlled by both minerals, the parent generally being the more influential.

The rate of solid diffusion, and therefore exsolution, is dependent

largely on the state of the sample during cooling. At low temperatures, solid diffusion is insufficiently rapid to swell existing intergrowths, and local nucleation occurs with the formation of small intergrowths interspersed between the larger pre-existing ones. The writer's observations indicate that fine intergrowths become increasingly dominant near the solvus curves - especially the bornite one. It is suggested that the paucity of chalcopyrite with respect to bornite near the bornite solvus curve results in a distance between adjacent intergrowths that is great enough to favour nucleation of new bodies in preference to long-distance solid diffusion. Furthermore, samples cooled through the solvus curve, especially with lower temperature intersections, have a limited time in which to exsolve the incompatible phase.

The above considerations are supported by the frequent occurrence of thin lattice intergrowths between, and parallel to, distinctly thicker lamellae in the composition range mentioned.

The effect of analysis of three-dimensional structures (specifically lattice intergrowths of chalcopyrite in bornite) by a two-dimensional plane (the polished section) warrants further consideration at this stage.

In a random orientation of three-dimensional planar structures, a complete range of lattice intersections from 0° to 90° would be expected on the transcutting polished surface. Furthermore, the thicknesses of the intergrowths should range from the true width to increasingly broader apparent widths as the angle of intersection of the polished surface with the individual intergrowth planes becomes more acute. The fact that only a small range of thicknesses and angles of intersection of lattice intergrowths has been observed in the synthetic bornite-chalcopyrite system is significant, and the following suggestion seems to constitute the most plausible explanation.

Bornite, as the host mineral of the intergrowths, is isometric with a habit dominated by the development of hexahedral (100), dodecahedral (110) and more rarely octahedral (111) forms. The cleavage and exsolution planes are represented by the octahedral form.

As indicated in the present experiments, crystallisation is rapid and appears to be accompanied by the formation of good crystal faces (figs. 18 and 19). During the compression of the semi-solid dental plastic in the construction of pellets, crystal faces of minerals in contact with the block piston surface very likely become oriented parallel to the piston surface (fig. 13). Time and again in the polished section, crystal masses appear to have been ruptured as if conforming with a more compatible orientation to the piston surface.

The preferred orientation of faces of the hexahedral and dodecahedral forms parallel to the piston surface appears to be responsible for the restricted angle of intersection of lattice intergrowths, and possibly forms triangular and orthogonal intersections respectively. The same process should also restrict the variation in thicknesses of the intergrowths. Slight deviations from the above preferred orientations most probably reflect an incomplete reorientation of the individual crystals owing either to minor obstructions on the piston surface or else to an incomplete separation of the crystal masses. Neither factor detracts however from the tendency of crystals to assume a preferred orientation during the construction of pellets. Furthermore, the prealignment of the pellet surface with the edge of the glass slide (page 27) favours the removal of a minimum amount of sample material during polishing processes.

In the consideration of blebs, segregation textures and chalcopyrite areas stable at high temperatures, it is difficult to assess the relative importance of solid diffusion. It is very probable however, that chalcopyrite masses adjacent to bornite crystals increase in volume during cooling owing to the addition of material by exsolution processes.

The distinction between exsolved chalcopyrite blebs within bornite crystals and separate chalcopyrite masses also constitutes a problem that has been difficult to resolve. Excellent examples of both occur in nearly all samples containing bornite and chalcopyrite, but separate masses are more conspicuous in the central part of the two-phase region (fig. 31). Gradations between the extremes are common. The following considerations may have an important bearing on this problem and the formation of bleb and lattice intergrowths in general.

Buerger (1948) notes that rapid diffusion in isostructural crystals favours the formation of blebs rather than lattice intergrowths owing to the presence of a large number of planes mutually compatible for exsolution. Bornite and chalcopyrite are face-centred cubic and isostructural at high temperatures, but only the high-temperature form of chalcopyrite is quenchable. The high-temperature form of bornite is stable above 230 $^{\circ}$ C, therefore above this temperature, exsolved chalcopyrite may be expected to occur as blebs. Lattice intergrowths cannot be excluded however, and, although further information is generally lacking on this aspect, it is suggested here that both bleb and lattice structures may form during cooling in the elevated temperature range. Examples such as the elongated blebs in figure 24 most likely represent intermediate structures formed between the two extremes. Below the inversion temperature (230 $^{\circ}$ C) of bornite to the metastable face-centred cubic form with a larger unit cell, exsolved chalcopyrite most probably forms lattice intergrowths in accordance with the considerations discussed on page 12.

Exsolution structures formed at elevated temperatures may persist in the lower temperature ranges in a metastable condition. If solid diffusion is rapid enough however, such structures, which are incompatible with those of the host mineral, will try to change to a more compatible, lower energy form. Accordingly, bleb structures should tend either to diminish in size as lattice intergrowths form in their place, or else to form lattice-like intergrowth extensions with, or without, a diminution in the size of the bleb. Results of the present investigation indicate that the latter process is probably the more important (fig. 29).

The considerations discussed above imply :- a) that solid diffusion in the bornite-chalcopyrite synthetic system is an important process and occurs fairly rapidly in water-chilled samples, even at temperatures below 230 °C, and (b) that chilling is insufficiently rapid to prevent extensive solid diffusion at low temperatures. The rate of cooling decreases exponentially as the temperature falls, and the insulating properties of the vitreosil capsule walls (thermal conductivity 0.0035 cals/sec/cm/cm²/°C) most probably sustain temperatures at a level sufficiently high to facilitate solid diffusion for a limited period of time.

