EXPERIMENTAL STUDIES OF TRANSPORTATION AND DEPOSITION OF SOME SULPHIDES IN AN OPEN SYSTEM AT HIGH TEMPERATURES AND PRESSURES

by

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INTRODUCTION

General Statement

Throughout historical time men have attempted to explain the origin of mineral deposits. Many theories were presented during this period, to be contested or supported according to the experience or beliefs of the critic, but few have been discarded because the genesis of mineral deposits can be explained in many ways. This lack of agreement on the origin of mineral deposits testifies to their diversity, to the ambiguity of information we gather concerning them, and particularly to our lack of knowledge of the earth's internal structure, composition, and physical-chemical processes.

Rapid technological advancement in the last thirty years has permitted us to attain certain conditions which simulate natural geologic environments. Studies of phase relations of minerals, mineral assemblages, solubilities, states of equilibrium under different pressure-temperature conditions, solid state diffusion, and a host of other studies have added greatly to our knowledge; yet we are rarely able to state the specific mechanisms active, or the physical and chemical conditions present, during the primary emplacement of a mineral deposit.

Experiments with sulphides have not contributed greatly to an understanding of the processes involved in their transport and deposition. Moreover, it is not possible from the information we have to eliminate any of the theories of sulphide ore genesis, although experimental results have placed restrictions upon the effectiveness of proposed methods of transport.

Hydrothermal theories require that great quantities of water traverse the host rocks to produce small sulphide bodies, for the solubilities of sulphides in water are extremely low and appear to remain so at moderate temperatures despite the presence of compounds or ions which increase solubilities. Highly alkaline or highly acidic solutions increase solubility, but most field evidence indicates that near-neutral conditions existed during mineralization. Transport of metals as soluble compounds in concentrated solutions as halides or sulphates, to be precipitated later as sulphides, has been suggested to overcome the water volume problem; but it is difficult to visualize how such solutions could be formed at depth if in equilibrium with a sulphide phase.

Theories of colloidal transport receive some support from field observations, and experiments show that colloids could be potent agents of transport. Gaseous transport of minerals implies that high temperatures would have existed near the site of deposition, but temperature determinations rarely indicate that they did. Volatilization of the halides of many metals takes place at acceptable temperatures, however, and movement as halide vapours in equilibrium with sulphurous vapours is quite possible.

Theories of transportation of sulphides as melts have received the least support of all, even though the concentration problem does not exist with melts and most mineralogical relationships can be explained. Mobile liquid phases are not present in common sulphide systems at the temperatures of deposition assumed for most ore deposits. It has been shown, however, that many double alkali sulphides melt at relatively low temperatures, and it is possible that such melts exist in nature. Failing this, the ore magmatist must search for a means of mobilization which will effect transport at sub-liquidus temperatures.

Evidently no single theory of ore genesis can explain all the features observed in a mineral deposit, because several different processes may have been operative throughout its history. By correlating experimental information and field observations, however, we may ultimately be able to trace that history.

Scope of the Present Study

The lack of agreement on the fundamental processes of transport and deposition of sulphides indicated to the writer that further experimental studies were necessary to assist in understanding this basic problem. Some comparisons between the ability of different materials to effect transport of sulphides under conditions which could feasibly be obtained in geological environments appeared to be needed. This required that an open system be set up in which a sulphide source could be connected to a site of deposition, a temperature difference could be maintained, pressure could be applied, and transporting media could be varied.

Hydrothermal solutions appear almost invariably to have been associated with ore deposition, and therefore most of the work was directed toward studying the relative effectiveness of different solutions in mobilizing sulphides. Two pressure vessels connected in series with a hydraulic pump provided all the conditions needed. Six different solutions were used, all of which had a pH greater than 7. Natural chalcocite, bornite, pentlandite, pyrite and pyrrhotite were used as source sulphides, and igneous rock materials, quartz, and calcite were used in the sites of deposition.

Further work involved study of the movement of sulphides by surface diffusion and directive pressure at subsolidus temperatures. The activating medium used was elemental sulphur. These systems were essentially closed, as equilibrium conditions were desired, but movement could be effected. Investigation in these experiments as with hydrothermal experiments, was confined to the Cu-Fe-S and Cu-Fe-Ni-S systems.

THEORIES OF GENESIS OF ORE DEPOSITS

General Statement

A complete summary of the details of theories on ore genesis would require more time and space than was available in this thesis. Within the past few years, moreover, many eminent geologists have realized the need for gathering together the views and information of the theorists so that comparisons could be made more easily than previously. Of the recent publications containing these important reviews and discussions the broadest coverage on the genesis and classification of ore deposits is given by: (1) Reports from 18th International Geological Congress (1950); (2) 50th Anniversary Volume of Economic Geology (1955); (3) Third Inter-University Geological Congress Papers (1955); and (4) Symposium on the Genesis of Massive Sulphide Deposits (Can. Inst. Min. and Met., 1958). Singewald (1956) and Edwards (1956) should be noted particularly for their reviews and discussions of classifications and theories.

Prior to the last quarter of the 19th century students of ore deposits classified them largely on the basis of morphology, Agricola being the most notable fore-runner of that school. Near the turn of the century the modern genetic groupings appeared, which quickly relegated morphological features to a secondary role in classifying deposits. Kemp (1893), Posepney (1894), Vogt (1895), Beck (1903), Lindgren (1907), Emmons (1908), Spurr (1923), and Niggli (1923), to mention a few, expounded their theories of origin, drew up classifications, and generally cleared the way for a better, if only rudimentary, understanding of the process of ore deposition. A brief review of the dominant theories on the source and evolution of mineral deposits follows.

Abyssal Theories

Most theories of ore genesis consider the ore metals to have risen from a sub-crustal source, where they had been concentrated by unknown processes. Studies of mineralized basic rocks such as the Skaergaard, Bushveld, and Stillwater intrusives indicated that in these rocks sulphides and oxides of heavy metals were syngenetic. Segregation of the valuable minerals was thought to have been accomplished partly by separation of immiscible liquid silicate and sulphide phases and partly by fractionation during crystallization, to give a sulphide-rich residual liquid or "ore magma" (Vogt, 1914; Spurr, 1923; Wager, 1955) which could be mobilized independently and deposited beyond the confines of the primary chamber. C.H. White (1945) postulates that sulphides and other ore minerals separated from the silicates as a liquid phase during cooling of the primeval earth, and localized within the mantle prior to consolidation of the crust. Later, during earth movements, this abyssal source of sulphides would be tapped by major fault systems.

J.S. Brown (1950) further revived the ore magma theory in his provocative book "Ore Genesis". He visualized, also, a segregation of sulphides and arsenides during early cooling stages of earth history. This molten ore magma formed a layer up to 1500 feet thick somewhere between the top of the peridotite layer (60 Km) and the base of the granitic crust (25-35 Km). The magma is thought to have separated into three phases: matte (Fe-Cu-Zn sulphides) on top, speiss (various arsenides) in the central part, and lead-silver sulphides at the bottom, analogous to the separations found in metallurgical furnaces. Irregularities produced by warping of the earth during cooling could eliminate or collect, by squeezing, one or more of the layers within this ore magma shell. Later tapping of the layer would yield only the remaining fractions.

Mineral deposits having such a source as those postulated by White and Brown are considered to be associated with igneous activity only in that related crustal dislocations and high temperatures would facilitate movement of the "ore magma" to the upper crust of the earth. Water is not considered necessary as a sulphide transporting medium, but it is likely to be picked up at higher levels, where it becomes a potent agent of metasomatism.

Posepney (1894) considered that heavy metals originated in a deep-seated "barysphere" similar to Brown's segregated shell and were brought to the surface through fissures by juvenile waters. Van Hise (1900) attacked this theory, because he considered that the pressures at great depth would close off any openings; he felt that movement of the metalliferous materials to the present sites was accomplished largely by circulating connate water, and the materials had first to be brought within the earth's upper fracture zone, probably by major orogenic processes or volcanic ejection.

Magmatic Theories

Fundamental Processes

The more popular theories of ore genesis relate mineralizing "solutions" directly with more recent igneous activity. During emplacement of intermediate to basic magmas crystallization and differentiation processes are thought to gradually remove the higher temperature magnesium, iron and calcium minerals (Bowen, 1933; Osborn, 1950) and the residual liquid phase becomes progressively richer in soda, potash, silica, most ore-forming elements, and volatile materials. Removal or localization of this residual acidic magma followed by further crystallization of the granite-forming minerals leaves the primary ore solutions concentrated and ready to move into the overlying rocks to form ore deposits.

Hydrothermal Theory

The classical hydrothermal theory, championed by Lindgren (1909-1936), Emmons (1908-1929), and others, sprang from this concept of crystallization-differentiation of a magma. No other theory has enjoyed such wide and lasting acclaim. Its main thesis is that water is a major constituent of juvenile ore solutions, and is therefore the principal medium of transport of the ore minerals. Evidence of the effectiveness of water in dissolving, transporting, and re-depositing materials is found in any supergene deposit; observations of active volcanoes show fairly conclusively that water is frequently evolved in large quantities from magmas; and the development of hydrous minerals in the vicinity of ore deposits offers abundant proof of the presence of water in the channels of the ore-forming fluids. It is not to be wondered that the hydrothermal theory was and still is popular, as is reflected in the mass of literature published on the subject in the last hundred years (Bischof, 1866 to Schwartz, 1959).

Yet, the theory has certain grave shortcomings, of which the most serious are the extremely low solubility of sulphides in water and the reversal of deposition of minerals according to their solubility in water. Lindgren was one of the first to admit the difficulties. Ingerson (1954) sought to overcome such negative evidence by proposing that volatile materials (H_2O, H_2S, CO_2 etc.) would be expelled first, condense, and be replaced by metals carried as soluble compounds in solution introduced later.

Volatile Transfer Theory

Fenner (1933) neatly bridged the gap between the ore magmatist and the hydrothermalist. He visualized a magma as separating into several fractions, which are as follows: (1) immiscible sulphides which may form bodies of orthomagmatic ores; (2) silicates and oxides that form rock bodies or oxide mineral deposits; (3) residual liquid portion of magma (pegmatitic fraction); and (4) gaseous emanations. The residual liquid and gaseous fractions are believed to collect most of the constituents of mineral deposits and therefore represent the mineralizing solutions, although the gases are considered to be best adapted for moving the materials. Bubbles of H_2O, CO_2, HCl and H_2S rising through the magma are thought to collect other gases of very small vapour pressure and "sweep" them out of the magma chamber into the surrounding rock. Condensation at cooler levels would result, but the materials would continue to move as solutions or be remobilized as gases again with increased temperature. Meteoric water could be incorporated in the upper levels.

Fenner's theories were not greeted enthusiastically, chiefly because the existence of a mobile gas phase within a deep-seated magma is difficult to accept. The theory of movement of materials as vapour distillates has been received more favourably (Zies, 1929; Brown, 1950), but the ability of gases to cause rock replacement has been consistently doubted.

Remobilization Theories

Many writers in the last two or three decades have stressed the importance of remobilization of heterogeneous materials, whether sedimentary or igneous, in producing mineralizing solutions. Such thinking is a natural off-shoot of the theories of granitization which have developed in opposition to the magmatist's ideas of vast intrusive bodies of magma. Probably the ore metals originally were distributed sparsely through the primary rock aggregate, but upon deep burial, melting, and mobilization of the rock mass they were localized into ore deposits by some unknown process of segregation, perhaps by natural affinity, or by water freed during the metamorphic processes. Locke (1941), Dunn (1942), Guimaraes (1947), Goodspeed (1952), and Gavelin (1955) are a few proponents of these theories.

Sullivan (1948) has several suggestions to make in support of remobilization. He proposes that the chalcophile and siderophile elements in the upper crust progressively increased as basic source material from deeper levels of the crust moved upward. Granitization processes would remobilize the rocks of a given area and the chalcophile and siderophile elements would be rejected from the lattices of the common rock-forming minerals. This reasoning added nothing new to the general theory or to the possible methods of concentration of ore minerals, but in a later paper Sullivan (1954) introduced the idea that the metallic elements migrated under the influence of an electrical potential. He states (page 566), "---granitization and ore deposition are viewed as the neutralization of an electrochemical disequilibrium set up during sedimentation and volcanic activity". Still later (1957) he expanded the idea of "electrochemical directionalism", suggesting that the relatively electropositive cations of the ferromagnesian minerals migrated downward (up the thermal gradient), while the relatively electronegative chalcophile and siderophile cations migrated upward (down the thermal gradient). Sullivan suggested also that the melting point of an element is an indication of the temperature at which it may begin or cease to move. The studies of Ingerson (1955) indicate that such is not the case.

Experimenters are at present not in a position to comment effectively on such theories, but a continuation of more practical studies such as those of Shaw (1953), Saull (1955), and Cameron (1956) could possibly bring a note of credence to this sort of reasoning.

A metamorphic source for ore minerals, presuming the rock materials are mobilized by total or partial melting, is no more difficult to visualize than a magmatic source, since primary and secondary (anatexis) magmas probably would undergo similar processes of differentiation. Hawley (1956) compares the two, but favours the magmatic source because it explains more readily metallogenic provinces and the textural relations of ore minerals. Proof of the effectiveness of metamorphic processes in mobilizing disseminated metals is meagre or lacking (Shaw, 1953), but Hawley grants it for the re-distribution of previously formed deposits.

Hillebrand (1955) suggests that sulphide mineralization is related to granitization only indirectly. He believes the sulphides were originally segregated in the sub-crust, but were picked up during 'magmation' processes involving both crustal and sub-crustal material.

Miscellaneous Theories

Sedimentary Origin Concepts

The remarkably continuous distribution of metallic minerals in particular strata of many sedimentary rock formations, such as those of the Kupferschiefer, Witwatersrand, and Rum Jungle beds, led to proposals that the main sources of ore minerals were sedimentary basins (Deans, 1950; James, 1954; Knight, 1957; Walpole, 1958; and others). The ore metals are thought to have been leached from the surrounding sparsely mineralized rocks by surface water, and were carried to the basin and precipitated as sulphides or oxides. Volcanic activity is thought to play an important role in the supply of metals to the sedimentary basin, because their concentration within specific stratigraphic horizons is most easily explained by correlation with an outburst of volcanism (Ramdohr, 1953; Friedman, 1959; McAllister, 1959). Later metamorphism and metasomatism may have been necessary to produce the present minerals, or to cause localization into concentrated deposits whose features are exclusively epigenetic (Schneiderhohn, 1941; Guimaraes, 1947; Skinner, 1958). Schouten (1946) favours later replacement of syngenetic iron sulphides by epigenetic ore solutions; an alternative process may be the replacement of syngenetic oxide or hydroxide minerals by epigenetic sulphur-bearing solutions.

The field evidence is far too abundant to discard sedimentation as a major factor in localizing ore minerals in specific strata. Whether or not they can be mobilized to form massive deposits is, however, a separate problem.

Cosmic Origin Concept

Skerl (1957) wrote an article suggesting that the origin of minerals was extra-terrestrial. He visualized intense bombardment of the earth, at irregular intervals, by metallic meteorites originating from the break-up of cosmic bodies. The target areas developed into metallogenic provinces either directly as sedimentary deposits or indirectly through later assimilation, granitization, or hydrothermal action.

Skerl realized that one theory is as good as another until proven wrong.

Conclusions

No single theory of ore genesis can satisfactorily explain all the features of an ore deposit; the more detailed its study, the more complex appears its depositional history. New theories, or modifications of old theories, are constantly being introduced to explain separate features, until gradually the array of hypotheses of transportation and deposition has become formidable indeed.

Part of the problem is this: we most often interpret that which we see in ore deposits as representing that which once was, whereas there may not be the least resemblance between present and past mineral associations. The statement made by Williams (1955) should sober the most enthusiastic of theorists:

> "It is, indeed, intriguing to reflect on the mineralogical and textural changes that may be induced by the metamorphism of sulphide ores, and rather disturbing to realize that the true origin of their original emplacement can be wholly masked by post-deposition metamorphic effects."

Perhaps because of this geologists have repeatedly overlooked details which would yield information regarding the true origin or mineral deposits.

The lack of experimental data to support hypotheses of ore deposition has also been a major factor in producing the great diversity of opinions regarding them. Advancing technology is now providing the means of studying geologic processes, but progress is necessarily slow because the field of study is vast and complex. In dealing with natural processes we usually must deal with multi-component systems, and knowledge of their physical chemistry is generally lacking. It is easier to theorize. At the same time, however, we should recall Galileo's words:

> "One conclusive experiment will batter to
> the ground a thousand probable theories."

EXPERIMENTAL INVESTIGATIONS RELATING
TO ORE GENESIS

Despite the slow progress made by experimenters in the study of geological processes, the results achieved are beginning to influence our interpretation of geological information. Ambiguous or inconclusive experimental results are being checked carefully by using different techniques, and new discoveries are being examined even more closely. The total effect on field study is to reduce generalization and to induce a more critical evaluation of geologic and mineralogic details.

The experiments carried out in the present study were intended to test, by comparison of results, a wide range of theories of ore transportation and deposition. To describe even in brief detail all experimental contributions to the study of ore genesis within this broad field would be impossible here, therefore only the more significant general investigations, and those dealing with the systems examined in the present experiments, will be mentioned.

Classification of Experiments

Experimental studies have been highly diversified, but they can be classified generally into three major groups.

(1) Solubility and Mobilization Experiments. These include studies of ionic, colloidal, 'complex' and gaseous solutions and their effect on different materials. Their ultimate purpose is to test theories of transportation, deposition, and replacement.

(2) Phase Relations Experiments. These studies are made to define the conditions of formation of minerals or mineral assemblages. Experiments designed to examine states of equilibrium, solid-liquid-gas relations, critical conditions, mineral associations, solid solution phenomena, and solid state transformations, to mention a few, may be included here.

(3) Statistical Analyses. Although not truly experimental, studies of the distribution of minerals, elements, and isotopes in specific areas may eventually contribute more to our knowledge of geological processes, geochemical conditions, and paragenesis than all other types of experiments. Examinations of the zonal distribution of elements or of mineral and element gradients, ratios of specific elements, age determinations, liquid inclusion compositions, and other comparative studies involving quantitative analyses of natural materials are included in this group.

The present study deals with transport and deposition of sulphide minerals. The following resume of experimental work is therefore largely confined to a review of the studies included in the first group.

Thermodynamic Calculations

The application of thermodynamic and thermochemical calculations to determine equilibrium relations between components in any system is receiving increasing attention as the calculated data are confirmed or corrected by experiments. In many fields of study we are still dependent solely upon data compiled by calculation or extrapolation with the aid of thermodynamics, and experimenters at least owe much to the works of Verhoogen, Ingerson, Kracek, Kelley, Goranson, Krauskopf, and many others.

Because of the existence of unknown species or of unknown complexing factors, the physical chemist is most often forced to work with simplified systems, which probably leads to some inaccuracy in his extrapolated results. There is no doubt that his contributions will become increasingly important as experimental studies converge on multicomponent systems. The work of Holland (1959) is illustrative of this fact.

Hydrothermal Solutions Studies

Experimental work involving water was begun long before the classical hydrothermal theory was presented. Daubree in 1841, for example, showed that cassiterite formed by reaction between perchlorate of tin and water vapour. Such studies were few, however, until experimental techniques and equipment were improved in the early 1900's.

Ionic and Complex Solutions

General Studies

Stokes (1907) was an early worker in the field of ionic solutions. He examined the effect of alkali carbonate solutions on pyrite and marcasite, and found that these minerals decomposed to hematite and other oxides, hydroxides, and sulphides. Thiosulphate and sulphate apparently formed, while sulphur was freed as H_2S and elemental sulphur. He considered that these products could react later with metallic salts to give alkali sulphates and sulphides. Oxidizing agents were apparently not necessary to convert pyrite to limonite.

Wells (1915) examined the effect of solubility on precipitation and sequence of deposition of ore-forming compounds. He noted that pH changes varied the sulphide ion concentration considerably and that components of precipitated mixtures can be separated by heating to dissolve compounds successively. Both pH and temperature, therefore, could be important factors in controlling deposition of minerals from solution. Wells tested the solubilities in water of sulphides of Pd, Hg, Ag, Cu, Bi, Pb, Zn, Ni, Co, and Fe. Weigel (1907) had previously tested the solubility of Hg, Ag, Pb, Cu, Zn, Ni, Fe and Mn sulphides and found that the sequence of deposition in nature did not follow the solubility sequence. He suggested that the formation of multi-metal compounds during ore deposition might cause these discrepancies, and implied that synthetic solutions differed from natural hypogene solutions.

Alkaline and Complex Basic Solutions

S.F. Emmons (1886) and Becker (1888) noted the high solubility of certain alkali sulphide fusion products, and laid the foundation for the alkali sulphide theories of transport.

Allen, Crenshaw and Merwin (1912) formed crystals of ZnS by heating amorphous ZnS in a solution of Na_2S at 350°C.

Freeman (1925) examined the double sodium sulphides of lead and zinc, and showed that they are decomposed by water to form Na_2S solution and unstable colloidal solutions of lead and zinc sulphides. Foreman (1929) indicated that neither pyrrhotite nor pyrite are soluble in Na_2S solutions at high temperatures and pressures. This was confirmed by pyrrhotite in K_2S solutions by Schouten (1934), but Stevens (1933) reports that a dark green colloid forms when pyrite is treated with Na_2S solutions whereas there is no effect with NaHS. Gruner (1933) found that NaHS is produced when SiO_2 is present in Na_2S solutions.

Lindner and Gruner (1939) examined the effects of H_2S, NaHS, and Na_2S solutions on thin sections of fourteen iron-rich minerals at 300°C and 85 atmospheres pressure. Silica dissolved in all solutions and did not, as suggested previously, appear to prevent dispersion or solution of iron. The Na_2S solution produced hematite and magnetite precipitates with FeS and silica in colloidal suspension, but the NaHS and H_2S solutions yielded abundant pyrite and minor amounts of FeS, magnetite and hematite. Gold from the container was readily dissolved by the NaHS solution (up to 2500 parts per million), but was not dissolved to any great extent by the other two solutions. The experiments suggested that oxidation of sulphur played an important role in the alteration of minerals; any iron removed formed pyrite, magnetite, or hematite.

Smith (1940, 1943) studied the effect of alkali sulphide solutions on many common sulphide minerals. His methods consisted of charging solutions of (1) soluble salts of metals,

(2) Na_2S-metal sulphide fusion products, and (3) shavings of the more soluble metals into a closed system bomb containing Na_2S solutions. The bomb was heated, cooled slowly, and all products were analyzed. Smith drew up solubility tables, grouping the minerals as follows:

(a) Sulphides poorly soluble in Na_2S_x melts;
(b) Sulphides very soluble in Na_2S_x melts but insoluble in aqueous solutions of polysulphides;
(c) Sulphides very soluble in Na_2S_x melts and in aqueous solutions of polysulphides.

His conclusions were that metals are carried in the double sulphide form and are precipitated as simple sulphides when the double "complex" is broken down. Dilution by meteoric water, reaction of concentrated sulphide solutions with host minerals, escape of H_2S, and sulphur oxidation would tend to reduce sulphide concentration and cause precipitation.

More recently, emphasis has been placed upon sulphur complexes higher than the double sulphides proposed by Smith. Garrels (1944) suggests from a study of Höltje and Beckert's (1935) results that CuS_3^{-4} exists in copper sulphide solutions, but Cloke (1958) determined the complexing ion to be CuS_5^{-4}.

Beland (1943) and Robinson (1948) respectively synthesized the sulphantimonites of lead and sulpharsenites of silver, using Smith's methods. Both sulphosalts and simple sulphides could be produced, simultaneously or individually depending on the ratios of metals used. An increase in sulphide ion increased the solubility of the metals in Na_2S solutions; also, higher pH and higher temperatures favoured more rapid solution and deposition. Robinson examined also the effect of Cl^-, HCO_3^-, and $CO_3^=$ ions on the formation of lead sulphantimonites. He found only a small increase in yield with Cl^-; the other ions did not appear to affect the rate of growth.

Olshanskii and Rafalsky (1956) studied solution and deposition of a few minerals in 0.5 - 1.0 N solutions of sodium thiosulphate at 300°C. Covellite, galena, and bornite recrystallized on a glass rod suspended near a quartz ampoule containing the minerals. The writers state,

> "One way or another the portion of the solution touching the surface of the rod slowly changed its composition, and this apparently causes a decrease in the solubility of the sulphide, which immediately crystallizes."

This is fairly convincing evidence of solution and migration of sulphides, whatever the ionic or molecular state may have been.

Hemley (1953) tested the solubility of lead sulphide in H_2S-saturated saline solutions. He showed that the concentration was approximately 10^{-6} gram per litre through a pH range of 1 to 8 at atmospheric pressure and temperature. This solubility is considerably in excess of the calculated value given by Verhoogen (1938 - See Table 1) or Czamanske (1959 - See Table 8). The existence of the complexes $Pb(HS)_2$ and $Pb(HS)_3^-$ is indicated from Hemley's concentration curves. The effect of pH on the solubility of some sulphides, as determined by Hemley, is shown in Table 2.

Barnes (1958) measured the solubility of ZnS in

TABLE 1

Solubility of Sulphides up to 400°C, for a pH of 7 (grams/litre)

Sulphide	25°C	100°C	200°C	300°C	400°C
ZnS	$1.4(10^{-7})$	$3.6(10^{-4})$	$2.2(10^{-2})$	0.8	5.9
PbS	$8.6(10^{-9})$	$8.9(10^{-8})$	$2.1(10^{-6})$	$1.6(10^{-5})$	$2.1(10^{-4})$
CuS	$2.4(10^{-13})$	$4.1(10^{-13})$	$4.6(10^{-12})$	$2.3(10^{-11})$	$7.8(10^{-11})$
HgS	$1.0(10^{-18})$	$2.2(10^{-17})$	$6.4(10^{-16})$	$5.6(10^{-15})$	$3.1(10^{-14})$
Ag_2S	$3.8(10^{-13})$	$5.7(10^{-13})$	$3.3(10^{-12})$	$1.4(10^{-11})$	$2.3(10^{-11})$
Cu_2S	$4.8(10^{-10})$	$4.0(10^{-11})$	$5.6(10^{-10})$	$2.6(10^{-9})$	$7.3(10^{-9})$

(after Verhoogen, 1938)

TABLE 2

Solubility of Some Sulphides in 0.1 M H_2S Solution (Grams/Litre)

pH	Cu	Pb	Ag	Hg
4	$4(10)^{-23}$	$2(10)^{-8}$	$1(10)^{-6}$	$1(10)^{-14}$
7	$3(10)^{-21}$	$2(10)^{-8}$	$3(10)^{-5}$	$7(10)^{-9}$
10	$2(10)^{-14}$	$4(10)^{-11}$	$2(10)^{-3}$	$1(10)^{-5}$

(After Hemley, 1953)

TABLE 3

Copper Concentration of Vein Solutions in Moles/Litre with Different Sulphur Content

Sulphur (mg./l.)	pH 1	pH 5	pH 7	pH 11	pH 13
0.10	$2(10)^{-16}$	$2(10)^{-24}$	$6(10)^{-18}$	$1(10)^{-10}$	$1(10)^{-6}$
0.010	$2(10)^{-15}$	$2(10)^{-23}$	$6(10)^{-20}$	$1(10)^{-12}$	$1(10)^{-8}$
0.001	$2(10)^{-14}$	$2(10)^{-22}$	$6(10)^{-22}$	$1(10)^{-14}$	$1(10)^{-10}$

(After Garrels, 1944)

H_2S-saturated water, and found that at 75°C and 300 psi the solubility was 10 mg. per litre. This figure is 100 times the calculated value for water alone (Czamanske, Table 8). Complex ions of the type $ZnS.xH_2S$ are suspected.

Acidic Solutions

Transport of sulphides in acidic solutions has received far less attention, experimentally, than has transport in basic solutions. Most students of geology admit the likelihood of rapid neutralization of acid solutions while traversing host rocks, but others suggest the possibility of local changes (Graton, 1940), total change from originally basic to acidic solution (Graton, et al, 1936), or total change from originally acid to basic solutions (Schmedeman, 1935). Zies (1929) noted an abundance of acid gases in the volcanic exhalations at Katmai.

Calculations of solubilities from solubility product data (Garrels, 1944) indicate that acidic solutions are capable of carrying notable quantities of metals only if acid is present in high concentrations. His results for copper are shown in Table 3. Increasing temperature increases the solubility, but markedly less than increasing the sulphur content, or the pH when above the neutral point.

Experiments with gold were carried out by Ogryzlo (1935). He found that gold can be dissolved in dilute HCl solutions at 300°C and 10 atmospheres pressure; oxygen aids the reaction. NaHS solution appeared to be a far stronger solvent, however, and Cl_2 in steam also attacked gold readily.

Kristofferson (1936) conducted some notable experiments with sphalerite, galena, and lead in acid environments. He passed a stream of gaseous 20% HCl across the minerals placed on a boat in a tube furnace and measured the weight loss over two to four days. Some of his results are given in Table 4. Chlorides were formed in all cases, and it is assumed the metals were transported in the volatile state. At higher temperatures H_2S and chlorides were driven off. Chloride solutions could presumably condense out at lower temperatures if H_2S were removed.

The widespread occurrence in ore deposits of sulphates (Butler, 1956) and acid-stable minerals (Jicha, 1951), and of chlorides or fluorides in fluid inclusions (Smith, 1954) indicates that more experimental work should be carried out with acidic solutions.

Colloidal Solutions

Some writers have stressed the importance of colloidal solutions as agents of transport of metals. Clark and Menaul (1916) were early experimenters in this field with respect to sulphides. They placed a known weight of a finely ground sulphide in a bottle with 0.01 N KOH solution, passed H_2S intermittently through the solution for several weeks, and analyzed the resulting liquid. All minerals examined, with the exception of argentite and proustite, went into colloidal solution. The concentrations are shown in Table 5.

It was found that the colloids coagulated when H_2S was driven out of the solution; also, limestone either inhibited formation of the colloids or precipitated them.

