EXPERIMENTS WITH COPPER SULPHIDES

at

ELEVATED TEMPERATURES

by

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A thesis submitted to the Faculty of Graduate Studies and Research of McGill University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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April, 1959.

ACKNOWLEDGEMENTS

The writer gratefully acknowledges the encouragement, guidance and constructive criticism of Dr. J.E. Gill and Dr. V.A. Saull of the Department of Geology, McGill University, who jointly directed this thesis. The many hours they spent discussing the problems with the writer were greatly appreciated.

Thanks are also due to Mr. H. Dehn for doing the copper assays and for constructing the vacuum tubes used in several of the experiments.

The research work was supported by Geological Survey of Canada Research Grant No. 274-68.

TABLE OF CONTENTS

INTRODUCTION	1
THEORIES OF ORE GENESIS	3
PREVIOUS EXPERIMENTATION AND OBSERVATIONS	
Solid Diffusion of Sulphides	8
Replacement	10
Gaseous Transportation of Sulphides	11
EXPERIMENTAL PROCEDURE	
Initial Material	• 16
Apparatus	17
Experimental Procedure	19
Examination of the Specimens	20
DESCRIPTION OF EXPERIMENTAL RESULTS	
General Results	21
List and Outline of Experiments	23
Description of Experiments	26
DISCUSSION OF RESULTS	
Solid Diffusion of Sulphides	40
Replacement	46
Gaseous Transportation of Sulphides	51
CORRELATION WITH GEOLOGICAL EVIDENCE	55
FUTURE EXPERIMENTAL WORK	60
SUMMARY AND CONCLUSIONS	63
BIBLIOGRAPHY	80

LIST OF ILLUSTRATIONS

Figures

Figure 1.	Diagram of Apparatus	18
Figure 2.	X-Ray Diffraction Patterns. Experiment AM-1.	49
Figure 3.	Approximate Iron Content of Copper Sulphide by X-Ray Fluorescence.	52

Photographs of Specimens

Plate 1.	Experiment AC-1. Chalcocite which has migrated in the direction of flow of sulphur vapour. Oblique view.	65
Plate 2.	Experiment AC-1. Top view of the same specimen as Plate 1.	65
Plate 3.	Experiment AC-1. Side view of the same specimen as in Plates 1 and 2.	66
Plate 4.	Experiment AH-1. Oblique end view of a mixture of PbS and Cu ₂ S showing upward migration.	66
Plate 5.	Experiment AH-1. Side view of the specimen shown in Plate 4.	67
Plate 6.	Experiment AH-1. Top view of the specimen shown in Plates 4 and 5.	67
	Photomicrographs of Polished Sections	
Plate 7.	Experiment AH-1. Pseudo-eutectic unmixing texture at 300°C.	68
Plate 8.	Experiment AH-1. Pseudo-eutectic unmixing texture at 450°C.	68

i

Plate 9.	Experiment AH-1. Pseudo-eutectic unmixing texture at 550°C.	69
Plate 10.	Experiment AH-2. Same conditions as in Plate 7, except for a lack of sulphur vapour.	69
Plate 11.	Experiment AH-2. Same conditions as in Plate 9, except for a lack of sulphur vapour.	70
Plate 12.	Experiment A-3. Chalcopyrite veinlet extending from bornite into magnetite.	70
Plate 13.	Experiment A-3. Chalcopyrite veinlets in magnetite.	71
Plate 14.	Experiment A-3. Exsolution of chalcopyrite in bornite.	71
Plate 15.	Experiment A-3. Segregated grains of chalcopyrite in bornite.	72
Plate 16.	Experiment R-1. Veinlet of chalcocite in chlorite.	72
Plate 17.	Experiment R-1. Same veinlet as in Plate 16 showing bornite in the chalcocite.	73
Plate 18.	Experiment R-1. Bornite in chalcocite.	73
Plate 19.	Experiment AF-1. Chlorite penetrated by digenite.	74
Plate 20.	Experiment AF-1. Partly replaced chlorite.	74
Plate 21.	Experiment AF-1. Partly replaced chlorite.	75
Plate 22.	Experiment AM-1. Partly replaced chlorite.	75
Plate 23.	Experiment AM-1. Partly replaced chlorite.	76
Plate 24.	Experiment AM-1. As in Plate 23, but with the nicol prisms almost crossed.	76
Plate 25.	Experiment AL-1. Chalcocite and bornite crystals on pyrrhotite. Proof of the gaseous transportation of copper-bearing molecules.	77

Plate 26.	Experiment AL-1. Chalcocite and bornite crystals on pyrrhotite.	77
Plate 27.	Experiment AL-1. Chalcocite and bornite crystals replacing pyrrhotite along a crack.	78
Plate 28.	Experiment AL-1. Chalcocite and bornite crystals on pyrrhotite.	78
Plate 29.	Experiment AL-1. Chalcocite and bornite crystals growing on and replacing pyrrhotite.	79
Plate 30.	Experiment AL-1. As in Plate 29.	79

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INTRODUCTION

At the present time there are no theories of the formation of epigenetic sulphide deposits that are in agreement with chemical and physical facts, theory and experimental results, and which explain all of the field observations that have been made.

Experimental data that would help to explain the nature of the ore-forming processes would be of great scientific and economic value.

Probably the most widely accepted theory of ore-formation is the hydrothermal theory, but many geologists have seriously questioned its validity. Ore magma, granitization, and volatile transfer theories are among the most reasonable alternatives to the hydrothermal theory that have been proposed.

In the present work the numerous theories and related experiments on the formation of ore deposits have been restudied. A brief outline of some of this work is presented, and a few pertinent points which most writers have failed to emphasize are discussed.

J.S. Brown (1948) proposed a theory that offered an explanation for many geological observations. One of the major weaknesses of this theory was that it relied on the volatile transport of the metallic elements as sulphides, for which there was no experimental evidence. Hsaio and Schlechten (1952) performed a series of experiments which indicate that many sulphides are only slightly volatile. Other workers, however, have made many experimental and field observations which they considered to indicate that sulphides are volatile under certain conditions. If their conclusions could be verified, and the conditions reproduced geologically, the hypothesis of Brown would be considerably strengthened.

MacDougall (1957) conducted a series of twenty-three experiments at McGill University, and he concluded that several sulphides were probably appreciably volatile in a sulphurous atmosphere, that some silicates appeared to have been replaced to a minor extent by sulphides, and that solid diffusion of some sulphides into each other takes place rapidly at elevated temperatures. The writer has continued MacDougall's work. Minor changes were made to his apparatus and procedure, and a series of forty-six experiments was carried out.

The original object of this work was to investigate more fully the volatility of certain sulphides, and the replacement of silicates by certain sulphides. Some of the early results indicated that a study of the migration of sulphides away from the main mass of the sulphides, by diffusion and related processes, was also warranted. Most of the experiments were carried out with copper sulphides.

Finally, an attempt was made to correlate the experimental results with geological observations.

- 2 -

THEORIES OF ORE GENESIS

Any coherent theory of the origin of epigenetic sulphide ore deposits should consider at least the following points: the source of the elements; the mechanism of transfer of the elements to the point of deposition; the temperature and pressure conditions during deposition; the reason for deposition; an explanation of the more or less consistent order of zoning and paragenesis; the mechanism and reason for replacement; an explanation of wall rock alteration; a reason for the occurrence of metallogenetic provinces.

There have been many theories presented to explain the origin of these deposits, but none of these have been universally accepted by geologists. When consideration is given to the experimental and field observations available, all theories have major shortcomings in one or more of the above points. There are numerous excellent summaries and criticisms of the theories (Economic Geology's 50th Ann. Vol., 1955 and Edwards, 1956), and the writer will only give an extremely brief description of some of the most important ones.

Probably the most widely accepted theory is the hydrothermal theory, which is outlined in the following paragraph.

Magmatic differentiation of a cooling magma gives rise to an aqueous end product which contains large quantities of the base metals originally present in the magma. The metals are transferred from the source as alkaline (Graton 1940) or acid (Lindgren 1936, Bowen 1933) solutions (Graton 1940), as a gaseous phase, which later condenses to form hydrothermal solutions (Fenner 1933), or colloidal dispersions (Garrels 1944). Deposition is caused by a decrease in solubility, due to cooling, and/or by replacement reactions altering the chemical nature of the transporting medium.

- 3 -

Some of the main arguments against the hydrothermal theory are the very low solubilities of sulphides in superheated steam (Morey 1951) or dilute acid or dilute alkaline aqueous solutions (Garrels 1944). The least soluble sulphides appear to have been transported farthest from the source to the coolest regions. High temperatures and the presence of electrolytes would tend to prevent the formation of colloidal dispersions.

The theory that sulphides have been intruded as a magma has been advocated by Spurr (1923), Bichan (1944) and others. Two of the arguments against these theories are: the high melting points of the sulphides as compared to the temperatures of formation determined for the deposits, and the difficulty of effecting replacement by a concentrated magma.

White (1945) and Brown (1948) have presented theories based on the premise that original differentiation of the cooling earth gave rise to deep-seated ore layers. Deep faults reaching these layers would allow the ore-forming minerals to escape as volatiles, which would rise upwards and form ore deposits. Water from the rocks near the site of ore deposition would effect the replacement of silicate minerals, or the silicate minerals themselves might be volatile under certain conditions. Other authors have postulated the volatile transfer of the metals as chlorides (Jicha 1951, Krauskopf 1957).

Some of the main arguments against these theories are that the only volatilities of the sulphides known are very low, and that chloride minerals are relatively scarce in ore deposits. The known volatilities of silicates are very low, and no adequate mechanism has been postulated to provide the large volumes of water deemed necessary to dissolve the replaced silicates.

- 4 -

Several ore deposition theories have been advanced which correlate granitization with the formation of ore deposits. Goodspeed (1952) postulates that the conversion of hydrous minerals to anhydrous minerals will release water which will leach out ore minerals from surrounding rocks and deposit them in structural traps. Sullivan (1954, p. 566) suggests that metallic elements will migrate, due to an electric field formed by "the neutralization of an electrochemical disequilibrium set up during sedimentation and volcanic activity." Some of the arguments against these theories are similar to those against the hydrothermal theories, and Sullivan's theories are considered to be lacking in adequate experimental corroboration.

There are a few considerations concerning the formation of ore deposits which do not seem to have been fully discussed. At the time of formation of an ore deposit, most theories consider the pressure on the ore-forming fluids, if it is mentioned at all, to be approximately equal to the weight of the overlying rocks per unit area. There appears to be no reason why the pressure could not be either much greater or less than this.

Large hydraulic pressures could be exerted by the same compressive forces which cause geosynclines to fold, or by many other mechanisms. For example, if the fluid is confined in a chamber which has the general shape of an "L", the pressure of the fluid at the top of the chamber will be greater than the pressure exerted by the overlying rocks by an amount approximately equal to the difference in weight per unit area of the vertical column of fluid and the adjacent column of rock.

Fault breccias are common, and it is not inconceivable that the breccia zones could maintain open spaces, at moderate depths. If this is true, ore forming fluids could be under extremely low pressures.

- 5 -

One of the best methods of estimating the temperature of formation of ore deposits is based on the fact that the amount of FeS soluble in ZnS varies with the temperature. Kullerud (1953, p. 98 and 110), has shown that at 800° C, 36% FeS by weight is soluble, but at 500° C only 14.7% is soluble. The rate of exsolution decreases with a decrease in temperature. At 600° C equilibrium is reached in twenty-eight weeks, and at 500° C in two years.