A chalcopyrite-rich sample chilled from a high temperature retains its face-centred cubic structure in a metastable condition at room temperature. In the elevated temperature range, the slow rate of exsolution of bornite from chalcopyrite probably favours the formation of lattice intergrowths rather than blebs. Such intergrowths would most likely be

controlled by the numerous mutual planes of the two crystals and therefore form a maze of intersecting structures. At temperatures below that of the inversion of bornite to the low-temperature form, bornite would ideally try to attain a lower energy state and therefore exsolve along planes in the parent chalcopyrite most compatible with this. The rate of exsolution of bornite from chalcopyrite is extremely sluggish however (especially at low temperatures), and this situation is unlikely to arise.

Results of the present experimental investigation support these ideas, and the maze of fine, exsolved bornite intergrowths observed so consistently probably represent structures present during exsolution at elevated temperatures. With prolonged time, or an extremely slow cooling rate, good lattice intergrowths, similar to those observed by Schwartz (1931) and others in natural chalcopyrite-rich samples, may form parallel to the planes of the octahedral (111) form.

Sub-solidus phase and texture relation.

Results of the examination of samples heated at different temperatures for a limited period of time (approximately 30 hours) and chilled in cold water are represented in figure 31. Several areas with different textural relationships are discernable in the sub-solvus region.

Segregation and emulsion bleb textures are present throughout the two-phase region but decrease in importance in the vicinity of the solvus curves. In one sample (D80a[#]- D at 800 °C) they are completely lacking. In view of the difficulties involved in distinguishing between modifications of exsolved bleb structures and stable chalcopyrite masses (see page 43),

* See appendix.



• Homogeneous material; O Bleb & segregation masses of chalcopyrite;

 \times Intergrowths (Cp in Bo); - - - Intergrowths (Bo in Cp)



The figures below the samples represent the estimated amount of bornite present. The letters below the graph represent the sample compositions as determined in fig. 11. Points T and S denote the limits of bornite and chalcopyrite solid solution respectively, as determined by Yund & Kullerud (1960)

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it has been practically impossible to determine the correct positions of the solvus curves. It seems probable however, that the true solvus curves lie just inside the two-phase regions of figures 31 and 33. As a result therefore, although not shown in these figures, the true solvus curves are most likely bordered on their solid solution margins by narrow zones containing exsolution textures formed only during cooling.

Lattice intergrowths occur throughout the two-phase region, and three distinct fields have been recognised:

a) Chalcopyrite exsolved from bornite. Gradations from fine (0.001 mm.) to coarse (0.004 mm.) intergrowths occur, but variations between crystals in the same sample make it difficult to define specific trends. In general, fine intergrowths are more prominent in the vicinity of the bornite solvus curve, and the contrast between fine and coarse lattice intergrowths is most noticeable here.

b) Bornite exsolved from chalcopyrite. All samples marginal to the chalcopyrite solvus curve display the fine bornite exsolution pattern described previously. The intergrowth texture becomes increasingly finer towards the chalcopyrite solvus curve and in some samples is discerned only with difficulty (fig. 21). With an increase in the bornite content the exsolved bornite texture becomes more irregular and patchy (fig. 29). c) Mixed intergrowth textures. The above fields overlap over a small area between bornite 28 and 45 wt.% at 500°C and bornite 35 wt.% at 700°C (fig. 31). Samples within this area reveal double exsolution features in which chalcopyrite lamellae exsolved from bornite re-exsolve fine bornite intergrowths within their boundaries (fig. 28). The upper limit of this field is uncertain and has been left in abeyance for lack of







Fig. 33 - Sub-solidus phase relations of bornite and chalcopyrite.

- I Region of solid solution.
- II Transition solvus zone of Bo; lighter, mottled yellow coloration.
- III Transition solvus mone of Cp; pinkish coloration.
- IV Two phase field marginal to Cp solid solution; dominated by fine irregular exsolved Bo intergrowths.
- V Two phase field marginal to Bo solid solution; dominated by exsolved Cp lattice intergrowths.
- VI Main two phase exsolution field containing exsolved Cp as lattice intergrowths, emulsion blebs, segregation textures and separate masses.
- VII Mixed field of exsolved Bo and Cp.

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Relations below 500°C have been taken from Sugaki's investigation of natural samples (1955).

Relations between 500 and 800°C have been determined by the writer.

Relations above 800°C have been inferred from the results of investigations by Grieg, Jensen and Merwin (1955).

Phase Relations:

- I Mixed crystals plus melt.
- II Bornite solid solution.
- III Chalcopyrite solid solution.
- IV Two-phase bornite-chalcopyrite stability field.

further information between samples G and H at 700 °C and 800 °C.

The relative amounts of bornite and chalcopyrite have been estimated in approximately equidimensional crystals, and the results are shown in figure 31. An analysis of the chalcopyrite : bornite ratio reveals an apparent increase with decreasing temperature (see also fig. 32). The significance of this trend is questionable however, in view of the dependence of the ratio on the shape of the solvus curve. Values along composition I for instance, indicate a reversed trend dependent on the shape of the chalcopyrite solvus curve (fig. 31).

An idealised diagram of the sub-solidus textural relationships, based on present experimental investigations, is given in figure 33.