TABLE 4

Weight Losses of Sulphides in a Stream of Gaseous HCl

Temperature	Weight Loss ZnS	Change in Weight PbS	Weight Loss Pb Metal
300°C	0 - 1%	Gain ($PbCl_2$)	-
400°C	3 - 5%	Gain ($PbCl_2$)	-
450°C	6 - 12%	Gain of 5%	10%
500°C	20 - 30%	Loss of 6%	75%

(After Kristofferson, 1936)

TABLE 5

Concentrations of Sulphides in Suspension in H_2S-Saturated 0.1 M KOH Solution

Mineral	Percent of Original in Suspension	Concentration gm./litre
Bornite	3.79%	$3.8(10)^{-4}$
Covellite	28.88%	$2.9(10)^{-3}$
Smaltite	16.72%	$1.7(10)^{-3}$
Tetrahedrite	3.16%	$3.6(10)^{-4}$
[1]Sphalerite	15.88%	$1.6(10)^{-3}$
[1]Pyrite	20.13%	$2.0(10)^{-3}$
Stannite	29.77%	$3.0(10)^{-3}$
Pyrrhotite	2.22%	$2.2(10)^{-4}$
Realgar	24.71%	$2.5(10)^{-3}$

[1] 0.001 N KOH Solution

(After Clark and Menaul, 1916)

Colloids have been recognized in most alkaline solution studies, and it is possible that their importance has been underestimated. Garrels (1944) suggests that colloidal solutions have the ability to penetrate; therefore, they could be far more important than ionic solutions as transport media because the metal concentration of colloids is much greater. Boydell (1925) and Lasky (1930) noted from literature and field studies that colloids should be seriously considered in theories of ore deposition. One major difficulty is that colloids tend to precipitate gels rather than replace minerals; however, colloidal features could be largely or entirely obliterated by post-depositional metamorphism, or, as Garrels proposes, the metals could migrate outward as ions from sols held in 'trunk' fissures and be deposited as crystalline minerals, leaving no trace of their colloidal origin.

Non-Sulphide Systems

Hydrothermal experimentation with non-sulphide systems has been more extensive than it has with sulphide systems. This would be expected because an understanding of stability and phase relations of rock-forming minerals is prerequisite to an understanding of magmatic, metamorphic, and metasomatic processes. A knowledge of the geochemistry of minerals commonly associated with sulphide minerals is, moreover, of great importance to the study of ore deposits.

A satisfactory treatment in summarizing the work of the many individuals who have studied silicate, oxide, carbonate, and other systems is not possible here. A few of the more important studies and summaries are those of Griggs (1941), Kennedy (1950), Fairbairn (1951), Yoder (1957), and Boyd and England (1958) on metamorphism; of Ingerson (1930), Smith (1953), Morey (1957), Yoder (1957), and Roedder (1958) on solubilities, and of Jaffe (1951), Van der Heurk (1953), Shaw (1953), and Schairer (1957), on phase equilibria and stability relations.

Gaseous Transport Studies

A number of volatility studies have been made on minerals because much field evidence suggests gases are important agents of transfer. For example, Zies (1929) noted that in 1919 a magnetite deposit existed at one particular fumarole at Katmai; C.N. Fenner visited the same fumarole in 1923, and found no magnetite, but encrustations of siliceous materials on which were deposited well developed crystals of PbS, ZnS and copper sulphides. The exhalation temperature was 97°C at the time of Fenner's visit.

Kristofferson's (1936) experiments, described earlier, indicate that transfer of some minerals can be effected by volatilization of the metal chloride. He also notes that zoning in ore deposits is sometimes reversed from that expected from the vapour pressures of the chlorides; obviously other factors influence deposition if transport were due to chloride vapourization alone. Ogryzlo (1935) found gold was transported by gaseous chlorine in steam. Krauskopf (1951) determined from thermodynamic principles that mercury sulphide cannot exist above 250°C; the mercury and sulphur move independently even at much lower temperatures.

TABLE 6

Volatilities of Metals and Metal Compounds in Equilibrium with Solid Sulfides, Silicates and Oxides at 600°C Vapour Pressures in Atmospheres

Name and Valence of Metal	Vapour pressure of sulfide	Metal vapour in equil. with sulfide if (S_2) 10^{-6}	Vapour pressure of oxide	V.p. of chloride in equil. with most stable solid (H_2S=30, HCl=10 At.)
Fe II	$1.82(10)^{-11}$	$3.98(10)^{-20}$	Low	$7.95(10)^{-3}$
Mn II	$8.32(10)^{-11}$	$6.30(10)^{-18}$	Low	$2.51(10)^{-3}$
Co II	$3.80(10)^{-10}$	No data	Low	$1(10)^{-5}$
Ni II	$3.80(10)^{-7}$	No data	No data	$1.58(10)^{-6}$
Cu I	$4.57(10)^{-5}$	$3.98(10)^{-20}$	Low	$6.30(10)^{-10}$
Cu II	Dcpsd.	Dcpsd.	No data	Dcpsd.
Ag I	No data	$6.30(10)^{-10}$	Dcpsd.	$1.99(10)^{-7}$
Au I	Dcpsd.	$1(10)^{-16}$	Dcpsd.	Dcpsd.
Zn II	$7.76(10)^{-9}$	$1(10)^{-8}$	Low	$5.01(10)^{-4}$
Cd II	$2.19(10)^{-7}$	$3.98(10)^{-5}$	$1.99(10)^{-7}$	$3.98(10)^{-4}$
Hg I,II	Dcpsd.	High	Dcpsd.	High
Sn II	$5.50(10)^{-5}$	$2.51(10)^{-7}$	No data	$7.95(10)^{-4}$
Sn IV	Dcpsd.	Dcpsd.	Low	$7.95(10)^{-2}$
Pb II	$2.19(10)^{-6}$	$1.99(10)^{-8}$	$1(10)^{-7}$	$1.99(10)^{-2}$
Mo IV	$1.12(10)^{-12}$	$1(10)^{-36}$	No data	No data
As III	ca. 0.1	No data	High	ca. 0.1
Sb III	$3.32(10)^{-4}$	$1.99(10)^{-5}$	$3.16(10)^{-2}$	0.7

'High' means >10 atm.
'Low' means $<10^{-7}$ (M.P. > 1,100°C)
'Dcpsd.' means decomposed at 600°C

(After Krauskopf, 1957)

Hawley (1941) studied the effect of heat on sulphides. He observed that crystals of pyrite and pyrrhotite were deposited in cracks developed while heating pyrrhotite in a dry atmosphere. He concluded that the iron sulphides had moved to the sites of deposition in the vapour state. Hewitt (1938) had reached the same conclusion from similar results obtained in his pyrrhotite phase relations studies.

Hsaio and Schlechten (1952) measured the rate of weight loss of many metallic sulphides by heating them in vacuum. Using the experimental values, they calculated the vapour pressures of the sulphides with Langmuir's formula

$$Wt = P\sqrt{\frac{M}{2RT}}, \quad \text{where}$$

Wt = weight per unit of time
P = vapour pressure (mm.Hg)
M = molecular weight (gms)
R = gas constant
T = absolute temperature

By comparing these vapour pressures with dissociation pressures obtained by thermodynamic calculations, they were able to determine approximately the weight loss due to volatilization. The minerals tested were divided into two groups:

1. Volatiles: ZnS, CdS, HgS, SnS, PbS, As_2S_3 , Sb_2S_3
2. Non-Volatiles: MnS, FeS, CoS, Cu_2S, NiS, MoS_2

The apparent vapour pressures for the volatiles were much higher than the calculated dissociation pressures; for the non-volatiles, the vapour pressures were lower than the dissociation pressures. The values are listed in Table 7.

Later experiments by Schlechten (1954) showed that in a non-oxidizing atmosphere certain metal sulphides volatilize,

TABLE 7

Apparent Vapour Pressures of Certain Sulphides

Sulphides	Temperature Range, °C	Pressure Range in Atmospheres
	VOLATILE SULPHIDES	
ZnS	704 - 1006	$2.46(10)^{-8}$ to $1.02(10)^{-7}$
CdS	503 - 704	$1.20(10)^{-7}$ to $1.90(10)^{-6}$
HgS	230 - 330	$3.39(10)^{-7}$ to $5.01(10)^{-5}$
SnS	503 - 704	$1.62(10)^{-7}$ to $1.07(10)^{-3}$
PbS	503 - 654	$4.79(10)^{-8}$ to $2.95(10)^{-6}$
As_2S_3	180 - 330	$4.57(10)^{-8}$ to $3.47(10)^{-5}$
Sb_2S_3	352 - 553	$3.39(10)^{-8}$ to $4.78(10)^{-5}$
	NON - VOLATILE SULPHIDES	
MnS	904 - 1106	$8.12(10)^{-8}$ to $2.76(10)^{-7}$
FeS	804 - 1006	$9.11(10)^{-8}$ to $2.40(10)^{-7}$
CoS	804 - 1006	$1.29(10)^{-6}$ to $1.78(10)^{-6}$
NiS	604 - 804	$5.37(10)^{-7}$ to $6.61(10)^{-5}$
Cu_2S	604 - 904	$5.75(10)^{-8}$ to $4.57(10)^{-7}$
MoS_2	904 - 1106	$3.31(10)^{-8}$ to $6.31(10)^{-6}$

(After Hsaio and Schlechten, 1952)

TABLE 8

Solubility of Sulphides up to 600°C for a pH of 7 (grams/litre)

Sulphide	25°C	100°C	200°C	400°C	600°C
ZnS	$1.49(10)^{-7}$	$4.18(10)^{-7}$	$1.21(10)^{-6}$	$4.11(10)^{-6}$	$1.01(10)^{-6}$
PbS	$7.85(10)^{-9}$	$1.52(10)^{-7}$	$2.05(10)^{-6}$	$4.36(10)^{-5}$	$2.75(10)^{-4}$
CuS	$2.36(10)^{-13}$	$9.67(10)^{-12}$	$2.52(10)^{-10}$	$1.06(10)^{-8}$	$9.95(10)^{-8}$
HgS	$1.25(10)^{-21}$	$5.75(10)^{-18}$	$8.19(10)^{-15}$	$2.89(10)^{-11}$	$2.89(10)^{-9}$
Ag_2S	$1.44(10)^{-12}$	$5.63(10)^{-10}$	$8.90(10)^{-8}$	$2.83(10)^{-5}$	$7.28(10)^{-4}$
Cu_2S	$2.07(10)^{-12}$	$1.70(10)^{-10}$	$7.36(10)^{-9}$	$5.23(10)^{-7}$	$6.11(10)^{-6}$

(After Czamanske, 1959)

and may be separated from each other and from non-volatile materials by a process of distillation. Ge, Hg, As, Sb, Cd, and Zn sulphides lose weight almost in proportion to their molecular weights and the sulphides re-condense. Other sulphides, including those of Fe, Ag, Cu, Ni, Co, and Mn, lose sulphur upon heating, leaving a lower sulphide or the metal itself in the non-volatile residue. Another group, including Th, Hf, Zr, Ba, and rare earth sulphides, have little tendency to volatilize or lose sulphur. The most effective temperatures for volatilization were found to be high, ranging from 800°C to 1000°C.

Studies of metallurgical and blast furnace linings (Davis, 1915, and others) have yielded fairly convincing proof of volatile transfer of lead and zinc. Weyl (1955) notes that crystals of greenockite, marcasite, and arsenides are produced synthetically for commercial purposes by volatilization.

The solubility of several minerals in super-heated steam at high pressures was studied by Morey and Hesselgesser (1951). Silicates were shown to dissolve more readily with increasing temperatures and pressures. Several sulphides were tested at 500°C and 1000 bars using a closed system; they remained unaltered with the exception of pyrite, which converted to pyrrhotite.

Wilson (1954) and Koop (1956) synthesized copper and iron sulphides from their respective silicates by passing H_2S across the silicates. Temperatures of 600°C or more were required. Some migration of sulphides into cracks was evident. MacDougall (1957) caused copper and iron minerals to migrate into cracks in adjacent rock material at temperatures of 450-550°C. He suggested that volatile transfer was largely responsible.

Smith (1949), from liquid inclusion decrepitation studies, found that Cornish ores apparently were deposited at temperatures of 265-390°C. He considered, therefore, that the transporting media were 'fluids' and not high temperature gases. Several investigators claim decrepitation temperatures are erroneous, and most often low (McCulloch and Briggs, 1958).

Krauskopf (1957) calculated the possible composition of a vapour phase in equilibrium with a cooling instrusive at 600°C, using proportions of constituents given by previous analyses or calculations of volatiles given off by heated rocks and volcanoes. Some volatile metals are present in vapour at 600°C in sufficient quantity to form ore deposits, but the low volatilities of most free metals and metal sulphides suggest that another means of transport is likely. Verhoogen (1938) had reached this conclusion earlier. Table 6 (after Krauskopf, p. 800) lists the vapour pressures expected of several metals when in equilibrium with their most stable compounds.

Diffusion Studies

Diffusion as a major means of transport of materials has received only minor support in theories of ore genesis. An energy gradient is necessary to effect diffusion, whether it is an electrical or chemical potential, or a concentration gradient, and there is little evidence in ore deposits to indicate that the continuous gradients required to effect movement over great distances existed at the time of deposition. Some field studies suggest that elements do migrate from wall rocks into mineralized areas, but dominantly the movement is in the opposite direction and only of local extent.

Whitman (1928) studied the rate of ionic migration of potassium iodide through a slab of unfractured, water-saturated Vermont marble by analyzing the water in test holes placed at various distances from a 'source' hole containing potassium iodide crystals. The rate of diffusion was 135 mm. in 100 days, which is approximately equivalent to that of KI diffusion through pure water; this indicated that the ions migrated freely out from the center of concentration through water-filled pore spaces. The experiment proved that dense rocks were permeable to ions, but it also provided an excellent example of how ore deposits can be removed.

Duffel (1937) and Garrels, Dreyer and Howland (1949) carried ionic diffusion studies farther. The latter writers found that although the rate of advance of $KMnO_4$ through limestone was independent of permeability or porosity, the total amount of material transported was dependent upon these factors and also upon the maintenance of a concentration gradient. Under the ideal conditions of a concentrated source and removal of diffusing ions by precipitation or channelways, they determined experimentally that the maximum distance traversed by an ion would be 2½ miles per million years, at 100°C. The amount of material which could be deposited at this distance from the source is very small.

Migration along trunk channels must be invoked as an end process of diffusion, otherwise dispersion of elements will result rather than accumulation. A change of environment in such channels could then cause localization of minerals by precipitation.

The importance of diffusion in effecting local changes is fully recognized. Replacement of minerals requires that materials diffuse in and out of the mineral; crystal growth in any medium indicates that diffusion toward a preferred position takes place; and solid solution or exsolution studies render ample proof of the migration of elements to form stable compounds. Few experimental studies, however, have provided information regarding the processes of diffusion, particularly with reference to replacement. Relative stability of minerals in a given environment, electrical or chemical potentials, and concentration gradients alone or together could not effect diffusion and cause replacement, were not some means of migration possible.

Douglas, Goodman, and Milligan (1946) conducted experiments to study this problem. They immersed a copper grid anode in copper sulphate solution, and suspended a bakelite-mounted pyrite block above it. A hole drilled through the bakelite connected the pyrite with the well of a glass tube cemented to the side opposite the pyrite. The tube was filled with weak HCl, a platinum cathode was inserted, and a 6-volt potential was applied across the system. Study showed that native copper was deposited on the surface of the pyrite, but beneath it a film of Cu_2S developed. Abundant iron ions appeared in the glass well. The conclusion reached was that a copper ion, upon entering the pyrite lattice, 'shunted' a line of iron atoms along without disturbing the sulphur atoms, and displaced one iron atom from the opposite face.

Wagner (1952) carried out conductivity experiments with Ag, Pb, Ba, and alkali halides, and found that both cations and anions migrated under the influence of an electrical potential. He suggests that cations and anions may jump to interstitial (improper) lattice sites, push adjacent ions to interstitial sites, or move to vacant positions in the crystal lattice.

Such studies reveal possible means of diffusion of elements in replacement processes. Experimental work in the field of oxidation-reduction and electrical potentials is only beginning, as far as mineralization processes are concerned.

Studies of Sulphide Melts

Much negative evidence is found to oppose theories of transportation of sulphide minerals as melts. The most significant evidence is the apparent lack of high temperature alteration of host rocks, and the apparently low deposition temperatures of the sulphides themselves as determined from crystallographic inversion points, unmixing relations, vacuole fillings, ratios of elements in minerals, and other means. Ingerson (1955) reviews the various methods used. Uncertainty exists, however, as to the accuracy of these methods of determining temperatures, particularly because post-depositional changes may have taken place, and the ideas of emplacement of massive sulphide bodies by means of melts still persist strongly.

Melting or decomposition temperatures of all common sulphides were determined long ago, and are listed in standard references (Kracek, 1942) or individual papers (Ingerson, 1955). A few studies have been made to determine the lowering of the melting points of sulphides by adding different materials such as certain volatile compounds or components which form solid solutions. The addition of water to anhydrous systems, for example, usually lowers the melting point of the components, particularly the silicates; antimony and arsenic form low-temperature sulpho-salts with many refractory sulphides; and excess sulphur is an important reducer of the melting point of many sulphides, as phase relations studies have shown. Water seems to be the only one of these 'mobilizers' to appear in quantity in the majority of ore deposits, but this does not exclude the possibility that it could have been introduced independently, or that sulphur or Sb, As, and other low-temperature sulphides could have been expelled from the system during crystallization of a complex ore 'magma' containing them.

Most experimentation with melts has yielded unsuccessful or inconclusive results. Hewitt (1938) reports that pyrrhotite and galena form a eutectic at approximately 770°C. Olshanskii (1948) in his studies of the FeS-FeO-SiO_2 system determined that FeS could exist as a liquid at 800-900°C, and Vogel and Fülling (1948) found FeO and FeS separating as immiscible liquids down to 950°C. Even the lowest of these temperatures, however, is considered too high for most mineral deposits.

W.H. White (1943) after examining the distribution of gold, galena, and other sulphides in 27 major gold mines, reached the conclusion that metal-rich differentiates from quartz-rich magmas were sufficiently mobile at 250-300°C to move into cataclastic zones in quartz bodies. Bichan (1944) proposed his silico-thermal theory on the basis of White's studies and on the fact that a gold alloy containing 6% silicon remains liquid down to 320°C and gold alloys containing up to 85% lead can remain liquid down to 220°C (Int. Crit. Tables). It is possible that silicon and lead could exist in the elemental state in natural environments, but there is no evidence of it in the visible portions of the earth's crust.

Freeman (1925) and others noted the great reduction of melting point of several sulphides by fusion with Na_2S. His experimental results are given in Table 9. Precipitation of the metallic sulphide and removal of the alkali sulphide is effected by introducing water into the system. Such compositions appear unlikely for natural melts, because the distribution of sulphides in rocks of known magmatic origin give no clue that they were

TABLE 9

Comparison of Melting Points of Some Sulphides with Respective Double Sodium Sulphides

Sulphide	M.P.°C	Double Sulphide	M.P.°C
PbS	1130	$PbS.Na_2S$	650
FeS	1000	$FeS.Na_2S$	660
ZnS	1650	$ZnS.Na_2S$	620
Cu_2S	1100	$Cu_2S.Na_2S$	560

(After Freeman, 1925)

present. On the other hand, little is known of the stability relations of complex silicate-sulphide systems.

Apart from the possible existence of low temperature complexes such as double sulphides, there is little to support theories of ore magmatism, even though they can answer the concentration problem with ease. The study of phase relations in many sulphide systems has shown that low temperature melts are not obtained in simple systems containing refractory sulphides. Should fully dependable geothermometric methods show undoubted proof of low temperature emplacement of the common sulphides, the ore magmatist will be forced either to abandon his theories or produce evidence that mass transport of sulphides can be effected below their melting points.

Solid State Transformations

A vast amount of experimental work has been carried out on phase relations of sulphides in solidus and sub-solidus regions. The importance of this work in determining the conditions of equilibrium of components in a system need not be stressed, for such fundamental knowledge is essential to an understanding of the conditions of mineralization and replacement.

It is necessary, however, to handle the information with caution when ore transportation and deposition are being considered. Minerals can be deposited in different ways, at different times, yet subsequent metasomatism caused by solid state diffusion under certain thermal or chemical conditions may completely obliterate those features by which the primary history of deposition could be traced. The work of Ross (1954) on the formation of intermediats sulphide phases by diffusion in the solid state illustrates the point well. It is doubtful that primary textures can be differentiated from similar secondary textures at the present time; in this respect, careful field study of a mineral deposit could yield information that would solve the problem.

The present study includes parts of the Cu-S, Cu-Fe-S, Fe-S, Fe-Ni-S, and Cu-Fe-Ni-S systems. The more recent studies relating to these systems are those carried out at the Geophysical Laboratory, Washington, D.C.; the results appear in the Institute's annual reports.

Summary

The many experiments that have been carried out to study possible means of transport and deposition of metallic sulphides have not limited the number of acceptable theories to any great extent. They have defined neither the physical and chemical nature of the ore-transporting medium, nor the causes and processes of movement from source to site of deposition. The studies have, however, provided us with some knowledge of the effectiveness of postulated means of transport.

At present the problem of transport and deposition of sulphide ores is not resolved. Hydrothermal transport, the most popular of all theories, requires that vast quantities of water be impelled through the enclosing rock because of the extremely low solubility of sulphides in water. Complexing materials increase solubilities of several metallic sulphides, but few sulphides appear to be present in ratios greater than one part to one million. Solutions with high pH and high sulphur content appear to be more effective solvents than acidic solutions for some sulphides, but many writers maintain field evidence does not support the alkaline sulphide theory. The composition of fluid inclusions and volcanic gases indicate that near neutral conditions probably existed. If this is so, much water and also much time would be required to deposit large sulphide bodies, assuming that the water is available to transport the sulphides.

Transportation of the metals as soluble compounds such as halides and sulphates has been suggested, the precipitation as sulphides taking place when sulphur-bearing solutions or gases are encountered or when replacement is effected. This theory has merit. The concentration problem is overcome to a great extent, and diffusion processes could operate at optimum rates. However, it may be questioned that halides and sulphates are present in quantity at any great depth in the earth and therefore that they could be dominant in primary solutions.

Colloidal solutions have been shown to be capable of transporting large quantities of sulphides; however, evidence of their existence in primary ore bodies is not common, and therefore few geologists consider them to have played more than a minor role in ore deposition. It is to be noted that post-depositional changes could have removed all traces of their presence.

Gaseous transport theories require high temperatures to cause vapourization of most sulphides, although the presence of HCl considerably reduces the temperatures necessary to volatilize certain sulphides. Laboratory studies and studies in fumarole areas show that heat is not dissipated readily by rocks, and that extremely high temperatures are easily maintained in trunk fissures along which vapours travel; consequently, considerable volumes of sulphides could in time be transported as gases despite low vapour pressures. Experimental work apparently supports volatile transfer theories to the extent that local movement has been effected in completely dry systems at temperatures which produce only low vapour pressures; however, definite proof that volatilization occurred is still lacking.

The theory of transport of sulphides as melts has little support experimentally because high temperatures are always necessary to produce a liquid phase from the more refractory common sulphides. Because field evidence generally suggests much lower temperatures existed at the time of deposition, the magmatic theory is not widely favoured; however, the possibility of moving large quantities of sulphides with only minimum amounts of liquids or gases is sufficient reason to search for a possible means of achieving mass transport by movement at sub-liquidus temperatures.

The problem of sulphide transport and deposition remains unsolved. None of the more dominant theories of hydrothermal, gaseous, or magmatic transport have been eliminated as a result of laboratory studies, although limitations of their effectiveness have been defined.

EXPERIMENTAL APPARATUS

General Statement

The high costs of research apparatus, particularly of high pressure-temperature vessels and their necessary accessories, frequently prevents experimental work from being carried out in many desirable fields. This problem is being gradually overcome with the appearance of less costly, commercially-produced equipment, and by the increase in funds provided for apparatus by governments and other organizations.

All basic equipment for high pressure experimentation was available at McGill University, and a government research fund was available to purchase additional apparatus for specific projects. A brief description of the high pressure, analytical, and other equipment used in the present experiments is given.

Hydraulic Pump Circuit

Components and Utility

An American Instrument Company electrically driven, total displacement pump capable of delivering either 15,000 or 30,000 psi was used to supply pressure to the reaction vessels. The pump circuit included the Aminco pump, 30,000 psi (minimum) tubing, control valves, tubing joints, pressure gauges, an automatic pressure control apparatus, a dead-weight pressure relief apparatus, and a 30,000 psi surge tank which could also be employed as a fluid separator. These parts are shown in Figures 1 and 2.

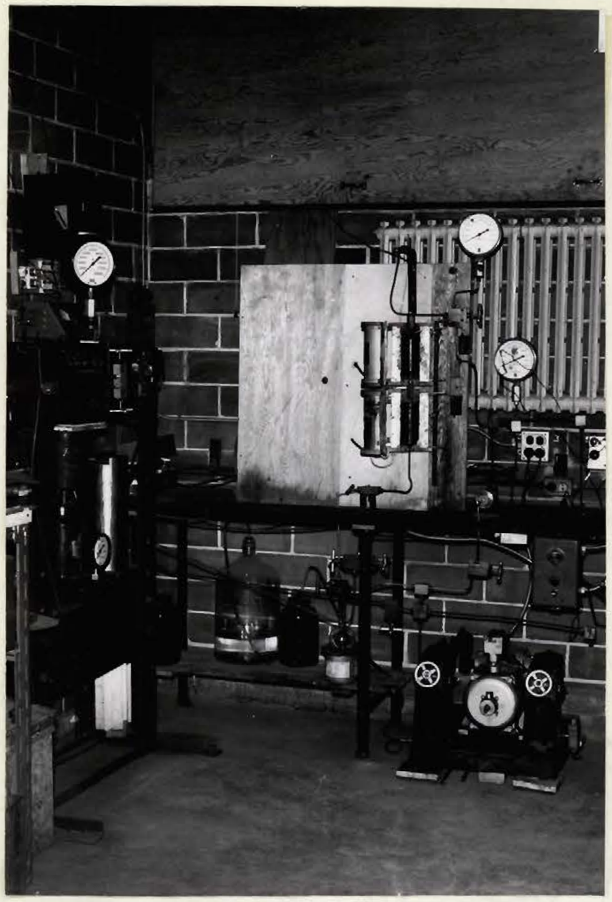


Figure 1

General view of pump and pressure vessel systems.

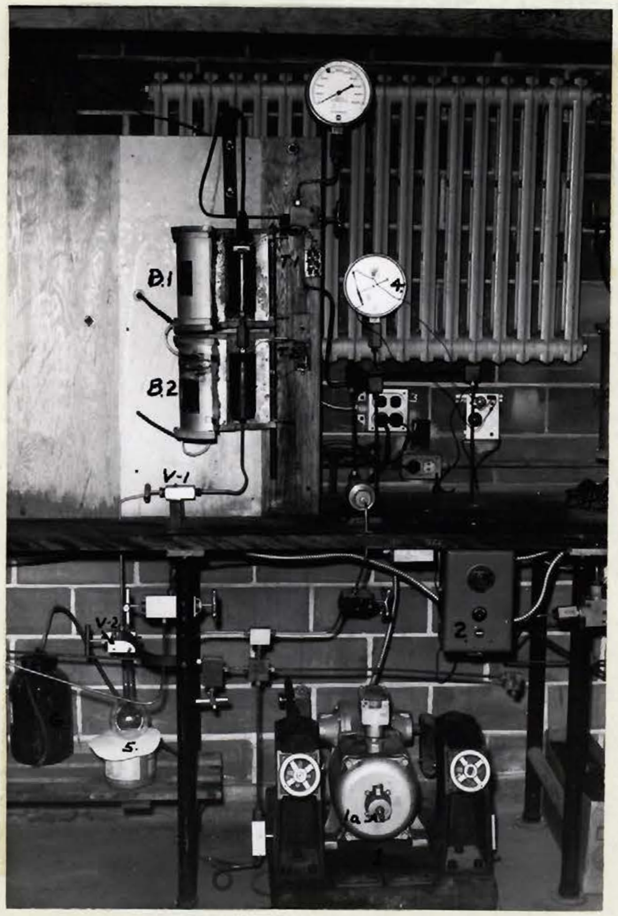


Figure 2

Circuit for Open System Experiments

1. Hydraulic Pump
1a. Manual operation bolt
2. Pump control box
3. One-way line valve
4. Pressure gauge
5. Fluid collector
6. Fluid reservoir

B.1 High temperature vessel
B.2 Low temperature vessel

T.1
T.2 Thermocouple switches

V.1
V.2 Circuit metering valves

This pump circuit can supply hydraulic pressure to any number of experimental systems at a specific pressure, or at different pressures when individual systems are isolated. Simultaneous operation of more than one dynamic system can be carried out only if the desired pressures are similar.

Pressure Relief Apparatus

A safety feature designed particularly for use with the open system bombs is the dead-weight pressure relief apparatus shown in Figure 3. The removable lever arm, which has a mechanical advantage of 10:1, forces a 60° coned shaft into the seat of a standard T-joint connected to the pump pressure line. A pan attached to the lever can be loaded with any desired weight to close the aperture against the pump pressure. This type of pressure release has an advantage over the blow-out type in that pressure will be maintained within the system should the upper pressure limit switch fail to shut off the pump.

Automatic Pressure Control

A sensitive, positive electrical contact for energizing the relay solenoid of the pump control box is necessary for automatic pump operation, otherwise excessive chattering of the relay results. Commercial pressure control relays are costly because of the precision required in manufacture. The system used here incorporated a low cost, highly sensitive electronic relay designed by E.J. Serfass (1941) and constructed by Dr. V.A. Saull of McGill University. The electronic relay is connected to the automatic pump relay, and is activated during

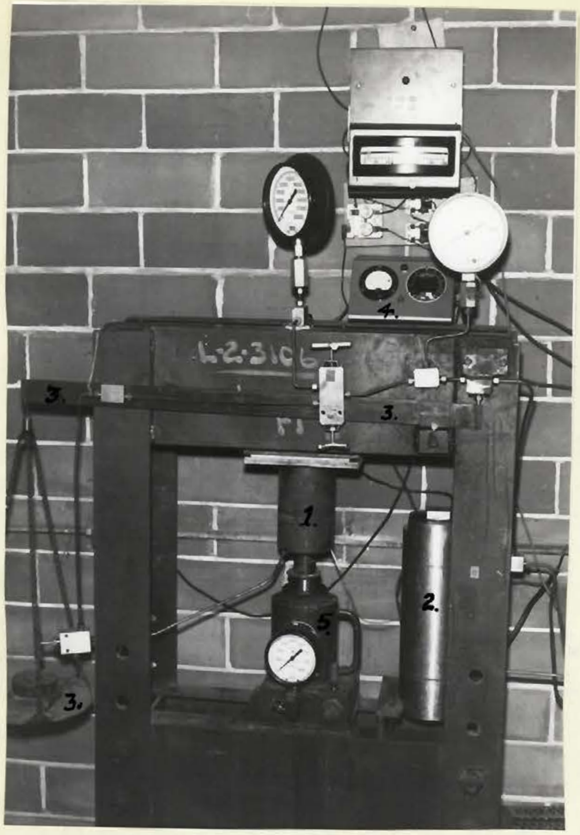


Figure 3

Differential Pressure Vessel in operating position, external furnace removed.