A deposit such as Broken Hill is estimated (Kullerud) to have taken thousands of years to cool, but the ZnS shows almost no exsolution of FeS although it contains enough FeS to give an estimated temperature of formation of 700°C.

Schwartz (1931, p. 192) has shown that solid solutions of chalcopyrite and bornite cooled from 600°C to room temperature in five minutes have already started to exsolve. If the cooling takes sixty minutes, the exsolution texture is very well developed, and some segregation at grain boundaries has started to take place. If the cooling takes twenty-four hours, the two minerals are completely segregated. Exsolution starts at 475°C and becomes extremely sluggish at 220°C.

If the Broken Hill ore body took thousands of years to cool, it is difficult to understand why the FeS was not almost completely exsolved from the sphalerite, and, similarly, why bornite and chalcopyrite exsolution textures are ever found in nature. Kullerud's statement that "In large deposits formed at considerable depth the cooling process must have taken thousands of years", is probably based on the fact that the wall rock is a good insulator. The effect of heat conduction away from sulphide deposits by the wall rock will be practically negligible.

There are, however, several other mechanisms which could cool an ore deposit fairly rapidly. Gaseous expansion is an effective cooling

- 6 -

process but it is unlikely that sufficient space would be available for this to take place to any large extent. It is possible that the net effect of the replacement and removal of silicate minerals, and the deposition of sulphide minerals, is endothermic. Very little is known about the mechanism of replacement, the nature of the ore-bearing fluids, the nature of the fluids which remove the replaced material, or the thermodynamic properties of minerals under high temperatures and pressures and in various atmospheres. No reasonable calculations can be made at the present time, even to indicate whether this effect is endothermic or exothermic.

One of the most feasible processes which would rapidly cool an ore deposit is a flow of a cooler fluid through and around the deposit. This process might also serve as a mechanism for replacement. Morey (1951) has shown that quartz and certain silicates are quite soluble in superheated steam. If the steam is in contact with quartz and the soluble silicates at all times, the steam will always tend to be saturated. To effect replacement at the site of an ore deposit, the temperature and/or the pressure of the steam must be elevated at or near the ore deposit.

Any theory that postulates that the metallic minerals arrive at the location of an ore deposit in a hot dilute solution, will have difficulty in explaining two things: first, how the ore was chilled (and this process must necessarily also cool the tremendous volume of solvent, as it would be impossible to keep the ore body cool if hot fluids were passing over it) and, secondly, if the solutions are cooled at the deposit, why replacement rather than deposition of silicates takes place.

- 7 -

PREVIOUS EXPERIMENTATION AND OBSERVATIONS

Solid Diffusion of Sulphides:

The majority of the experimental work on the solid diffusion of sulphides has concerned the formation of intermediate phases by the diffusion of atoms from one sulphide into another with which it is in contact. There have been a number of experiments indicating that such diffusion can take place quite rapidly at reasonably low temperatures. Two of the most recent studies are those of Virginia Ross (1954) and MacDougall (1957).

Virginia Ross found that the formation of intermediate phases in the systems Cu₂S-CuS, Cu₂S-Sb₂S₃ and Cu₂S-As₂S₃ was rapid at temperatures of 200°C in an argon atmosphere. In forty-eight hours, 1.2mms., 0.9mms., and 0.6mms. of the intermediate phase had formed in the respective systems. MacDougall (1957, p. 33) found similar results in a nitrogen and sulphur atmosphere for the system Cu₂S-FeS. In 24 hours the thickness of the intermediate phase was 0.2mms. at 350°C, 3.5mms. at 450°C, 5mms. at 550°C and 8mms. at 650°C.

Experimental and field observations on phenomena which have been described by most workers as due to volatilization may have been caused by a complex process involving surface diffusion, volume diffusion, very local volatilization and condensation, and plastic flow. A discussion of this process is given in the discussion of the experimental results.

Davis (1915, p. 664) observed chalcocite, bornite and chalcopyrite along lines of weakness in fire-brick of the copper blast-furnace at Trail, B.C. The brick was out of contact with the matte but migration could have been effected either by diffusion or volatilization.

Schwartz (1931) heated bornite and chalcopyrite in evacuated sealed

tubes, and found that specimens heated at 500°C or more, for 24 hours or longer, developed crystals of bornite with intergrown chalcopyrite on their surfaces. Schwartz believed this was due to volatilization.

Edwards (1956) describes a brick from a stoping wall at Broken Hill which had been strongly heated in a fire. The brick was impregnated with galena and chalcocite and the original mortar replaced. He ascribes this to volatilization. Edwards reports experimental work on Pine Vale copper ore heated at 450°C in an evacuated glass tube. Bornite and chalcopyrite crystals developed on the polished surface.

J.E. Hawley (1941) heated a polished section of pyrrhotite in air for two hours at 640°C, and noted that, after heating, fractures in the gangue contained stringers of pyrite. He also heated a specimen containing pyrrhotite and magnetite at 775°C, for 18 hours, in H_2S . Pyrrhotite veinlets developed in fractures in the magnetite. Hawley ascribed both these results to volatilization.

MacDougall (1957) has carried out numerous experiments. Chalcocite crystals developed on the surface of CuS heated in a nitrogen and sulphur atmosphere for 16 hours, at temperatures as low as 450°C. In one of his experiments at 550°C, bornite crystals developed on the surface of bornite after 24 hours (p. 44). At 650°C, bornite crystals were found on the surface of chalcopyrite as well as on bornite (p. 45). In experiments dealing with sulphides wired to rock specimens and heated in nitrogen and sulphur at 550°C, veinlets of chalcocite, bornite and chalcopyrite formed in rock fractures, and some magnetite and pyrite grains were transformed into bornite or chalcopyrite.

- 9 -

Replacement:

Replacement, according to Bateman (1950, p. 137), is the most important process in the emplacement of epigenetic mineral deposits. Bateman defines replacement as "a process of essentially simultaneous capillary solution and deposition by which a new mineral is substituted for one or more earlier formed minerals." The resulting body may occupy the same volume and retain the identical structure of the original body. The new mineral may be partly or wholly different in chemical composition.

The process of substitution is imperfectly understood, but in reactions where no volume change occurs the exchange can not be molecule for molecule, as this would involve a considerable difference in volume for most reactions. Ridge (1949) has shown that, to maintain electrical balance, oxidation or reduction must accompany most reactions, and, when sulphides replace other sulphides, an addition or subtraction of sulphur usually occurs. Jensen (1957) has verified this by comparison of sulphur isotope ratios.

Sulphides replace other sulphides and gangue minerals, but are rarely replaced by gangue minerals. The iron in most sulphide minerals is ferrous, but ferric iron is common in silicate minerals.

Solid diffusion is considered to be very important in replacement. Experimental work, as discussed under the section on diffusion, has shown how rapidly adjacent sulphides which are not in equilibrium can be replaced by intermediate phases.

Garrels (1925, p. 325) has shown experimentally that "the reaction of hydrolyzed, slightly acid solutions provided replacement (of limestone by supergene copper minerals) always essentially volume for volume and with duplication of textures."

MacDougall (1957, p. 66) found a veinlet of chalcopyrite, which appeared to have replaced some chlorite, in one of his experiments where pyrrhotite and chalcocite were separated by a pellet of chlorite rock. The specimens were heated for 24 hours at 550°C in a nitrogen and sulphur atmosphere. The walls of the fracture were irregular, and a new mineral was noted in places along the contact between the chlorite and the chalcopyrite. MacDougall suggests that the chalcocite reacted with the chlorite to form chalcopyrite and another chlorite much lower in iron than the original material.

Koop (1956) has shown that hydrogen sulphide will react with iron-bearing silicates to form pyrrhotite at minimum temperatures between 670°C and 835°C for biotite, less than 835°C for epidote and olivine, between 835°C and 980°C for hornblende, and between 1000°C and 1055°C for augite. X-ray investigation showed a structural breakdown of all the silicates except augite. Minor pyrrhotite formed on chlorite at 980°, and none at **8**90°C.

Gaseous Transportation of Sulphides:

The possibility of gaseous transportation of sulphides depends on two phenomena: the vapour pressure of the sulphides, and the solubility of the sulphides in the surrounding gases.

The vapor pressure of a solid is not constant but increases with the total pressure on the solid (Gucker and Meldrum, 1950, p. 634). If the volume of the solid is considered to be constant, and if the vapour is considered to be a perfect gas, the following equation expresses this effect:

$$\binom{P2}{p_1} = \frac{V_s}{RT}$$

- 11 -

 V_s is the molal volume of the solid, R is the gas constant, T is the temperature, p_1 is the initial vapour pressure at a total pressure of P_1 , and p_2 is the final vapour pressure at a total pressure of P_2 .

A sample calculation for the change in the vapour pressure of pyrite at 550°C, when the total pressure is changed from one atmosphere to 10,000 atmospheres, shows that the final vapour pressure will be 32 times as large as the original vapour pressure. This effect is appreciable, but it is probably not nearly as important as the effects of solubility.

Almost the only experiments on the volatility of sulphides have been conducted by Hsaio and Schlecten (1952). This work was performed by heating sulphides in a vacuum at various temperatures, for different periods of time. The weight loss was measured, and the vapour pressure was calculated from the equation $W = p (M/2RT)^{\frac{1}{2}}$. W is the weight loss in grams per square centimeter per second, p is the vapour pressure, M the molecular weight, R the gas constant and T the temperature. This equation will give an apparent vapour pressure lower than the actual vapour pressure, as some molecules will be recaptured by the solid instead of being sucked away in the vacuum.

For most of the sulphides classed as non-volatile by Hsaio and Schlecten, the observed vapour pressures were very close to the dissociation pressures determined by other workers. These sulphides are MnS, FeS, CoS, NiS, Cu₂S and MoS₂. The condensate was examined in each experiment and it was found that some cobalt and some iron had been transferred. With regard to the iron, it was concluded that about 20% of the total weight loss was due to FeS transfer in the range 900°C. to 1100°C. The results for Cu₂S were somewhat ambiguous, but this was believed to be due to the formation of fine copper wool on the surface of the sulphide specimen. No mention was made of Cu being found in the condensate.

Hsaio and Schlecten give the apparent vapour pressures of certain volatile sulphides as follows:

Sulphides	Temp. Range OC.	Pr. Range Log P mms.	Approx. Pr. at 550 ^o P mms.		
HgS	230 - 330	-4.41 to -2.58	7.58 x 10^{-1}		
As ₂ S ₃	180 - 330	-5.54 to -2.42	3.02×10^{-2}		
Sb ₂ S ₃	352 - 553	-5.41 to -2.59	2.75×10^{-3}		
PbS	503 - 654	-5.56 to -3.35	$6.17 \ge 10^{-5}$		
CdS	503 - 704	-5.96 to -3.16	$6.31 \ge 10^{-6}$		
ZnS	704 - 1006	-5.27 to -1.89	$9.55 \ge 10^{-9}$		

A.M. Schlecten (1954) reports that a good separation of PbS and ZnS in the gaseous state can be achieved with only a small zone of overlapping. The ZnS condenses first, and the PbS later in a colder zone.

The phenomenon of a solid being soluble in a gas has been recognized since the work of Hannay (1880). This process is not fully understood.