Bornite and chalcopyrite solid solution phase boundary positions at 700 $^{\circ}$ C, as determined by Yund and Kullerud (1960) (fig. 11), show minor discrepancies with the positions of the solvus curves plotted in figure 31. Coincidence of the bornite curve is fairly close, but the chalcopyrite curve is displaced substantially towards the chalcopyrite end-member. A possible explanation of the latter discrepancy is that the solvus curve plotted in figure 31 is nearer the chalcopyrite end-member than the true solvus curve in accordance with the discussion on page 47. The same reasoning however, does not account for the discrepancy in the bornite curve as plotted, but it should be noted that the difference in positions of these boundaries at 700 $^{\circ}$ C falls within the error of plotting the curve. A steeper bornite solvus curve would satisfy the phase relations in the diagram and also include the solvus point indicated by Yund and Kullerud. An interesting implication of this explanation is that the exsolution zones marginal to the solvus curves, as suggested on page 47,

should be narrow adjacent to the steep bornite curve and much broader adjacent to the flatter chalcopyrite solvus curve. The rate of exsolution of the phases concerned would very likely affect the widths of these exsolution zones, but the relative positions of the solvus boundaries at 700 ^oC in figure 31 seem to support the above suggestion as an explanation of the discrepancies observed. An alternative explanation for the discrepancy in the chalcopyrite solvus curve is that sample H is more deficient in sulphur than has been assumed. As indicated in figure 11, a slight loss in sulphur would displace the chalcopyrite solvus curve a considerable distance towards the chalcopyrite end-member.

A tentative sub-solidus diagram for the binary system bornite (Cu_5FeS_4) - chalcopyrite $(CuFeS_{1.76})$ is suggested in figure 34. The relationships above the temperature range investigated by the writer are based on work by Grieg, Jensen and Merwin (1955, p. 132). The extension of the bornite solvus curve below 500 °C represents a very tentative suggestion by Sugaki (1955, p. 126). In view of the sharp inflection indicated at 500 °C, the writer feels that little significance can be attached to Sugaki's results as applied here, and further work must be done on synthetic systems to delimit the extension of the solvus curves below 500 °C.

Chilling effects

A sample of composition D (near the transition region of the solvus curve) was chilled from 800 $^{\circ}$ C in cold water, liquid air and air at room temperature to test the influence of the rate of cooling.

When chilled in cold water (800 °C to 15 °C) and liquid air (800 °C



Fig. 35 - Sample chilled in water from 800°C to 11 °C in a few seconds.

Distinct lattice intergrowths of chalcopyrite have been exsolved from the darker bornite. (Sample run D80a)*

0.05 mm. 0.0 Scale

Fig. 36 - Sample chilled in liquid air from 800°C to -193°C in a few seconds.

Resultant textures are very similar to those of fig. 36. (Sample run D80c)*

0.05 mm. 0.0 Scale





Fig. 37 - Sample cooled in air from 800°C to 23°C in 15 minutes.

All chalcopyrite has exsolved at the crystal boundaries forming good segregated textures. (Sample run D80b)*

0.05 mm. 0.0 Scale

to -193 °C), the sample did not show any noticeable difference in the type or amount of exsolution texture (figs. 35 and 36). The sample cooled in air (800 °C to room temperature in 15 minutes) showed complete exsolution of chalcopyrite to the margins of the bornite crystals (fig. 37).

These results demonstrate : (a) the high rate of solid diffusion in the bornite-chalcopyrite synthetic system, and (b) the very efficient insulating properties of the 'vitreosil' glass.

Time effects.

To study the effects of time on exsolution phenomena, observations were made firstly, on changes in samples heated at different temperatures for different lengths of time and then chilled in water, and secondly, on changes in samples at room temperature and in contact with the atmosphere over a period of one year.

Samples heated for different periods of time. - Samples of compositions D,E,F,G,H and I (spanning the sub-solvus exsolution field, fig. 31) were used in the investigation. Both bornite-rich and chalcopyrite-rich samples, though heated for different lengths of time, showed little difference in the resultant type and form of the exsolution texture for the specific sample (figs. 38 to 41). The fine nature of the bornite intergrowths with respect to the thicker lines of the occular grid made analyses difficult and often unreliable, and statistical studies have therefore been confined mainly to the more readily observed chalcopyrite intergrowths exsolved from bornite host material. General observations on approximately equidimensional bornite-rich crystals indicated that there might have been a slight increase in the amount of chalcopyrite



Fig. 38 - Bornite-rich sample heated at 800 °C for 34 hours then chilled in water Lattice intergrowths of chalcopyrite have formed in the darker bornite. (Sample run D80a)*





Fig. 39 - Same sample heated at 800°C for 164 hours then chilled in water. The lattice intergrowths are very similar to those of fig. 38 but appear to be associated in places with thicker forms resembling elongated bleb-like structures. (Sample run D80d)*



Fig. 40 - Chalcopyrite-rich sample heated at 700°C for 17 hours then chilled in water. Bornite intergrowths have exsolved from chalcopyrite as fine, discontinuous, dark grey lamellae (see arrow). (Sample run I70a)* 0.0 0.05 mm

Scale



Fig. 41 - Same sample heated at 700°C for 125 hours then quenched in water. Resultant textures are very similar to those of figure 40. (Sample run I70b)*

formed during an extended period of heating. Accordingly, an analysis, using the adapted Chayes point-counter method described previously, was made to test the variation of the following parameters:

	Total bornite	:	Total chalcopyrite
	Total bornite	:	Total crystal area
	Chalcopyrite intergrowths	:	Total bornite
Corrected	chalcopyrite intergrowths	:	Total bornite

The last mentioned measurement was made in an attempt to distinguish between exsolved lattice and bleb-segregation material. Difficulties were often encountered in distinguishing between some of the exsolution textures - especially emulsion blebs from adjoining segregation textures, and thick lattice intergrowths from elongated, oriented, emulsion blebs. The results of statistical analyses of samples D and E for temperatures ranging from 500 °C to 700 °C, and duration of heating ranging from 17 to 168 hours, are indicated in figures 42 and 43.