1. Pressure vessel
2. High pressure surge tank
3. Pressure relief apparatus
4. Temperature controller
5. Hydraulic jack
6. Steel frame

Figure 4

Pressure Control System

1. Electronic relay
2. Pressure gauge
3. Electrical contact leaves

pumping when the needle of a standard pressure gauge forces together two copper leaves mounted on the face plate of the gauge (Figure 4). The moving leaf is shaped so that the needle can continue past it, thereby shutting off the pump permanently should a blow-out in the bomb system occur.

Additional Equipment, and Modifications

A large volume pressure intensifier was manufactured to produce pressures between 30,000 and 120,000 psi, but repeated failures of the steel prevented its use. The intensifier has been re-designed for future use. A drawing of the modified vessel is included in the Appendix.

Much difficulty was encountered with the Aminco pump through leakage from the pump cylinder. The plastic sealing washers usually employed in the cylinder were finally replaced by polythene-impregnated leather washers, and the difficulty was overcome. Other modifications to the pump included the insertion of hardened steel bushings in lever arm pivots, and the introduction of a bolt (Figure 2, la) in the pump motor shaft to permit manual operation of the motor.

Should future replacement of this hydraulic pump become necessary, or if additional pumps are required, it should be noted that relatively inexpensive air-driven pumps can be purchased from Sprague Engineering Limited*. These pumps are highly efficient, dependable, and produce a steadier pressure than the Aminco type.

*Distributors: Rousseau Controls Ltd., Montreal

The standard Aminco pipe coning tool produced rough cone surfaces which frequently leaked under pressure. This tool should be discarded and replaced by a superior double-sided coning tool distributed by Autoclave of Canada, Limited, Toronto. When possible, pipes should be mounted in a lathe for proper coning with a file and fine emery cloth.

Pressure Vessels

Two different types of pressure vessels, or 'bombs' were used in the experiments, according to the conditions required. These were:

(1) Open-end, high pressure-temperature vessels, used for open system experiments or when confining pressures only were needed;

(2) A high pressure-temperature, differential pressure vessel, used when a positive moving force was required in addition to a confining pressure.

These pressure vessels were used in circuit with the hydraulic pump described earlier.

Open System Vessels

Requirements

An assembly drawing of the open-end pressure vessel designed by the writer is included in the Appendix, and a simplified diagram is given in Figure 8. This bomb was constructed so that the entire vessel could be heated, thereby reducing temperature gradients within the bomb to a minimum. A large internal diameter was desirable, so that a considerable volume of experimental material could be accommodated, but at the same time the vessel had to withstand high pressures and temperatures. The bomb had to be open at both ends to permit the passage of fluids or gases through it and to allow its connection on either end with other parts of a circuit, particularly with a second bomb in series. A thermocouple entry port, sufficiently close to the interior to give fairly accurate temperature readings, was necessary. Finally, the vessel parts had to be extremely resistant to corrosion. These requirements were all met, although some not too satisfactorily.

Vessel Body

The vessel body was manufactured from the highly corrosion-resistant, tough cobalt-nickel-chromium alloy No. 25 produced by Haynes Alloys Company, Kokomo, Indiana. With one exception, described later, the bomb was almost completely unaffected by the solutions and pressure-temperature conditions used in this series of experiments. The alloy also possesses great strength at high temperatures, which permits the design of pressure vessels having large inside to outside diameter ratio.

Pressure Seals

The large internal diameter of the bomb made it necessary to use, at the access end, a seal whose closure was maintained by the internal pressure. A modified Bridgman unsupported-area type of seal (Bridgman, 1931; Morey and Hesselgesser, 1951) was used in conjunction with a removable stem. This seal proved to be highly effective, and no failures occurred during the experimental runs. The sealing washers could be made of any desired material on a small lathe, provided that they were smoothly finished. Copper or nickel washers were used in these experiments.

At the exit end of the vessel and at the small end of the bomb stem, simple 60° cone-in-cone compression seals were used to attach the bomb to standard high pressure line fittings. These cone seals leaked frequently at high temperature connections, either when the effective sealing pressure was reduced by creeping of the pipe cone metal, or when a surge of cool fluid rapidly contracted the pipe cone.

Bomb Stem

The bomb stem was made from 316 stainless steel, because a 5/64-inch diameter hole could not be drilled through a 3½-inch length of the cobalt alloy at the time of manufacture of the vessel. The stainless steel was generally unsatisfactory because it corroded easily and pierce holes, which were difficult to locate, commonly developed.

Thermocouple Well

The thermocouple well was placed in the screw head of the bomb adjacent to the bomb stem (see Vessel Assembly Drawing). This position allowed penetration of the thermocouple to within one-half inch of the end of the central cavity, and did not weaken the vessel walls. A test run revealed only a 2-degree temperature difference between the interior of the bomb and the external position of the thermocouple.

Suggested Modifications

The major modification suggested for the existing open-system vessel is to substitute a more resistant alloy for the present bomb stem metal. Tungsten-carbide tipped dental drills cut the tough new alloys readily, and could be employed to drill long, fine holes of 3/32 or 5/64-inch diameter when mounted on special shanks (Figure 6, No. 6). The round-end burr is the best type to use for this work. The short length of pipe used to connect two or more vessels should also be made of material superior to that provided in commercial high pressure tubing.

Differential Pressure Vessel

The differential pressure vessel used was an externally heated, large diameter bomb designed by Cameron (1956) and Wolofsky (1957) at McGill University. With this vessel, a directive force from a jack can be impressed on the experimental materials while a confining pressure is being applied, and at the same time fluids or gases can be passed through the experimental chamber. The vessel was designed to reproduce conditions of hydrothermal-dynamic metamorphism, using an open system. In the present experiments the central, open circuit was closed off. The component parts of the vessel are shown diagrammatically in Figure 9, and a picture of the vessel in operating position is given in Figure 3.

Serious difficulties were encountered with this vessel in maintaining a seal at the moving end when temperatures exceeded 350°C. The seal, an unsupported area type, consisted of copper and teflon washers. The teflon washer volatilized near this temperature, and upon movement the copper alone was unable to fill the irregularities in the bomb wall sufficiently quickly to maintain the pressure. For more critical experiments, the bomb should be reamed out, plated with cadmium or nickel, and honed internally to a 5-micron finish, or be replaced by a vessel made from a more corrosion-resistant material such as the Haynes cobalt alloy.

Strength of Materials

The determination of the strengths of pressure vessels under high temperature and pressure conditions has received much attention in the past twenty years. No completely satisfactory equation is available for determining the limiting conditions of operation for thick-walled cylinders, but for general purposes the equation given by Timoshenko (1956) can be used to calculate stresses set up by pressures and temperatures. The resulting values can be compared with strengths of a material at given temperatures as published by the manufacturer.

Timoshenko shows that the tensional and radial stresses set up in a thick-walled cylinder by an internal pressure of Pi will be approximately as follows.

$$St = \frac{a^2 \; Pi}{b^2 - a^2} \times \left(1 - \frac{b^2}{r^2}\right) \qquad (1)$$

$$Sr = \frac{a^2 \; Pi}{b^2 - a^2} \times \left(1 - \frac{b^2}{r^2}\right) \qquad (2)$$

St = tensional stress
Sr = radial stress
r = arbitrary radius
b = external radius
a = internal radius
Pi = internal pressure

As there is not a large thermal gradient between the inside and outside of an externally heated bomb at equilibrium, thermal stresses need not be considered.

Calculations to determine the pressure limitations of the open system bomb were made, using the manufacturer's ultimate tensile strengths of the cobalt alloy at various temperatures. Equation (1) was used because the tensional stress is the greater of the two. For the arbitrary radius (r), the internal diameter was used since the equation shows it to be the radius of greatest stress. Reduction of the equation gives:

$$P_i = St_t \times \frac{(b^2 - a^2)}{a^2 - b^2}$$

or

$$P_i = 0.923\ S_t$$

for the bomb, where S_t equals the ultimate strength. Some pressure limitations obtained in this way are given in Table 10.

TABLE 10

Some Calculated Pressure Limitations of the Open System Pressure Vessel

Temperature	Pressure	Temperature	Pressure
70°F	139,000 psi	1500°F	60,6000 psi
1000	100,000	1650	39,400
1200	89,800	1800	30,400
1350	68,200		

The stress-rupture graph in Figure 5 was drawn from the manufacturer's ruptural stress values for failure in 10 hours. These empirical yield points, as would be expected, are considerably lower than those indicated from the ultimate strengths. Tests of cold seal bombs at McGill University revealed, however, that the bombs could withstand pressures of 72,000 psi at 1350°F (732°C) for minimum periods of 24 hours with no detectable increase of external diameter. This value exceeds even the ultimate strength of the vessel, as calculated above. Obviously bombs made of the cobalt alloy will be quite safe when operated at the upper limits given by the graph in Figure 5.

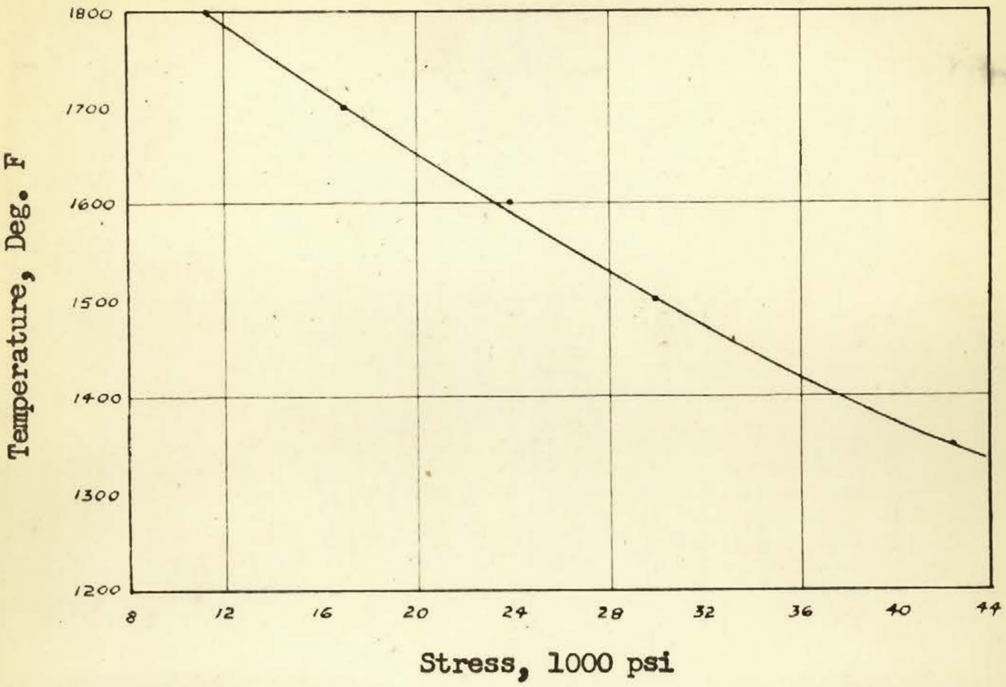


Figure 5

Stress-Rupture properties of Haynes Alloy 25 at higher temperatures. From Manufacturer's data for rupture in 10 hours.

Calculations of strengths of the differential pressure vessel have been made by Cameron (1956). At 550°C the yield strength is 30,000 psi.

The weakest points in the hot seal bomb systems will be the heated pipes leading from the bomb, or the bomb stem itself when that is made of inferior metal. The upper pressure limitations of the system should therefore be set by the yield strengths of pipe materials in the critical areas; similar to the pressure vessels, these yield strengths should give an ample pressure safety factor.

Cleaning Equipment

Tools for cleaning and polishing cone seats, clogged pipes and stems, and the interiors or sealing surfaces of pressure vessels are indispensable to the efficient operation of the pressure systems. Figure 6 shows several small tools used for different cleaning purposes. The unfinished interiors of bombs were cleaned with a wire brush, or with a mounted cloth impregnated with coarse grinding compound such as that seen in Figure 6, No. 4.

Low Pressure Apparatus

Two experiments were carried out in a water-free environment at atmospheric pressure. The experimental apparatus consisted simply of high-temperature glass tubing inserted in a ceramic shield, the latter being placed in a tube furnace. Figure 7 shows the various parts.

This apparatus is well suited to atmospheric pressure experiments. It can be set up rapidly, and the experimental materials can be subjected to any desired liquid or gaseous environment.

Analytical Equipment

All equipment necessary for the study of specimens and experimental products was available at McGill University.

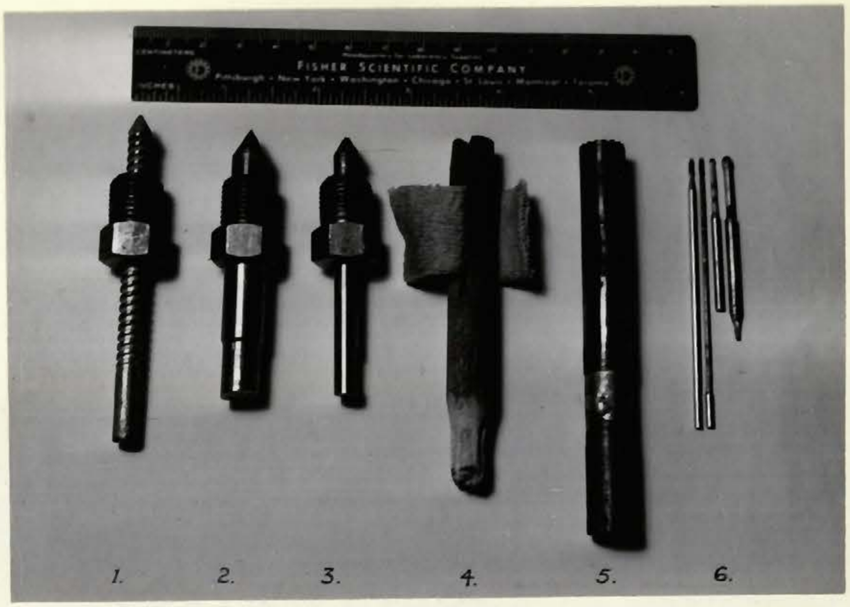


Figure 6

Tools for Cleaning Pressure Vessel Circuit Parts

1. 60° Carbide tipped drill for cone seat reaming
2. 60° Hone for fine grinding of cone seats
3. 60° Polisher, cloth tipped
4. Polisher for cleaning seal wall of Open System Bomb
5. Toothed Augur for removing coagulated materials from Open System Bomb
6. Dental drills for clearing pipes and bomb stems

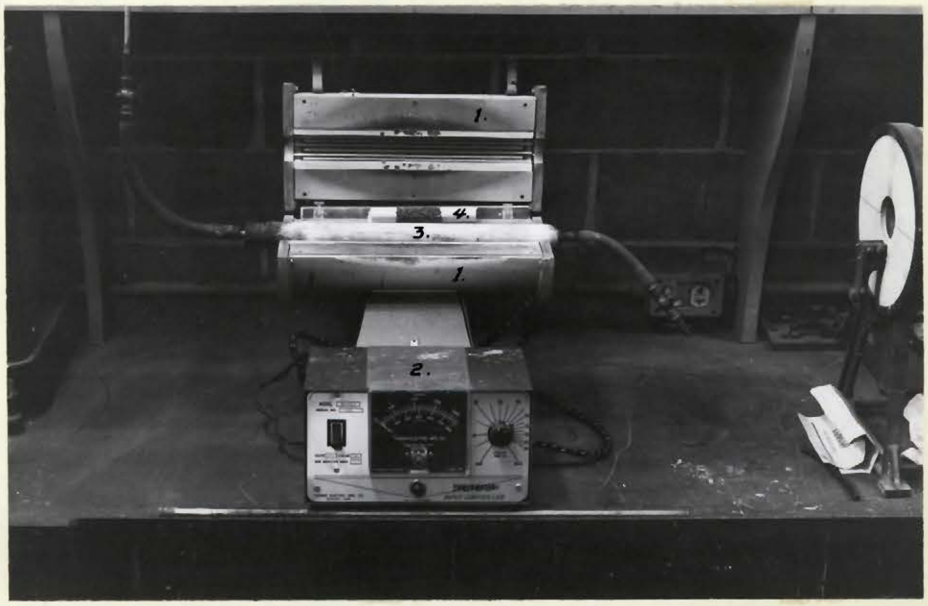


Figure 7

Low Pressure Apparatus

1. Tube furnace 2. Temperature controller
3. Ceramic shield connected to gas lines
4. Glass tube containing experimental materials

A General Electric XRD-3 X-ray diffractometer was used to determine by diffraction the crystalline products formed, and to assess semi-quantitatively by fluorescence the distribution of certain transported elements. Diamond polishing equipment enabled the production of good polished surfaces on friable products, which would have been difficult to achieve otherwise. Quantitative chemical analyses were made in the department's geochemical laboratory.

EXPERIMENTAL PROCEDURES

Preparation of Materials

Natural materials were used in all experiments, as it was desired to observe any changes in textures and mineral relationships produced by the experimental conditions. Purity of material was not a requisite, but the proportions of minor constituents in minerals to be used in the primary reaction vessel was kept below ten percent.

Mineral specimens for use in 'primary' environments were crushed and screened to obtain grains ranging from 2.5 mm. to 4.0 mm. in diameter. This minimum diameter was necessary to prevent the grains from moving out of the reaction vessels and through the pipes. The grains were tumbled briefly to break off loose particles, were washed, and examined under the binocular microscope. Grains which contained a high percentage of impurities were rejected.

Rock or mineral specimens for use in 'depositional' environments were crushed and screened to obtain grains ranging in diameter from 2.5 to 6.0 mm. These grains were also tumbled and washed to remove loose particles.

Operational Procedures

The experiments in this study fall into three different groups:

1. open system, hydrothermal experiments,
2. closed system, differential pressure experiments,
3. closed system, low pressure experiments.

The experiments of the first and second groups were carried out in pressure vessels, and those of the third either in pressure vessels or in glass tubing.

Open System Hydrothermal Experiments

The open-end pressure vessels were used when it was necessary to pass solutions or gases through the reaction vessels while they were being subjected to specific conditions of temperature and pressure. The vessels were charged with the experimental materials and connected in series to the pump circuit, as shown in Figure 8. The pressure vessels and external circuit were filled with the fluid or gas to be used, the exit metering valves were closed, and pressure was built up to check for leaks in the system. The external tube furnaces were then closed and the bombs heated to the temperatures required. The pressure was maintained during heating by bleeding off the excess liquid through the metering valves.

When the desired pressure-temperature conditions were reached the hydraulic pump was set to operate automatically, one metering valve was opened fully, and the other was adjusted to control the rate of flow of solution through the bombs. For more experiments a flow rate of 0.2 to 0.4 ml. per minute was maintained when possible. A lesser rate of flow, although desirable, resulted in rapid blockage of the system because fine materials precipitated from solution readily clogged the meter valve openings.

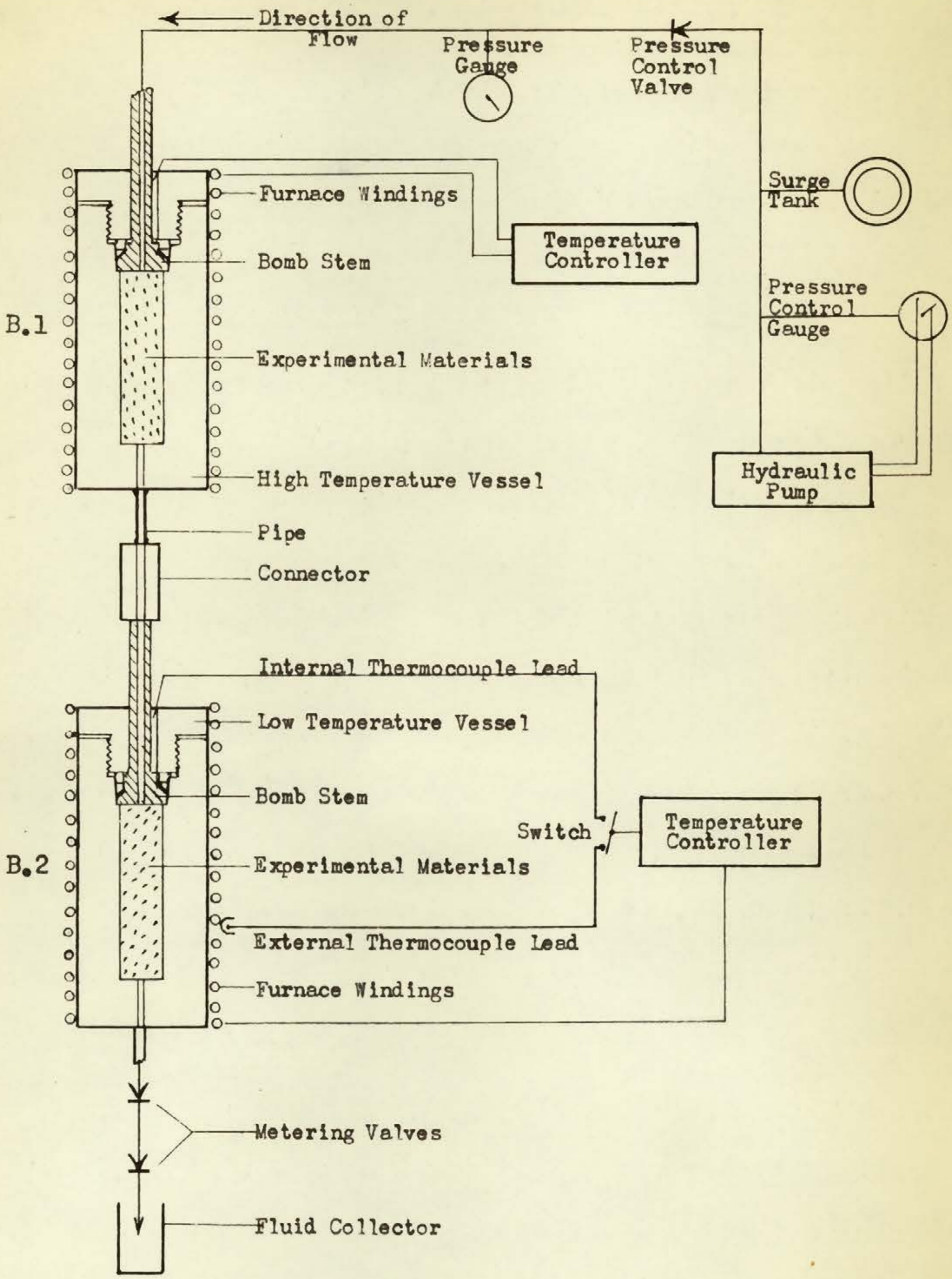


Figure 8

Circuit Diagram for Open System Experiments

Blockage of the circuit occurred frequently from collection of materials at the control metering valve. By closing the idle valve and opening the control valve fully the blockage could be cleared without allowing a surge of fluid to pass through the vessels. The sudden passage of a large volume of liquid commonly caused leakage when the hot cone seats contracted; it also dislodged materials deposited in lower parts of the system. When blockage of other parts of the circuit occurred, however, the experiment was usually terminated.

Closed System Differential Pressure Experiments

Differential forces to cause a directed movement of experimental material were produced in two ways.

One method used was to subject a two-compartment sealed capsule, of which only one end was collapsible, to a hydrostatic pressure (Experiments N and O). The material to be tested was placed in the collapsible end, while the non-collapsible end and central restriction were left empty. The capsule was welded shut, inserted in a pressure vessel, heated, and subjected to pressure. A peristaltic force developed as the charged end collapsed, causing materials to flow through the restriction into the rigid end. Figure 39 shows a section through the collapsed end of such a capsule.

The second method of producing a deforming force required the use of the differential pressure vessel described previously. Complete instructions for its operation are given by Wolofsky (1957). In the present experiments (Q,R,S,T) the

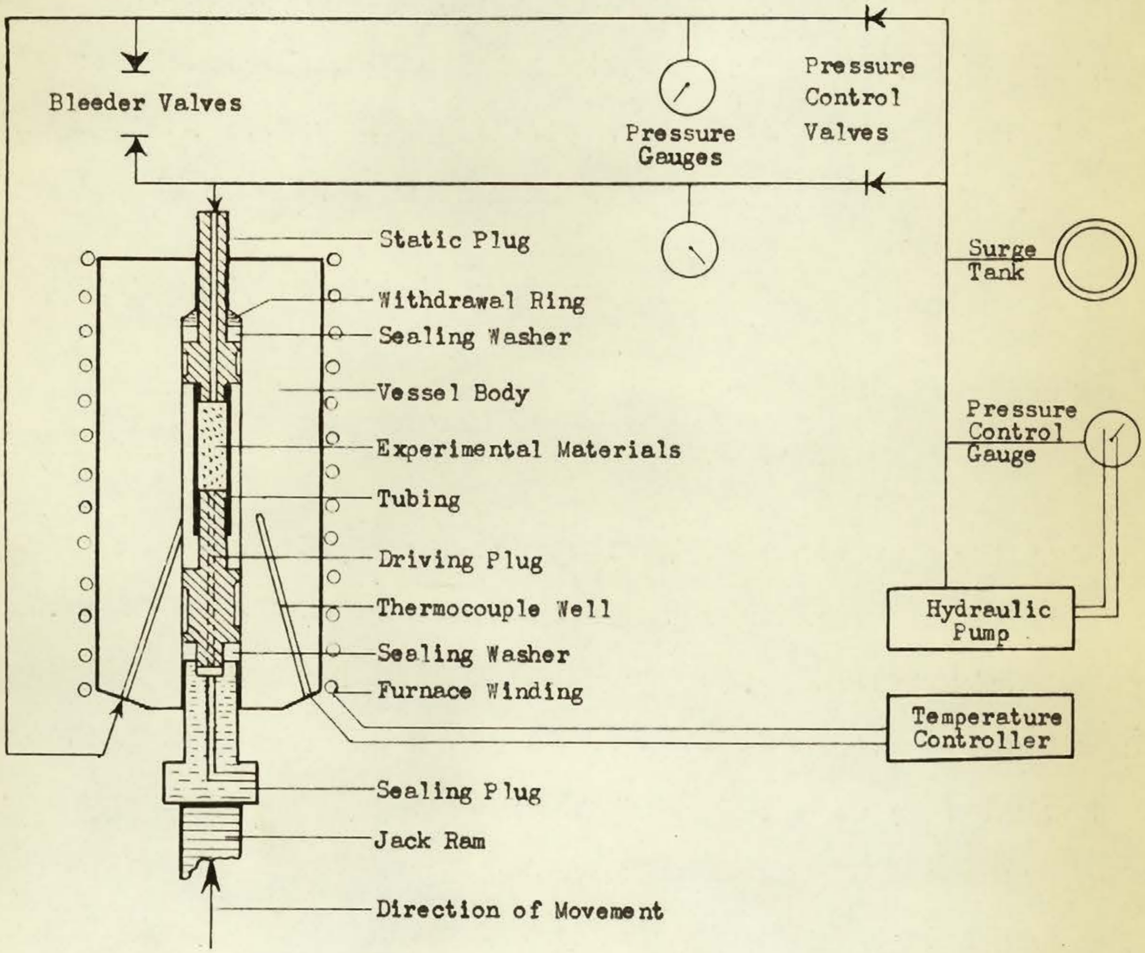


Figure 9

Circuit Diagram for Differential Pressure Experiments driving plug was lengthened to give a larger displacement, and the reaction tube was cut from thick-walled pipe to provide more resistance to deformation. Grains of refractory materials were loaded in the static end of the tube to maintain open spaces, and the sulphide minerals were loaded at the dynamic end, as shown in Figure 10. The bomb was assembled and connected to the hydraulic system (Figures 3 and 9), pressure was built up against the jack ram, and heating was begun. When equilibrium temperatures were reached, steady pressure was applied by the jack and the driving plug was moved slowly into the tube chamber against the central hydrostatic pressure and frictional resistance of the moving seal. The tube collapsed or was compressed as the plug moved, and a directive force was thereby continuously applied on the experimental materials.

Closed System, Low Pressure Experiments

Low pressure experiments were made to determine whether or not confining pressure had an effect on the mobilization of sulphide minerals or their elements. When possible, an electrical potential was also placed across the reaction chamber to examine its effect on the movement of materials.

Pressure vessels were used in the U series of experiments; these experiments were conducted to determine the effect of full sulphur vapour pressure on mobilizing different sulphide minerals. The minerals were charged into the bombs with sulphur, the bombs were connected to a pressure gauge, and heating was begun. No attempt was made to exhaust air from the system.

The atmospheric pressure experiments, M and W, were run to study the effect of lack of water, temperature

Figure 10

Assembled internal components of differential pressure vessel, showing cut-away of reaction tube. Moving end is to the right.

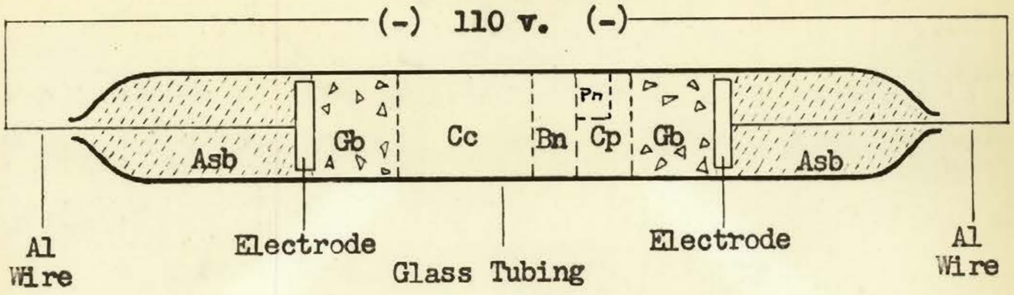


Figure 11

Atmospheric Pressure Experimental Set-up

Gb: Peridotite Cc: Chalcocite Bn: Bornite
Cp: Chalcopyrite Asb: Asbestos

gradients, and electrical potential on the migration rates of sulphides. The sulphide grains were introduced into Vycor glass tubing, and were enclosed on either side by peridotite grains, aluminum electrode plates, and asbestos wool packing, as shown in Figure 11. The electrode wires were extended out either end of the tube and connected through a variable resistor to a direct current source of 110 volts. The tubes were then placed in the furnace and heated. In these two experiments the use of a thermocouple was avoided by testing and pre-setting the temperature controller.

ANALYTICAL PROCEDURES

Selection of Material

The procedure for selection of experimental material for analysis varied somewhat with the type of experiment. Closed system and differential pressure experiments required only: (a) the close examination of products under the stereoscopic microscope; (b) the selection of individual grains or particles for preparing X-ray mounts and polished sections; or (c) the mounting of the entire recovered specimen as a polished section.