Kennedy (1950) concluded that the property of a solvent which makes it a gas has little or nothing to do with its efficacy as a solvent. He found no break or change in the slope of the solubility curve of SiO₂ in water when the water changed from the liquid to the gaseous state. Brady (1953) concluded that the silica in Morey's experiments (1951) was probably transported as Si(OH)₄ at steam pressures greater than a few hundred atmospheres, and possibly as Si₂O(OH)₆ at lower pressures. Ewald, Jepson, and Rowlinson (1953) feel that the solubility is due to a clustering of gas molecules around one molecule of the solute. The work of Ölander, A. and Liander, H., as reported by Morey (1957), has shown that, at 440°C and 403 Kg. per square centimeter, superheated steam will dissolve 5% NaCl by weight. The partial pressure of NaCl is therefore of the order of 20 atmospheres. The vapour pressure of NaCl calculated from the free energy equation given by Kelley (1935) is 4×10^{-8} atmospheres at 440°C, so the amount of NaCl is fifty million times that corresponding to its vapour pressure. Morey reports that no indication of the formation of HCl was noted, and that Spillner found that steam containing dissolved NaCl had no electrical conductivity.

Morey and his co-workers (1951, 1957) have investigated the solubility of numerous substances in water vapour under high temperatures and pressures. The following are some of their results for quartz: at 400° C the weight percent of quartz in steam was 0.064% at 333 bars, 0.155% at 1000 bars, and 0.231% at 2000 bars; at 600°C it was 0.036% at 333 bars, 0.296% at 1000 bars, and 0.765% at 2000 bars. Enstatite was partly dissolved at 1000 bars, at 600°C. The weight percent of the oxides in the superheated steam was 0.0088% for MgO and 0.069% for SiO2. The enstatite has been decomposed, and an extraction of an amount of silica far in excess of the metasilicate ratio has taken place. Similar results were found for albite at low pressures, but at high pressures the material dissolved in essentially albite composition. At 500°C, at 2000 bars, the weight percent of the combined oxides was 0.2675%, and the molecular ratios were 1:0.98:6.10 for Na2O. Al2O3 and SiO2. Microcline gave results similar to those for albite, and, under the same conditions, the weight percent of the combined oxides was 0.248%. and the molecular ratios were 1:0.93:6.76. The molecular ratios of

both feldspars are 1:1:6.

Using a static method and attempting to measure weight changes, bornite, covellite, bismuthinite, chalcocite, sphalerite and pyrite were found to be practically insoluble in superheated steam at 500° C, at 1000 bars. Using a dynamic method on sphalerite under the same conditions, it was found to be soluble to the extent of 0.017% by weight.

There has been some definite evidence that gaseous transportation of sulphides does occur, but most of the phenomena ascribed to the volatility of sulphides could also have been formed by a complex diffusion process, described by the writer under solid diffusion. Davis (1915, p. 671) observed lead sulphide and lead silicate minerals in bricks in the upper part of the stack of the lead blast furnace at Trail, B.C. It was found that the higher the sulphur content of the charge, the more galena was deposited. MacDougall (1957, p. 45) states that a ring of iron oxides was found at the cool end of the combustion tube, after an experiment in which pyrrhotite was heated at 650°C in a sulphur and nitrogen atmosphere. The fact that iron oxides, rather than sulphides, were formed, slighly detracts from the value of this otherwise notable result, and MacDougall does not mention this occurrence in his deductions, summary or conclusions.

- 15 -

EXPERIMENTAL PROCEDURE

Initial Material

Sulphides:

Artificial sulphides prepared by Fisher Scientific Co. were used in all experiments. Mounted grains of the sulphides were examined with a reflecting microscope and found to be quite pure. The pyrite used in the experiments was prepared by heating Fe₂O₃ and sulphur in a nitrogen and sulphur atmosphere, at 550°C, for one hour. The resulting product was reground and the process repeated three times, to ensure that the pyrite was saturated with sulphur.

Non Sulphides:

Natural minerals were used, except for the sulphides. These minerals were donated by the McGill University mineralogical collection or by fellow students. Identification and the degree of purity of the minerals were determined microscopically. Chemical assays were available for the two iron-rich chlorites used, and the iron content of the third chlorite was determined by the X-ray diffraction method developed by W. Petruk (1959).

Sublimed sulphur was obtained from Fisher Scientific Co., and the nitrogen was supplied by the Canadian Liquid Air Co. and was 99.9% pure.

Pellets:

The sulphide pellets were prepared by first compressing the sulphide powder in a hydraulic press at a pressure of 10,000 pounds per square inch. The pressure was maintained for fifteen minutes at a temperature of 175°C. The compressed material was then cut and ground to form a cylinderical pellet approximately 12mms. in diameter and 8mms. thick. This method was also used to form pellets of silicate grains in a sulphide matrix. The magnetite and chlorite pellets were cut from large specimens and ground to the same size as the sulphide pellets.

In the experiments where two or more pellets were bound together, pure aluminum wire was used. Although the aluminum wire is inert in the sulphur and nitrogen atmosphere, it is not very strong, and the contact between the pellets was not too satisfactory.

Apparatus

Figure 1 is a diagram of the apparatus.

The specimens were placed in a tube of Corning 172 glass inside a McDanel combustion tube. The combustion tube has an outside diameter of 1-1/4". It fits perfectly the heating chamber of the horizontal Hevi Duty Electric Co. furnace which was used. Rubber tubing was fitted to the reduced end of the combustion tube, and a clamp sealed the gas inside the combustion tube from the atmosphere. The other end of the tube was fitted with a two-hole rubber stopper. Nitrogen could be introduced through a short piece of glass tubing in one hole, and a sillimanite thermocouple protector occupied the other. The bead of the chromel alumel thermocouple inside the protecting tube could be placed less than half an inch from the sample. The protecting tube prevented corrosion of the thermocouple by the sulphur vapour. Loose asbestos was packed around the thermocouple to prevent convection currents, and the temperature recorded in this manner was found to be the true temperature of the sample.

- 17 -



In several of the experiments the specimens were heated in vacuum tubes which were made from Corning number 172 glass tubing. The outside diameter of the tubing was 20mm. and the wall was $2\frac{1}{2}$ mm. thick. To melt the glass, a mixture of oxygen, natural gas and compressed air was used. One end of the tube was closed and the sample was inserted. The other end of the tube was then drawn out into a thin tube. The gas inside the tube was evacuated and replaced by nitrogen three times, then the final seal was made by melting the thin tube. The pressure inside the tube at room temperature was four millimeters of mercury.

Experimental Procedure

The experimental procedure was identical in all experiments except where otherwise indicated.

The specimen and about two grams of sulphur were placed in the Corning 172 glass tube. This tube was inserted in the McDanel combustion tube, and the specimen placed in the centre of the furnace. The rubber stopper holding the thermocouple protector was coated with grease and emplaced. The length of the thermocouple protector inside the tube had previously been adjusted so that the end of it would just reach the sample. The glass tube leading to the nitrogen supply was inserted through the hole in the stopper, and nitrogen was flushed through the tube. During the flushing, the temperature was held at about 90°C to drive off any moisture.

After twenty-five minutes the nitrogen was shut off and the tubing clamps were closed. The furnace was rapidly heated to its ultimate temperature, and during the heating excess pressure was released by slightly opening the clamp at the reduced end of the combustion tube.

- 19 -

Once the desired temperature had been reached, the clamp was closed and the variable resistance and temcometer were adjusted to maintain this temperature. It took about fifteen minutes to heat the furnace from 90° C to 550° C.

At the end of a run, the furnace was shut off and opened, and the combustion tube was slightly raised to allow air to circulate underneath it. The tube cooled from 550°C to 100°C in about twenty-five minutes.

Examination of the Specimens

On completion of an experiment, the specimens were examined under a binocular microscope. Most of them were then mounted in bakelite or plastic, polished, and examined under a reflecting mineralographic microscope.

A semi-quantitative copper assay was made of the altered iron nut in experiment AE-2 using dithizone. Semi-quantitative iron assays were made in experiments AD-1, AG-1 and AG-2, using X-ray fluorescence. X-ray diffraction was used to compare the silicate minerals before and after experiment AM-1, and also to compare them with a portion of the original sample heated at the same temperature, for the same length of time as the original experiment, but in a pure nitrogen atmosphere. General Results:

Approximately two grams of excess sulphur were heated with the specimen in all the experiments except where otherwise indicated. The sulphur vapour pressure inside the combustion tube is not known, but probably varied during the experiment. As the sulphur at the center of the furnace was heated, it would melt and then boil, and the sulphur vapour would condense in the cooler part of the tube as liquid sulphur where the temperature was greater than the melting point of sulphur, and as solid sulphur where it was colder than this. The liquid sulphur would gradually evaporate and in turn condense as solid sulphur.

Most of the sulphur was found at the end of a run to be condensed in the tube in the region where the temperature would have been approximately 100°C. The final and minimum sulphur vapour pressure was probably that of solid sulphur at 100° C, approximately 8.97×10^{-5} atmospheres (West 1950). The maximum sulphur vapour pressure during an experiment was less than one atmosphere, but, regardless of the exact pressure, a certain amount of excess sulphur was available to the reactions proceeding at the specimen at all times.

Covellite was the initial copper sulphide in all the experiments. Under low sulphur vapour pressures, covellite dissociates to form digenite and sulphur vapour at approximately 235°C (Kullerud 1956). The maximum temperature at which covellite can exist in equilibrium with sulphur vapour is 490°C (Kullerud, 1958). Digenite dissociates to form chalcocite and sulphur at approximately 550°C under low sulphur vapour pressures (Kullerud, 1956). One phenomenon occurring in all the experiments, except where otherwise mentioned, was the formation of complexly twinned subhedral crystals and/or needles of copper sulphide on the surface of the dissociated covellite. The size, shape, concentration and location of these crystals varied erratically from one experiment to the next. In many of the experiments where the original material was a rectangular block of covellite, the crystals completely filled the space between the bottom of the specimen and the glass tube. The crystals and the main body of the dissociated covellite were examined by X-ray diffraction, and the "d" spacings corresponded very closely to those listed for $\boldsymbol{\alpha}$ chalcocite (American Society for Testing Materials, 1957). In the experiments conducted under a high sulphur vapour pressure, the final copper sulphide was probably digenite, but, although some digenite may have been present in other experiments, chalcocite was probably the dominant mineral. Minor amounts of covellite were found on the surface of many of the altered specimens, and this was probably formed during the cooling process.

In the experiments which employed a vacuum tube, the calculation of the partial pressure of sulphur vapour was as follows:

Experiment AD-1 is used as an example.

The volume of the tube less contents was 31.4 cc.

The vacuum was 95% at $20^{\circ}C$.

The volume of the nitrogen left in the tube would be:

 $\frac{5}{100} \times 31.4 \times \frac{823}{293} = 4.4 \text{ cc. at } 550^{\circ}\text{C} \text{ and } 1 \text{ atmosphere.}$

The weight of the CuS was 0.411 g., and, if it is assumed that this was entirely dissociated to digenite, the weight of the sulphur released was $0.411 \times \frac{128.24}{860.67} = 0.0612g.$

Assuming that the total pressure at 550°C is approximately one atmosphere, the mole fraction of S₂ is 0.26, of S₆ is 0.56, and of S₈ is 0.18 (West, 1950). The effective gram molecular weight of the sulphur vapour is therefore 0.26 x 64.12, plus 0.56 x 192.36, plus 0.18 x 256.48, or 170.67. At 550°C and one atmos., the volume occupied by the sulphur vapour would be $0.0612 \times 22,400 \times \frac{823}{273} = 24.2$ cc. The total volume of gas at 550°C and 1 atmos. would be 24.2,

The actual total pressure must have been $\frac{28.6}{31.4} = 0.91$ atmos.