Ideally a large number of samples are required for an accurate statistical analysis. Only a small number (usually less than 10) of equidimensional crystals larger than 0.07 mm. diameter were available in each sample in the analysis. It has been necessary therefore, to apply Bessel's correction for small numbers (Moroney, 1957) in order to obtain the best estimate of variance.

Significance tests using Snedecor's Variance Ratio test and Student's t test show that time statistically has an insignificant effect on the variation of textural relationships. Sample E at 700 °C shows the most significant variation, and a sample calculation pertaining to the total chalcopyrite : total bornite ratio is given on pages 59 and 60.





Data from Chayes analyses:	E70a*				E705*				
		<u>17 h</u>	ours	-		<u>125</u>	hour	5	
Crystal samples**	1	2	3	4	1	2	3	4	
Bornite	57	47	53	50	3 8	83	80	52	
Coarse intergrowths	7	6	11	13	9	27	30	10	
Fine intergrowths	6	5	5	1	2	2	0	1	
Emulsion blebs	2	0	0	2	1	1	0	6	
Segregation material	6	2	5	2	10	5	7	2	
Total	78	60	74	68	61	118	117	71	

Sample calculation of statistical analyses of texture relations

in sulphides heated for different periods of time then chilled.

In order to evaluate the effect of time on the total chalcopyrite : total bornite ratio - perhaps the most meaningful parameter - it is necessary to determine if there is a significant difference between the results of the two compositions indicated in the tables above.

The Student's t test, which is based on the Null Hypothesis that all samples are derived from the same parent population, is a sensitive test suitable for use in the present problem.

In order to obtain the best estimate of population variance for the Student's t distribution, it is desirable, in view of the small number of samples analysed, to pool the individual sample variances. A logical initial step therefore is to test the significance of the difference between sample variances to see if it is low enough to show that the sample variances could be independent estimates of the same population. This is readily done using the following test.

Snedecor's F test (Variance Ratio test; Moroney, p. 234)

 $F = \frac{\text{Greater estimate of the variance of the population}}{\text{Lesser estimate of the variance of the population}}$

* See appendix for composition.

** In this calculation, sample refers to the number of crystals analysed in the sulphide compositions indicated above. (Sample calculation continued).

		E7	'0 a				E	70Ъ	
<u>Calculation of variance:</u> Sample	1	2	3	4		1	. 2	3	4
Total chalcopyrite Total bornite	21 57	<u>13</u> 47	<u>21</u> 53	<u>18</u> 50		<u>2</u> 2 30	2 <u>35</u> 8 83	<u>37</u> 80	<u>19</u> 52
Ratio values (x 100) x'= Mean of ratio values x'= Number of samples n'=	37 35 4	28	39	3 6	x# X# n#	= 58 = 41 = 1	3 4 2 1	46	37
Std. dev. (s') = $\sqrt{\frac{(x'-\bar{x}')^2}{n'}}$ =	4.	18			(s#)	2	7•58		
Therefore variance $(s')^2 =$	17.	5		(s*)2	= 5	7•5		
Apply Bessel's correction for sma	11 n	umbe	rs t	o ob	tain	the	best	esti	mate

Apply Bessel's correction for small numbers to obtain the best estimate of variance: $(\hat{s}!)^2 = (\frac{n!}{n!-1})(s!)^2 = 23.3$ $(\hat{s}^n)^2 = 76.6$

$$F = \frac{\text{Greater variance}}{\text{Lesser variance}} = \frac{76.6}{23.3} = 3.3$$
1% level of variance ratio = 29
5% level of variance ratio = 9.3

Since the observed value is noticeably less than the 5% value, the difference between the sample variances is sufficiently insignificant to warrant further investigation by the t test as follows:

Student's t test (Moroney, p.227).	Difference of means
	Std. error of diff. of mean

Assuming the Null Hypothesis, it is necessary to pool the sample variances in order to obtain the best estimate of the population variance. Best estim. of pop. var. $(\hat{\sigma})^2 = \frac{n'(s')^2 + n''(s'')^2}{n' + n'' - 2} = \frac{4 \times 17.5 + 4 \times 57.5}{4 + 4 - 2} = 50$ Best estim. of pop. std. dev. $(\hat{\sigma}) = 7.07$ Best estim. of pop. std. dev. $(\hat{\sigma}) = 7.07$ Therefore t = $\frac{+(\bar{x}' - \bar{x}'')}{\hat{\sigma}_W} = \frac{+(35 - 41)}{5} = 1.2$ Degrees of freedom = 4 + 4 - 2 = 6

For 6 degrees of freedom, reference to the graph for Student's t distribution (Moroney, p.230) shows that the above t value is well below the 5% level of 2.5. <u>Conclusion</u>: There is no significant difference between the total chalcopyrite : total bornite ratio in E70a and E70b.

The insignificance of the effect of time indicates that at elevated temperatures the relative abundances of bornite and chalcopyrite rapidly reach a state of equilibrium. For a specific sample, exsolution is dependant on the rate of cooling, which is uniform for the experiments considered, and therefore does not affect the relative amounts of bornite and chalcopyrite formed in that sample by exsolution processes.