The selection of products for analysis from open system hydrothermal experiments required far more care, however, because direct comparisons between experiments were to be made. The procedure used was as follows:

(1) Experimental materials were removed section by section from the pressure vessels. Mineral or rock grains placed in certain sections of the bombs were then separated from the different grains of adjacent sections;

(2) A careful study under the stereoscopic microscope was made of all materials from the bombs to detect megascopically any evidence of solution, alteration, transportation, or deposition;

(3) Sample grains were taken from the various sections and mounted for polished section study;

(4) The remaining grains of a given section were tumbled

gently in a glass vial to remove for X-ray analysis any deposited material;

(5) Bomb stems, pipes, and joints were examined critically for alteration and deposition, and products were selected for analysis when necessary;

(6) Discharge fluids were filtered. The solids recovered were mounted for X-ray analysis, while the liquids were stored for chemical analysis.

Preparation of Samples

Polished Sections

Grains selected for polished section study were arranged as desired in a small container along with a few grains of natural minerals for comparison. Quick-setting liquid plastic was poured into the container to form the mount. When hardened, the mount was ground down to the desired level, polished, and labeled. Gendron (1959) describes a similar method of preparing mounts.

X-Ray Mounts

The volume of material recoverable from various parts of the reaction vessels was rarely enough to mount on standard dished X-ray slides (Klug, Alexander, 1954). A special technique, which also partly compensated for the great range in volume of the samples, was therefore used in mounting the experimental products.

A small conical dispenser which held approximately

0.01 cc was made so that the volume of material used for each mount could be controlled. Paper discs for powder mounts were cut from a high grade filter paper to obtain a basal material having a low radiation background. The discs were cut a standard one-half inch in diameter so that a constant surface area would be presented to the radiation.

Materials to be X-rayed were carefully examined to remove recognizable, unwanted minerals or rock fragments. As it was desirable to know the total amount of a deposited element in a given section of a vessel, every attempt was made to remove particles of original materials so that the total volume would not exceed that of the dispensing cup. The cleaned sample was ground finely in an agate mortar, and the resulting powder was mixed with collodion on the paper mounting discs. When there was an excess of powder, the fraction measured for analysis was noted; if the volume was less than the volume of the dispenser, flour was added.

Materials mounted only for X-ray diffraction identification of minerals were not closely controlled with respect to volume used, unlike those to be analysed by X-ray fluorescence.

X-Ray Fluorescence Analyses

Standard mounts of known copper and iron content were made so that a semi-quantitative evaluation of the content of these elements in the experimental mounts could be obtained by X-ray fluorescence. These standards were run each time a suite of experimental mounts were X-rayed. The total metals content in each mount was then determined by comparing the characteristic radiation intensities with those of the standards. Normally, readings on individual peaks were made, the values being taken directly from the X-ray geiger scaler unit, but an occasional mount was scanned to check for interference by other elements if they were expected to be present. Figure 12 shows such a graph.

No great accuracy was to be expected from this method of analysis. Loss of material, either during selection of the sample or removal of the various sections from pressure vessels, probably would cause the greatest error. Variation in particle size and irregularity of the irradiated surface were probably important sources of error, although re-orientation of the standard mounts on the machine seldom changed line intensities by more than 2%. A few non-systematic errors became apparent when chemical analyses of the mounts were obtained; in these instances the X-ray analyses are likely suspect. X-ray fluorescence and chemical extraction analyses for copper in mounts from the hydrothermal experiments are compared in Tables 15 to 26.

Although chemical and X-ray analyses of the same mount differed by as much as 30%, a comparison of results from experiment to experiment clearly shows that X-ray fluorescence analysis of selected mounts is sufficiently accurate to detect the effects of changing the environment in studies of transportation and deposition of materials. If greater accuracy is required, an internal standard should be used. One method of introducing the standard is to add a drop of solution of the standard element to the mineral powder, when the latter is being mounted.

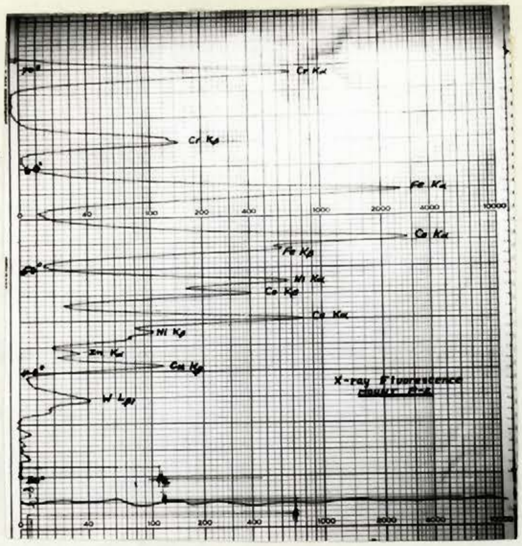


Figure 12

Typical X-Ray Fluorescence graph
Taken with General Electric XRD-3
Diffractometer.
(X 1/4)

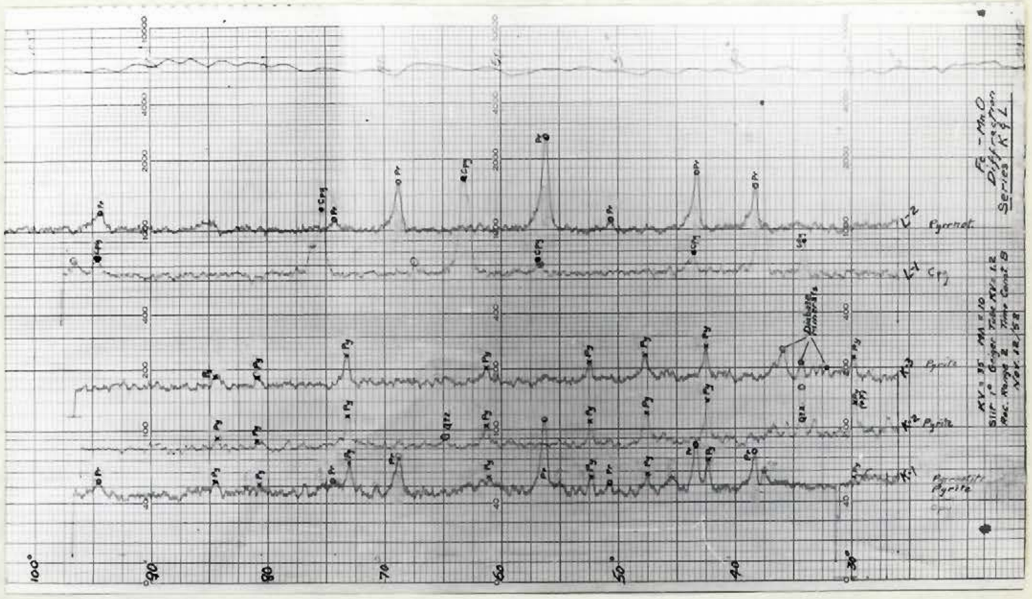


Figure 13

Typical graph of X-Ray diffraction patterns (Expts. K, L).
Before the peaks of minor products are studied, the
respective peaks of major products are eliminated by direct
comparison with graphs of natural minerals.
(X 1/3)

Chemical Analyses

Chemical analyses were made on different experimental products either when a check on X-ray fluorescence analyses was desirable, or when tests for specific ions or radicals were required.

The standard procedures of dry fusion, acid extraction, and colorimetric analysis using diphenyl-thiocarbazone were used when analyzing X-ray mounts chemically for copper content. The analysis of discharge liquids from the open system experiments was more difficult, because it was desired to know the relative amounts of sulphur radicals produced during an experiment. The spontaneous break-down of H_2S to sulphur and oxidized radicals proceeded quickly, giving positive tests in most cases. The sulphide ion produced during the experiment was finally precipitated by cadmium ion placed in the collecting flask, and a fairly reliable analysis of the sulphur radicals existing at the discharge point was then obtained.

Separate tests were made for the copper content of the discharge liquids. Using the standard colorimetric 'dithizone' method. The liquid under test was evaporated with HNO_3 and the copper ions extracted with HCL. Only qualitative tests were made for other elements in solution, such as cobalt and nickel; these two elements would appear when the vessels corroded. Table 14 summarizes the results of all analyses of the discharge liquids.

Mineral Identification by X-Ray Diffraction

Minerals crystallized or re-deposited in various parts of the reaction vessels were sometimes identified by polished section study, but the majority were recognized only by their characteristic X-ray powder diffraction patterns. The graphical recording unit of the General Electric XRD-3 diffractometer greatly facilitated the study of patterns from these multi-mineralic fractions.

Graphical powder patterns of the several common minerals used or expected to appear in these experiments were run in order to eliminate these minerals, by direct comparison, from the patterns of the X-ray mounts. The 2θ values of unidentified peaks on any graph were then checked against the ASTM tables for identification of unknown minerals. A typical graph sheet containing the diffraction patterns of several mounts appears in Figure 13. Tables 15 to 26 give the lists of minerals detected in the X-ray mounts from the open system experiments.

The X-ray method was fast and normally effective, but occasionally the identification of unknown minerals was difficult or impossible. In some instances the X-ray pattern was weak because the mineral was either poorly crystallized or present only in minor amounts. In other instances the X-ray pattern was masked by patterns of more abundant minerals. Such a situation existed, for example, when X-ray fluorescence revealed that copper was abundant but no copper mineral was identified from the diffraction pattern.

RESULTS OF EXPERIMENTS

Grouping of Experiments

The main purpose of this research was to produce data from which a study could be made of the relative ability of different materials to mobilize or transport sulphide minerals. The experiments can be divided into four groups according to the environmental or physical conditions used. The divisions and corresponding experiments are as follows:

1. Hydrothermal Experiments - Low Sulphur Environments
   Experiments A to I, inclusive.
2. Hydrothermal Experiments - Excess Sulphur Environments
   Experiments J, K, L, P and V.
3. Non-Aqueous, Low Pressure Experiments - Excess Sulphur Environments
   Experiments M,W, and U series.
4. Differential Pressure Experiments - Aqueous Environments
   Experiments N, O, Q, R, S and T.

The hydrothermal experiments include those in which water was the main agent of transport; the system was usually open and subjected to high pressure. The low-sulphur group includes experiments in which no sulphur was added to the system. The excess sulphur group includes those experiments in which sulphur in one form or another was introduced so that the proportions of sulphur or sulphur compounds in the bomb atmosphere would exceed the probable equilibrium proportions for the sulphides alone. At the temperatures and pressures used, water existed as a vapour whose density for the high pressure experiments ranged from 0.32 to 0.39 g/cc.

The low-pressure experiments were made to test the degree of mobilization of sulphides in atmospheres containing little or no water, but abundant sulphur. The differential pressure experiments were conducted to test the ability of experimental materials to move readily by physical deformation when a positive, directive force was applied.

An outline of the experiments is included in the Appendix for immediate reference. All the physical and chemical conditions of each experiment are given. In the following paragraphs the conditions and results of each experiment are described briefly.

Hydrothermal Experiments - Low Sulphur Environments

Chemical and X-ray analyses of the products of these experiments are given in Table 11 and Tables 12 to 19 inclusive. Table 11 lists chemical analyses of discharge liquids and weight losses of 'primary' copper sulphides. Tables 12 to 19 list X-ray, chemical, and mineralogical data obtained from different sections of the pressure vessels.

EXPERIMENT A

Purpose:	To test solubility of chalcocite and its degree of mobilization in pure water, and to examine features of solid state diffusion which might occur between pyrrhotite and chalcocite.

TABLE 11

TABLE 11

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

Weight Loss of Primary Sulphide and Discharge Liquids Analyses

Expt.	Wt. Loss Cu Sulphide from B.1 (Percent)	Time Run (hrs.)	Volume Liquid Collected (ml.)	pH of Soln.	Copper in Solution (mg./l)	Sulphur Compounds Present H_2O (mg./l)	 SO_2 (mg./l)	 SO_3 (mg./l)	 S_2O_3 (mg./l)	Remarks, Other Ions in Soln.
					LOW SULPHUR ENVIRONMENT					
A	—	14	Nil	—	—	—	—	—	—	Closed System
B	0.05	48	1250	8.2	$1.0(10)^{-7}$	10	14	27	50	Fe Abundant
C	0.3	72	1250	8.7	$1.0(10)^{-7}$	5	22	39	200	Fe, SiO_2
D	0.07	10	150	7.8	$4.0(10)^{-7}$	Trace	18	44	100	Fe
E	1.4	5	80	9.2	$1.0(10)^{-6}$	Not Detected	4	9	Not Detected	Fe, $CaCl_2$
F	0.8	48	850	8.5	$1.4(10)^{-7}$	13	21	25	32	Fe
G	0.3	15	110	8.3	$1.2(10)^{-7}$	3	2	3	5	Fe
H	0.8	26	900	8.2	$2.5(10)^{-7}$	60	8	7	25	Fe
I	(Bornite) 7.2	10.5	220	8.1	$5.0(10)^{-7}$	120	17	40	Not Detected	Fe, Cr, Mn
					EXCESS SULPHUR ENVIRONMENT					
J	—	3	Nil	—	—	—	—	—	—	No liquid passed
K	(Gain) 3.3	6	24	7.9	$1.5(10)^{-7}$	Present	4	12	Not Detected	Fe
L	(Gain) 2.8	96	10	8.2	$1.8(10)^{-7}$	Present	8	20	10	Fe
P	2.4	12	200	12.2	$5.0(10)^{-7}$	Present	Not Tested	Present	Not Tested	Co, Cr, Ni, Fe, Mn
V	(Bn, Cc) 0.7	27	100	8.1	$2.0(10)^{-7}$	Present	5	50	20	Fe

Materials and Conditions:

Chalcocite[1] and pyrrhotite grains in contact in high temperature 'primary' vessel ; peridotite in low temperature 'depositional' vessel
Environment: Distilled water
Temperatures: B.1[2] = 510°C; B.2[3] = 210-160°C[4]
Pressure: 15,000 psi. Time run: 14 hours
No liquid collected

Results:

A leak developed in the low temperature vessel and the system was closed, but the run was continued to examine any diffusion products which might form in the primary vessel.

The chalcocite fragments had remained angular, and had altered only slightly during the run. Some minute crystals later identified as chalcocite had developed locally on corners and faces of the original chalcocite. A dark tarnish covered some grains. All grains had recrystallized; on their irregular surfaces, minute crystal faces had developed which were crystallographically oriented over diameters of 1 to 2 millimeters. At the contact between pyrrhotite and chalcocite the chalcocite grains usually were attached to pyrrhotite grains and to each other. The pyrrhotite grains were blackened but otherwise unchanged.

Polished section study revealed that chalcopyrite and bornite had formed where chalcocite and pyrrhotite grains

[1] All natural chalcocite used contained minor bornite, pyrite, and quartz.
[2] Hereinafter termed 'B.1'.
[3] Hereinafter termed 'B.2'.
[4] High temperature at entry end, low temperature at exit end.

were in contact. The originally isotropic chalcocite had become a mosaic of slightly anisotropic chalcocite grains.

EXPERIMENT B

Purpose: To test chalcocite mobilization as in Experiment A, and to examine the effect of different materials in precipitating copper sulphides.

Materials and Conditions:
B.1: Chalcocite at entry end, pyrrhotite grains in contact at exit end
B.2: Peridotite nearest entry; pyrrhotite in center; peridotite at exit
Environment: Distilled water
Temperatures: B.1 = 520°C; B.2 = 200-160°C
Pressure: 16,500 psi. Time run: 48 hours
Volume of liquid collected: 1250 ml.

Results:

Bomb 1. The chalcocite grains in the primary vessel presented the same features of tarnishing, recrystallization, local cohesion, and scattered growth of fine surface crystals as had been observed in experiment A. In the pyrrhotite zone, however, an abundance of fine black crystals had developed on the surface of the grains and on the bomb stem at the exit end. A few unidentified yellow crystals were also scattered on the surface of the bomb stem. The analyses of fractions selected from various parts of the system (Table 12) revealed that magnetite had formed in the pyrrhotite zone, and that copper had been deposited as chalcopyrite and bornite at the exit end of the vessel. There was a loss of 0.01 gram (0.05%) of chalcocite from the primary vessel.

Polished section studies of chalcocite and pyrrhotite grains which were in contact revealed that bornite and chalcopyrite had formed along the common boundary (Figure 14). These minerals could only have been produced by solid state diffusion of copper

Figure 14

Experiment B (20 X)

Diffusion of iron and copper at boundary of chalcocite (Cc) and pyrrhotite (Pr) grains, producing mixed phases of chalcopyrite (Cp) and bornite (Bn), and iron-rich chalcocite

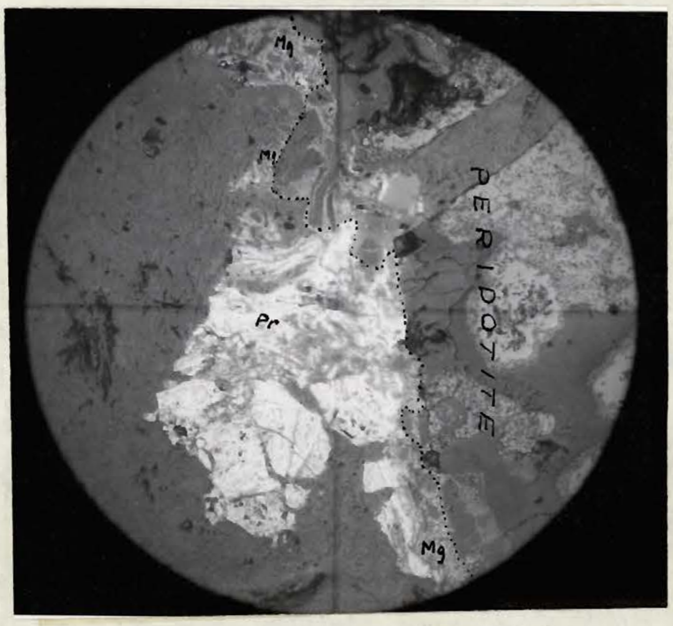


Figure 15

Experiment B (90 X)

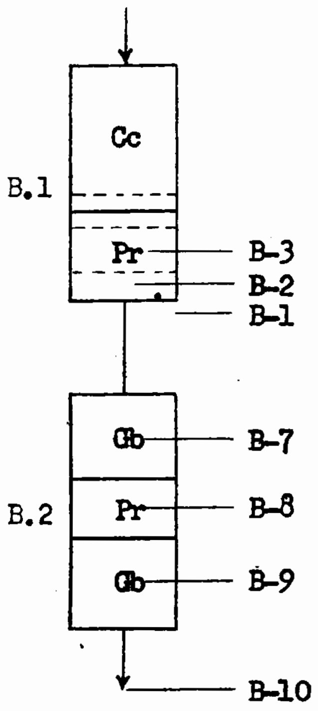
Deposition of pyrrhotite (white) and magnetite (speckled) on irregular surface of peridotite grain.

TABLE 12

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT B

Distribution of Materials within Bombs — Positions of X-Ray Mounts



Mount	X-Ray Fluorescence Counts per Second			Copper Analyses (mg)		X-Ray Diffraction
	CuK_β	CuK_α	FeK_α	X-Ray	Chemical	Minerals Detected
B-3	44	190	12,050	0.08	—	Mg, Pr
B-2	108	520	13,250	0.30	—	Mg, Pr, Cp
[1]B-1	1520	9200	1950	4.0	—	Bn
B-7	34	120	7840	0.05	—	Mg
B-8	43	170	8460	0.07	0.08	Pr
B-9	51	220	7290	0.10	—	Mg
B-10	39	140	560	0.05	0.03	Sulphur

Symbols

Minerals : See Table No. 24

B-x : X-ray Mount

Remarks

[1] Black crystals on stem base.

Loss of chalcocite from B.1: 0.05%.

Apparent solubility of Cu_2S: $2.1(10)^{-4}$ gm/l.

and iron from their respective minerals.

Bomb 2. Peridotite fragments and pyrrhotite grains in the secondary vessel appeared to be unaltered, and only a thin coating of fine crystals had been deposited on the entry end peridotite; polished section study (Figure 15) and X-ray analysis (Table 12) revealed that the coating contained magnetite and pyrrhotite. The analyses showed no significant increase of copper through the vessel.

The liquid recovered was yellowish and contained abundant H_2S. A dark grey precipitate which settled out slowly was later identified as sulphur. Analysis of the liquid (Table 11) showed a copper concentration of less than 0.1 mg. per litre. Sulphite, sulphate, and thiosulphate ions were detected at the time of analysis. The discharge precipitate contained only 0.03 mg. of copper.

X-ray fluorescence analyses of fractions selected from the vessels (Table 12) showed that little copper had moved into or through the second vessel, although the copper content of the lower peridotite section was higher than normal (see Table 24).

EXPERIMENT C

Purpose:	To test chalcocite mobilization in a distilled water environment, particularly in the pyrrhotite zone in the primary vessel.	
Materials and Conditions:	B.1:	Chalcocite at entry end, separated from pyrrhotite grains at exit end by an alundum filter.
	B.2:	Peridotite, pyrrhotite, and calcite layers, successively from entry end

Environment: Distilled water
Temperatures: B.1 = 620°C; B.2 = 200-140°C
Pressure: 16,000 psi. Time run: 72 hours
Volume of liquid collected: 1250 ml.

Results:

<u>Bomb 1.</u> Chalcocite grains presented the same general appearance as in experiments A and B; however, a greater abundance of new, fine, black crystals had developed on points and faces of original grains, and the grains were often cemented loosely to one another. Polished section study showed the cementing material to be chalcocite (See Experiment D). Pyrrhotite grains were tarnished as previously, and adhered together near the exit end of the vessel, where an abundant growth of fine, black crystals had taken place. Black specks had appeared on the remnants of the filter, which had largely decomposed. There was a weight loss of 0.05 gram (0.3%) of chalcocite from the chalcocite section.

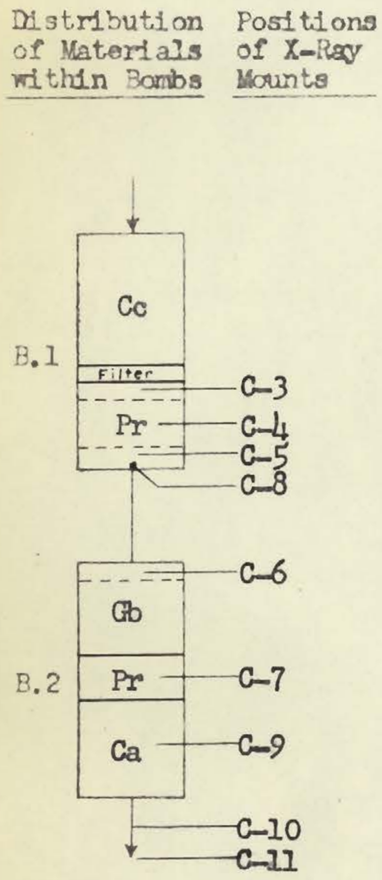
<u>Bomb 2.</u> Surfaces of fragments of peridotite at the entry end were slightly stained and lightly coated with dark, loose, scale and powder, most of which was magnetic. Both magnetite and pyrrhotite had been deposited (Table 13). The pyrrhotite grains lower in the vessel were stained irridescent on some surfaces, but no deposition had occurred. The calcite fragments had been corroded, and only one-half of the original remained.

The discharge liquid was again yellow, contained abundant H_2S, and deposited a grey-black precipitate. Analyses (Table 11) revealed a copper concentration of less than 0.1 mg. per litre. Sulphite, sulphate, and thiosulphate ions were present at the time of analysis. The discharge precipitate contained 0.06 mg. of copper.

TABLE 13

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT C



Mount	X-Ray Fluorescence Counts per Second CuK_β	CuK_α	FeK_α	Copper Analyses (mg) X-Ray	Chemical	X-Ray Diffraction Minerals Detected
C-3	53	248	17,000	0.10	- -	Mg
C-4	43	205	18,100	0.06	- -	Mg, Pr
[1]C-5	121	665	19,900	0.34	- -	Mg, Pr, Cp
C-6	88	470	7,490	0.20	0.14	Mg, Pr, Cp
C-7	51	240	15,300	0.10	- -	Pr
C-9	43	195	11,000	0.07	- -	Mg, Pr
C-10	41	170	180	0.05	0.04	Ca
[2]C-11	49	210	7,300	0.08	0.06	Indeterm.
[3]C-8	1660	9,940	7,400	5.0	- -	Mg, Bn

Remarks

[1] Contaminated by Cu from sealing washer.

[2] Blowout material.

[3] Fine, black crystals on stem base.

Loss of chalcocite from B.1: 0.3%.

Apparent solubility of Cu_2S: $2.8(10)^{-4}$ gm/l.

Symbols

Minerals : See Table No. 24

C-x : X-ray Mount

Table 13 shows the analyses of mineral fractions extracted from the vessels. It appears that copper had again moved through the pyrrhotite zone, as in experiment B, and deposited at the exit of the primary vessel. A copper concentration higher than normal was found at the entry end of the low temperature vessel, indicating that there had been some movement of copper through the connecting line.

EXPERIMENT D

Purpose:	To test the ability of salt solutions to mobilize chalcocite, and to study further the movement of copper in the primary vessel.
Materials and Conditions:	B.1: Chalcocite and pyrrhotite separated by alundum filter; pyrite in contact with pyrrhotite at exit end B.2: Calcite at entry end, followed by pyrrhotite and peridotite layers Environment: Artifical sea water, less sulphate Temperatures: B.1 = 620°C; B.2 = 200-140°C Pressure: 16,000 psi. Time run: 10 hours Volume of liquid collected: 150 ml.

Results:

Constant blocking of lines caused much difficulty in keeping the flow steady. Temperatures and pressures were maintained for 48 hours, of which time only 10 hours of flow was realized.

Bomb 1. The chalcocite grains remained angular, and were recrystallized as in previous experiments, but were coated more thickly with powder and fine, dark crystals. In the vicinity of the filter recognizable prismatic and octahedral forms had developed; these crystals often coalesced and attached adjacent chalcocite

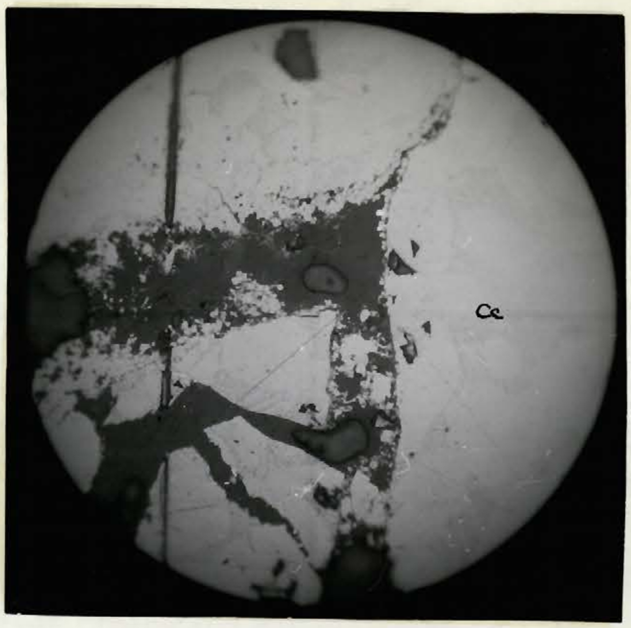


Figure 16

Experiment D (65 X)

Development of secondary chalcocite crystals and masses on surfaces of original chalcocite grains.

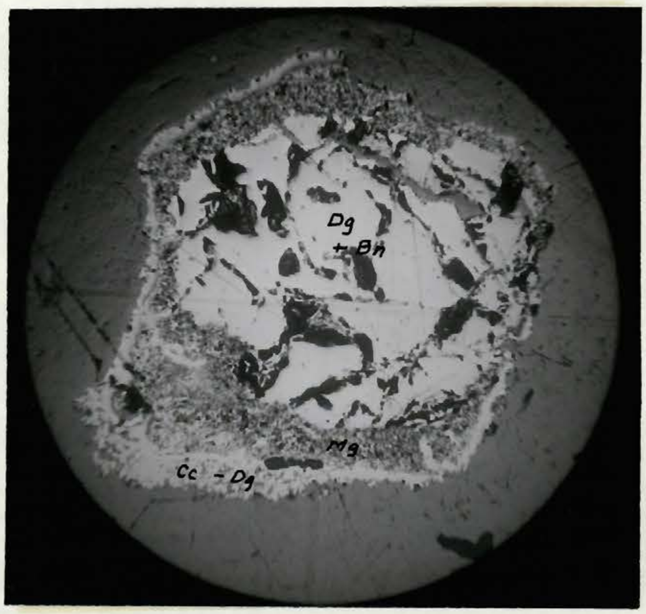


Figure 17

Experiment D (20 X)

Total replacement of pyrrhotite grain. Rim: Chalcocite (Cc) and digenite (Dg). Inner Band: Magnetite (Mg) and digenite. Core: Digenite, and bornite (Bn) of varying iron content. Native copper is present in veinlets and minute masses.

grains to each other, and occasionally rounded the edges of grains. Polished section study (Figure 16) showed them to be chalcocite. Magnetite was also present. At the filter much coalescence of these surface crystals had taken place, and small masses of newly-formed chalcocite penetrated the filter. In one area a mass of chalcocite had grown out from the chalcocite grains and around the edge of the filter, assuming the contour of the vessel. Where it contacted pyrrhotite grains on the downstream side, these had been either converted to chalcopyrite and bornite or had been replaced by an intimate mixture of digenite and bornite (Figures 17 and 18). Native copper was also present in minute masses and veinlets. Magnetite which had formed previously on the other pyrrhotite surface had not been replaced. The loss of chalcocite was 0.01 gram, or 0.07% by weight of the original chalcocite.

Pyrrhotite grains in the vessel had been blackened and were coated abundantly with fine magnetite crystals; the grain forms remained angular. Polished section study revealed that much of the pyrrhotite had been converted to magnetite. The pyrite had been completely converted to columnar pyrrhotite and magnetite (Figure 19).

On the face of the bomb stem at the exit end of the vessel much deposition had taken place. Minute crystals of native copper appeared on the outer rim, succeeded by bornite and then chalcopyrite (Table 14) toward the exit hole. It was evident from this depositional series that copper had migrated not from the chalcocite zone, but from the copper sealing washer 1/2 inch higher on the bomb stem. The concentration of copper at the same place in experiments B and C is likewise explained.