The partial pressure of sulphur was $\frac{24.2 \times 0.91 = 0.77}{28.6}$ atmos.

In the experiments involving chlorite, a small amount of water would be released. No water condensed on cooling, so presumably this was taken up by other minerals or by the unidentified material.

The error in the calculated partial pressure of sulphur due to inaccuracies of measurement, is approximately plus or minus 0.06 atmospheres.

List and Outline of Experiments:

plus 4.4, or 28.6 cc.

A-l to	Magnetite -	CuS.	550°C	24	hrs.	Bornite	formed	at	interface,	
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- A-5 and chalcopyrite veinlets in magnetite.
- B-1 FeS Chlorite PbS, ZnS, CuS mixture. 550°C 48 hrs. Minor diffusion of chalcocite.
- C-1 FeS Chlorite CuS, Sb₂S₃, SnO₂ mixture. 550^oC 48 hrs. Stibnite volatilized.

D- 1	FeS - 2mm. space - CuS. 550°C 24 hrs. Nil.
E-1	CuS - chlorite. 550°C 24 hrs. Minor diffusion.
F-1	CuS - limestone. 550°C 24 hrs. Minor diffusion.
G-1	FeS in CuS. 550°C 48 hrs. Chalcopyrite nodules formed.
H-1	Gabbro in CuS. 550°C 48 hrs. Minor diffusion.
I-1	Chlorite in CuS. 550°C 48 hrs. Minor diffusion.
J-1	FeS - 2mm. space - Sb_2S_3 . 550°C 48 hrs. Sb_2S_3 volatilized.
K-1	Gabbro in Sb2S3. 550°C 48 hrs. Sb2S3 volatilized.
L-1	Chlorite in Sb ₂ S ₃ . 550 ^o C 48 hrs. Sb ₂ S ₃ volatilized.
M-1	CuS - $l\frac{1}{2}$ mm. space - FeS. 550°C 48 hrs. Minor bornite between the pellets and on the Cu ₂ S.
N-1	CuS - $l\frac{1}{2}$ mms. sulphur - FeS. 550°C 48 hrs. Same as M-1.
P-1	CuFeS ₂ , FeS veinlet in chloritic rock. 550°C 8 hrs. Nil.
Q- 1	Chlorite in CuS. 550°C 48 hrs. Diffusion and possibly minor replacement.
R-1	Iron-rich chlorite in CuS. 550°C 48 hrs. Diffusion and re- placement. Minor bornite in Cu ₂ S.
S-1 to S-2	CuS - Magnetite. 550°C 24 hrs. Attempt to set up an elec- trical potential failed. Results as in A-1 to A-5.
	Bronzite in CuS. 550°C 24 hrs. Minor diffusion.

- V-1 PbS, CuS, FeS mixture. 200°C 550°C 24 hrs. Diffusion.
- V-2 PbS, CuS mixture. 200°C 550°C 24 hrs. Diffusion.
- W-1 Augite in CuS. 550°C 48 hrs. Minor diffusion.
- X-1 Biotite in CuS. 550°C 64 hrs. Minor diffusion.
- X-2 Biotite in CuS. 550°C 40 hrs. H₂O present. As in X-1.
- Y-1 Augite, epidote and siderite in CuS. 550°C 48 hrs. H₂Opresent. Minor diffusion.
- Z-1 Chlorite, biotite, epidote and augite in CuS. 825°C 48 hrs.
 Minor diffusion and possibly replacement of chlorite.
- Z-2 Chlorite, biotite, epidote and augite in CuS. 285°C 169 days. Nil.
- AB-1 CuS 1" space Fe. 680°C 21 hrs. Copper transferred.
- AC-1 CuS. Stream of sulphur and nitrogen. 550°C 6 hrs. Appreciable diffusion.
- AD-1 FeS₂ 3" space CuS. 550°C 24 hrs. Sulphur pr. 0.77 atmos. Fe transferred.
- AE-1 CuS 3" space Fe. 475°C 24 hrs. Nil.
- AE-2 CuS 3" space Fe. 775°C 17 hrs. Copper transferred.
- AF-1 Three chlorites in CuS. 550°C 48 hrs. Sulphur pr. 0.75 atmos. Two iron-rich chlorites definitely partly replaced.

- AG-2 FeS₂ 3" space CuS. 550°C 37 hrs. All vapour evolved in first two hours flushed out. Nil.
- AH-1 PbS, CuS mixture. 200°C to 550°C 24 hrs. Diffusion.
- AH-2 PhS, CuS mixture. 200°C to 550°C 24 hrs. All vapour evolved in first two hours flushed out. Minor diffusion.
- AJ-1 CuS 3" space Fe. 655°C 24 hrs. No excess sulphur. No copper transferred.
- AK-1 Repeat of AF-1.
- AL-1 CuS pellet 3" space Fe. 675°C 24 hrs. Copper transferred.
- AM-1 Iron-rich chlorite in CuS. 550°C 48 hrs. Sulphur pr. 0.75 atmos. Chlorite crystals partly replaced.

Description of Experiments:

A-1 to A-5 Magnetite pellet wired to CuS pellet. 550°C. Nitrogen and sulphur atmosphere. 24 hrs.

Five similar runs were made, and although qualitatively the results were the same, quantitatively they were different. The most marked reaction took place in experiment A-3. In this experiment a pellet of magnetite 5mms. thick and 12mms. in diameter was bound with aluminum wire to a CuS pellet. After heating, the CuS was altered to chalcocite, and subhedral crystals of chalcocite covered most of the surface. A layer of bornite had formed between the two pellets and extended down the side of the magnetite almost to the end of the pellet. The bornite adjacent to the chalcocite contained no visible chalcopyrite, but approximately 2mms. from the chalcocite exsolved and segregated chalcopyrite grains were evident (Plates 13, 14 and 15). The bornite layer was 1mm. thick at the interface and decreased in thickness down the side of the magnetite. Copper-bearing sulphides penetrated the magnetite along cracks. These veinlets were mainly chalcopyrite, but near the bornite layer, from which they originated, they contained some bornite (See plates 12 and 13). Small pyrite veinlets formed at the end of the magnetite pellet farthest from the chalcocite.

In the five runs the thickness of the bornite layer at the interface varied from 0.05 to 1.0mms., and the amount of replacement of magnetite by copper iron sulphides along cracks, varied accordingly.

In each run approximately the same amount and size of chalcocite crystals grew on the surface of the altered CuS pellet.

B-1 FeS pellet, chlorite pellet and pellet of a mixture of PbS,
 ZnS, and CuS, wired together. 550°C. Nitrogen and Sulphur atmosphere. 48 hrs.

The FeS and chlorite pellets do not appear to be altered to any great extent. The pellet formed of PbS, ZnS, and CuS showed little zoning except for a thin layer of chalcocite crystals on the outside of the pellet. One minute veinlet of chalcocite penetrated a crack in the chlorite rock, and a very minor amount of chalcopyrite occurred at the end of the veinlet. C-1 FeS pellet, chlorite pellet and pellet of a mixture of CuS, Sb₂S₃, and SnO₂. 550°C. Nitrogen and sulphur atmosphere. 48 hrs.

> The FeS and chlorite pellets do not appear to be altered to any great extent. Some flowage of the sulphide mixture had occurred and some of the stibnite had volatilized. No definite zoning could be seen in the pellet.

D-1 FeS pellet, CuS pellet 2mms. apart. 550°C. Nitrogen and sulphur atmosphere. 24 hrs.

> Minor pyrite was formed in cracks in the magnetite. Chalcocite crystals formed.

E-1 Chlorite pellet, CuS pellet, wired together. 550°C. Nitrogen and sulphur atmosphere. 24 hrs.

> Chalcocite crystals formed on the altered CuS and between the two pellets. Some of the fractures in the chlorite were filled with chalcocite.

F-1 Limestone pellet, CuS pellet, wired together. 550°C.Nitrogen and sulphur atmosphere. 24 hrs.

Chalcocite crystals formed on the altered CuS and between the two pellets. Chalcocite had migrated into some of the cracks in the limestone.

G-1 Pyrrhotite grains in a matrix of CuS. 550°C. Nitrogen and sulphur atmosphere. 48 hrs.

The specimen was entirely altered to chalcopyrite. The specimen was originally rectangular, but the chalcopyrite formed in nodules.

H-1 Grains of gabbro in a CuS matrix. 550°C. Nitrogen and sulphur atmosphere. 48 hrs.

Chalcocite crystals formed on the surface and chalcocite penetrated cracks in the gabbro.

I-1 Grains of chlorite in a CuS matrix. 550°C. Nitrogen and sulphur atmosphere. 48 hrs.

Chalcocite crystals formed on the surface and chalcocite penetrated cracks in the chlorite. The texture suggested that minor replacement might have occurred, and one minute grain of chalcopyrite had formed.

J-1 Pyrrhotite pellet, Sb₂S₃ pellet 2mms. apart. 550^oC. Nitrogen and sulphur atmosphere. 48 hrs.

> Needles of stibnite occurred throughout the tube, but there was no evidence of any reaction between the pyrrhotite and the stibnite.

K-1 Gabbro grains in a matrix of Sb_2S_3 . 550°C. Nitrogen and sulphur atmosphere. 48 hrs.

Needles of stibnite occurred throughout the tube, but there was no evidence of any reaction between the stibnite and the other minerals. The stibnite penetrated cracks in the gabbro only very slightly, near the contact.

L-1 Chlorite grain in a matrix of Sb₂S₃. 550^oC. Nitrogen and sulphur atmosphere. 48 hrs.

Same results as in K-1.

- 29 -

M-1 CuS pellet, asbestos washer $l\frac{1}{2}$ mms. thick, FeS pellet wired together. 550^o Nitrogen and sulphur atmosphere. 48 hrs.

The pyrrhotite did not appear to be altered to any great extent, but a few grains of bornite had formed on the side of the hole in the washer, and minor bornite occurred at the surface of the altered CuS pellet adjacent to the washer.

N-1 CuS pellet, asbestos washer with the hole packed full of sulphur, FeS pellet, all wired together. 550°C Nitrogen and sulphur atmosphere. 48 hrs.

> The pyrrhotite did not appear to be altered to any great extent, but a globule of bornite had formed on the side of the hole in the washer, and minor bornite occurred at the surface of the altered CuS pellet adjacent to the washer.

P-1 Natural polished specimen of a veinlet of pyrrhotite and chalcopyrite in a chloritic rock. 550°C Nitrogen and sulphur atmosphere. 8 hrs.

No definite changes could be noted.

Q-1 Chlorite grains in a matrix of CuS. 550°C Nitrogen and sulphur atmosphere. 48 hrs.

Chalcocite crystals formed on the surface and chalcocite penetrated the chlorite along cracks and cleavage planes. The texture suggested that some replacement had occurred but there was no conclusive evidence.
R-1

Iron-rich chlorite grains in a matrix of CuS. 550°C Nitrogen and sulphur atmosphere. 48 hrs.