Changes in samples at room temperature. - A re-examination of samples after one year has revealed a few interesting textural changes. Most samples within the sub-solvus field show little change in texture including chalcopyrite-rich varieties which should have reordered to the low-temperature, tetragonal form in this period of time (Frueh; 1958). Bornite-rich samples quenched from near the solvus curve (D at 800 °C) show some interesting changes (figs. 44 and 45). Yellow chalcopyrite shadow zones seem to be slightly enriched with fine chalcopyrite lattice intergrowths. More noticeably, fine stringers of chalcocite sometimes occur in the centers of the chalcopyrite intergrowths. Where small cracks are present in the bornite crystals, fine threads of chalcocite, bordered by a thin chalcopyrite zone on the side adjacent to the bornite, occur in a persistent relationship (fig. 45).

These results most probably reflect the effects of oxidation at room temperature, because the mounted samples were stored in contact with the atmosphere. The oxidation of bornite to chalcopyrite and chalcocite probably conforms with the following reaction :

 $Cu_5 FeS_{4} + (1+x)O_2 \longrightarrow CuFeS_{(1+x)} + 2Cu_2S + (1+x)SO_2$

6í







Fig. 45 - Bornite-rich sample one year later showing oxidation features along cracks and cleavage planes. Chalcocite (Cc:white) is rimmed by chalcopyrite (Cp) adjacent to the darker bornite (Bo). (Sample run C80b)*

Application of results.

The results of the present experimental work are applicable, either directly or indirectly, to two main fields of economic geology in the following manner.

In the study of natural sulphide deposits.

Application can only be made with caution in view of the radically different environmental conditions of naturally occurring deposits in contrast to those used in the writer's research. Natural bornite occurs most commonly in mesothermal environments (170 °C to 300 °C - Edwards, 1954) and appears to coincide with a paragenetic break between the earlier formed sulphides, such as pyrite, chalcopyrite, sphalerite and galena, and the later formed copper sulphides (Ray, 1930). The present series of experiments were conducted at temperatures well above the mesothermal range, but some of the results outline basic principles very likely involved in the formation of natural ore textures.

A comparison of the results of the present experiments with those of other research workers using natural copper-iron sulphides indicates that solid diffusion processes in natural minerals are very much slower than those observed in the equivalent synthetic systems. This relationship may possibly be extended to include other sulphide systems. Impurities in natural samples are the most probable cause of this discrepancy, but other factors, such as confining pressure and the nature of the ore solution, cannot be ignored. The persistence of natural intergrowths under conditions that, experimental work indicates, should have caused complete segregation of the minerals concerned, further emphasises the practical importance of these factors.

Results of the present investigation show that lattice intergrowths with pinching intersections, segregation textures and very probably bleb structures can be formed by exsolution processes. Although this does not refute the activity of other processes, such as replacement, it must be considered as important positive evidence in favour of exsolution in the exsolution-replacement dilemma (page 4) and its associated problem of ore paragenesis. It is significant in this respect that textures very similar to the exsolution varieties mentioned above have been observed frequently in natural minerals and in the products of experimental investigations of natural sulphide systems.

Oxidation of bornite-rich samples, with the liberation of sulphur dioxide, causes the formation of textures that could readily be mistaken for a paragenetic replacement series. This observation is directly applicable, as a limiting factor, to the interpretation of textures in natural copper-iron sulphide deposits, and it may possibly even be extended to include other sulphide systems.

The practical application of the bornite-chalcopyrite system to geothermometry has not been realised in the present research, but several interesting, pertinent features have been recognised and are considered below.

An evaluation of sub-solidus relations gives a basis for determining temperatures of mineral formation, provided that the amount of material exsolved during cooling (exsolution textures) can be distinguished accurately from the amounts of the relative phases present at the temperature of formation.
For a sample formed in the solid solution region, the minor phase is present only in exsolution textures. Subsequent heating therefore will yield a minimum temperature of formation which is reached when all the exsolved material is reabsorbed by the host mineral. For a sample formed in the two-phase region, all material exsolved during cooling will likewise be reabsorbed when the temperature of formation is reached during subsequent heating. This should yield a phase ratio that can be correlated with the relative amounts of the phases indicated in the sub-solidus diagram to confirm the temperature of formation (see fig. 30 and discussion on page 39). Identification of the exsolved material is imperative, because continued heating usually increases the solvent powers of the host mineral and therefore enables solid solution of the minor phase originally present at the temperature of formation.

An advantage of the above method is that a sub-solidus diagram is not essential for a determination of the temperature, or minimum temperature of formation. The presence of such a diagram however, provides a check on the temperature of formation when used in conjunction with a bulk composition analysis of the sulphide. Alternatively, it provides a ready means for evaluating the bulk composition of the sulphide in the following manner. Identification of a predetermined minimum temperature of formation on the correct solvus curve, or a determination of the relative amounts of the phases present at the temperature of formation - for example, point R, or the ratio x : y in figure 30 - enables a rapid evaluation of the bulk composition of the sulphide - AC projected in figure 30.

The direct application of the above techniques to natural sulphide deposits faces many problems, not least of which is the general inability to distinguish between the resultant products of processes commonly active in the formation of ore textures - exsolution, replacement, oxidation, primary deposition etc. Furthermore, sub-solidus relations and processes in natural samples probably deviate from those indicated in pure, synthetic systems. The extent of deviation is largely unknown and therefore inhibits the application of observations of synthetic products, and especially those of copper-iron sulphides, to the interpretation of natural ore textures.