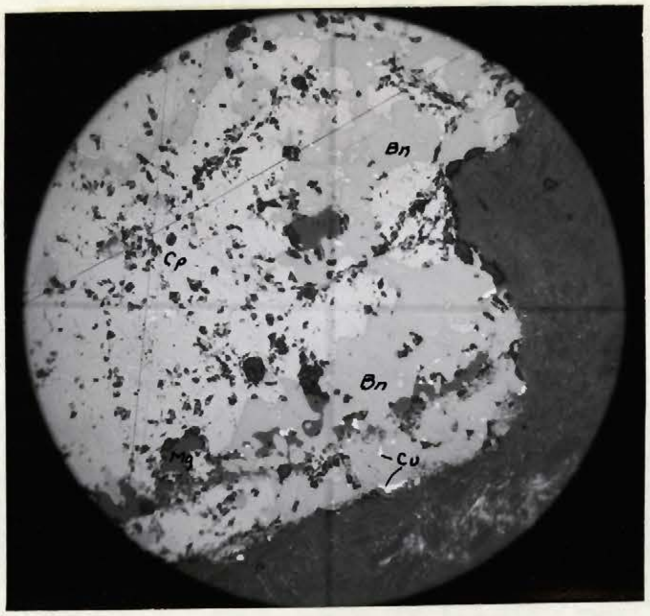


Figure 18

Experiment D (20 X)

Partial replacement of pyrrhotite grain, first by magnetite (Mg) and later by chalcopyrite (Cp) and bornite (Bn). Late native copper (Cu) is also present.

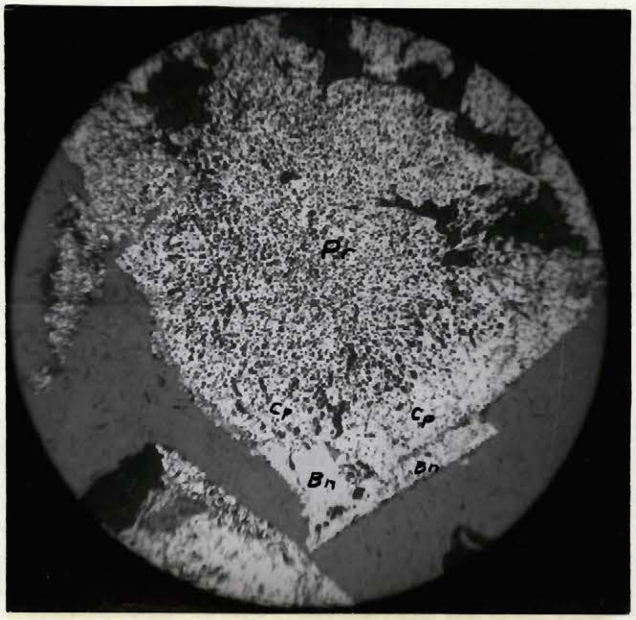


Figure 19

Experiment D (20 X)

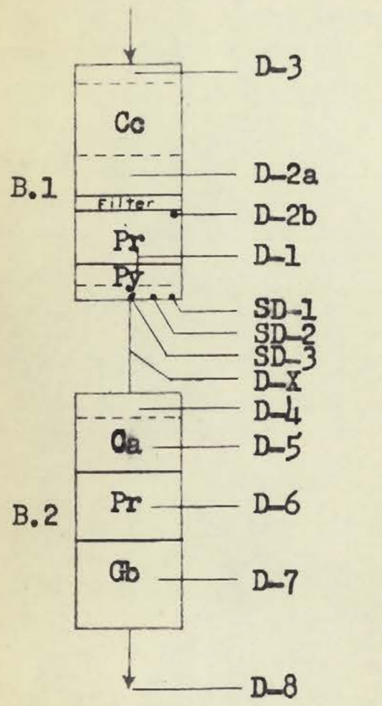
Cellular texture of pyrrhotite (Pr) after pyrite, and subsequent replacement of chalcopyrite (Cp) and bornite (Bn) adjacent to bomb stem (straight edge).

TABLE 14

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT D

Distribution of Materials within Bombs | Positions of X-Ray Mounts



Mount	X-Ray Fluorescence Counts per Second			Copper Analyses (mg)		X-Ray Diffraction
	CuKβ	CuKα	FeKα	X-Ray	Chemical	Minerals Detected
D-3	395	2570	440	1.2	- -	Bn
D-2a	1930	11,300	1640	5.0	- -	Bn
D-2b	2230	12,100	935	5.8	- -	Cc, Bn
D-1	47	225	14,500	0.09	- -	Pr, Mg
[1] SD-1	1050	6050	7250	3.0	- -	Bn, Pr, Cu
SD-2	820	4650	10,300	2.8	- -	Cp, Mg
SD-3	99	540	17,800	0.26	- -	Mg, Pr, Cp
D-X	37	150	10,700	0.05	- -	Pr, Mg
D-4	31	110	13,200	0.04	- -	Pr
D-5	36	155	9,700	0.05	- -	Py, Pr
D-6	59	290	9,600	0.12	- -	Pr
D-7	58	280	7,550	0.12	0.10	Pr
D-8	66	340	880	0.15	0.05	Sulphur

Symbols

Minerals : See Table No. 24

D-x : X-ray Mount

Remarks

[1] SD 1-3: Crystals on stem base.

Loss of chalcocite from B.1: 0.07%

Apparent solubility of Cu_2S: $2.4(10)^{-3}$ gm/l.

Bomb 2. The calcite fragments at the entry end of the secondary pressure vessel had been little affected, and were coated with a light-coloured material and abundant fine yellowish crystals (Figure 20). X-ray diffraction revealed that pyrrhotite was present near the entry, succeeded partly by pyrite lower in the calcite section. The pyrrhotite and peridotite grains remained unchanged, and little or no deposition had taken place on them.

The discharge liquid was clear after and an abundant tan-coloured sediment had settled out. Only traces of H_2S were detected by the lead nitrate test. Sulphite, sulphate, and thiosulphate ions were present (Table 11). Analysis for copper showed a concentration of 0.40 mg. per litre. The discharge residue contained 0.05 mg. of copper.

Analyses of fractions selected from the vessels (Table 14) showed that copper had not moved far, in appreciable quantity, from its original site. Migration around the filter was restricted to less than 1/4 inch, and terminated at pyrrhotite grains. The movement from the copper washer along the stem was almost 1/2 inch. It appears, however, that more copper was carried in solution than in previous experiments, for the concentration increased in successively lower fractions of the secondary vessel. The concentration of copper in the discharge residue was no higher than in previous experiments. If the total amount of copper deposited in the secondary vessel, pipes, and discharge residue had been transported in solution, the approximate solubility of chalcocite at 620°C in this sea water would be $2.4(10)^{-3}$

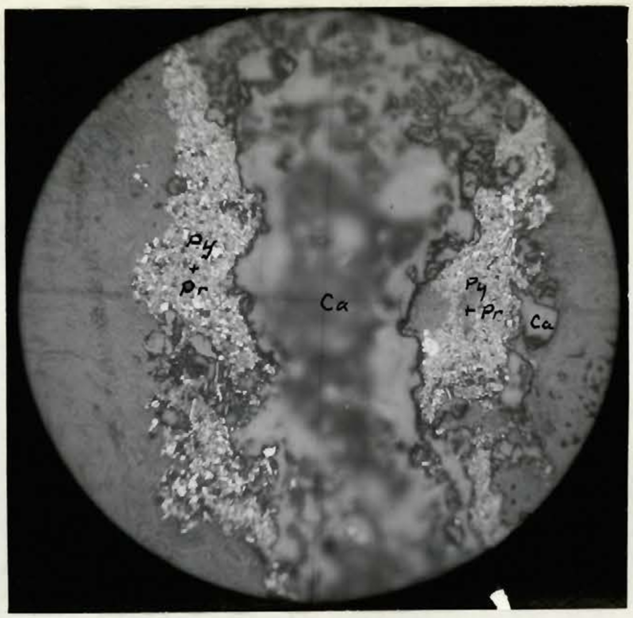


Figure 20

Experiment D (90 X)

Deposition of pyrite and pyrrhotite (white) on disrupted surfaces of calcite (Ca) grain.

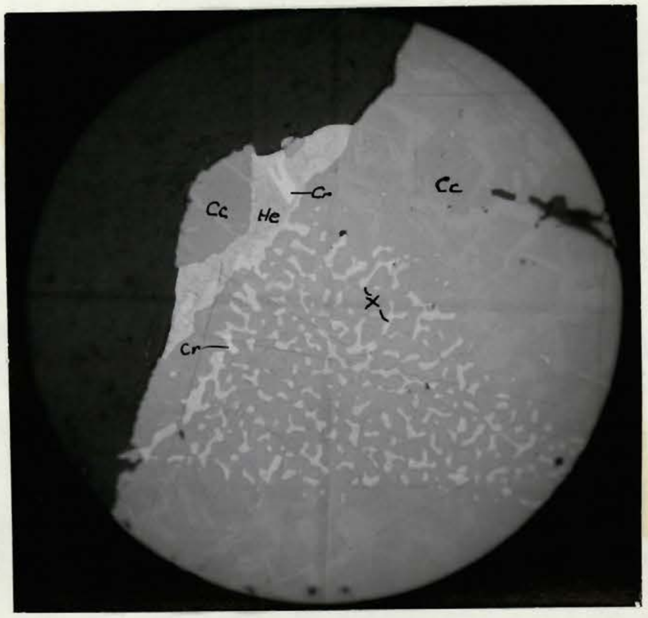


Figure 21

Experiment E (65 X)

Unusual cone structure suggesting expulsion of hessite (He), carrollite (Cr), and an unknown mineral (X) from recrystallized chalcocite (Cc), forming a nodule on the surface.

gram per litre.

EXPERIMENT E

Purpose:	To test the degree of mobilization and solubility of chalcocite in chloride solutions.
Materials and Conditions:	B.1: Chalcocite alone; alundum filter at exit B.2: Diabase at entry end, followed by calcite at exit end Environment: 1.0 N solution of NH_4Cl Temperatures: B.1 = 550°C; B.2 = 220-150°C and 350-250°C Pressure: 14,400 psi. Time Run: 5 hours Volume of liquid collected: 80 ml. The primary vessel was reversed so that the stem would be at the entry end; also, nickel sealing washers were substituted for copper washers.

Results:

The lines blocked frequently because of rapid deposition of material precipitating from solution. Temperatures of the secondary vessel were increased later to 350-250°C so that volatilization of NH_4Cl might take place, but blockage continued.

Bomb 1. Chalcocite grains remained angular; occasionally some corrosion appeared to have taken place at grain edges, but elsewhere in the upper parts of the bomb small growths of fine dark crystals were observed. Minute, pinkish metallic nodules were observed on a few grains. Two minerals in the nodules were identified, with reservation, as carrollite and hessite; a third could not be identified. The distribution of the minerals suggests that they had been expelled from the lattice of the recrystallizing chalcocite (Figure 21); their original distribution in the chalcocite was unknown. A mat of fine, yellowish, elongated crystals, mixed with dark crystals, was deposited on most grains nearer the lower end of the vessel. The light-coloured crystals were tested, and proved to be chlorides. Minute masses of chalcocite had been deposited on both the upstream and downstream sides of the filter. The bomb stem (at the entry end) contained abundant black flakes and crystals, which were identified as magnetite. The weight loss of chalcocite from the vessel was 0.32 gram, or 1.4%.

A few minute flakes of native copper were observed in the powder extracted from the pipe and joint connecting the vessels.

Bomb 2. An abundance of brown powder composed chiefly of chlorides had been deposited in the bomb stem and throughout much of the upper two-thirds of the vessel. The powder was leached with dilute HCl; a dark insoluble fraction remained, which contained much magnetite (Table 15). The diabase, when washed, was noted to have occasional black unidentified spots which increased in number toward the calcite section. In the boundary zone of diabase and calcite small amounts of green copper carbonate were precipitated. Some solution of calcite had taken place, and magnetite was deposited as a black powder on the calcite grains along with the chloride mentioned earlier.

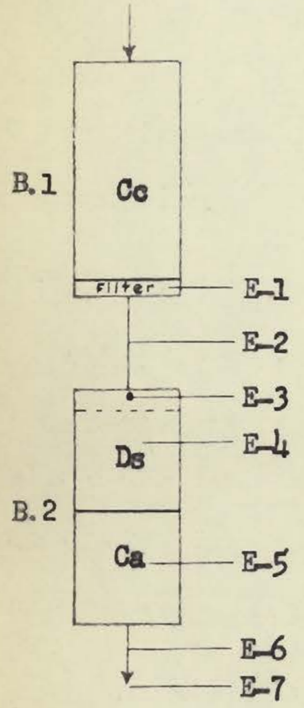
The discharge fluid was colourless after a tan-coloured sediment had settled out. Ammonia was present in abundance, but no H_2S was detected. Analysis of the fluid (Table 11) showed that minor sulphite and sulphate were present, but thiosulphate was absent. The copper content of the fluid was 1.0 mg. per litre.

TABLE 15

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT E

Distribution of Materials within Bombs   Positions of X-Ray Mounts



Mount	X-Ray Fluorescence Counts per Second CuK_{β}	 CuK_{α}	 FeK_{α}	Copper Analyses (mg) X-Ray	 Chemical	X-Ray Diffraction Minerals Detected
[1]E-1	2080	12,600	1310	5.3	- -	Cc
E-2	230	1340	16,500	0.65	- -	Mg, Cu
E-3	76	380	21,400	0.18	- -	Mg
E-4	88	510	15,300	0.12	0.15	Mg
E-5	45	200	16,500	0.08	0.14	Mg
[2]E-6	37	120	2360	0.05	0.35	Ca
[3]E-7	27	120	2500	0.03	0.04	Indeterm.

Symbols

Minerals : See Table No.24

E-x : X-ray Mount

Remarks

[1] Mineral by-passing filter.

[2] Discharge residue.

[3] Blowout material.

Loss of Cc from B.1: 1.4%

Apparent solubility of Cu_2S: $1.1(10)^{-2}$ gm/l.

The discharge residue contained 0.35 mg. of copper.

Analyses of fractions selected from the vessels (Table 15) show that copper had moved in appreciable quantities. In this experiment there had been no contamination from a copper sealing washer, hence all copper had originated in the primary vessel, and had been transported by the chloride solution. Most of the copper was deposited in the collecting flask, which suggests that it may have remained in solution in the low temperature vessel as well as in the primary vessel. By summing the amounts of copper deposited in the various sections of the vessel, an apparent solubility at 550°C of $1.1(10)^{-2}$ gram per litre of Cu_2S is obtained.

EXPERIMENT F

Purpose:	To test further the mobilization of chalcocite by pure water, and to check the effect of different materials on its deposition.
Materials and Conditions:	B.1: Chalcocite alone; alundum filter at exit B.2: Calcite at entry end, followed by pyrrhotite and diabase Environment: Distilled water Temperature: B.1 = 550°C; B.2 = 210-130°C Pressure: 15,500 psi. Time run: 48 hours Volume of liquid collected: 850 ml. NaOH solution was added to the collecting flask to reduce decomposition of H_2S in the discharge liquid.

Results:

One rapid release of pressure through the exit valve occurred midway through the experiment when blockage material suddenly released while an attempt was being made to clear the system.

Bomb 1. Recrystallization of chalcocite, retention of angular shapes of grains, and local growth of fine surface chalcocite crystals had taken place, similar to that observed in experiments A, B, and C. At the exit end of the vessel some cohesion of grains resulted from fusion by the migrating surface chalcocite. A thin coating of magnetite had been deposited on some surfaces of the grains. The alundum filter had disintegrated. The weight of chalcocite lost from the vessel was 0.19 gram, or 0.8%.

Bomb 2. The calcite at the entry end of the vessel showed the usual signs of corrosion, and its volume had decreased. Rare spots of green copper carbonate indicated that some copper had moved into the vessel and been deposited. A sooty material identified as magnetite had been deposited lightly on the grains.

The pyrrhotite grains were blackened as in previous experiments, and many were spotted with rust. Green copper carbonate spots were common on the pyrrhotite near the calcite contact. The diabase appeared to be slightly bleached and was coated in places with magnetite powder. A green copper carbonate was also present in this section.

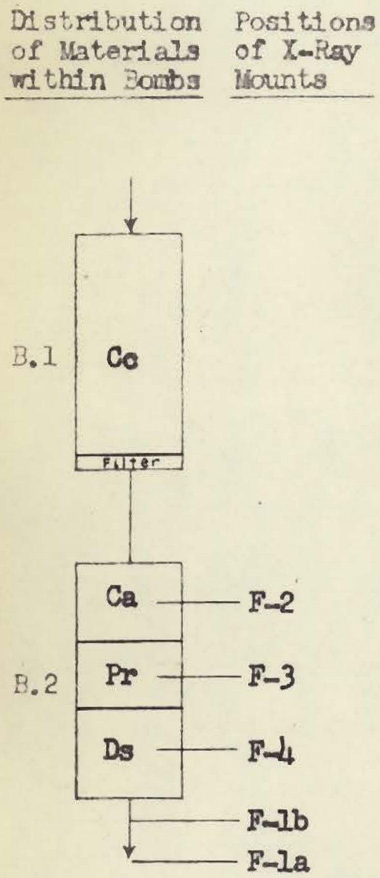
The discharge liquid was yellowish, contained abundant H_2S, and yielded a black precipitate. As in previous distilled water experiments sulphite, sulphate, and thiosulphate ions were present when the liquid was analysed (Table 11). The liquid contained 0.14 mg. of copper per litre, and the discharge residue 0.05 mg. of copper.

Analyses of fractions selected from the vessels

TABLE 16

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT F



Mount	X-Ray Fluorescence Counts per Second CuKβ	 CuKα	 FeKα	Copper Analyses (mg) X-Ray	 Chemical	X-Ray Diffraction Minerals Detected
F-2	53	230	5300	0.10	0.15	Mg
F-3	53	245	15,600	0.10	- -	Pr, Mg
F-4	76	370	10,900	0.18	0.15	Mg
[1]F-1b	33	110	310	0.04	0.05	Inderterm.
[2]F-1a	178	965	14,100	0.50	0.60	Mg

Remarks

[1] Discharge residue.

[2] Blowout material.

Loss of Cc from B.1: 0.8%

Apparent solubility of Cu_2S: $5.3(10)^{-4}$ gm/l.

Symbols

Minerals : See Table No.24

F-x : X-ray Mount

(Table 16), as well as the grain studies, showed that some movement of copper had been effected. The results must be treated with caution, however, because the blowout material contained much copper. Much of the material deposited during the first half of the run was obviously flushed out of the second vessel, and probably some of the loosely attached new crystals were dislodged from the primary vessel.

There was no clear evidence of preferential deposition of copper minerals in different sections of the second vessel. No replacement of rock minerals was detected from polished section studies. The higher concentration of copper in the diabase section could have resulted from displacement, as the calcite dissolved, of material originally deposited in the calcite section.

EXPERIMENT G

Purpose:	To check the solubility and mobility of chalcocite in pure water, and to observe the extent of decomposition of chalcocite to yield sulphur compounds.
Materials and Conditions:	B.1: Chalcocite alone; alundum filter at exit Second vessel not used Environment: Distilled water Temperature of B.1 = 550°C Pressure: 15,500 psi. Time run: 15 hours Volume of liquid collected: 350 ml. The chalcocite was carefully selected to reduce the iron content to a minimum.

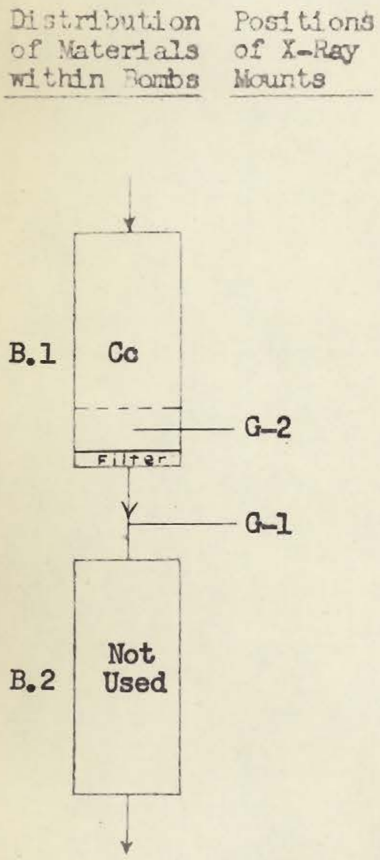
Results:

The chalcocite grains retained their conchoidal surfaces and angular shapes as in previous experiments. The grains were recrystallized as usual, and small chalcocite masses had

TABLE 17

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT G



Mount	X-Ray Fluorescence Counts per Second CuK_β	 CuK_α	 FeK_α	Copper Analyses (mg) X-Ray	 Chemical	X-Ray Diffraction Minerals Detected
G-2	3290	17,600	1950	11.0	--	Cc, Mg
[1]G-1	33	105	21,400	0.03	0.02	Indeterm.

Remarks

[1] Probably contaminated by magnetite while clearing pipes.

Loss of chalcocite from B.1: 0.34%

Apparent solubility of Cu_2S: $1.8(10)^{-4}$ gm/l.

Symbols

Minerals : See Table No.24

G-x : X-ray Mount

grown out from corners and edges to fuse occasional grains together. A black, partly magnetic deposit containing a curved, platy mineral had formed on most chalcocite grains in the lower part of the vessel. Close examination of the grains beneath the deposit revealed that the chalcocite was finely pitted. The deposit contained some magnetite, apparently derived from the inlet pipe, but it was composed chiefly of chalcocite (Table 17). The weight loss of chalcocite from the vessel was 0.08 gram, or 0.34%.

The discharge liquid was almost clear, and only a small amount of black sediment settled out. Sulphide, sulphite, sulphate, and thiosulphate ions were all present in small amounts (Table 11). The copper content of the solution was 0.12 mg. per litre. The discharge residue contained 0.02 mg. of copper.

It appears that a thin surface layer of chalcocite had been mobilized, but had re-deposited immediately as discrete crystals. No native copper was observed on the grain surfaces or in polished sections; therefore the H_2S and sulphur compounds found in the discharge liquid must have been derived largely from the break-down of small amounts of bornite and other iron sulphides not detected in the natural chalcocite.

EXPERIMENT H

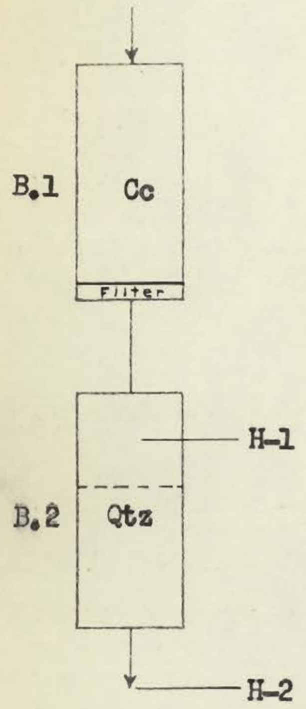
Purpose:	To check the solubility and mobility of chalcocite and to identify the minerals deposited.
Materials and Conditions:	B.1: Chalcocite alone; alundum filter at exit B.2: Quartz Environment: Tap water Temperatures: B.1 = 550°C; B.2 = 180-110°C Pressure: 15,500 psi. Time run: 26 hours Volume of liquid collected: 900 ml. NaOH solution was added to the collecting flask.

TABLE 18

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT H

Distribution of Materials within Bombs	Positions of X-Ray Mounts



Mount	X-Ray Fluorescence			Copper Analyses (mg)		X-Ray Diffraction
	Counts per Second CuK_β	CuK_α	FeK_α	X-Ray	Chemical	Minerals Detected
H-1	68	315	3150	0.16	0.05	Py, Qtz
H-2	35	120	970	0.05	—	Indeterm.

Remarks

Loss of Cc from B.1: 0.8%

Apparent solubility of Cu_2S: $1.7(10)^{-4}$ gm/l.

Symbols

Minerals : See Table No.24

H-x : X-ray Mount

Results:

Bomb 1. Fine surface crystals of chalcocite had developed on the original grains in the primary vessel, and the grains were tarnished and recrystallized as in previous experiments. A few ragged, deep pits were noted in the grains; evidently dissolution of some impurity had taken place. The loss of chalcocite from the primary vessel was 0.10 mg., or 0.84%.

Bomb 2. The white quartz in the second vessel had become clear, indicating that most vacuoles had either disappeared or had been filled, and a thin surface coating of a yellow mineral had been deposited on the grains at the entry end. The mineral was identified as pyrite (Table 18).

The discharge liquid was dark green, due probably to colloidal FeS in the strongly basic solution of the collecting vessel. A dark green amorphous precipitate settled out upon standing. The discharge solution contained H_2S and sulphite, sulphate, and thiosulphate ions (Table 11). The liquid contained 0.25 mg. of copper per litre, and the discharge residue 0.05 mg. of copper.

The natural chalcocite used in this experiment contained visible bornite and sparse pyrite, and the discharge fluid contained abundant H_2S. It is evident from a comparison of this experiment and experiment G, in which the original chalcocite contained no visible Fe-S minerals, that the production of H_2S and oxidized sulphur is dependent on the presence of iron sulphides, which decompose under these conditions. Chalcocite and magnetite are produced if the iron mineral is bornite.

EXPERIMENT I

Purpose: To test the solubility and mobility of bornite, to determine the minerals formed, and to check the degree of oxidation of sulphur released.

Materials and Conditions:
B.1: Bornite alone; alundum filter at exit
B.2: Quartz
Environment: Tap water
Temperatures: B.1 = 550°C; B.2 = 180-110°C
Pressure: 15,500 psi. Time run 10.5 hours
Volume of liquid collected: 240 ml.

$Cd(NH_3)_2Cl$ solution was placed in the collecting flask to precipitate sulphide ion in solution.

Results:

The lines blocked frequently, and the pressure was released twice while blockage material was being cleared.

Bomb 1. Bornite grains in the primary vessel were blackened, cracked extensively, and coated with a thin mat of fine black crystals, most of which were magnetite. Freshly broken surfaces of the grains were steel blue in colour. The filter had disintegrated and much of it had been carried into the second vessel. The loss of bornite from the primary vessel was 1.45 grams, or 7.2%. The majority of the bornite is considered to have been moved as small particles which broke off from the grains while flushing the lines.

Bomb 2. The quartz grains near the entry were coated with a thin layer of finely crystalline material which resembled tarnished pyrrhotite, but X-ray diffraction patterns (Table 19) showed it to be magnetite and bornite.

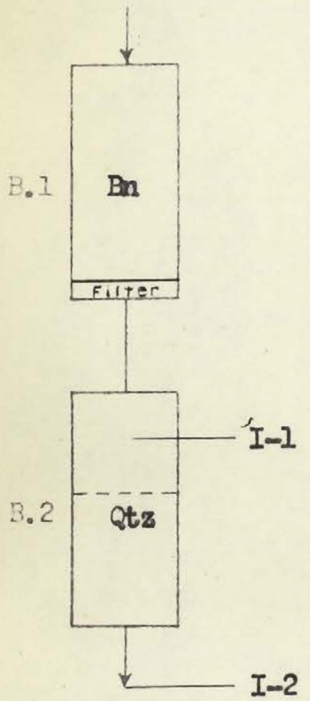
The discharge liquid was light yellow and contained

TABLE 19

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT I

Distribution of Materials within Bombs — Positions of X-Ray Mounts



Mount	X-Ray Fluorescence			Copper Analyses		X-Ray Diffraction
	Counts per Second			(mg)		Minerals Detected
	CuK_{β}	CuK_{α}	FeK_{α}	X-Ray	Chemical	
[1]I-1	490	3130	18,600	1.5	2.5	Mg, Qtz, Bn
I-2	41	130	1050	0.06	0.05	Indeterm.

Remarks

[1] Suspected contamination by bornite chipped off and carried into B.2 while clearing pipes. Filter pulverized.

Loss of Bn from B.1: 7.2%

Symbols

Minerals : See Table No.24

I-x : X-ray Mount

abundant H_2S. A dark green solution similar to that of experiment H was obtained when strong NaOH was added to a fraction of the fresh solution. Much CdS was precipitated in the collecting flask. Analysis of the decanted solution (Table 11) showed that sulphite and sulphate were present, but thiosulphate was not. The decanted solution contained 0.5 mg. of copper per litre, and the cadmium sulphide precipitate contained 0.05 mg. of copper.

Polished section study showed that the majority of the bornite grains had been greatly altered. The development of intermediate bornite-chalcocite and bornite-digenite solid solution phases had apparently taken place, and cooling had produced products which showed variations in colour from chalcocite-white through bluish-red to orange and finally to the normal bornite pinkish-brown. This colour relationship was identical to that observed in Experiment D, where chalcocite had replaced pyrrhotite. Close examination revealed that fine exsolution textures had developed occasionally between the new chalcocite formed and the bornite. The changing colours were due partly to the proportions of each mineral in a given area, and partly to change in colour of bornite as the iron, copper, and sulphur content varied. Figures 17 and 22 show the colour gradations, although indistinctly.

It is evident that some of the bornite decomposed under these conditions, yielding H_2S, magnetite, and chalcocite, as had been suggested by experiments G and H. Solid diffusion appears to have been the dominant process effecting the change.

Hydrothermal Experiments - Excess Sulphur Environments

Chemical and X-ray analyses of the products of these

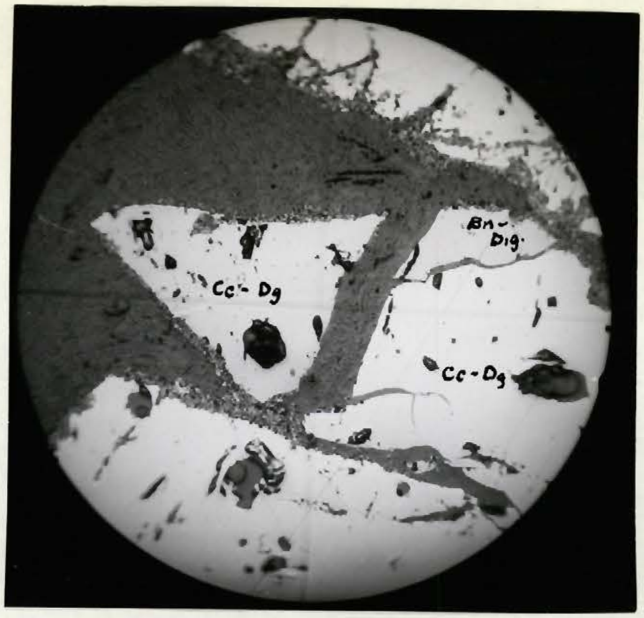


Figure 22

Experiment I (65 X)

Magnetite crystals coating original bornite grains now consisting of a chalcocite-digenite (Cc,Dg) mixture which is locally intergrown with pale bornite (Bn).