Chalcocite crystals formed on the surface and chalcocite penetrated the chlorite along cracks and cleavage planes. The texture suggested that some replacement had occurred. Minor bornite had formed in the chalcocite, and what appeared to be new silicate minerals had formed (Plates 16, 17 and 18). An attempt was made to separate the sulphides and the silicates with an isodynamic separator. The sulphide-poor fraction was examined under a petrographic microscope. Most of the grains were cloudy and almost opaque and had numerous minute specks of opaque sulphides associated with them. One grain of quartz and one grain of piedmontite were identified but it is possible that these were original minerals, although the original material was examined under a binocular microscope and appeared to be pure chlorite. The material replacing the chlorite crystals was probably the same as the material found in experiment AM-1. (See discussion of results).

S-1 and 2 CuS pellet. Magnetite pellet, wired together. 550°C Nitrogen and sulphur atmosphere. 24 hrs.

> It was attempted to set up an electrical potential across the pellets. Aluminum wire was used to carry the current, and the wire to pellet contact was made with a solder. This connection was unsatisfactory and the results were inconclusive. The results were very similar to those of experiments A-1 to A-5, and reversing the current made no discernible difference.

- 31 -

U-1 Bronzite grains in a matrix of CuS. 550°C Nitrogen and sulphur atmosphere. 24 hrs.

Chalcocite penetrated along cracks in the bronzite, but no evidence of replacement was visible.

V-1 PbS, CuS, FeS mixture in four rectangular prisms. Temperature gradient from 200°C to 550°C. 24 hrs.

> The two hotter pellets had become very compact due to flowage, and some migration towards the cool end of the tube was evident. The other two pellets were affected to a lesser degree, but they were both markedly thicker at their cooler ends. The overall composition appeared to be uniform throughout the specimens. A vague pseudoeutectic texture was developed similar to that shown in Plates 7, 8 and 9.

W-1 Augite grains in a matrix of CuS. 550°C Nitrogen and sulphur atmosphere. 48 hrs.

> Chalcocite crystals formed on the surface. There is no evidence that chalcocite had replaced the augite, although it had penetrated the grains along cracks.

 X-1 Biotite grains in a matrix of CuS. 550°C Nitrogen and sulphur atmosphere. 64 hrs.

> Chalcocite grains formed on the surface and chalcocite slightly penetrated the biotite along cleavage planes.

X-2 Biotite grains in a matrix of CuS. 550° C Nitrogen, sulphur and H₂O atmosphere. 40 hrs.

Same results as in X-1.

Y-1 Three separate pellets of augite in a CuS matrix, epidote in a CuS matrix, and siderite in a CuS matrix. 550°C Nitrogen, sulphur, and H2O atmosphere. 48 hrs.

Chalcocite crystals formed on the surface and chalcocite penetrated the minerals along cracks. There was no evidence of replacement or reaction between the chalcocite and the other minerals.

Z-1 Four separate pellets of iron-poor chlorite in a matrix of CuS, biotite in a matrix of CuS, epidote in a matrix of CuS, and augite in a CuS matrix. 825°C Nitrogen and sulphur atmosphere. 48 hrs.

> Coarse crystals of chalcocite (1-2mms. in diameter) formed on the base of the specimens and completely filled in the space between the specimen and the tube. Chalcocite veinlets had formed in cracks in all of the silicates. The texture suggested that minor replacement of the chlorite had occurred, and a few minute grains of chalcopyrite had formed. There was no evidence of replacement of the other silicate minerals.

Z-2 Four separate pellets of iron-poor chlorite in a matrix of CuS, biotite in a matrix of CuS, epidote in a matrix of CuS, and augite in a CuS matrix. 285°C Nitrogen and sulphur atmosphere. 169 days.

> The CuS pellet had mostly dissociated to form what was probably digenite. Some covellite was present in the altered specimens, but this might have been formed on cooling. There were no crystals formed on the surface of the specimens,

- 33 -

little penetration of cracks, and no evidence of replacement.

AB-1 CuS pellet, iron nut, l" apart. 680°C Nitrogen and sulphur atmosphere. 21 hrs.

The following sequence of minerals formed on the altered iron nut. A minute layer of covellite formed on a thin layer of chalcocite which overlaid magnetite, which overlaid pyrrhotite, which overlaid unaltered iron. The actual contact between the chalcocite and magnetite was not visible in the polished section as the polishing process had plucked away most of the copper sulphides. Only a few grains of chalcocite were seen. The uniform covering of the bolt was deduced from the distinctive blue colour of the covellite film.

AC-1 Semicircular prism of CuS. 550°C A stream of nitrogen and sulphur. 6 hrs.

> The apparatus was modified for this experiment. The McDanel combustion tube was removed so that direct observations of the specimen could be made through the Corning 172 glass. Nitrogen was passed through a flask of boiling sulphur and then through the glass tube. Additional sulphur was present in the tube at the start of the experiment.

The downstream end of the specimen appeared to melt and flow downstream (Plates 1, 2 and 3). The material started to climb up the walls of the glass tube as well as flowing downstream. The material extended 0.3" past the original end of the specimen. An oxygen leak developed after about four hours. Flowage appeared to slow down very markedly and the specimen began to turn red, especially in the mobile portions. X-ray diffraction later identified this new mineral as Cu₂O.

AD-1 12 grams of FeS₂ with a surface area of 6.86 square cms.
3" away from 0.411 grams of CuS with a surface area of
1.0 square cms. 24 hrs.

550°C Nitrogen and sulphur atmosphere. Partial pressure of sulphur was 0.77 atmos., total pressure was 0.91 atmos. The CuS pellet dissociated to form what was probably digenite, and crystals formed on the surface. X-ray analysis indicated that the digenite contained approximately 0.46% iron at the end of the experiment. No copper was transferred to the pyrite. The digenite was examined under a reflecting microscope, but no iron-bearing sulphide minerals were evident.

- AE-1 CuS pellet 3" away from an iron nut. 475°C Nitrogen and sulphur atmosphere. 24 hrs. Chalcocite crystals formed on the surface of the dissociated CuS pellet. A minor amount of pyrrhotite formed on the iron nut, but there was no indication that any copper had been transferred to the nut.
- AE-2 CuS pellet 3" away from an iron nut. 775^oC Nitrogen and sulphur atmosphere. 17 hrs.

The new minerals formed on the nut, as seen under the binocular microscope, appeared to be similar to the minerals formed in experiment AB-1. 0.307 grams of the outer surface of the nut were dissolved, and a copper assay by the dithizone method indicated that the material contained 0.25% Cu. No copper could be detected by a similar assay of an unaltered iron nut. It was presumed that all of the transferred copper had been dissolved, as all of the alteration products on the nut and some of the unaltered iron had been dissolved.

AF-1 Three separate samples of chlorite grains in a CuS matrix. 550°C 48 hrs.

> The experiment was designed to have a total pressure of 0.9 atmos. and a sulphur pressure of 0.75 atmos. After initially heating to 550°C, the enclosing tube appeared to be intact, but at the end of the experiment one end of the glass tube was cracked, and the digenite was slightly oxidized to Cu_2O .

The Fe/Fe plus Mg ratios of the three chlorite specimens were 0.22, 0.46, and 0.76.

Crystals of digenite formed on the surface of all three samples. Digenite penetrated the iron-poor chlorite along cleavage planes and some of the textures suggested that minor replacement had occurred. These replacement textures were much better developed in the two iron-rich chlorites (Plates 19, 20 and 21). The material replacing the chlorite crystals was probably the same as the material found in experiment AM-1 (See discussion of results). AG-1 9.542 grams of FeS₂ with a surface area of 6.86 square cms. 3" away from 1.22 grams of CuS with a surface area of 2.77 square cms. 550°C Nitrogen and sulphur atmosphere. 37 hrs.

> Chalcocite crystals formed on the surface of the dissociated CuS pellet. X-ray fluorescence indicated that the chalcocite contained approximately 0.2% Fe. No copper was transferred to the pyrite.

AG-2 Same initial material and conditions as in AG-1.

A stream of nitrogen flushed out all evolved gases for the first two hours of the experiment. The CuS specimen had been placed downstream from the FeS2, but an analysis by X-ray fluorescence indicated that no iron had been transferred to it during the experiment. No crystals formed on the dissociated CuS specimen.

AH-1 PbS - CuS mixture in a piece of Corning 172 glass tubing that had been split longitudinally. Temperature gradient from 200°C - 550°C. Nitrògen and sulphur atmosphere.
 24 hrs.

The material was originally packed into the container as firmly as possible, and the surface was levelled. The results indicated that some movement towards the cool end of the tube had occurred. Plate 5 shows the wave-like structures that formed on the surface, with the gentle slopes towards the hot end of the tube, and the steep slopes towards the cool end. Crystals and structures that looked as if they had been formed by gas bubbles breaking through a very viscous liquid had formed on the surface (Plate 6). Along the edge of the surface, curved wedges of the mixture had begun to migrate up the walls of the glass tube (Plate 4).

A pseudo-eutectic unmixing texture was developed (Plates 7, 8 and 9). The unmixing was much more nearly complete at the hot end of the specimen than at the end that had been colder. X-ray fluorescence indicated that the Pb/Cu ratio was identical throughout the length of the tube.

AH-2 Same initial conditions as AH-1.

A nitrogen stream flushed out any gases evolved for the first two hours. Minute crystals formed on the surface but otherwise the surface was flat. At the hottest part of the tube the amount of material present had slightly decreased, as there was a space between the sulphides and the wall of the tube. A pseudo-eutectic unmixing texture had been developed to about the same extent throughout the specimen (Plates 10 and 11).

AJ-1 CuS pellet, iron nut 3" apart. 655°C Nitrogen atmosphere. 24 hrs.

> A minor amount of pyrrhotite but no visible copper sulphides formed on the nut. No chalcocite crystals formed on the dissociated CuS pellet.

AK-1 Repeat of AF-1 with identical results.

When the tube was broken at the end of the experiment the distinctive sound made by the air rushing in proved that there had been no leakage during the experiment. In spite of this a minor amount of Cu_2O had formed.

AL-1 CuS pellet, iron nut 3" apart. 675°C Nitrogen and sulphur atmosphere. 24 hrs.

The iron nut had been partly altered to pyrrhotite, and fern-like crystals of an intimate mixture of chalcocite and bornite had grown on the outside of, and partly replaced, the pyrrhotite (Plates 25 to 30).

AM-1 Chlorite grains having an Fe/Fe plus Mg ratio of 0.46, in
 a matrix of Cu₂S. 550°C Nitrogen and sulphur atmosphere.
 The partial pressure of sulphur was 0.75 atmos. and the
 total pressure was 0.9 atmospheres. 48 hrs.

Digenite crystals formed on the surface, and digenite penetrated the chlorite along cracks and cleavage planes. What appeared to be a new mineral (see the discussion of experimental results) replaced some of the chlorite pseudomorphically (Plates 22, 23 and 24).

DISCUSSION OF RESULTS

Solid Diffusion of Sulphides:

Volume solid diffusion was observed in several of the experiments, and the results were in accord with those found by previous workers.

In experiments A-1 to A-5 chalcocite and magnetite reacted to form the intermediate phases bornite and chalcopyrite. The amount of the intermediate phases formed varied erratically due to the variable nature of the contact between the pellets. The aluminum wire used was too weak to bind the pellets tightly together, and when the wire expanded on heating the contact must have been very poor. MacDougall (1957) used nichrome wire and obtained reproducible results.

In experiment G-1 a better method was devised. A pellet was made by compressing FeS cubes 5mms. on a side in a matrix of CuS. The time interval used was too long, as, after heating at 550°C for 48 hours, the entire pellet had been altered to chalcopyrite.