Another aspect of sub-solidus phase relations that may be applicable to geothermometry in natural sulphide deposits is the determination of approximate temperatures, or temperature ranges, of formation from exsolution textures present in natural samples. The common occurrence of exsolution textures in natural bornite-chalcopyrite samples indicates that these textures persist in a metastable form under pressure and temperature conditions present at the earth's surface. By establishing the thermal stability limits of the various sub-solidus textures present in natural samples, it should be possible to equate the bulk composition of a sample with the textures observed in that sample to determine the approximate range of temperature of formation. An analogy of this application may be drawn with reference to figure 33 on the assumption that the diagram represents sub-solidus textural relations able to persist in a metastable form under surface conditions of temperature and pressure. Seven textural fields have been recognised in figure 33 and any sample of a composition represented on the diagram may be expected to contain textures present at temperatures below, but not above, its temperature of formation. For example, a sample comprising 70% chalcopyrite may contain textures of regions III, IV and VII if formed at approximately 900 °C, but

only textures of region VII may be expected if it formed at 500 °C.

Much work will have to be done on studies of natural and synthetic systems before this method can be applied satisfactorily, but once perfected, it should provide a useful check on approximate temperatures of formation of natural sulphide deposits.

In the study of synthetic systems.

Present results indicate that synthetic systems comprising a few pure components provide an ideal situation in which basic processes, such as solid diffusion, appear to be developed to a high degree. Rigid control of composition and environment therefore, should enable a systematic analysis of the effects of changes of different physico-chemical parameters. Theoretically the results of such studies should be applicable ultimately, when natural environments can be simulated in the laboratory, to a reliable interpretation of textures observed in natural sulphides. The practical complications of the physical and chemical changes involved are enormous however, and may even defy this ultimate goal.

Exsolution textures only form during cooling. The rate of cooling, and general rate of change of the physical environment, therefore, should have an important effect on the final products of synthetic systems, and especially those featuring rapid solid diffusion. It is necessary then, when comparing results, to ensure that environmental changes have been been identical for the products under consideration. In the writer's research, some deliberate digressions from the water-chilling technique used for most of the experiments supported this fact. Had different cooling methods been employed, it seems certain that the final sub-solidus exsolution texture relations would have differed, even radically, from those observed.

Results of the present research indicate that crystallographic forms and polymorphic changes of the respective host and exsolved phases seem to have an important effect, in some instances, on the form and temperature range of certain exsolution textures. The effects appear to be governed by the rate of solid diffusion (which is dependent mainly on the specific synthetic system and crystallographic structures involved) and also by the rate of cooling (which may be controlled).

In a consideration of the final products of synthetic systems, all the features discussed so far should be taken into account, and special attention should be paid to the rate of solid diffusion which appears to be a predominant process on which most other exsolution features depend.

Conclusions

A preliminary investigation of exsolution textures and processes in the synthetic bornite-chalcopyrite system has revealed the following features. 1) A grid-ocular/point counter analytical technique is suitable for a quantitative study of phase relations in the polished section. 2) Lattice intergrowths of chalcopyrite in bornite and vice versa, emulsion blebs and segregation textures appear to represent the main products of exsolution. Near the solvus curves, bornite and chalcopyrite become yellowish-orange and pinkish, respectively, and frequently bornite contains irregular yellowish patches apparently representing the incipient exsolution of chalcopyrite. Statistical analyses of the phases are often complicated by the difficulty of distinguishing between different textural forms (e.g. coarse lattice intergrowths and elongated emulsion blebs) and defining the precise boundaries of some of these textures.

3) The sub-solidus textural relations observed appear to be controlled by the rate of chilling. Restricted solid diffusion during chilling in the lower temperature ranges seems to be responsible for the predominance of finer lattice intergrowths in compositions near the solvus curves. Near the bornite solvus curve, the occurrence of fine chalcopyrite laths parallel to coarser varieties probably implies that local nucleation occurs in preference to long-distance solid diffusion.

A comparison of the results of other research work (Yund and Kullerud; 1960) with those plotted in figure 31 (p. 46) indicates that the correct positions of the solvus curves, and especially the chalcopyrite one, are probably displaced slightly towards the centre of the two-phase region. This modification implies that in figures 31 and 33 there is a narrow zone comprising only exsolution textures on the solid solution side of both solvus curves.

4) The formation of exsolution textures appears to be controlled mainly
by solid diffusion within individual crystals. Exsolution of chalcopyrite
from bornite is faster than the reverse process - approximately 24 times
as fast in natural systems (Schwartz; 1931). The rate of exsolution of
chalcopyrite from bornite in synthetic systems appears to be approximately
95 times as fast as the same process in natural systems. Impurities such
as Co, Ni, Zn and Mn most likely inhibit solid diffusion in natural samples.
5) The relations of exsolution textures in the synthetic bornite-chalcopyrite system appear to be affected by the following factors :

a) The rate of cooling appears to control the extent of solid diffusion. Rapid chilling in a few seconds favours the formation of chalcopyrite exsolution textures within the bornite host whereas slower cooling over approximately 15 minutes results in the segregation of chalcopyrite at the host crystal margins.

b) The insulating properties of the silica glass capsules appear to cause a uniform rate of exsolution in rapidly chilled samples. As temperature drops off exponentially with time, solid diffusion at the lower temperatures may be maintained for a relatively long period.

c) The relative crystallographic symmetry of the host and exsolving phases seems to control the form of some exsolution textures. The hightemperature, isostructural, face-centred cubic forms of bornite and chalcopyrite seem to favour the exsolution of chalcopyrite as bleb and/or lattice structures and the exsolution of bornite as a maze of fine intergrowths. Below approximately 230 °C, the low-temperature, face-centred cubic form of bornite appears to favour the exsolution of chalcopyrite only as

lattice intergrowths within the bornite crystal.

d) In bornite crystals less than approximately 0.07 mm. diameter, segregation textures appear to form at the expense of other exsolution textures.

e) During the compression of sample material in the construction of polished section pellets, crystal faces of bornite appear to be preferentially oriented parallel to the surface of the pellet press block piston (see fig. 13; p. 26). This preferential orientation is believed to be responsible for the restricted range of angles of intersection and lamellae widths of the chalcopyrite lattice intergrowths.