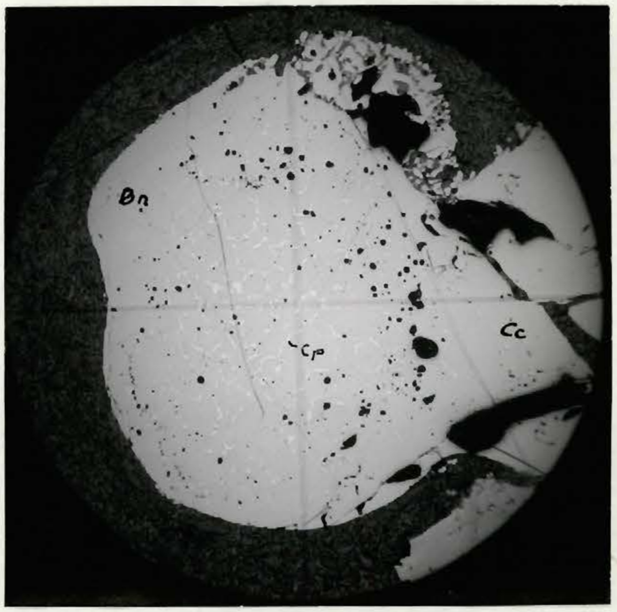


Figure 23

Experiment J (30 X)

Boxwork exsolution of chalcopyrite (white) in bornite (Bn) which is gradational into iron-rich chalcocite (Cc) on right.

experiments are given in Table 11 and Tables 20 to 24 inclusive.

EXPERIMENT J

Purpose:	To test the degree of mobilization and solubility of chalcocite in an excess sulphur hydrothermal environment.
Materials and Conditions:	B.1: Chalcocite mixed with flowers of sulphur B.2: Quartz at entry end, followed by diabase Environment: Distilled water, sulphur Temperatures: B.1 = 550°C; B.2 = 350-200°C Pressure: 15,000 psi. Time run: 3 hours Volume of liquid passed: None.

Results:

The line blocked before liquid could be passed through the system; however, the run was continued for 3 hours to examine any new products formed in the primary vessel.

Examination of the chalcocite within the primary vessel revealed that the grains were loosely attached to one another. The corners of most grains were rounded, and pronounced deposition of a new mineral as botryoidal encrustations had taken place. Small octahedral and prismatic crystals had developed upon the surfaces of the globular masses. The bomb stem at the entry end of the vessel had been deeply corroded and converted to pyrrhotite, or to copper minerals where the stem contacted the chalcocite. Fine crystals of bornite, with admixed magnetite, had developed on chalcocite grains near the stem.

Polished section study revealed that the original chalcocite grains now consisted of an intergrowth of chalcocite and digenite. Covellite partially rimmed the majority of grains, and the digenite was found in greater amounts near the covellite. Occasional bornite globules containing chalcopyrite were observed (Figure 23); these had developed by the diffusion of iron from pyrite enclosed in the original chalcocite grains.

EXPERIMENT K

Purpose: To check the degree of mobilization and test the solubility of chalcocite in a high sulphur environment. Repeat of experiment J.

Materials and Conditions:
B.1: Chalcocite mixed with flowers of sulphur
B.2: Quartz at entry end, followed by diabase
Environment: Distilled water, sulphur
Temperatures: B.1 = 550°C; B.2 = 550-450°C
Pressure: 15,000 psi. Time run: 6 hours
Volume of liquid collected: 24 ml.

Water was bled slowly through the system, at an average of one to two drops per minute. $Cd(NH_4)_2Cl$ was added to the collecting flask.

The vessels were cooled slowly in their furnaces; thirty minutes were required to lower the temperature to 300°C.

Results:

The lines blocked readily because of the slow feed, and constant attention was required.

Bomb 1. The experimental products were similar to those found in experiment J. Smooth, globular masses partly encrusted with fine prismatic and octahedral crystals had developed throughout the primary vessel. Figures 24 and 26 show some typical forms. The grains at the exit end were blue due to an abundance of covellite on the surface. At the entry end less mobilization had occurred and less covellite had developed, because sulphur was removed as water entered. Rare, small globules of bornite were observed, and

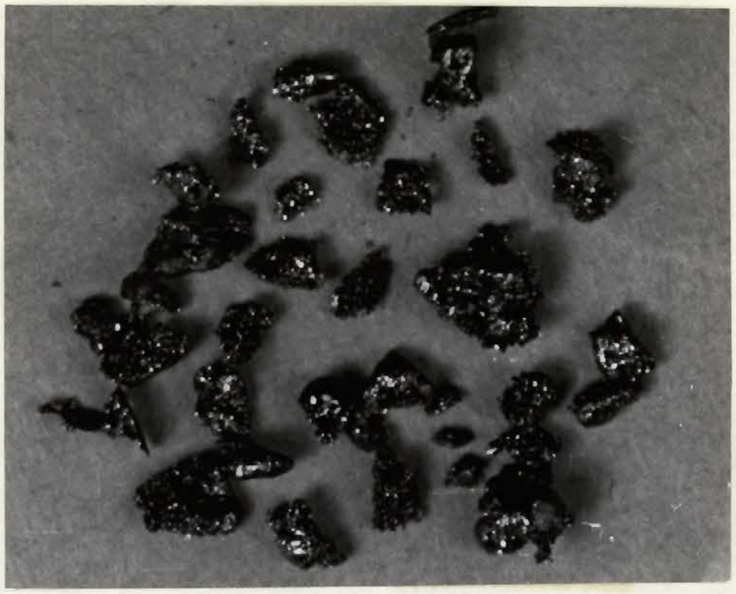


Figure 24

(3 X)

Typical rounded, smooth-surfaced masses, partly encrusted with crystals, formed when chalcocite grains are heated in high sulphur environments.

Figure 25

Experiment K (20 X)

Section showing globular grains of chalcocite (Cc) and digenite (Dg) rimmed by late replacement laths of blue covellite (Cv). Bornite (Bn) grain contains residuals of pyrite (Py) and exsolved chalcopyrite (Cpy), and is rimmed by blue and brown covellite (Cvb). The latter is found only where iron is present.

a little free sulphur was present near the exit end of the vessel. The bomb stem had been corroded and altered to pyrrhotite, pyrite, and chalcopyrite. The weight of the products exceeded the weight of original chalcocite by 0.75 gram (3.3%).

Polished section study of the grains removed from the vessel revealed that they consisted largely of an intergrowth of chalcocite and digenite, as in experiment J. Covellite laths rimmed the majority of grains, including bornite grains. In the latter case, however, an unusual brown covellite was also observed. This synthetic mineral appears to be associated only with an iron-rich host; it appears to be a distinct mineral species having a composition between CuS and Cu_5FeS_4. Figure 25 shows the various mineral relationships.

<u>Bomb 2.</u> The stem of the second vessel was corroded and altered to magnetite, pyrrhotite, and pyrite. Multitudes of fine hairlike crystals had grown on both quartz and diabase; X-ray analyses revealed that they were pyrite. Sulphur was scattered throughout the vessel.

The discharge liquid was light yellow and contained H_2S, which was removed with $Cd(NH_4)_2Cl$ in the collecting flask. Analyses of the liquid (Table 11) revealed the presence of sulphite and sulphate ions, but thiosulphate was not detected. The liquid contained 0.15 mg. of copper per litre, and the cadmium sulphide precipitate 0.06 mg. of copper.

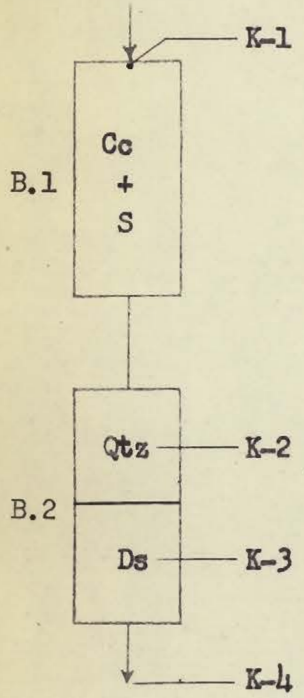
Analyses of fractions from the second vessel (Table 20) indicated, by comparison, that greater amounts of copper had been transported by the sulphur-rich solutions than by distilled water.

TABLE 20

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT K

Distribution of Materials within Bombs	Positions of X-Ray Mounts



Mount	X-Ray Fluorescence Counts per Second CuK_β	CuK_α	FeK_α	Copper Analyses (mg) X-Ray	Chemical	X-Ray Diffraction Minerals Detected
K-1	425	2510	2750	1.2	—	Pr, Py, Cpy
K-2	93	470	7300	0.24	0.40	Py, Qtz
K-3	75	355	7020	0.18	0.25	Py
K-4	41	270	5120	0.06	—	Py

Remarks

Gain in weight of sulphide in B.1: 0.75 gm. (3.3%)

Apparent solubility of Cu_2S: $2.9(10)^{-2}$ gm/l.

Symbols

Minerals : See Table No.24

K -x : X-ray Mount

Summation of the weights of copper deposited in the lower parts of the system gives a Cu_2S solubility of $2.9(10)^{-2}$ gram per litre, assuming the copper to have been transported in solution.

EXPERIMENT L

Purpose:	To check the degree of mobilization and solubility of chalcocite in an excess sulphur environment; to further check production of oxidized sulphur compounds; and to attempt replacing rock minerals.
Materials and Conditions:	B.1: Chalcocite at entry end in direct contact with peridotite at exit end; flowers of sulphur packed into interstices B.2: Quartz at entry end, peridotite at exit end Environment: Distilled water, sulphur Temperatures: B.1 = 550°C; B.2 = 300-190°C Pressure: 15,000 psi. Time run: 96 hours Volume of liquid collected: 10 ml. Approximately 1 cc. of water was released from the system every 5-10 hours. No sulphur fixing agent was added to the collecting flask. The vessels were cooled rapidly in air; the temperature of B.1 dropped to 250°C in five minutes.

Results:

Bomb 1. The products in the chalcocite section of the primary vessel were similar to those observed in experiments J and K. Magnetite, pyrrhotite, pyrite, chalcopyrite, and bornite had developed on the bomb stem. The chalcocite grains had totally lost their angular shapes and become glassy-surfaced globules and masses; obviously the copper sulphide had been in a highly mobile state, for it had the appearance of solidified slag. Many of the smooth surfaces were coated with well-developed octahedra and a few prisms (Figures 24 and 26), the crystals being somewhat larger near the entry end. The grains were often attached together by short necks of the mobilized copper sulphide. Covellite was rare, unlike in the

Figure 26

Experiment L (8 X)

Typical development of octahedra of chalcocite and digenite, formed in open spaces in excess sulphur experiments. All crystals grew from smooth-surfaced chalcocite masses having the appearance of solidified slag.

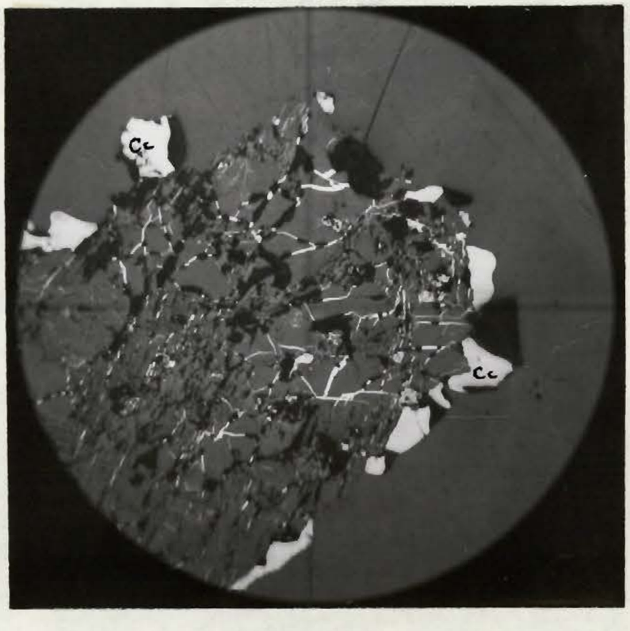


Figure 27

Experiment L (30 X)

Deposition of chalcocite (Cc) as shapeless masses and crystals on surface of peridotite grain, and penetration into grain along fractures and grain boundaries.

two previous experiments. The weight of the products exceeded the weight of original chalcocite by 0.22 gram (2.8%).

Polished section study revealed mineral assemblages similar to those observed in the two previous experiments, with the exception that covellite was present only in small amounts. The major phase was chalcocite; digenite was present in lesser amounts than previously.

The peridotite grains appeared unaltered on the surface. Some deposition of fine, black crystals, most of which were magnetite, had taken place. At the chalcocite boundary zone, however, a few grains were partially coated with chalcocite 'slag' and crystals which had migrated from the chalcocite section. A polished section of the grains showed that chalcocite had been deposited on the surface of the peridotite and had penetrated into the peridotite along fractures and minute intergranular fissures (Figure 27). No extensive replacement of rock minerals was observed; however, chalcopyrite and bornite were produced occasionally when the migrant chalcocite encountered magnetite.

<u>Bomb 2.</u> The quartz grains had become clear, but otherwise were unchanged. A brown crystalline coating on the quartz consisted largely of pyrrhotite. The peridotite grains likewise were unaltered and were coated with lesser amounts of new pyrrhotite.

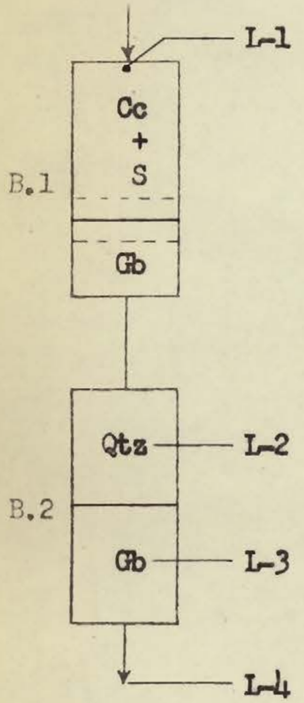
The discharge liquid was the usual light amber colour and contained H_2S; small amounts of grey-black precipitate settled out upon standing. Analyses of the liquid showed the presence of sulphite, sulphate, and thiosulphate (Table 11). It is apparent that unless the reactions are prevented by removal of sulphide ion, H_2S oxidizes readily to produce thiosulphate and other oxygen-sulphur

TABLE 21

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT L

Distribution of Materials within Bombs | Positions of X-Ray Mounts



Mount	X-Ray Fluorescence			Copper Analyses		X-Ray Diffraction
	Counts per Second			(mg)		Minerals Detected
	CuK$_\beta$	CuK$_\alpha$	FeK$_\alpha$	X-Ray	Chemical	
L-1	1660	9900	14,550	4.4	—	Cpy
L-2	90	465	19,800	0.23	—	Pr
L-3	62	350	15,500	0.14	—	Pr
L-4	48	310	9800	0.09	—	Indeterm.

Symbols

Minerals : See Table No. 24

L-x : X-ray Mount

Remarks

Gain in weight of sulphide in B.1: 0.22 gram (2.8%)

Apparent solubility of Cu_2S: $4.6(10)^{-2}$ gm/l.

compounds. The copper content of the liquid was 0.19 mg. per litre; the discharge precipitate yielded 0.09 mg. of copper.

Analyses of fractions selected from the vessels (Table 21) showed that copper had been deposited in the secondary vessel in amounts similar to those found in experiment K. If the total amount of copper found in the second vessel and discharge materials had been transported in solution, the approximate solubility of chalcocite at 550°C in this environment would be $4.6(10)^{-2}$ gram per litre.

EXPERIMENT P

Purpose:	To test the mobilization and degree of solubility of chalcocite in sodium sulphide solution.
Materials and Conditions:	B.1: Chalcocite alone B.2: Calcite at entry end, followed by peridotite; pyrrhotite at exit end. Environment: 1.0 M solution of Na_2S Temperatures: B.1 = 550°C; B.2 = 285-230°C Pressure: 14,400 psi. Time run: 12 hours Volume of liquid collected: 200 ml.

Results:

The run was stopped once because of total blockage of the exit line. Two valves were placed in series to permit clearance of lines without losing pressure from a sudden release of blockage material.

Bomb 1. Intense corrosion of the primary vessel had taken place; a thickness of approximately one millimetre had been converted to linnaeite and other metal sulphides. The chalcocite grains had fused together completely into a somewhat porous, impermeable cylinder which was removed by boring out the friable alteration products of the vessel with a thin saw-toothed tube (Figure 5, No. 5). The weight of chalcocite lost from the vessel was 0.57 gram, or 2.4%.

Examination of the chalcocite product in polished section showed that the mass consisted largely of digenite and lesser exsolved chalcocite. Some areas were pale bluish-red to bornite-pink, indicating that iron from contained bornite and pyrite had dispersed in the chalcocite to produce the intermediate sulphide phases described earlier. Minute specks of pyrite were scattered throughout the entire mass; they were for the most part randomly distributed, but occasionally outlined original surfaces of chalcocite grains. No reaction had taken place between chalcocite and the alteration products of the vessel.

Evidently the chalcocite had been mobilized readily by the Na_2S solution, and the grains had fused together rapidly. The solution could pass through the friable vessel products that were forming, and as the intergranular central passages were closed the external pressure compacted the mass.

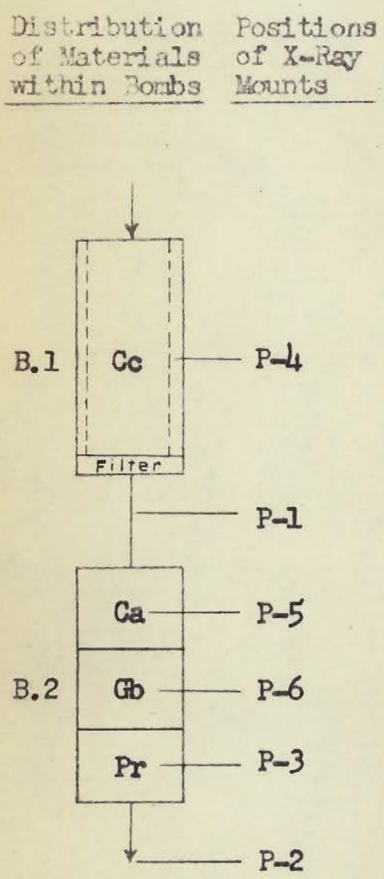
Bomb 2. The calcite grains had remained angular, and little dissolution of them had taken place. A dark brown coating had been deposited on the surfaces, and minute yellow and black crystal faces could be discerned throughout the coating. The peridotite grains were apparently unchanged and had a thin coating similar to that on the calcite. The pyrrhotite had been tarnished, and occasionally grains were coated locally with a black deposit.

The discharge liquid was light green. Qualitative analyses showed that cobalt, nickel, chromium and iron were present

TABLE 22

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT P



Mount	X-Ray Fluorescence Counts per Second			Copper Analyses (mg)		X-Ray Diffraction
	CuK_β	CuK_α	FeK_α	X-Ray	Chemical	Minerals Detected
P-4	150	930	1880	0.42	—	Bn, Linnaite
P-1	86	430	7550	0.21	0.12	Indeterm.
P-5	440	2660	7900	1.25	1.20	Linnaite
P-6	235	1400	7280	.67	0.25	Linnaite
P-3	72	395	20,050	.17	0.25	Pr
P-2	380	2340	8550	1.1	3.0	Linnaite

Remarks

Loss of chalcocite from B.1: 2.4%

Apparent solubility of Cu_2S: $2.4(10)^{-2}$ gm/l.

Symbols

Minerals : See Table No.24

P-x : X-ray Mount

in abundance. No tests were made for oxidized sulphur compounds since they were undoubtedly present before the experiment was run. Sulphates were present as solids in the discharge residue and within the exit pipes. The copper content of the liquid was 0.50 mg. per litre (Table 11). The discharge residue contained 3.0 mg. of copper in 21 mg. of solid.

Analyses of selected fractions from the secondary vessel (Table 22) revealed that much greater quantities of copper had been transported by the Na_2S solution than by any solution used in previous experiments. If the total weight of copper deposited in the pipes, secondary vessel, and discharge residue had been transported in solution, the approximate solubility of chalcocite at 550°C in the Na_2S environment would be $2.4(10)^{-2}$ gram per litre.

EXPERIMENT V

Purpose:	To test the extent of mobilization and solubility of chalcocite and bornite in an H_2S - water vapour environment.
Materials and Conditions:	B.1: Chalcocite at entry end, separated from bornite at exit end by an asbestos filter; filter at exit B.2: Quartz at entry end, chlorite schist in central part, and pyrrhotite at exit end Environment: H_2S gas, distilled water Temperature: 550°C Pressure: 300 psi. Time run: 27 hours Volume of liquid collected: 100 ml. Water was introduced into the system very slowly, with intermittent surges to clear the lines. The vapour pressure of the H_2S would therefore approximate the bottle pressure most of the time. The vapour was passed through the system at an approximate average rate of 5 cc per minute.

Results:

The system blocked twice; the experiment was terminated after the second blockage.

Bomb 1. The chalcocite grains remained angular with the exception of one grain on which local fusion had taken place. The surfaces were frequently coated with a thin, finely-crystalline black deposit, beneath which the chalcocite grains appeared slightly corroded. The bomb stem was surfaced by the usual copper-iron sulphides.

The bornite grains also remained angular, and were mostly covered with a coating of fine-grained, slightly pinkish material containing abundant fine, black crystals. The filter between the two was blackened and coated on either side with dark crystals and masses. The weight loss of bornite and chalcocite from the vessel was 0.15 gram (0.7%).

Polished section studies and X-ray analyses showed that chalcocite crystals with minor digenite and bornite had developed on the surfaces of chalcocite grains, and bornite and chalcocite had been deposited on the surfaces of bornite grains. The asbestos filter had been permeated by chalcocite on the upstream side and by lesser amounts of chalcocite, bornite and chalcopyrite on the downstream side (Figure 28). The chalcocite had apparently penetrated the filter readily by moving down flow and concentration gradients; bornite had moved less readily upstream.

Bomb 2. The quartz grains were clean except for a few scattered, fine, dark crystals; if any significant deposition had taken place

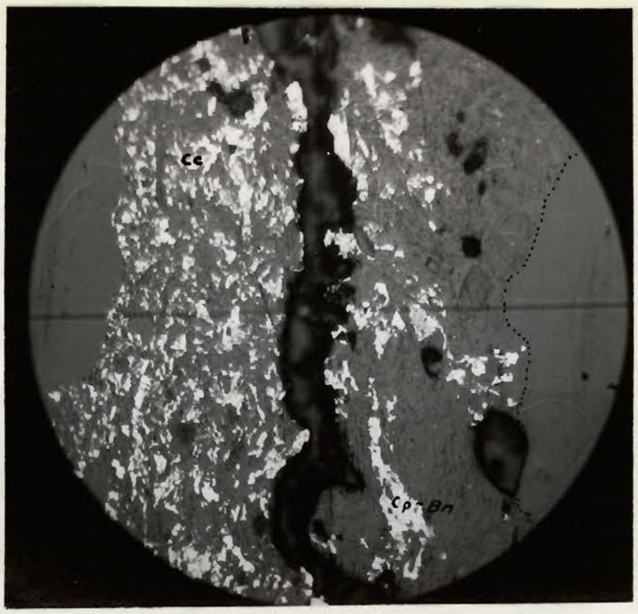


Figure 28

Experiment V (30X)

Intrusion and deposition of Chalcocite (Cc), Chalcopyrite (Cp) and Bornite (Bn) in asbestos filter used to separate Bornite grains (right) from Chalcocite grains (left).

Figure 29

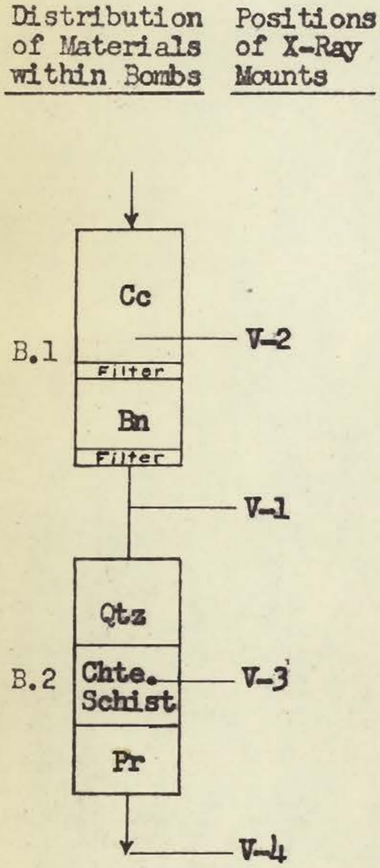
Experiment M (8 X)

Well developed prisms and octahedra of chalcocite formed in open spaces in excess sulphur 'dry' systems.

TABLE 23

COMPARATIVE RESULTS OF HYDROTHERMAL EXPERIMENTS

EXPERIMENT V



Mount	X-Ray Fluorescence Counts per Second CuK_β	 CuK_α	 FeK_α	Copper Analyses (mg) X-Ray	 Chemical	X-Ray Diffraction Minerals Detected
V-2	4270	21,800	2460	13.0	—	Bn, Cc
V-1	48	220	20,900	0.10	0.20	Pr
V-3	355	2180	8900	0.95	0.80	Chlorite
V-4	192	1080	6150	0.54	0.60	Indeterm.

Remarks

Quartz and Pyrrhotite: No evident deposition on grains, therefore no x-ray mounts were made.

Loss of Bn and Cc from B.1: 0.7%

Apparent solubility of Cu_2S: $1.6(10)^{-2}$ gm/l.

Symbols

Minerals : See Table No.24

V -x : X-ray Mount

the materials had subsequently been removed. The chlorite schist was slightly coated with black powder, but otherwise the grains appeared unaffected. Pyrrhotite at the exit end of the vessel appeared unaffected except for local development of a rusty film.

The exit pipe and bleeder valve contained a light brown solid which was soluble in dilute HCl; it was predominantly iron sulphate.

The yellowish discharge liquid yielded a grey-black precipitate. Chemical analyses showed that sulphite, sulphate, and thiosulphate were present (Table 11) as well as H_2S. The liquid contained 0.20 mg. of copper per litre, and the discharge residue 0.60 mg. of copper.

A study of the analyses of the selected fractions shown in Table 23 reveals that significant quantities of copper had been moved by the H_2S - water vapour. Bornite had not been broken off and transported as fine particles in this experiment, because no bornite peaks appeared in the diffraction pattern. The copper compounds were apparently non-crystalline. The reason for localization of copper in the chlorite schist is not known; no copper minerals were detected in polished section. If all the copper detected had been transported by the vapour, the solubility of chalcocite at 550°C in this environment would be $1.6(10)^{-2}$ gram per litre.

TABLE 24

X-Ray Fluorescence Data

Miscellaneous Mounts

X-Ray Mount	Mineral Symbol	Impulse Counts Per Second				Copper mg.
		CuK_{β}	CuK_{α}	FeK_{β}	FeK_{α}	
Calcite	Ca	32	110	70	360	-
Diabase	Ds	33	115	840	4660	-
Flour	Fl	37	135	40	185	-
Peridotite	Gb	34	120	995	5780	-
Hematite	Hm	26	92	4950	23,300	-
Marcasite	Ma	34	124	2990	14,000	-
Magnetite	Mg	25	90	5010	23,900	-
Pyrite	Py	31	110	2250	12,100	-
Pyrrhotite	Pr	49	225	2500	13,380	-
Pentlandite	Pe	30	170	2420	12,100	-
Quartz	Qtz	30	95	49	235	-
Sulphur	S	24	88	42	200	-
Bornite	Bn	2480	13,300	780	4260	6.0
Chalcocite	Cc	3160	16,100	54	240	13.0
Chalcopyrite	Cp		See Standards			

Standard Mounts

X-Ray Mount	Mineral Symbol	CuK_{β}	CuK_{α}	FeK_{β}	FeK_{α}	Copper mg.
Copper	Cu	3100	17,200	140	745	35.0
Cp 1/2, Fl 1/2		532	2925	570	2825	2.00
Cp 1/5, Fl 4/5		366	1975	350	1930	1.00
Cp 1/10, Fl 9/10		190	990	185	1010	0.55
Cp 1/20, Fl 19/20		95	470	105	560	0.25

Diffractometer Conditions For X-Ray Fluorescence Analysis (General Electric XRD-3)

Radiation : Tungsten
Tube voltage : 50 Kv.
Tube amperage : 50 mA
Analysing crystal : LiF
Slit : 0.010

Geiger tube voltage : 2.15 Kv.
Recorder range : 3
Time constant : B

Non-Aqueous Low Pressure Experiments -

Excess Sulphur Environments

Study of the results of these experiments was restricted to observations made under stereoscopic and mineralographic microscopes.

EXPERIMENT M

Purpose:	To test the mobility of chalcocite in a 'dry' sulphur-rich atmosphere, and to examine the effect of an electrical potential on the rate and direction of migration of chalcocite
Materials and Conditions:	Vycor glass tubing charged with grains of chalcocite and flowers of sulphur moistened with water. Peridotite grains were placed on both ends of the chalcocite, followed by aluminum electrodes. The materials were held in place by asbestos packing (See Figure 14). The tubing containing the charge was heated in a standard tube furnace (Figure 7). Furnace Temperature: 550°C Pressure: Atmospheric. Time run: 40 hours Environment: Sulphur vapour, air Impressed voltage: 6 volts The reaction tube was cooled rapidly in air when the run was terminated.

Results:

The water rapidly boiled off as the tubing was heated, and the resistance across the system increased from 40,000 ohms to 2 megohms.

The sulphur vapour migrated through the packing to the cool ends of the tube and condensed. As the sulphur moved from the high temperature area the sulphur vapour pressure probably decreased to less than one atmosphere.

The central chalcocite zone had undergone complete change. The grains had been fused together into a vesicular cylinder in which original grains had been remolded into smooth rounded and globular masses joined by necks and filaments of mobilized copper sulphide. The new sulphides were frequently coated with well-developed octahedra and prisms (Figures 26 and 29).

The migrated sulphide was determined in polished section to be chalcocite with, locally, small amounts of exsolved digenite. The products were extremely fine-grained. Small pyrite masses were observed in a few areas.

A striking feature observed in this experiment was the growth of fine needles of chalcocite which projected outward into open spaces from the slag-like masses of chalcocite surrounding the voids (Figure 30). Octahedral faces had developed occasionally at the tips of the needles. Binocular microscope study revealed that the needles pointed toward two diametrically opposite bands on the surface of the specimen; these bands had been in juxtaposition with the breaks between the two halves of the furnace. Marked deposition of chalcocite on the glass tube had taken place in these two relatively cool areas (Figure 31).