MacDougall has shown that this particular phenomenon of volume solid diffusion proceeds at approximately the same rates whether the system is in a sulphur and nitrogen atmosphere or whether the sulphur is flushed out with nitrogen. This is in marked contrast to the effect of sulphur on those processes which govern the migration of material away from the main mass of the sulphides.

The formation of veinlets in specimens, and crystals on the surface of specimens has been cited by previous workers (MacDougall 1957, Hawley 1941, and Schwartz 1931) as probably due to volatilization. MacDougall considered that diffusion played a part in the formation of some of the veinlets. The writer believes that these phenomena are caused by solid diffusion and related processes.

- 40 -

In experiments C-1, J-1, K-1 and L-1, stibnite was present, and at 550°C, the temperature at which the experiments were performed, stibnite is quite volatile. Although the stibnite had partly volatilized, no stibnite veinlets were found in cracks in the adjacent specimens, and no crystals had formed on the surface of the remaining stibnite. Stibnite had been deposited on the walls of the tube and was especially concentrated near the cold end of the tube.

Chalcocite behaved in a markedly different manner. In the numerous experiments at 550° C in a sulphur and nitrogen atmosphere, chalcocite crystals formed on the surface of the chalcocite pellets, and chalcocite veinlets penetrated cracks and cleavage planes in adjacent minerals to a depth of as much as 10mms. in 48 hrs. (Plates 16 and 19). No chalcocite was found deposited on the walls of the tube.

The force of gravity appears to have some effect on individual mobile molecules, as in many of the experiments the space between the bottom of the tube and the glass containing-tube was completely filled with crystals. In experiment AC-1 the chalcocite pellet appears to have sagged downwards (Plate 3). This might be due to the action of the force of gravity on individual diffusing molecules, but more probably is due to a decrease in the strength of the pellet as a whole.

Experiment AC-1 also showed that in six hours chalcocite migrated 0.3" along the bottom of a glass tube in the direction of flow of a stream of nitrogen and sulphur vapour (Plates 1, 2 and 3). The mobile chalcocite also migrated up the side of the tube, presumably due to the fact that this was down a concentration gradient. Migration against gravity was also noted in experiment AH-1 (Plate 4).

Experiments V-1, V-2, AH-1 and AH-2 indicated that a mixture

- 41 -

of PbS and Cu₂S will move down a temperature gradient as a unit. No large scale mineral zoning takes place. X-ray fluorescence studies of six samples taken from different parts of the specimen in experiment AH-1 revealed that the Cu/Pb ratio was identical no matter what the temperature of the sample had been. The pseudo-eutectic unmixing texture that had been developed did not indicate that flowage had occurred, but the macro-structure gave good evidence of migration (Plate 5). Where the specimen had been hottest there was less material, and waves of material had built up on the surface with a gentle slope towards the end that had been hottest, and a very steep slope towards the end that had been cbldest. The material which had originally been a tightly packed powder was a porous solid after the experiment. The mobile part of the chalcocite in experiment AC-1 was also porous.

Experiments AG-2 and AJ-1 indicate that in the absence of sulphur vapour there is no evidence that surface diffusion had occurred at temperatures as high as 655°C. The covellite altered to chalcocite, but no large chalcocite crystals were formed on the surface, and the original rectangular prism retained its shape.

In a sulphurous atmosphere, bornite, bornite and chalcopyrite solid solutions, and chalcopyrite migrated away from the main mass of the sulphides. This was evident in experiments A-1 to A-5 (Plates 12 to 15). There is a slight possibility that the migration occurred when the sulphide was chalcocite, and that this chalcocite later reacted with magnetite to form chalcopyrite and bornite. This seems very unlikely, as no unaltered chalcocite was found associated with the iron-bearing sulphides.

- 42 -

One of the fundamental concepts of thermodynamics is that the free energy decrease in a reaction is a measure of the driving force of the reaction. If the solid state is stable, there will be a tendency for one large crystal fo form, rather than many small ones, the reason for this being that the decrease in the surface area decreases the surface energy of the solid. The crystals of sulphides on the surface of the specimens may have been formed by this driving force. The surface of the specimens was originally composed of numerous very small crystals, so if the molecules were free to migrate, the tendency would be for large crystals to grow at the expense of the small ones. Diffusion in the surface layer of the solid would aid in the transportation of material to the growing crystals. Surface diffusion has been described by Barrer (1951, p. 312-363), and the following paragraphs summarize some of his findings and opinions.

There can be two types of film on solids, those which are stable in monolayers, and those which tend to aggregate into three-dimensional structures. The three-dimensional crystalline state is very readily formed, and a rise in temperature can cause an orientation of crystallites to agree with that of the underlying solid lattice. Sometimes alloy systems may occur, evidencing mobility and interdiffusion of atoms. In a great many of the systems studied, the crystal grains grow very rapidly as the temperature is raised, due to more rapid migration of atoms.

An experiment with a film of silver showed that crystallites formed at 500°C. "It was concluded that the most freely mobile part of the film was the surface layer, which for a silver layer on a silver film (of 50 layers),

- 43 -

was mobile at temperatures 700°C below the melting point of the metal."

The rate of surface diffusion increases with temperature and concentration, and is greater than grain boundary diffusion and much greater than volume diffusion. The different rates of diffusion for thorium diffusing into or over tungsten at 1655°K are, in cms. 2 /sec., 1.51 x 10⁻¹⁷ for volume diffusion, 9.33 x 10⁻¹³ for grain boundary diffusion, and 9.12 x 10⁻¹⁰ for surface diffusion. This is in the ratio of 1 : 61,800 : 60,400,000.

Crystal needles often project above the surface of a melt, and the needles can only form in this way if lateral diffusion of ions on its surface takes place.

This brief summary of some of Barrer's observations indicates that many of the phenomena observed in the writer's experiments may have been, at least in part, caused by surface diffusion.

Veinlets formed in cracks in adjacent specimens, and chalcocite migrated away from the main mass of chalcocite down temperature and concentration gradients and in the direction of flow of sulphur vapour. If these phenomena were caused by large-scale volatilization of chalcocite, one would expect that most of the chalcocite would have condensed at the cold end of the tube as happened when sulphur and stibnite volatilized. This did not occur but very local volatilization and condensation may have been important.

Herring (1952, p. 35), in discussing the "transportation of matter through appreciable distances" in order that materials may attain their equilibrium shape, states that, "There are four mechanisms by which such transport can conceivably take place, namely, plastic flow, evaporation and condensation, volume diffusion, and surface or grain-boundary migration." Local volatilization and condensation might explain why the sulphide migrated rapidly in the direction of flow of a stream of nitrogen and sulphur vapour, the volatilizing molecules being driven forward slightly by the impact of the sulphur and nitrogen molecules, before they condensed again.

Volume diffusion may have been important in the migration of the sulphides. Herring (1952) states that "A change brought about by volume diffusion involves two types of elementary processes, namely, diffusion of lattice defects through the crystal and the building-up or annihilation of lattice defects in the portion of the crystal immediately beneath the surface." Volume diffusion is considered to be very important in sintering, especially at high temperatures. Kuczynski (1949, p. 174-177) studied the rate of growth of the neck joining an individual sphere of copper to a flat plate of copper, and he considered this to be due mainly to volume diffusion at high temperatures, and mainly to surface diffusion at low temperatures.

Soles (1959) has shown that chalcocite at 550°C will flow plastically in the presence of sulphur vapour when a differential pressure is applied to the specimen. This process would be very important in the migration of sulphides under differential pressure. The effect of the absence of sulphur vapour on the ability of chalcocite to flow plastically is not definitely known.

At 550°C in the absence of sulphur vapour, when no differential pressure is applied, chalcocite will not migrate appreciably down a concentration or temperature gradient or in the direction of flow of a stream of nitrogen passing over the specimen.

Harrison, Morrison and Rose (1957) investigated the isotopic exchange between gaseous chlorine and solid sodium chloride. The chlorine

- 45 -

in the sodium chloride was radioactive. At low temperatures there was an exchange of chlorine atoms of the surface of the crystal with chlorine atoms of the gas. At 264°C, exactly half the melting point of the NaCl, bulk diffusion of the chlorine in the solid took place. The chlorine of the entire crystalline solid was in equilibrium with the surrounding chlorine gas, the ratio of radioactive chlorine to non-radioactive chlorine being the same in both phases.

Barrer (1951) states that in a solid and gas system at high temperatures, an equilibrium exists between the gaseous component and the component in excess in the lattice, and that the plasticity and tensile strength are affected by this.

It seems possible that the presence of sulphur vapour acts in some way to weaken or partly destroy the bonds holding the atoms in the solid sulphides. The fact that sulphides are slightly soluble in sulphur vapour may be related to this. There will also be formed a finite amount of other sulphides (such as CuS in the case of copper sulphides) which may be more mobile at the existing temperatures.

Mobile atoms and/or molecules will tend to migrate down temperature and concentration gradients; gravity and an applied differential pressure will force them to move in definite directions; and if they are capable of local volatilization and condensation, they will be driven in the direction of flow of a passing stream of gas.

Replacement:

In experiments A-1 to A-5 sulphur vapour and magnetite reacted to form pyrite; magnetite and chalcocite reacted to form bornite and chalcopyrite; and bornite and magnetite reacted to form chalcopyrite. The replacement may have taken place volume for volume, but there

- 46 -

was no good evidence for this as none of the minerals appeared to be pseudomorphic after magnetite.

At atmospheric pressure, at 550°C and in a nitrogen and sulphur atmosphere, the following minerals appeared to be unreplaced by chalcocite: calcite, siderite, biotite, epidote, bronzite and augite. Even when they were heated at 825°C for 48 hours, biotite, epidote and augite did not appear to be even slightly replaced by chalcocite.

In several of the early experiments chlorite with a low iron content was heated with chalcocite, and, although the resulting texture suggested that minor replacement had occurred, there was no definite evidence. The chlorite grains had been penetrated by chalcocite, and many of the veinlet walls did not match each other, but only rarely was a minute speck of an iron-bearing sulphide observed, and no new silicate minerals appeared to have been formed.

In experiment R-1 an iron-rich chlorite was used, and replacement of the chlorite crystals by a different type of material (see below) took place (Plates 16 to 18). Minor bornite occurred in the chalcocite. Similar results were found in experiments AF-1, AK-1 and AM-1, which were performed under a sulphur vapour pressure of 0.75 atmospheres. In these experiments no bornite was found in the copper sulphide, there was no definite evidence for the replacement of the iron-poor chlorite although the texture suggested that some replacement had occurred, but in the ironrich chlorites, the replacement texture had been very well developed (Plates 19 to 24).

The nature of the material replacing the chlorite crystals is not definitely known. The material obtained in experiment R-1 was examined with a petrographic microscope and was cloudy and almost opaque. When a polished specimen of experiment AM-1 was examined under a reflecting

- 47 -

microscope with an oil immersion lens, the material appeared to be neither a single grain of a sulphide mineral nor a single grain of a silicate mineral (Plates 23, 24). It did have a distinct pink colour, but all reactions with the standard chemical reagents were negative.

The altered specimen of experiment AM-1 was crushed, and by heavy liquid separation, a fraction containing approximately 90% chlorite and 10% of the material replacing the chlorite crystals was obtained. This fraction was compared by X-ray fluorescence and X-ray diffraction to the original chlorite and to a specimen of the original chlorite which had been heated in nitrogen for forty-eight hours at 550°C. This latter specimen was examined with a binocular microscope and no visible replacement of the chlorite crystals had occurred.