6) Results of the present research reveal principles applicable to the ultimate study of natural sulphide deposits as follows :

a) A systematic study of the effects of controlled physico-chemical changes on synthetic systems may provide a means of simulating and interpreting exsolution textures observed in natural sulphide systems.

b) The temperatures of formation of sulphide deposits can be determined by reheating the sample and observing the temperature at which exsolution textures are reabsorbed by the host mineral. For initially homogeneous samples only a minimum temperature determination is possible, but for a sample formed in the sub-solidus two-phase region an exact temperature of formation may be determined, provided that exsolved material can be distinguished accurately from material stable at the temperature of formation.

c) Exsolution textures have been observed frequently in natural sulphide deposits. It is possible that a determination of the sub-solidus textural relations in natural sulphides will provide a means of evaluating a temperature range of formation by correlating the textures and composition of the sample with those plotted in specific areas of the sub-solidus temperature - composition diagram.

As a final conclusion it should be noted that relatively little is known of the processes responsible for most textures observed in sulphide systems. Numerous problems confront the investigator, but only by overcoming these with systematic investigations of synthetic, and possibly natural, systems can the results of experimental research be used to interpret the genesis and formation of natural sulphide deposits.

Suggestions for further investigations.

The following are suggestions for future investigations which may enable a clearer understanding of the behaviour of sulphide systems and especially the bornite-chalcopyrite system.

1) Analyse samples intermediate between those used in the present research to enable a more precise location of the solvus curves and a clearer determination of the sub-solidus texture relations illustrated in figures 31 and 33.

2) Determine the exact rate of cooling of the capsule interior by sealing a thermocouple (preferably platinum to prevent oxidation during sealing) in an evacuated capsule and then chilling it in cold water, air and liquid air.

3) Determine the effect of different cooling rates on sub-solidus bornitechalcopyrite relations by chilling the samples in media with different thermal conductivities and at different temperatures.

4) Use high-temperature X-ray camera techniques or a polished section heating stage and inert atmosphere to study the phase relations of bornite and chalcopyrite as a function of temperature. This should enable an accurate determination of the solvus curves and serve as a means of evaluating the amount of exsolved material observed in synthetic or natural samples at room temperature - a fact that is probably complicated by the entry of exsolved material into 'stable phase' structures without noticeably altering their shape.

5) Using techniques similar to those described by Sugaki and Tashiro (1956), determine the rate, and if possible mechanism, of solid diffusion of Cu and Fe atoms in the synthetic bornite-chalcopyrite system.

6) Evaluate the effects of different impurities on the bornite-chalcopyrite system by using synthetic samples containing controlled amounts of impurity. This type of study constitutes an important, though possibly tedious, means of investigating conditions likely to simulate those present in natural sulphide deposits.

7) Extend the present research to an investigation of sub-solidus phase relations and exsolution processes below 500 °C. The restriction of experimental research to the sub-500 °C. temperature range is probably of great practical importance in view of the reduced technical complications and more realistic application to natural environments. Furthermore, results of the present investigations indicate that the time required for phases to reach equilibrium prior to quenching is unlikely to hamper research until systems become considerably more complex.

8) Extend the present research to investigations of other sulphide and sulphosalt systems. Such studies of phase relations and processes under ^controlled physico-chemical conditions should facilitate the interpretation of textures observed in the equivalent natural deposits. They may also provide a means of assessing the expected behaviour of the constituent elements where these occur as impurities in other sulphide systems.

9) Investigate the effects of known solutions (simulating natural solutions) on the predetermined textures of specific sulphide systems. Such studies, following up on investigations by Ray (1930) and others, should elucidate the effects of other processes such as replacement. The resultant textures may then be compared with those obtained by exsolution to evaluate the relative importance of the respective processes on the formation of textures observed in natural sulphide deposits.