The peridotite grains on either end of the chalcocite section had been cemented firmly together by chalcocite masses which had migrated outward from the central section. The mobile chalcocite was smeared across surfaces of the peridotite grains in slag-like coatings one millimeter or less in thickness (Figure 32). Chalcocite prisms and octahedrons were commonly superimposed upon these slag-like basal masses. The majority of the crystals were well

Figure 30

Experiment M (8X)

Needles of chalcocite growing out from globular masses of chalcocite into voids (white). Needles point in the direction of lower temperatures.

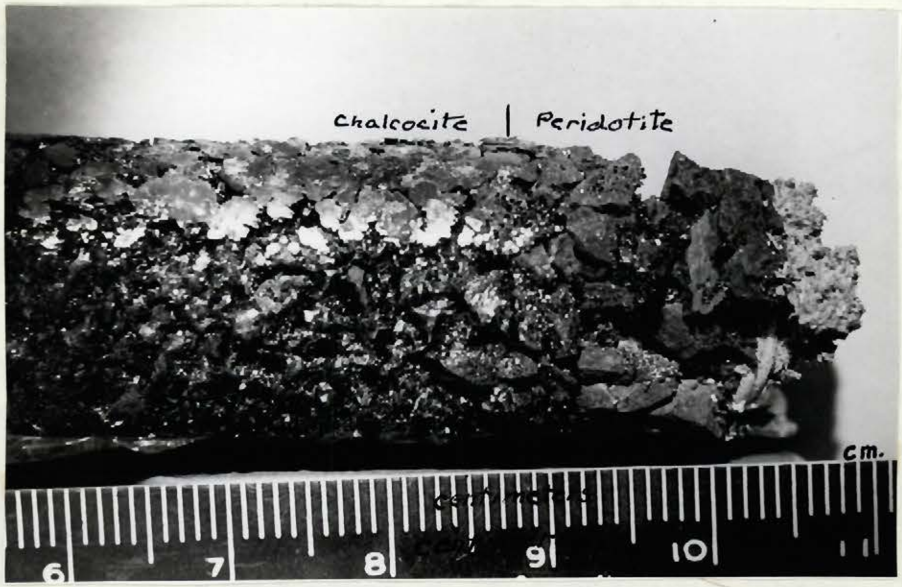


Figure 31

Experiment M (2X)

Experimental products removed from glass tubing to illustrate cementation of peridotite grains and asbestos fibers by migrant chalcocite, and deposition of chalcocite at glass wall (white band) in low temperature areas. Chalcocite moved approximately 2 cm.

Figure 32

Experiment M (5X)

Showing migration of chalcocite across grains of peridotite and superposition of crystals upon the slag-like coatings. Upper large grain is completely coated on the left side with 'slag' chalcocite; elsewhere, crystals grow from 'slag' base.

Figure 33

Experiment M (30X)

Chalcocite crystals (right side) and chalcopyrite-bornite mixture (left side) coating surface of peridotite grain, penetrating grain via cracks, and surrounding serpentinized olivine grains.

developed, but many were observed to have only partially developed crystal faces on one side, and blended into the structureless mass from which they grew. Polished sections of peridotite grains revealed that chalcocite had penetrated the peridotite fragments along fissures and grain boundaries as it had in experiment L; bornite and chalcopyrite were also present in minor amounts (Figure 33).

The chalcocite had moved outward through the peridotite section into the asbestos section, and filaments of chalcocite cemented asbestos fibres together 1/4 inch beyond the peridotite grains (Figure 31). The distance traversed by the chalcocite was approximately two centimeters.

No difference was apparent in the features of the migrant chalcocite, or the distance moved, on either side of the chalcocite section. The low impressed voltage did not appear to have directed the movement of chalcocite.

The results obtained in the experiments indicate that chalcocite moved down a temperature gradient, and possibly down a concentration gradient.

EXPERIMENT W

Purpose:	To check the rate and direction of movement of chalcocite in a 'dry', sulphur-rich atmosphere, to examine the effect of a high electrical potential on the movement, and to observe the influence of iron and nickel on mobilized copper sulphides.
Materials and Conditions:	Vycor glass tubing charged in center with chalcocite, bornite, chalcopyrite, and pentlandite grains. Peridotite grains, aluminum

electrodes, and asbestos packing were placed on either end (Figure 14). The tubing was inserted in a ceramic shield and heated in a standard tube furnace.
Furnace Temperature: 650°C (Pre-set to avoid using a thermocouple)
Environment: Sulphur vapour, air
Pressure: Atmospheric. Time run: 72 hours
Impressed voltage: 110 volts.

The reaction tube was cooled slowly in the furnace, the temperature dropped to 300°C in one-half hour.

Results:

The glass tube had fractured in many places, especially at the chalcopyrite end.

The enclosed sulphide grains had been fused together into a coherent, porous cylinder as in experiment M. On the chalcocite end peridotite grains and a narrow band of asbestos were cemented firmly to the end of the sulphide mass; the mobile chalcocite had migrated 2.5 centimeters from its original position. On the chalcopyrite end only those peridotite grains immediately adjacent to the sulphide mass were attached together.

The peridotite grains on the chalcocite end were coated with chalcocite masses and crystals, duplicating the features described in experiment M. Strikingly, the smooth, slag-like chalcocite predominated on those grain surfaces facing the original chalcocite section, and the new crystals of chalcocite predominated on those grain surfaces facing away from the original chalcocite. The chalcocite thus appeared to have moved down both temperature and concentration gradients as a mobile 'liquid' phase, as it had in experiment M; the final process appears to have been the formation of crystals on the migrant slag-like masses. No needles of chalcocite had developed in this experiment, however; apparently the ceramic shield had distributed the heat evenly around the glass tubing. If the electrical potential had in any way influenced the movement of chalcocite, it was not recognizable.

The peridotite grains on the chalcopyrite end of the sulphide mass had been bleached, and were stained red by hematite which had formed at the expense of chalcopyrite. Some chalcopyrite at the extreme end had apparently broken down in the oxygen-rich atmosphere introduced after the sulphur had distilled off. Hematite, minor magnetite, and chalcocite had been produced, but no cuprite was recognized.

The surface of the sulphide cylinder changed gradually in appearance through the different mineral sections. The bright metallic globular surfaces and crystals typical of the chalcocite section gave way to tarnished nodular surfaces representing the position of original bornite; the nodules became less pronounced in the blackened pentlandite-chalcopyrite section, and reduced to sub-angular protrusions in the black, lusterless end chalcopyrite zone. Figure 34 partly illustrates the changes observed. Increasing iron content evidently restricts the degree of surface mobilization of copper sulphide.

A longitudinal polished section of the sulphide cylinder revealed that copper and iron had diffused throughout the sulphide mass. Fine-grained chalcocite, pyrite, and a little magnetite were the only minerals observed except in the pentlandite area, and except for the latter the originally distinct mineral sections could not be differentiated. The pyrite was dispersed through the chalcocite in small masses and specks, and occasionally outlined original grain boundaries. Magnetite was restricted to

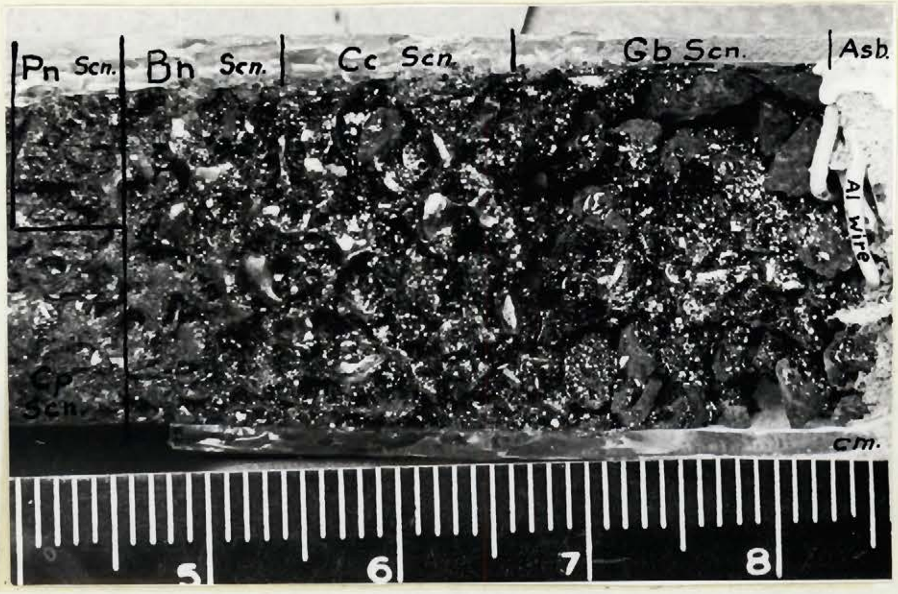


Figure 34

Experiment W (2.5X)

Showing migration of chalcocite (Cc) across surfaces of peridotite (Gb) grains toward the outer asbestos (Asb) packing, and illustrating the progressive decrease in degree of surface mobilization with increasing iron content through bornite (Bn) into the pentlandite (Pn) and chalcopyrite (Cp) sections of the tube.

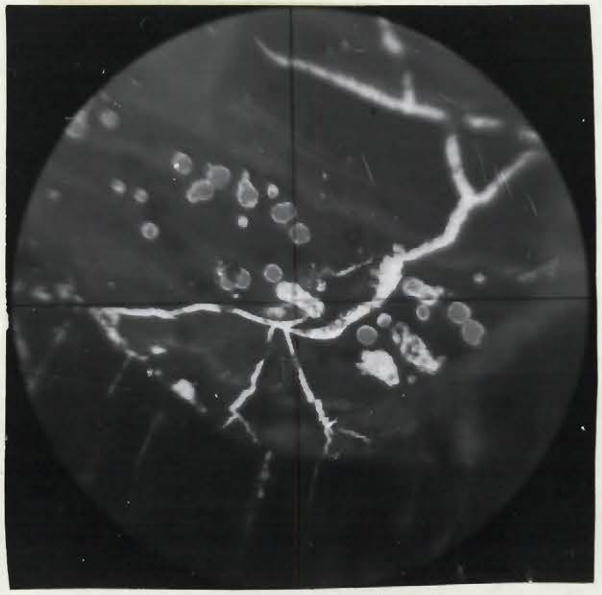


Figure 35

Experiment W (250X)

Chalcopyrite-bornite veinlets in peridotite fragment. Spheres of magnetite within serpentine (after olivine) are being replaced by chalcopyrite (white). Veinlets consist of chalcopyrite and bornite.

narrow zones at grain boundaries; it was more abundant near the chalcopyrite end. Although the original pentlandite had been considerably modified on the surfaces of grains, the polished section revealed that diffusion between pentlandite and the copper minerals was restricted to the border zone, where the two distinct phases co-existed. No intermediate phase was observed in this experiment.

Polished sections of peridotite grains revealed that chalcocite had penetrated the fragments as it had in previous experiments. In a few areas bornite and chalcopyrite were observed, and close study showed that these minerals were frequently associated with the magnetite formed during serpentinization of the olivine (Figure 35). The intruding chalcocite had reacted with the magnetite to produce stable chalcopyrite-bornite phases which tended to segregate as migration continued.

EXPERIMENT U_A

Purpose:	To examine the products formed and the degree of mobilization obtained when minerals are subjected to full vapour pressure of sulphur at the temperature used.
Materials and Conditions:	Pressure vessel connected to low pressure gauge. Natural bornite and marcasite charged into vessel with flowers of sulphur. Minerals separated by copper foil. Temperature: 580°C; Pressure: 77 psi*; Time run: 18 hours Excess sulphur was flushed from the vessel after cooling it slowly to 300°C.

* The vapour pressure of sulphur is taken from the determinations of West (1950), as his apparatus permitted greater accuracy in measuring vapour pressures.

Results:

The bomb stem had reacted; pyrrhotite and pyrite were the major products formed.

Most marcasite grains had been only slightly altered on the outside, where a thin coating of an undetermined mineral had been deposited in places. Occasional specks of bornite, chalcopyrite, and digenite were attached to the grains. Chalcopyrite had developed about the points of contact of marcasite and the copper foil used to separate the bornite and marcasite grains. The copper foil had been converted to digenite and covellite.

The bornite grains had become rounded on corners and edges, but cementation had been very weak. Polished sections revealed that most grains were rimmed by a mosaic of small masses of bornite which had been mobilized. Digenite specks were also commonly present in this outer layer. The central parts of most grains had changed little; the bornite product was paler in colour than the original and rapidly tarnished to a blue-white colour identical to that of digenite. A few grains of the original bornite had been strongly altered throughout, and had become vesicular masses partly replaced by blue and brown covellite; the mineral relationships are described in experiment U_B.

EXPERIMENT U_B

Purpose:	Similar to U_A
Materials and Conditions:	Natural bornite and nickeliferous pyrrhotite charged into pressure vessel with flowers of sulphur. Minerals separated by copper foil. Temperature: 550°C; Pressure: 56 psi*; Time run: 19 hours.
	The vessel was cooled slowly to 250°C prior to flushing out excess sulphur.
	*From West's (1950) determinations.

Results:

The distinctive rectangular outlines of the pyrrhotite had become slightly rounded by a thin surface deposit containing much pyrite. Freshly broken grains showed the pyrite extended into cracks and along cleavage planes within grains (Figure 36). Grains adjacent to the copper foil were spotted with covellite and were replaced locally with bornite and chalcopyrite (Figure 37). Minute, unidentified white specks were present in the chalcopyrite. The copper foil had been converted to covellite.

The bornite grains had been rounded on the edges, and some were attached loosely to each other; most were coated with covellite. Polished sections revealed that all grains had been greatly altered, and that multitudes of small vesicles had developed throughout the grains. The major phase was pale bornite which contained scattered masses of chalcopyrite. Blue covellite rimmed both the outsides of grains and the peripheries of the randomly distributed vesicles within the grains. The blue covellite was succeeded by the unusual red-brown covellite described in experiment K, and this was in turn bounded by laths of

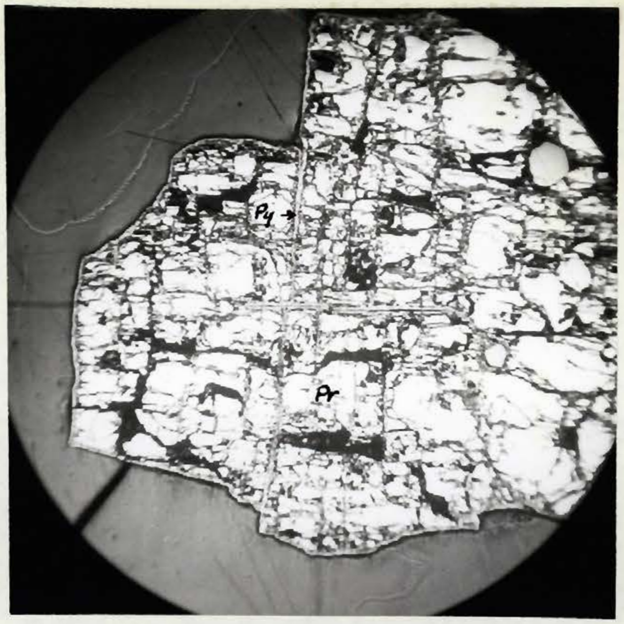


Figure 36

Experiment U_B (20X)

Development of pyrite (Py) on surface, and along cleavage planes and fractures within nickeliferous pyrrhotite (Pr)

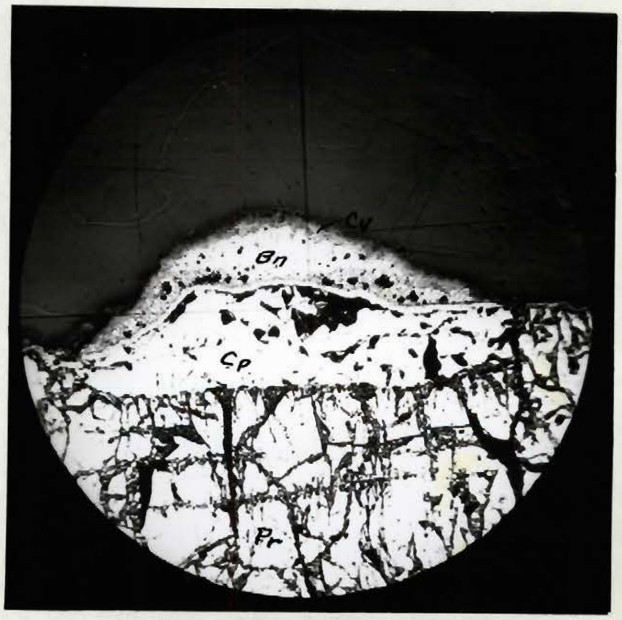


Figure 37

Experiment U_B (30X)

Chalcopyrite (Cp) and bornite (Bn) replacing nickeliferous pyrrhotite (Pr) at point of contact with copper foil, converted to covellite (Cv). Trace of the previously altered pyrite rim, now chalcopyrite, is evident.

chalcopyrite adjacent to the bornite. Figure 38 shows the mineral relationships.

EXPERIMENT U_C

Purpose:	Similar to U_A
Materials and Conditions:	Natural chalcocite and nickeliferous pyrrhotite charged into pressure vessel with flowers of sulphur. Minerals were in contact with each other. Temperature: 550°C; Pressure: 56 psi ; Time run: 19 hours. The vessel was cooled slowly in its furnace; excess sulphur was flushed out at 250°C. From West's (1950) determinations.

Results:

The pyrrhotite had changed markedly in its surface appearance. Grains had been rounded noticeably, and were coated with a thin, bronze-coloured surface layer which also penetrated the grains along fractures and cleavage planes. Covellite was observed on a few grains near the contact of chalcocite and pyrrhotite.

The chalcocite had been mobilized as in previous excess sulphur experiments, and the resulting nodular masses adhered firmly to each other. At the contact chalcocite enfolded grains of pyrrhotite or bound them together. Covellite had developed on most surfaces of the chalcocite grains.

Polished section study showed that the surface layer

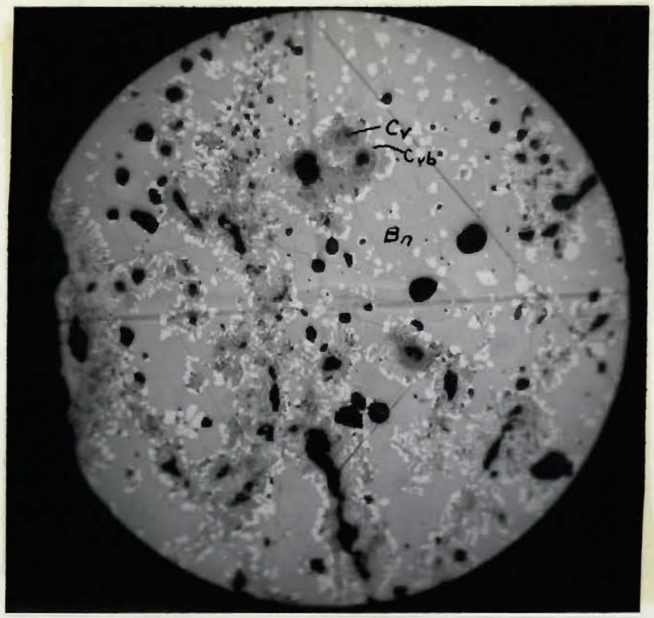


Figure 38

Experiments U_A, U_B (90X)

Vesicular mass produced by heating bornite in sulphur held at full vapour pressure. Main mass is orange-coloured bornite (Bn). Blue covellite (Cv) rimming grains and peripheries of vesicles is succeeded by brown covellite (Cvb), which in turn is bordered by chalcopyrite (Cp) adjacent to the bornite.

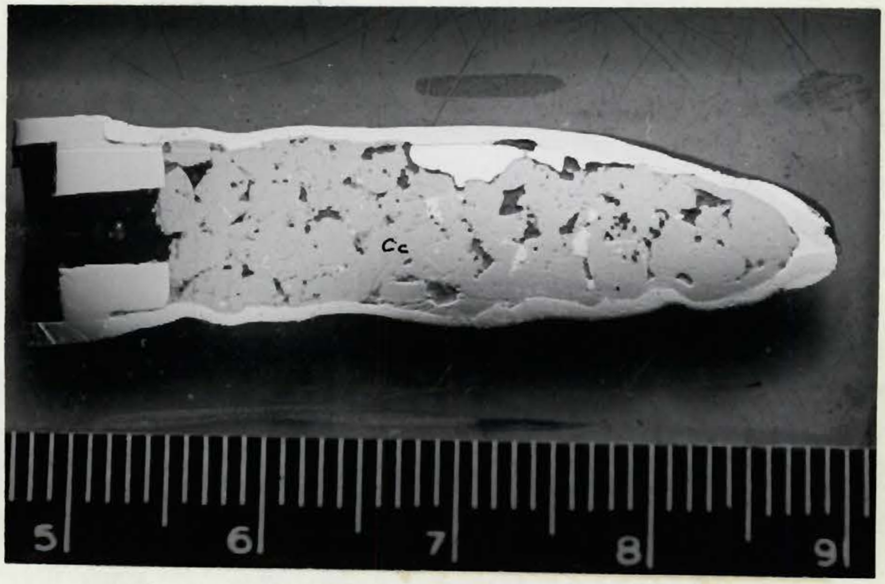


Figure 39

Experiment O (2.5X)

Mounted section of capsule used in differential pressure experiment. Native copper (white) is scattered through or rimming rounded, compressed chalcocite (Cc) grains. Rigid end of capsule is to the left.

on the pyrrhotite was an extremely fine-grained mixture of pyrite and magnetite. Some water or oxygen must have been present in the system to produce the latter mineral. No nickel mineral was recognized. The original chalcocite grains now consisted of chalcocite and digenite, the latter being more evident adjacent to covellite, which rimmed the grains. Brown covellite had developed where iron was available.

Diffusion of iron and copper had been noticeably less in this experiment than in many previous experiments; for example, intermediate Cu-Fe sulphide phases had seldom developed where covellite surrounded pyrrhotite grains. The alteration rim had apparently formed on the pyrrhotite prior to mobilization of the copper sulphide and in some way had inhibited further reaction.

Differential Pressure Experiments

Study of the results of these experiments was restricted to observations made under stereoscopic and mineralographic microscopes.

EXPERIMENTS N and O

Purpose:	To test the ability of copper sulphide to move under a differential pressure applied by a peristaltic force.
Materials and Conditions:	Two-part capsule, one end collapsible. Chalcocite and flowers of sulphur were charged into the collapsible (copper) end, the capsule was sealed, and was placed in a high pressure vessel. The vessel was heated to 550°C and a hydrostatic pressure was applied.

Pressures: Experiment N: 7,500 psi
Experiment O: 10,000 psi

The hydrostatic pressure collapsed the copper end of the capsule, and the resulting peristaltic force tended to drive moveable materials into the rigid end.

Results:

The capsules collapsed in both experiments, indicating that the seal had held at the start of the experiments. Penetration of water into both capsules had taken place later, however, and the differential pressure obtained at the start was nullified.

Polished sections through the capsules (Figure 39) showed that the original discrete chalcocite grains had been compressed into a solid mold consisting of a mixture of chalcocite and exsolved digenite. Native copper was scattered through the sulphides as masses and specks, and commonly outlined original grain boundaries. The copper sheath was partly converted to chalcocite. Examination at the edges of voids revealed that the chalcocite had been mobilized as in previous experiments. Small globular masses and crystals of chalcocite had formed on the surfaces of the original grains, and grew into the open spaces remaining.

Mass movement of the copper sulphides into the rigid end of the vessel had not been effected, although surface crystals had grown into, and chalcocite grains had been deformed at, the neck between the ends of the capsules. The experiments show that the mobilized copper sulphide did not behave as a liquid, although it had deformed readily to fill unoccupied areas. The structural rigidity of the chalcocite lattice apparently had been reduced in the high-sulphur atmosphere, thereby facilitating 'plastic flow'.

EXPERIMENTS Q and R

Purpose:	To test the ease with which copper sulphide is moved by differential pressure while in an excess sulphur hydrothermal environment.
Materials and Conditions:	High temperature differential pressure vessel shown in Figure 9. Copper reaction tubing, loaded at the static end with quartz and peridotite grains, and at the moving end with chalcocite grains (See Figure 10). Flowers of sulphur was packed in with minerals. The vessel was connected to the hydraulic circuit and heated. Pressure was applied to the moving piston by the jack, in amounts sufficient to cause the piston to move into the bore against the hydrostatic pressure and frictional resistances.

	EXPERIMENT Q	EXPERIMENT R
Hydrostatic Pressure	10,000 psi ± 200 psi	5,000 psi ± 200 psi
Temperature	550°C	550°C
Time Run	2 hours	2 hours
Cooling 550°C-300°C	1/2 hour	1 hour
Force on Piston	2500 pounds	2500 pounds

Results:

In both experiments the teflon pressure seal on the moving piston blew out between 500 and 550°C, but the copper washer slowly sealed the leak. The runs were continued under a hydrostatic pressure of 200 psi until high resistance on the jack ram indicated that the reaction tube had collapsed and filled the vessel bore.

The chalcocite grains within the reaction tube had become sub-rounded from movement of the migrant surface chalcocite described in earlier experiments, and had been distorted by the different force components set up during collapse of the tube. Chalcocite had been pressed into spaces between quartz grains and into folds in the copper casing.

Polished sections revealed that the original chalcocite grains had recrystallized to granular mosaics of anisotropic chalcocite. A secondary intergranular digenite phase had developed which contained exsolved laths of chalcocite; the digenite had a reddish cast in places, suggesting that some iron was incorporated in the lattice. Native copper was not observed.

Although the copper sulphides had moved readily into open spaces, a calculation of the force on the sulphide grains could not be made because the resistance of the reaction tubing varied as it collapsed. Possibly 2000 pounds of the force on the moving piston would have been supported by the collapsing reaction tube and its contents.

EXPERIMENT S

Purpose:	Repeat of experiments Q and R. To examine the degree of mobilization of copper sulphides by a positive uniaxial force while in an excess sulphur hydrothermal environment.

Materials and Conditions:

Differential pressure vessel shown in Figure 9. Brass reaction tubing loaded at static end with quartz and peridotite grains, and at moving end with chalcocite grains and a partial section of pentlandite grains. Flowers of sulphur was packed between grains.

The driving piston (See Figure 10) was lengthened, and modified so that it would enter the reaction tubing without collapsing the tubing. This modification ensured that the force moving the piston would be transmitted to the grains themselves.

Hydrostatic pressure: 500 psi
Temperature: 550°C; Time run: 4 hours
Cooling time 550°C-300°C: 1 hour
Force on piston: 3100 pounds

Results:

The piston seal held at the 500 psi hydrostatic pressure used, and the force on the piston was maintained at 3100 pounds. This force caused the piston to move into the vessel bore in short, intermittent increments as the grains yielded and the static frictional resistance of the seal was overcome. Calculations showed that a maximum force of 2500 pounds was applied to the chalcocite grains.

The brass tubing had buckled at a late stage in the experiment. The chalcocite grains had been molded into a solid mass which filled the distorted brass container, and the original grains had been deformed beyond recognition. The sulphides had streamed around the nose of the piston as it was forced into the tube, and had flowed into spaces between the quartz and peridotite grains. Examination of polished sections revealed that fine flow lines contoured the space occupied by the nose of the piston, and extended into tails on either side of the nose position.

Figure 40 shows most features; the flow lines were too fine to appear in the photograph.

Polished section study revealed that the chalcocite had recrystallized and digenite had formed, identically to that described in experiment Q. At the pentlandite-chalcocite boundary marked alteration had taken place. Chalcocite was replaced by digenite, which became progressively richer in iron as the pentlandite was approached. In the boundary area the copper sulphide phase had all the visual characteristics of bornite. Pentlandite had been carried along by the copper sulphides in the boundary area, and here was in equilibrium with the bornite phase. It is evident that iron in excess of that required to form pure pentlandite had reacted with the chalcocite to give bornite and intermediate Cu-Fe-S phases. Figure 41 shows the textural relationships. The pentlandite away from the contact zone had retained its original brittle nature, and the grains had fractured rather than yielded. An increase in the content apparently increased the ability of the sulphide phases to deform with ease.

EXPERIMENT T

Purpose:	To test the degree of mobilization of chalcocite by a positive uniaxial force while in a low sulphur hydrothermal environment.
Materials and Conditions:	Differential pressure vessel shown in Figure 9. Iron reaction tubing loaded at static end with nephrite and peridotite grains and at moving end with chalcocite and pentlandite grains as in experiment S. The driving piston and reaction tubing were constructed similar to those used in experiment S.

Figure 40

Experiment S (2.5 X)

Section through reaction tube, showing flowage of chalcocite to fill container and spaces left by driving plug. Fine flow lines parallel to outline of the driving plug (lower part). Pentlandite (Pn) removed from chalcocite remained brittle.

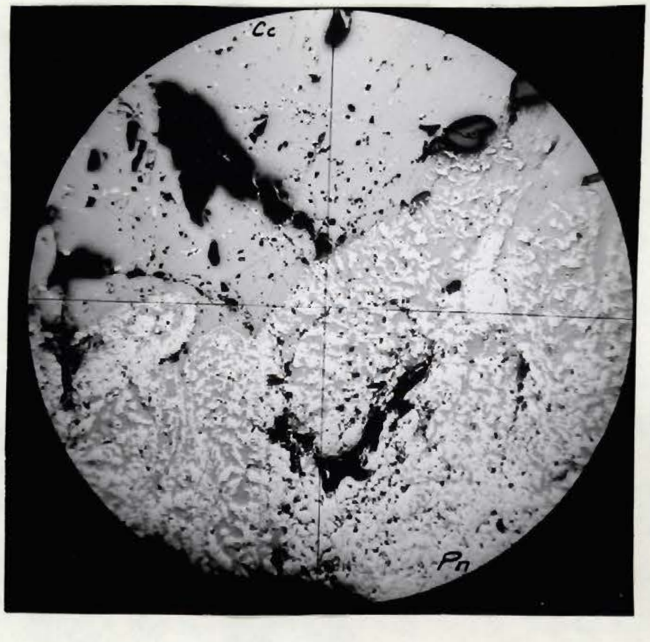


Figure 41

Experiment S (30 X)

Segregation of iron-rich copper and nickel sulphide phases at common boundary of chalcocite (Cc) and pentlandite (Pn). Note streaming of pentlandite masses through Cu-Fe-S phase.

Hydrostatic pressure: 500 psi
Temperature: 550°C; Time run: 18 hours
Cooling time 550-300°C: 1 hour
Force on piston: 3100 pounds

Results:

The rate of movement of the piston into the vessel bore was considerably less than it had been in experiment S. A longitudinal section through the reaction vessel (Figure 42) showed that the chalcocite grains had been crushed by the moving piston, rather than molded as in the excess sulphur experiments. Fracturing of the grains was sub-parallel to the direction of the applied force, and although the shattered grains filled the slightly distended tube, no flowage of the chalcocite had taken place.