X-ray fluorescence showed that all three specimens contained the same amount of iron. In experiment AM-1, therefore, no iron migrated from the chlorite into the adjacent copper sulphide.

The X-ray diffraction curves of the three specimens are shown in Figure 2. Most crystalline materials will cause discernible diffraction peaks if they are present in amounts greater than a few percent. For example 1% quartz in chlorite is readily detected (Petruk, 1959). As no new peaks showed up in the X-ray diffraction curve of the specimen from experiment AM-1, and as the material replacing chlorite formed about 10% of the specimen, it is assumed that either this material was poorly crystallized, or that it also was a chlorite.

Brindley (1950) showed that heating magnesian chlorites to 600° C drives off four out of six OH groups from the brucite part of the structure. This material still gives chlorite diffraction peaks, but the intensity of the 001 peak (8°) is increased, and the intensities of the 002 and 003 peaks (15.9° and 23.8°) are decreased.

- 48 -



The intensities of these peaks, in counts per second, were respectively; 308,1130, and 272 for the unaltered chlorite, 860, 375, and 95 for the heated chlorite, and 113, 233 and 60 for the heated and partly replaced chlorite of experiment AM-1.

The differences in the peak intensities of the unaltered chlorite and the heated chlorite may be due to a partial dehydration as described above.

The peak intensities of the heated chlorite are greater than those of the heated and partly replaced chlorite. This does not appear to be due only to dilution of the chlorite by poorly crystallized material, as if this were so the peak ratios should be identical. If the replacing material is a second well crystallized chlorite, the intensities of the reflections of the two chlorites combined would have been greater than those observed. Variations in the intensities of the X-ray reflections may be due to variations in the iron content, variations in the degree of dehydration, and slight variations in the mounting technique causing preferred orientations of the chlorite, as well as to variations in the amount of chlorite present.

Minor amounts of bornite may be present in the material which replaced the chlorite. Less than 0.1% would probably not be detected by X-ray diffraction, but might still be enough to cause the pink colour noticed under the reflecting microscope.

X-ray photographs, detailed chemical analyses of the chlorite and the material replacing it, and heating the material for a longer period of time would aid in the determination of exactly what occurs in the replacement reaction. The reason why this reaction takes place cannot be ascertained until the replacing material is identified. It must be due to the interaction of copper sulphide and/or sulphur vapour with the OH radicals and/or iron or other atoms of the chlorite.

Gaseous Transportation of Sulphides:

To the writer's knowledge, no previous experiments or observations have shown that copper, in some form, (probably as a sulphide) can be transported as a gas when the original material is a copper sulphide. There have been two previous experiments which indicate that iron in some form can be transported as a gas when the original material is pyrrhotite. Hsaio and Schlecten (1952) consider that in their experiments in a vacuum iron was transferred, presumably as gaseous pyrrhotite, at temperatures between 900°C and 1100°C. MacDougall (1957) states that a ring of iron oxides was formed at the cool end of the combustion tube after an experiment in which pyrrhotite was heated at 650°C in a sulphur and nitrogen atmosphere.

The most satisfactory method of observing gaseous transportation of sulphides would be to pass a stream of whatever atmosphere was desired over enough of the sulphide so that the gas would be saturated with the sulphide. An analysis of the final gas or condensate would give the true solubility of the dissolved sulphide. This method would involve many complications, so a static method was devised.

At 550°C chalcocite or digenite will absorb iron, and pyrite will absorb copper. Three experiments were performed with pellets of pyrite and what was originally covellite placed 3" apart. In experiment AD-1 the sulphur vapour pressure was 0.75 atmos,; in experiment AG-1 excess sulphur was present, and although the sulphur pressure was not known, it was probably less than 0.75 atmos. In experiment AG-2 there was no sulphur vapour present.

X-ray fluorescence studies revealed that no copper had been

FIGURE 3

- 52 -



transported to the pyrite, but that iron had been transported to the chalcocite in experiments AD-1 and AG-1. The results are presented in Figure 3 and show that in experiment AD-1 after 24 hrs. the digenite, which weighed 0.350 grams, had absorbed 0.46% iron, and in experiment AG-1 the chalcocite, which weighed 1.015 grams, had absorbed 0.2% iron in 37 hrs.

To make a crude comparison of these results with the apparent vapour pressures found by Hsaio and Schlecten (1952), one must assume that the copper sulphides were as efficient as a vacuum-pump in removing iron from the atmosphere. Calculations using the equation $W = p \left(\frac{M}{2RT}\right)^{\frac{1}{2}}$ give the partial pressure of pyrite (assuming the iron was in the gas as pyrite molecules) as 1.23×10^{-7} atmos. in experiment AD-1; and 1.01×10^{-7} atmos. in experiment AG-1. The apparent vapour pressure of PbS in a vacuum is 6.17×10^{-5} atmos., and of ZnS is 9.55×10^{-9} atmos. (Hsaio and Schlecten).

To study the gaseous transportation of copper, chalcocite and an iron nut were placed 3" apart and experiments AB-1, AE-1, AE-2, AJ-1 and AL-1 were performed. It was found that copper was transported at temperatures above 675°C if excess sulphur was present in the atmosphere. No iron was transported to the copper sulphides.

In experiment AB-1 an air leakage caused the outside layer of the pyrrhotite (which had formed by the reaction of the sulphur vapour with the iron nut) to be altered to magnetite. Chalcocite was deposited on the magnetite, but, due to plucking during the polishing process, the actual chalcocite - magnetite contact could not be observed. The chalcocite had a definite pink tinge, which was probably due to a high iron content acquired by reaction with the magnetite.

In experiment AL-1 chalcocite appeared to have been deposited on

- 53 -

the pyrrhotite, and much of the chalcocite had reacted with the pyrrhotite to form bornite. Fern-like crystals formed on the surface of, and replaced pyrrhotite (Plates 25 to 30).

In the calculations made to determine the apparent partial pressure of pyrite, it was assumed that the copper sulphides were capable of absorbing iron from the atmosphere as rapidly as a vacuum would have removed it. No iron-bearing minerals occurred on the surface of the pellet, so this seemed to be a reasonably approximate assumption. In the case of copper absorption, the outer surface of thepyrrhotite was quickly covered with a layer of copper minerals, indicating that the copper was not being absorbed to the extent that it was available. In experiment AE-2 the outer 0.307 grams of the altered nut contained approximately 0.25% copper. The figure obtained for the partial pressure of chalcocite (assuming the copper was transported as chalcocite) is probably much too low. It is 2.01×10^{-7} atmos. at 775° C.

The nature of the gaseous molecules in these experiments is not known. Gaseous transportation could not be effected except in the presence of sulphur vapour, so it seems likely that some type of sulphide molecules were involved.

CORRELATION WITH GEOLOGICAL EVIDENCE

The most satisfactory way of correlating the experimental results with geological evidence, would be to devise a reasonable theory for the formation of epigenetic sulphide deposits which would satisfy all of the requirements discussed in the early part of this paper. It has not been possible to do this, but the following paragraphs outline an hypothesis which might be applicable to a few deposits, and at least serves to illustrate the potentialities of the observed phenomena.

The source of the ore deposit is assumed to have been a cooling batholith in which the metallic elements were concentrated in an immiscible sulphide liquid. That this process of concentration is feasible, is indicated by the formation of relatively immiscible silicate slags and sulphide mattes in blast-furnaces.

After the batholith had partly cooled, and the sulphides and silicates in this deeper part of the batholith had crystallized, contraction cracks and joints would probably develop in the surrounding rocks.

The sulphides would move up these fractures by solid diffusion (and related processes as described in the discussion of the experimental results) and by plastic flow (Soles, 1959), in the presence of sulphur vapour caused by the dissociation of some of the sulphides due to the decrease of pressure caused by contraction. The weight of the overlying rocks would squeeze the sulphides upwards towards a zone of lesser rock pressure, and this movement would be aided by the tendency of the sulphides to migrate down the temperature and concentration gradient, and in the direction of flow of any streams of sulphur vapour.

Fault zones extending upwards from the edge of a batholith are common, and the sulphides could migrate up these through the metamorphosed rocks adjacent to the batholith. In this metamorphosed zone, and in the batholith itself, there would be little chlorite, so the sulphides would not react with the enclosing silicate minerals.

The wall rock would act as a good insulator and there would be little heat conducted away from the moving sulphide mass. Assuming that the sulphides left the source at a temperature of about 800° C, it is conceivable, therefore, that they could still be at a temperature of 600° C by the time they were far enough from the batholith that the surrounding rocks, except for those immediately adjacent to the sulphides, were at a temperature of 300° C. Conduction and convection currents in the sulphides would help to maintain their high temperature.

At this point the fault zone along which the sulphides were travelling might have been intersected by another fault which tapped the juvenile water vapour above the batholith. This water vapour is assumed to have been cooled by expansion and other processes, and to have arrived at the junction of the faults at approximately the temperature of the surrounding rocks. At this temperature the water vapour would be saturated with silicates, but when it encountered the hot sulphides it would be heated, the expansion would cause an increase in pressure, and the vapour would begin to dissolve the surrounding silicates. The sulphides would advance into the space formerly occupied by the silicates, and the water vapour would continue to move up the fault, removing the dissolved material.

Selective replacement of some iron-bearing silicates might be aided by reactions between them and the sulphides. In the writer's experiments it was shown that such reactions occurred with iron-rich chlorite. It seems logical that reacting material would be more readily dissolved than other coherent crystals.

Most of the sulphides in the ore body would be close to the interface

- 56 -

between the water vapour and the sulphides. The interface will have a very large surface area because the sulphides tend to form a myriad of stringers and veinlets. The sulphides will be rapidly cooled by the stream of water vapour to a temperature of possibly 450°C at the interface.

The process of replacement would continue until the source of the sulphides failed. Water vapour would continue to cool the deposit and the final temperature would be that of the surrounding rocks. The sulphides, therefore, would have been rapidly cooled from 600°C to 450°C, and then fairly rapidly to 300°C. Iron-rich sphalerite would have exsolved very little pyrrhotite more than that which had been exsolved at 600°C.

Throughout the migration of the sulphides, the highly volatile minerals such as cinnabar and stibnite, and minor amounts of the less volatile sulphides and those sulphides which are soluble in sulphur vapour, would have been driven ahead of the main sulphide mass. Zoning would be partly due to relative rates of solid diffusion, and partly to original zoning at the source. The paragenesis would also be affected by these factors, and by slight variations in temperature and sulphur vapour pressure. Solid volume diffusion would cause intermediate phases to form between earlier and later minerals that were not in equilibrium.

Sulphides migrating up the fault would penetrate cracks and openings, but as the steepest temperature gradient and most of the flow of sulphur vapour would be up the main fault, and as the sulphides would be highly cohesive, such penetration would only take place to a minor extent. Sulphur vapour would penetrate much more deeply into the adjacent rocks. If the rocks contained pyrrhotite, or magnetite which would be converted to pyrrhotite, a static system similar to the experimental conditions would exist. Copper would be transported through the sulphur vapour and would react with the pyrrhotite to form bornite or chalcopyrite.

The foregoing is no more than an hypothesis, but additional experiments (see section on future work) may further substantiate some of these ideas.

Brown (1948) postulated a deep-seated source and an upward migration of the metallic elements as volatile sulphides. Hsaio and Schlecten's experiments (1952) proved that most of the sulphides are not very volatile. The present experiments have shown that some sulphides are soluble to a very slight extent in sulphur vapour.