Appendix

List of experiments

Abbrev	iatic	ns:	-						
1)	<u>Samp</u> (A60	<u>ole</u> - a)	Letter Figure Letter	A = composition (see figures 11 and 31) = Cu_5FeS_4 60 = temperature x 10 ⁻¹ = 600 °C x 10 ⁻¹ . a = order of the experiment = first one for A60.					
2)	Obse	rvati	Lons – I I Coa	Bo = bornite; Cp = chalcopyrite; i/g = intergrowth; Fine lamellae = approximately 0.001 mm. thick; arse lamellae = approximately 0.004 mm. thick.					
Percentages indicated below are only approximate values.									
Sample	Time hrs	in mins	Temp. C	Observations on polished sections.					
A80a	40	00	800	Only Bo.					
C80a	35	30	800	Only Bo - yellowish in colour.					
D80a	34	00	800	Bo with 5% Cp as fine lattice i/g .					
E80a	35	30	800	Bo with 20% Cp as lattice i/g + bleb & good segreg- ation textures.					
F80a	34	00	800	Bo with 30% Cp as medium-fine lattice i/g + a few irregular small blebs.					
G80a	3 8	00	800	Bo with 45% Cp as irregular patches, blebs and lattice i/g.					
H80a	40	00	800	Cp with 25% Bo as patches & fine irregular i/g .					
180a	36	30	800	Only Cp - pinkish-yellow in colour.					
J80a	239	00	800	Only Cp.					
K80a	40	00	800	Only Cp.					
A70a	17	00	703	Only Bo.					
C70a	17	00	703	Only Bo.					
D70a	17	00	703	Only Bo - yellowish in colour with vague mottled tones.					
E70a	17	00	703	Bo with 20% Cp as lattice i/g + minor blebs and segregation textures.					
F70a	17	00	703	Bo with 35% Cp as lattice i/g + a few Cp patches with lattice i/g extending away from them.					
G70a	17	00	698	Bo # Cp; Bo as irregular patches with Cp lattice i/g & blebs.					
H70a	17	00	698	Cp with 20% Bo as small irregular patches & minor fine irregular i/g.					

Sample	Time in hrs mins	Temp.	Observations on polished sections.
170a	17 00	698	Cp (pinkish) with 5% Bo as scattered patches, lenses & minor very fine irregular i/g.
J70a	239 00	700	Only Cp.
K70a	17 00	698	Only Cp.
A60a	24 00	601	Only Bo.
C 60a	24 00	601	Only Bo.
D 60a	24 00	601	Bo with 15% Cp as lattice $i/g \&$ minor blebs.
E 60 a	24 00	601	Bo with 30% Cp as irregular patches, coarse lattice i/g & minor segregation textures.
F60a	24 00	601	Bo with 45% Cp as irregular patches & coarse lattice i/g.
G60a	24 00	605	Cp patches, blebs & coarse lattics i/g with 40% Bo as fine irregular i/g & scattered patches.
H60a	24 00	605	Op with 20% Bo as fine irregular i/g + scattered irregular patches.
I60a	24 00	605	Cp with 5% Bo as minor patches & fine irregular i/g .
J60a	176 00	608	Only Cp.
K60a	24 00	605	Only Cp.
A 50a	36 00	508	Only Bo.
C 50a	36 00	508	Dominantly Bo with poorly defined yellowish zones & lattice-like structures.
D 50 a	36 00	508	Bo with 20% Cp as lattice i/g & segregation textures.
E50a	36 00	508	Bo with 40% Cp as lattice i/g & minor segregation textures.
F50c	36 00	508	Bo with 40% Cp as lattice i/g & segregation textures.
G50a	36 00	498	Bo # Cp; Cp as patches & minor coarse i/g containing fine irregular i/g of Bo.
H50a	36 00	498	Cp with 20% Bo as fine irregular i/g & minor patches sometimes containing lattice i/g of Cp.
I50a	36 00	498	Cp with 10% Bo as fine irregular i/g .
J50a	274 30	500	Pinkish Cp with minor very fine irregular i/g of Bo.
K50a	36 00	498	Only Cp.

Time and cooling experiments.

498

F50a

00 06

Bo with 35% Cp as fine-medium lattice i/g & scattered blebs.

Sample	Time in hrs mins	Temp. oC	Observations on polished sections.
F50b	10 00	508	Bo with 30% Cp as fine lattice $i/g \&$ minor blebs.
D80b	15 0 0	802 (Co	led in air) Bo with 10% Cp as segregation textures.
D80c	12 00	804 (<u>Ch</u>	illed in liquid air) Bo with 10% Cp as lattice i/g & minor blebs.
С80ъ	164 00	7 99	Only Bo with a yellowish, mottled colouration.
D80d	164 00	799	Bo with indistinct yellowish patches often containing fine lattice i/g of Cp.
E80b	164 00	799	Bo with 30% Cp as lattice i/g, minor blebs & segregation textures.
н80ъ	164 00	799	Cp with 20% Bo as fine irregular i/g .
180ъ	164 00	799	Cp with very minor fine i/g of Bo.
С70Ъ	125 00	705	Only Bo.
D70b	125 00	705	Bo with scattered fine lattice i/g of Cp.
Е70Ъ	125 00	705	Bo with 25% Cp as coarse lattice i/g, minor blebs & segregation textures.
Н 70 Ъ	125 00	705	Cp with minor Bo as fine irregular i/g & small scattered patches.
170b	125 00	705	Cp with minor Bo as very fine irregular i/g.
С60ъ	156 00	598	Bo with scattered fine lattice i/g of Cp.
D60ъ	156 00	598	Bo with minor Cp as lattice i/g & scattered blebs.
E 60b	156 00	598	Bo with Cp as coarse lattice i/g & segregation textures.
Н60ъ	156 00	598	Capsule incompletely evacuated and sample predom- inantly oxidised to cuprite & magnetite.
I60b	156 00	598	Cp with Bo as fine irregular i/g & scattered patches sometimes containing lattice i/g of Cp.
С 50Ъ	168 00	509	Only Bo - sometimes with a yellowish mottled tone.
D50b	168 00	509	Bo with minor Cp as fine & coarse lattice i/g, blebs & segregation textures.
E50b	168 00	509	Bo with Cp as lattice i/g, scattered blebs & minor segregation textures.
Н50ъ	168 00	509	Cp with Bo as fine irregular i/g & small scattered patches.
I50b	168 00	509	Cp with Bo as fine irregular i/g .

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