The partial pressure of chalcocite in sulphur vapour at 775°C was shown in the experiments to be more than 2.01 x 10⁻⁷ atmos. This figure is considered to be far too low because of the inadequacy of the mechanism for removing copper-bearing molecules from the gas. In the writer's opinion, however, this figure is probably not more than a hundred times too low. The experiments with pyrite suggested that an increase in the sulphur vapour pressure may increase the solubility of the sulphides, but the critical temperature and pressure of sulphur is 1040°C and 116 atmos. At 775°C the vapour pressure to 27.3 atmos. would, in the writer's opinion, probably only slightly increase the solubility of copper sulphides.

Soles (1959) has shown that chalcocite will migrate away from the main mass of the sulphide in the presence of H_2S just as readily as in the presence of sulphur vapour. It is conceivable that some water is present at depth, that under high temperatures and pressures H_2S or a

- 58 -

similar gas would form, and that the sulphides would be quite soluble in this gas, under these conditions.

If this is an important ore-forming process, the sulphides must be extremely soluble in the gas. Almost all of the excess sulphur which arrives at the location of the ore deposit must react with iron from the wall rocks to form iron-bearing sulphides. At sulphur vapour pressures of one atmosphere or more pyrite is the stable iron sulphide at temperatures less than 690°C (Kullerud and Yoder, 1956). Pyrrhotite is present in many ore deposits which have formed at temperatures below 690°C which indicates that there was not enough sulphur to alter all of the iron available to pyrite.

If an ore body is assumed to have been formed by the deposition of chalcocite which had been transported as chalcocite dissolved in gaseous H_2S , and if all of the sulphur in the H_2S united with iron of the wall rock to form pyrite at the site of the ore deposit, then, for a sulphide body to form with as high a pyrite: chalcocite ratio as 10:1, the minimum solubility of Cu₂S in H_2S must have been 15% by weight. The writer feels that this degree of solubility is unlikely.

Large scale transfer of copper over long distances by a static system such as was used in the experiments, is also deemed to be very unlikely. The evidence available at the present time minimizes the importance of gaseous transportation of metallic elements as sulphides.

FUTURE EXPERIMENTAL WORK

Additional experiments should be performed to investigate more extensively the phenomena that have been observed.

It has been shown that the presence of sulphurous vapour is necessary for the migration of sulphides away from the main mass of sulphides, and for the gaseous transportation of copper sulphides and iron sulphides to take place. The experiments with pyrite also indicate that an increase in the sulphur vapour pressure may increase the solubility of pyrite in the sulphur vapour. This is in accord with the results of Morey and Hesselgesser (1951), which showed that the solubility of quartz in water vapour increased with an increase in the water vapour pressure.

The sulphur vapour pressure cannot exceed 3.77 atmos. at 550° C (West, 1950), but it seems likely that some of the compounds formed by the reaction of sulphur and water at high temperatures and pressures will have the same effect on the sulphides as sulphur. As the critical temperatures of at least some of the compounds which are expected to form (H₂S, SO₂, etc.) are less than 550°C, very high vapour pressures can be obtained. The effect of such vapour pressures on the gaseous solubility of various sulphides should be investigated.

The fastest rate of surface diffusion was observed in experiment AC-1. A stream of sulphur vapour was passed over a pellet of Cu₂S at 550°C, and the Cu₂S diffused 0.3" in six hours. This is a rate of 36.5' per year, which is appreciable, but it would have been increased still more if a temperature gradient had existed.

Soles (1959) has shown that chalcocite will flow plastically under the influence of differential pressures at 550°C in the presence of sulphur vapour.

- 60 -

Future work should investigate quantitatively the effect on various sulphides and sulphide mixtures of : temperature, temperature gradients, differential pressures, various vapour pressures of different combinations of water and sulphur compounds up to 10,000 bars, and of passing a stream of these vapours over the sulphides.

The addition of one sulphide to another tends to lower the melting point of the mixture below the melting points of the pure compounds (Barth, 1952). Similarly, it is conceivable that mixtures of sulphides may diffuse more rapidly than pure sulphides. It is also conceivable that the compounds may diffuse independently of each other, and that given sufficient time, different rates of diffusion will produce zoning.

The experiments indicated that sulphides can diffuse through minute cracks but, in all cases, a steep concentration gradient existed. If it can be shown that small discrete grains of sulphides will migrate long distances by solid diffusion and related processes, the granitization and related theories of ore-genesis will be considerably strengthened.

The effect of an electrical potential on the rates of diffusion should be investigated. If the sulphides diffuse more rapidly, some of the ideas of Sullivan (1954) will be supported. Jost (1952, p. 183) presents evidence that volume diffusion of the metallic elements of some sulphides can be induced by the application of an electrical potential.

The normal effect of an increase in pressure is to increase the melting point of a compound (Gucker and Meldrum, 1950, p. 632), but the melting point of silicates decreases when the water vapour pressure acting on them is increased (Yoder, 1958). It is conceivable that watersulphur compounds might have a similar effect on the melting point of sulphides. If it can be shown that this effect does take place, the oremagma and related theories of ore-genesis will be considerably strengthened.

- 61 -

From the data available on the rates of ex-solution it was argued that many sulphide deposits must have cooled rapidly. The effect of impurities, pressure, and large vapour pressures of sulphur-water compounds on ex-solution rates of sulphides (especially of pyrrhotite from iron-rich sphalerite) should be studied.

One possible way to effect the postulated rapid cooling of sulphide deposits would be to pass cool water vapour over the hot sulphides. Morey and Hesselgesser (1951) have shown that quartz and certain other silicates are soluble in water vapour at high temperatures and pressures. If this reaction is endothermic, an effective process of originally cooling the water vapour is available. The ore deposit would also be rapidly cooled if the net effect of replacement and removal of the wall rock, and the deposition of sulphides is endothermic. The effect of the former process, at least, could be investigated.

SUMMARY AND CONCLUSIONS

Unless otherwise stated, the observations and conclusions listed below represent original contributions.

 A brief outline of a few of the main theories on ore genesis was given, and a few generally neglected points were emphasized. It was suggested that many ore deposits have cooled rapidly.

 An outline of previous experiments and observations pertinent to the present work was given.

3) A series of forty-six experiments was performed to investigate the behaviour, chiefly of copper sulphides, in regard to the migration of sulphides away from the main mass of the sulphides by solid diffusion and related processes, the replacement of silicates by sulphides, and the gaseous transportation of sulphides.

4) It was shown that volume solid diffusion between adjacent grains of chalcocite, and magnetite or pyrrhotite, takes place rapidly and intermediate phases are formed. This work is in accord with the results of previous workers.

5) Evidence was presented that solid diffusion and related processes rather than sulphide volatilization (as advocated by previous workers) is responsible for the formation of crystals on the surface of sulphides, and veinlets of sulphides along fractures in adjacent minerals or rocks. Such phenomena were evinced, both in these experiments and in those of previous workers, by chalcocite, digenite, bornite and chalcopyrite solid solutions, and chalcopyrite.

6) It was shown that chalcocite migrates by solid diffusion and related processes at appreciable rates, down a temperature gradient, down a concentration gradient, in the direction of flow of a stream of sulphur vapour, and downward due to the force of gravity.

7) Chalcocite does not migrate appreciably by solid diffusion and related processes in the absence of sulphur vapour.

8) Iron-rich chlorite crystals are partly replaced by unidentified material which does not appear to be well crystallized, when heated at 550°C in contact with copper sulphides in a sulphurous atmosphere. Under similar conditions calcite, siderite, biotite, epidote, bronzite and augite are not replaced.

9) When chalcocite is heated in a sulphurous atmosphere, gaseous transportation of copper can occur at temperatures as low as 675°C. This does not take place in the absence of sulphur vapour.

10) When pyrite is heated in a sulphurous atmosphere, gaseous transportation of iron can occur at temperatures as low as 550° C. Previous work has suggested that gaseous transportation of iron can occur when pyrrhotite is heated at 650° C in a sulphurous atmosphere, or at 900° C in a vacuum. Iron will not be transported at 550° C in the absence of sulphur vapour.

11) An attempt was made to correlate the experimental results with geological evidence, and to outline an ore-genesis hypothesis which might be applicable to some deposits.

12) The evidence available suggests that the gaseous transportation of sulphides is not a major process involved in the movement of the metallic elements, but that the migration of sulphides by solid diffusion and related processes and/or by plastic flow (Soles, 1959) in the presence of sulphurous vapour, may be.



PLATE 1: Experiment AC-1. Oblique view of specimen of chalcocite which has migrated 0.3" to the left, in the direction of flow of sulphur vapour.



PLATE 2: Experiment AC-1. Top view of the same specimen as that shown in Plate 1.



PLATE 3: Experiment AC-1. Side view of the specimen shown in Plates 1 and 2. The specimen is upside down.



PLATE 4: Experiment AH-1. Oblique end view of the mixture of PbS and Cu₂S. The peaks at the side are due to upward migration.


PLATE 5: Experiment AH-1. Side view of the specimen shown in Plate 4. The waves are due to migration down temperature, to the left.







PLATE 7: Experiment AH-1. Portion of the mixture (large grey areas) of chalcocite (grey bands) and galena (white) which was at 300°C.



PLATE 8: Experiment AH-1. As in Plate 7, but this portion was at 450°C.



PLATE 9: Experiment AH-1. As in Plate 7, but this portion was at 550°C.



PLATE 10: Experiment AH-2. Same conditions as in Plate 7, except for a lack of sulphur vapour.



PLATE 11: Experiment AH-2. Same conditions as in Plate 9, except for a lack of sulphur vapour.



PLATE 12: Experiment A-3. Chalcopyrite (Cp) veinlet extending from bornite (Bn) into magnetite (Mag).



PLATE 13: Experiment A-3. Chalcopyrite veinlets extending from segregated grains of bornite and chalcopyrite into magnetite.



PLATE 14: Experiment A-3. Exsolution of chalcopyrite in bornite.



PLATE 15: Experiment A-3. Segregated grains of chalcopyrite exsolved from bornite.



PLATE 16: Experiment R-1. Veinlet of chalcocite in chlorite.



PLATE 17:

Experiment R-1. Same veinlet as in Plate 16 showing the minor amount of bornite (white specks) in the chalcocite.



PLATE 18: Experiment R-1. Minor bornite in chalcocite.



PLATE 19: Experiment AF-1. Medium-iron-rich chlorite penetrated by digenite.



PLATE 20: Experiment AF-1. Medium-iron-rich chlorite partly replaced by unidentified material (U.M.).



PLATE 21: Experiment AF-1. Most-iron-rich chlorite partly replaced by unidentified material (U.M.).



PLATE 22: Experiment AM-1. Chlorite replaced by unidentified material (U.M.).



PLATE 24: Experiment AM-1. As in Plate 23, but with the nicol prisms almost crossed.





PLATE 26: Experiment AL-1. Chalcocite and bornite crystals on pyrrhotite.



PLATE 27: Experiment AL-1. Chalcocite and bornite crystals replacing pyrrhotite along a crack.



PLATE 28: Experiment AL-1. Chalcocite and bornite crystals on pyrrhotite.



PLATE 29: Experiment AL-1. Chalcocite and bornite crystals growing on and replacing pyrrhotite.



PLATE 30: Experiment AL-1. As in Plate 29.

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