Polished section study revealed that the chalcocite had been recrystallized; the fragments consisted of granular, anisotropic chalcocite similar to that observed in experiment D and others. The pentlandite grains at the chalcocite boundary had been partly replaced by bornite and iron-rich chalcocite or digenite phases referred to in earlier hydrothermal experiments. Isotropic pentlandite was scattered in small masses through the replaced fragments (Figure 43) as it had been in experiment S. The nickel had again been excluded, at least in part, from solid solution with the copper-rich phase.

In this experiment the chalcocite had not deformed readily under the applied force, as it had done in experiment S. The evidence indicates that sulphur in excess of that required to form chalcocite or digenite greatly increased the mobility of copper sulphide.

Figure 42

Experiment T (2X)

Fragmented chalcocite (Cc) in differential pressure experiment, low sulphur environment. Note longitudinal fractures paralleling the direction of the applied force (arrow). Unreplaced pentlandite remained brittle.

Figure 43

Experiment T (20X)

Almost total replacement of pentlandite (Pn) grain by Cu-Fe-S solid solution. White 'remnants' are isotropic pentlandite which did not form a solid solution series with copper-rich phase.

COMPARISON AND DISCUSSION OF EXPERIMENTAL RESULTS

The general grouping of experiments, as given on page 62 of the preceding section, is followed below in discussing the results of the experiments. In this discussion, the important features of the experiments are reviewed briefly; comparisons of results are then made between individual experiments in a single group, and between the groups of experiments themselves.

I. Hydrothermal Experiments - Low Sulphur Environments

These experiments were made primarily to determine the relative solubilities and apparent mobilities of some sulphides in dynamic hydrothermal systems having different environmental conditions. The low sulphur experiments were run firstly to obtain a reference datum of solubility in a distilled water environment, and secondly to examine any changes in solubility and mobility of a sulphide caused by adding soluble salts, without having to consider possible complexities arising from an additional sulphur phase.

Features of the Experimental Products

Several features, listed below, were common to the products of every experiment in this group.

(a) Sulphide mineral fragments had more or less retained their original shapes.

(b) Pyrite had lost sulphur and converted to pyrrhotite. Pyrrhotite had converted to magnetite, except where in contact with chalcocite. In the latter case, chalcopyrite, bornite, and iron-rich chalcocite had formed by solid-state interchange of copper and iron between the two original minerals. Magnetite, on the other hand, had resisted reaction with chalcocite to form Cu-Fe-S minerals.

(c) Massive, isotropic chalcocite had recrystallized to coarse-grained anisotropic chalcocite, and minor bornite had been absorbed by the recrystallizing chalcocite. Digenite had formed in areas where sulphur had been expelled during the decomposition of sulphur-rich minerals.

(d) Minute crystals and growths of new chalcocite had developed on the corners and edges of original chalcocite grains, occasionally fusing grains together or following the contour of the vessel when in contact with its wall.

(e) The fluids collected from the experiments contained H_2S, except in the cases where the original solutions contained salts (Experiments D and E). Sulphite, sulphate, and thiosulphate ions were also present, but the latter were apparently produced mostly during oxidation of H_2S after the fluids entered the collecting flask. The pH of the discharge fluids ranged between 7.8 and 9.2.

(f) No replacement of materials in the low temperature vessel had taken place. Calcite, when used, had been dissolved by the hot solutions, but generally magnetite and other compounds had been deposited on the surface of materials placed in the vessel.

Solubility of Chalcocite

The apparent solubility of chalcocite, as determined by the summation of weights of copper deposited in the lower parts of the experimental system, is much higher than was to be expected from free energy calculations. Distilled water experiments yielded apparent solubilities ranging from $1.8(10)^{-4}$ to $2.8(10)^{-4}$ gram per litre under the conditions 550°C and 15,000 psi. The solubility increased upon addition of salts; this is indicated from experiments D (artificial sea water) and E (ammonium chloride solution), in which the apparent solubilities of Cu_2S were respectively $2.4(10)^{-3}$ and $1.1(10)^{-2}$ gram per litre for the conditions used.

TABLE 25

Experimental Solubilities in Grams per Litre of Cu_2S in Different Environments, Compared with the Calculated Values of Verhoogen (1938) and Czamanske (1959)

Temperature	550°C		620°C
Distilled Water Experiments	$1.8(10)^{-4}$	to	$2.8(10)^{-4}$
Artificial Sea Water (Expt. D)	- - -		$2.4(10)^{-3}$
1M. NH_4Cl Solution (Expt. E)	$1.1(10)^{-2}$		- - -
1M. Na_2S Solution (Expt. P)	$2.4(10)^{-2}$		- - -
Saturated H_2S Solution (Expt.V)	$1.6(10)^{-2}$		- - -
Water plus Sulphur (Expt. K)	$2.9(10)^{-2}$		- - -
Water plus Sulphur (Expt. L)	$4.6(10)^{-2}$		- - -
Verhoogen (1938)	$2.3(10)^{-8}$		$3.5(10)^{-8}$
Czmanske (1959)	$3.5(10)^{-6}$		$7.0(10)^{-6}$

In Table 25 a comparison is made between the solubilities of Cu_2S obtained experimentally and the solubilities in water as calculated from free energy data by Verhoogen (1938) and Czamanske (1959). The experimental values appear to be extremely high compared with the calculated values, and it might be suspected that mechanical enrichment resulted from transportation of small particles broken loose from the 'source' material. This possibility is considered unlikely, however, because the chalcocite was carefully abraded and screened prior to use, and filters were used to arrest transport of small particles. Some copper was added to the system in experiments B, C, and D, but as copper sulphides had formed when the migrant Cu had entered the reaction chamber, near-equilibrium would still prevail. The copper is therefore considered to have been transported from the primary vessel as ions (simple or complex), molecules, or gels, which were formed in equilibrium with the sulphide minerals in the primary vessel. The apparent solubility values are considered, moreover, to be minimum values, because all experimental material was probably not recovered from depositional sites in the system.

The addition of soluble salts to the primary solution increased the solubility of Cu_2S greatly. The mass influence of additional ionic species in solution would, directly or indirectly, favour an increase in copper ion concentration according to Le Chatelier's principle, but quantitative evaluation under these conditions of probable non-equilibrium would be hazardous. The possibility also exists that soluble copper complex ions of indefinite composition formed, but their influence on solubility likewise cannot be defined. In the case of ammonium chloride solution, the formation of soluble copper-ammonia complex ions probably is responsible for most of the increase in solubility.

The thiosulphate radical is apparently unstable at higher temperatures (See also Feld, 1911; and Peschanskii and Valensi, 1949), and therefore should have little or no effect on sulphide solubility. An increase in the volatility of Cu_2S by addition of chloride ion is not responsible for the increase in amount of copper transported, since the vapour pressure of Cu_2S is greater than that of CuCl (See Tables 6 and 7).

Mobilization of Chalcocite

The development of minute new crystals of chalcocite or digenite on the surface and corners of original chalcocite grains indicates that in these experiments some inter-grain movement of copper sulphide had taken place in the high temperature vessel. The cause of movement of chalcocite and growth of new crystals is not evident. It may be due to local solution and concomitant deposition, to local volatilization and re-deposition, or to atomic migration down a local energy gradient. No features suggestive of melting were observed. The addition of soluble salts to the solution appeared to increase slightly the amount of sulphide mobilized, but the total mass affected remained small.

Migration proceeded more rapidly in the direction of flow, a fact which is illustrated best by the migration of chalcocite around the filter in Experiment D. This indicates that the mobile ions or molecules were free to be moved across surfaces by the small energy gradient of a slowly moving vapour.

Solid State Transformations

Copper and iron moved readily from one site to another by solid state diffusion processes. As noted previously, bornite, chalcopyrite, and intermediate Cu-Fe-S phases were formed readily where pyrrhotite and chalcocite were in contact. Copper apparently moved more easily into pyrrhotite than iron moved into chalcocite, for entire grains of pyrrhotite were converted to Cu-Fe-S minerals whereas only a relatively narrow band of the adjacent chalcocite grain consisted of iron-rich chalcocite or bornite. MacDougall (1957) has shown this to be so in dry systems as well.

Phase Relations

The present experiments were not intended to establish phase relations in the Cu-Fe-S system, inasmuch as Merwin and Lombard, Ross, and others have carried out far more accurate studies. The effect of adding water to the system requires a note, however. In an open Cu-Fe-S-H_2O system, pyrite decomposes to pyrrhotite and the sulphur freed forms H_2S and other sulphur compounds which are removed from the system. Pyrrhotite continues to break down, yielding magnetite and H_2S, and ultimately bornite loses sulphur to form magnetite and iron-rich chalcocite or digenite. Thus pyrite, pyrrhotite, and bornite are unstable in a hydrothermal low-sulphur open system under the conditions used.

In a closed Cu-Fe-S-H_2O system the stability of different minerals depends on the partial pressure of sulphur as well as the proportions of metallic components present. Magnetite is still formed at the expense of pyrrhotite when the sulphur pressure is below that of a saturated H_2S solution (See Experiment A); beyond this, no further conclusions regarding phase relations in closed systems can be drawn from the present hydrothermal studies.

II. Hydrothermal Experiments - Excess Sulphur Environments

The addition of sulphur to the experimental system produced noticeably different results from experiments of the low sulphur group, with the exception of experiment V in which sulphur was added as H_2S.

Features of the Experimental Products

The physical appearance of the products in the primary vessel of experiment V was much the same as that of the products of low sulphur experiments. Chalcocite and bornite fragments had more or less retained their original shapes; chalcocite had recrystallized; and fine growths of new minerals had developed on the original fragments, fusing them together occasionally or coating the interiors of openings. Some chalcocite fragments appeared slightly corroded in places.

The products in the primary vessel of experiments J, K, L, and P were totally different in appearance from the products of the low sulphur experiments. Smooth, rounded surfaces had developed on the original fragments of chalcocite and bornite, and masses of new crystals had grown upon these smooth surfaces.

There were no noticeable changes in the amounts of material deposited in the second vessel, even though much more copper was present than in the low sulphur experiments. No replacement of mineral fragments in the vessel was detected.

Solubility of Chalcocite

The experiments revealed (Table 25) that chalcocite is apparently much more soluble in sulphur-rich than in sulphur-poor solutions. The H_2S solution yielded a somewhat lower solubility value than the concentrated Na_2S solution or solutions containing native sulphur; the average value is approximately 100 times that obtained in distilled water experiments.

This high solubility is at variance with the calculated values of Garrels (1944) and the experimental results of Hemley (1953), given in Tables 2 and 3. The results of Clark and Menaul (1916), however (See Table 5), showed that large amounts of covellite and bornite may be suspended in H_2S -saturated KOH solutions, and it is possible that the high solubilities indicated in the present experiments result from the suspension of colloidal particles in the transporting media. The fact that the copper-rich products were non-crystalline, according to X-ray powder diffraction studies, may also support such a theory of transport. Barnes (1958) experimentally determined the solubility of ZnS in H_2S - saturated water to be much higher than the calculated value, and concludes that the solubility is controlled by the formation of complex ions of the type $ZnS.xH_2S$. His theory could apply equally well to the solubility of Cu_2S in H_2S solutions.

Ellis (1959) suggests that thiosulphate complexes could be responsible for increasing the solubility of ZnS in hydrothermal solutions; but this theory is not supported by the present experiments, which indicate that the thiosulphate ion is unstable in hydrothermal solutions.

Mobilization of Chalcocite

The chalcocite must have been highly mobile in order to form the slag-like masses described earlier, but it did not appear to flow as a liquid because no similar material was found outside of the primary vessel. Migration of chalcocite in the direction of the stream flow was less pronounced than in low sulphur experiments, but the tests for movement under flow pressures were inconclusive because the volume of liquid passed was small. The penetrating ability of the chalcocite was remarkable, however. Peridotite fragments near the chalcocite commonly were riddled with chalcocite which had migrated into fractures and along grain boundaries.

The means by which chalcocite moved and new crystals grew are no more evident in these experiments than in low sulphur experiments, but two features stand out which appear to be significant when considering means of transfer:

(1) Fractures in peridotite were completely filled laterally with sulphides, and there was no indication of inward or differential growth of crystals (for example, comb structures), which would be expected if the minerals had been deposited from a solution;

(2) Where bornite and chalcopyrite were found together in the veinlets, both minerals extended from wall to wall; that is,

zonal distribution of the minerals was totally lacking.

The features mentioned strongly suggest that chalcocite had either: (a) been injected into the fissures; or (b) advanced into the fissures as a mobile mass, by capillary action or under the influence of some physical or chemical gradient. Whatever the state of the migrant chalcocite, iron was absorbed, bornite and chalcopyrite had been formed, and the latter minerals continued to migrate along the passages.

Theories of deposition from a solution or a gas cannot be totally discarded because of the lack of diagnostic depositional features; however, there is no indication of a chemical change in the host rock which might have caused deposition from a solution, and no temperature gradient existed within peridotite grains to engender movement by volatile transfer.

Phase Relations

The most distinctive difference in the mineral assemblages of low and high sulphur experiments was the stability of sulphur-rich minerals in the latter. Mineral assemblages noted were pyrite-chalcocite-digenite, pyrite-bornite-chalcopyrite, and covellite-bornite-chalcopyrite. Covellite was found most commonly on the periphery of chalcocite or digenite grains, and is considered to have developed during the cooling process (See Kullerud, 1957); an unusual iron-rich covellite formed in grains which contained iron. These assemblages were expected from the phase equilibrium studies of Roseboom and Kullerud (1958).

III. Non-Aqueous Low Pressure Experiments-
Excess Sulphur Environments

The low pressure experiments were carried out primarily to determine whether or not water and confining pressure have an effect on mobilizing chalcocite and copper-iron sulphides, by comparing the results with those of high pressure hydrothermal experiments containing excess sulphur.

In experiments M and W an electrical potential was applied on the reaction chamber. However, the masking effect of the highly mobile sulphides eliminated any possibility of determining the influence of an electrical potential on migration of the sulphides.

Features of the Experimental Products

The surface features of the experimental products were generally similar to those of the related excess sulphur hydrothermal experiments. Chalcocite had reacted similarly in all the experiments, and globular masses, glossy surfaces, filaments of massive chalcocite, and abundant new crystals had been produced. Bornite had reacted to a lesser extent than chalcocite; the grains had become sub-rounded and were coated with fine bornite, digenite, or covellite crystals, but glossy surfaces were generally lacking. Marcasite was unaffected under these conditions. Pyrite had developed on the surfaces and along cleavage planes of pyrrhotite grains. Covellite had developed on the surfaces of copper-rich products in experiments of the U series in which the sulphur was confined and the cooling was slow, but had not formed in experiments M and W, where the sulphur vapour pressure was low and cooling had been rapid.

Mobilization of the Sulphides

Cu-S Minerals

All the features illustrative of movement that were observed in the high-sulphur hydrothermal experiments were duplicated in the 'dry' atmospheres of this group of experiments. The migrant chalcocite or digenite again fused the original grains, moved into adjacent areas to envelop peridotite and other sulphide grains, and penetrated peridotite grains along fractures and mineral grain boundaries, absorbing iron from dispersed magnetite particles to produce bornite and chalcopyrite.

Chalcocite in the atmospheric pressure experiments was particularly mobile, producing needles and filaments of chalcocite that were commonly terminated with partly developed octahedra, or spreading smooth coatings of chalcocite across large areas of adjacent peridotite grains. The needles produced in experiment M are of particular significance, because they point in the direction of lower temperature. In experiment W no needles developed, but the large crystals of new chalcocite formed on the surfaces of the slag-like chalcocite masses grew away from the source chalcocite towards the ends of the tube. Also, many of the crystals developed faces on one side only; the sides facing the chalcocite source were continuous with the formless chalcocite masses from which the crystals grew, whereas most crystal faces developed facing away from the source chalcocite and, to a lesser extent, away from the furnace wires.

Experiments recently carried out at McGill university by J. Guy-Bray also showed that in high sulphur environments chalcocite migrated away from the source and down the temperature gradient. His apparatus consisted of two boats separated in a furnace: the chalcocite in some instances migrated from the source boat, bridged a short gap, and descended into the second boat. The experiments more or less confirm the hypothesis that the major proportion of the migrating chalcocite is rigid, as was suggested by the unsupported growth of chalcocite needles in experiment M.

Cu-Fe-S and Fe-S Minerals

The mobility of bornite was visibly less than that of chalcocite, from observations made in experiments U_A and U_B; nevertheless bornite does move readily under these conditions, according to the evidence presented earlier from its penetration of rock fragments. B.J. Meikle also provided supporting evidence from recent experiments made at McGill university; in them, he found that bornite migrated short distances across foreign surfaces when hot, gaseous sulphur at atmospheric pressure was passed across the mineral. Marcasite and pentlandite showed much less tendency to move in the present experiments. In experiment W, copper and iron diffused throughout the recovered specimen, producing iron-rich chalcocite and digenite, pyrite, and magnetite. The latter was present only at the chalcopyrite end, where iron was abundant and some air had penetrated the tube. The surface features of migration decreased noticeably from the chalcocite end through the bornite section into the chalcopyrite-pentlandite section, where such features were almost lacking. It is evident that the mobility of Cu-Fe-S minerals is suppressed by increasing iron content.

IV. Differential Pressure Experiments

The differential pressure experiments were made to test the ease with which sulphides could be moved by deforming forces in high sulphur and low sulphur environments. The objective was twofold: (a) to determine the physical state of the 'mobile' sulphide phase observed in other experiments; and (b) to investigate the possibility that sulphides may be injected into open spaces at temperatures below their melting points.

Peristaltic Force Experiments

The usual features of mobilization of chalcocite were present in these two high-sulphur experiments (N and O), although native copper was an additional equilibrium phase. The weak end of the capsule collapsed as desired, and the hydrostatic pressure tended to extrude the enclosed sulphides into the non-collapsible end of the capsule. Extrusion was not effected, however, and although some grains were deformed at the neck (Figure 39), it was evident that the sulphides remained rigid. Chalcocite was therefore not melted under these conditions, and the features suggestive of a liquid state resulted from 'activation' processes which were effective only at or near the surface of the chalcocite grains.

Uniaxial Force Experiments

An equal directive force of known magnitude was applied in these experiments so that any apparent differences in mobility of the sulphides used in the separate experiments could be attributed either to compositional differences of the sulphides or to different environmental conditions, rather than to differences in stress.

The experimental results showed that chalcocite and digenite deformed easily in excess sulphur environments at 550°C, and moved readily to fill any openings (Figure 40). Lineations paralleling the surfaces of the moving piston showed that the minerals had flowed from one point to another without fracturing. The Fe-rich digenite and bornite phases formed by solid-state diffusion near the pentlandite section in experiment T had also moved readily, carrying small masses of a stable pentlandite phase as they migrated (Figure 41), but the pentlandite away from the chalcocite contact did not become mobile under these conditions, and only fractured under the deforming force.

In the low-sulphur environment (Experiment T) chalcocite reacted to the deforming force like a brittle solid. The grains were fractured and pulverized, and the resulting discrete particles were compacted or forced into available openings (Figure 42). Flow structures were totally lacking, despite the fact that the experiment had been run for a greater length of time than the high sulphur experiments. Diffusion of copper and iron to form different Cu-Fe-Ni-S phases at the pentlandite-chalcocite boundary apparently proceeded as rapidly in the low sulphur as in the high sulphur experiments.

Collectively, the differential pressure experiments yield conclusive proof that sulphur is a potent agent in reducing the structural rigidity of some copper sulphides to the point where they can be deformed plastically, moved rapidly, and therefore injected easily, provided that passages and deforming forces exist. The sulphur evidently diffuses throughout the sulphides at these temperatures, facilitating bulk movement as well as activating the surface layers of atoms.

Surface Mobilization of Cu-S Minerals

Throughout the experimental study, evidence of the mobilization of chalcocite, digenite, and low-iron copper sulphides was found. The experiments have not revealed the processes involved in effecting mobility; however, they have provided information which restricts the search for the cause of activation to a relatively small field. In review, it has been shown that:

(a) Sulphur in excess of that required to form a stable bornite-digenite-pyrite assemblage greatly increased the mobility of the sulphides. Native sulphur and sulphide ion were more effective mobilizers than H_2S. Water or non-sulphurous anions did not affect the mobility to any appreciable extent;

(b) The highest degree of activation appeared to be at the surface of sulphide masses, or more specifically, at solid - gas interfaces. This is more evident in high-sulphur experiments, where mobile atoms or atom groups tended to reduce the surface area of sulphide masses or grains, forming spherical surfaces analogous to those formed by a viscous liquid, while at the same time the masses themselves strongly resisted deformation as only a solid can;

(c) A thin, mobile sulphide layer migrated rapidly across foreign surfaces and penetrated materials along fine passages, suggesting that the mobile mass had moved under the influence of surface tension. The direction of movement was away from the source material and, preferentially, down a temperature gradient;

(d) Spherical or non-planar surfaces developed contemporaneously with crystal faces, indicating that the mobile sulphide phase was in equilibrium with a (temporarily) non-mobile phase.

The evidence allows but one conclusion: that the apparent mobility of the low-iron copper sulphides is the direct result of extreme agitation of surface molecules. Therefore, in determining the cause of movement of the sulphides it is necessary to consider: (1) the phenomena of adsorption and absorption at solid-liquid and solid-gas interfaces; (2) the processes causing disordering of crystal lattices at interfaces; and (3) the specific media involved in effecting disorder of crystal lattices.

The literature yields little applicable information on these complex subjects; however, radioactive isotopes are now providing a means of examining the phenomena of surface activity and mass diffusion, and some progress is at last being made experimentally. Harrison, Morrison, and Rose (1957) made a notable contribution when they examined isotopic exchange rates between gaseous chlorine and solid sodium chloride at temperatures ranging from 20°C to 400°C. They found that a complex series of reactions took place in three steps which involved both the surface and the bulk of the solid. The initial low-temperature reaction was rapid, and involved only the outermost surface layers of atoms. The writers attribute the reaction to strong adsorption of chlorine, causing low temperature lattice disordering; they suspect that structural irregularities exist at the surface of the NaCl crystal to account for the energy involved in disordering or removing ions from the halide lattice. The second reaction was much slower, initially reaching a steady reaction rate between 60°C and 80°C, and appeared to involve both adsorption and absorption of chlorine; the reaction was brought to completion more rapidly at higher temperatures up to 200°C. Only near-surface atom layers were affected. Above 200°C, a third type of reaction began which proceeded for much longer periods and produced much greater activity, until the isotope concentration "- - - approached the value corresponding to a uniform distribution of radioactive atoms throughout the gaseous and solid phases, showing that bulk diffusion had occurred.". This bulk diffusion reaction proceeded to completion at approximately 260°C, or one-half the melting point of NaCl.

The macroscopic features observed in the present experiments suggest that similar reactions occurred between sulphur and the copper sulphides. By analogy, structural disorder of the outermost layers of atoms in the sulphide lattice produced a high energy surface film which responded readily to physical differences such as temperature and concentration gradients or small surface stresses. The main mass of the sulphides would have a lower level of energy, but would respond readily to a deforming force because internal disordering of the lattices by bulk diffusion reduced the rigidity to the point where 'plastic flow' could be achieved.

Because the transition of Cu_9S_5 to Cu_2S begins at the experimental temperatures used (550°C), the sulphide lattice is probably already structurally unstable, and lattice disordering therefore may be effected readily by the free sulphur atoms. Further experimental work at lower temperatures, in both the Cu-S and Cu-Fe-S systems, may yield information which would establish the influence of this transition on the mobilization of the sulphides.

Some theoretical considerations of surface energies and configurations which require mention here are those given by Herring (1952). He assumes that the configuration of any crystalline body reflects a variation in the free energy across surfaces in thermal equilibrium and that at different points on a crystal the surface free energy will vary according to the Miller indices (more specifically, the atomic density). The surface tension (γ) is a function of the surface free energy and therefore can be related to the direction (n) of the unit normal to a surface plane. If the normal to another plane pierces the original surface plane, the two normals can be related in direction by an angular variable (δn), and the surface free energy of the second plane can be related to the first by a direction ($n + \delta n$). In this way, the surface free energy, and hence the surface tension, across any crystal face can be related to the unit normal to that face. A geometric polar plot, in which distances from the unit origin in the directions (n) and (n + δn) are proportional to (γ), will therefore give the configuration of the surface free energy of the unit. The theory is outlined in more detail by Seitz (1940, p. 97). A schematic plot given by Herring (p.26) is shown in Figure 44.

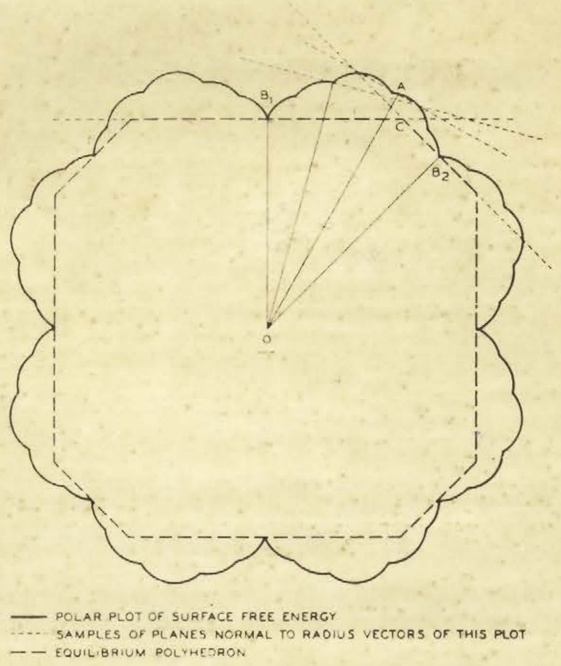


Figure 44

Schematic γ plot and the Wulff construction based on it. (After Herring, 1952, p.26)

Cusped minima appear on the plot where the surface free energy reaches minimum values. These do not appear in the case of liquids, since γ is isotropic and independent of orientation of the normal to the interface; the equilibrium shape will therefore be a sphere. With increasing anistropism, however, the equilibrium shapes may vary from ellipsoids (liquid crystals) to polyhedra (crystals), depending on the inherent physical properties of the material or the influence of external conditions. Thermal agitation and contamination of surface layers by adsorption of foreign substances are external factors which tend to blunt or eliminate cusps, since the surface tension is decreased; the equilibrium shapes may therefore shift from polyhedral to sub-polyhedral or even rounded forms, depending on the degree of disordering of the lattice.

In the present high sulphur experiments the apparent contemporaneous development of crystal faces and rounded, glass-like surfaces of chalcocite is explained by applying Herring's concepts. Surface contamination by adsorption of sulphur lowered the lattice disordering temperature and thermal agitation increased the surface free energy (both tending to eliminate cusped minima on the γ plot), and depending on local conditions either polyhedral or liquid crystal forms could develop. In the low-sulphur experiments no appreciable reduction of the disordering temperature was effected by adsorption of atmospheric constituents, and the increase in surface free energy by thermal agitation alone was insufficient to reduce anisotropism to the point where non-polyhedral configurations would be produced.

In low-sulphur environments, then, migration of sulphides would have to be effected by local solution and re-deposition, recrystallization, or volatilization, since the polyhedron was the stable form. But in excess sulphur environments the highly disordered state of the lattice in the outer layers would permit migration of the surface atoms, since the stable form would approach that of a liquid. The knowledge that sulphides move easily at relatively low temperatures is of extreme interest to the ore magmatist.

Suggestions for Further Experimental Work

The present investigation is considered to be only preliminary to more detailed studies of transportation and deposition of sulphides in dynamic systems. The writer is convinced that this type of experimental work is vital, for it provides a direct approach to the problems of transportation and deposition of ore minerals, and therefore to the problems of mineralization. The field for further experimental work is unlimited in all directions. Some experiments relating to the present study which may be carried out are:

(1) Experiments to determine the apparent solubilities of Cu-S and Cu-Fe-S minerals at lower temperatures, in atmospheres similar to or different from those used in the present experiments;

(2) Long-term hydrothermal experiments to attempt replacing minerals, using sulphide-bearing solutions;

(3) Experiments to examine mobilization of the copper sulphides in high-sulphur atmospheres at temperatures lower than those used in these experiments;

(4) High-temperature X-ray diffraction studies of the copper sulphides to determine the structural changes which take place as the sulphides are mobilized;

(5) Differential pressure experiments to determine the conditions under which the iron-rich sulphides may be deformed easily.

APPLICATION OF THE EXPERIMENTAL RESULTS TO NATURAL PROCESSES OF TRANSPORTATION AND DEPOSITION OF SULPHIDE MINERALS

This research was primarily intended to test the merit of the hydrothermal theory of transportation and deposition of sulphide minerals. As the study progressed, however, it became necessary to investigate 'dry' systems in order to compare the mobility of the sulphides in aqueous and non-aqueous environments. Finally, it was considered necessary to test the responses of some sulphides to deforming forces in order to determine whether or not the sulphides could be injected into openings as an 'ore magma' at temperatures below their melting points. Three possible means of emplacement of sulphide minerals are therefore to be considered with reference to the present experiments; these are: (1) hydrothermal transport; (2) surface migration; and (3) injection of sulphide 'melts'.

Hydrothermal Transport

The hydrothermal theory encompasses a vast field; therefore, restrictions in the scope of the experimental study had to be drawn, and some assumptions had to be made. The studies were restricted to the Cu-S and Cu-Fe-S systems; only high temperatures were applied to the 'transport' end of the experimental circuit; and the possible effect of varying confining pressure was not considered. Two assumptions were made: (1) the metal-bearing components to natural solutions were considered to be always in equilibrium with a sulphide phase; and (2) all metal ions or metal-sulphide compounds (complexes, molecules, gels, or suspensions) formed in the 'primary' experimental vessel were considered to be possible constituents of a natural ore-bearing fluid and could contribute to the formation of an ore deposit.

One of the major criticisms of the hydrothermal theory with regard to 'primary' sulphide mineralization is the low solubilities of common sulphides in water. When calculated sulphide solubilities are employed in determining the quantities of water required to form even small orebodies, astronomical figures are obtained; for example, one cubic kilometer of water will carry approximately one short ton of Cu_2S in solution if the solubility of the sulphide is taken as 10^{-6} gram per litre. Assume tentatively that the water is to be provided by melting or 'remobilization' of either igneous or sedimentary rocks containing 5% by volume of free water. From this source, a total of 20,000 cubic kilometers of rock (a cube 27.1 kilometers on each edge) would be required to produce 1000 tons of Cu_2S. Ideal conditions are necessary; that is, the solutions are saturated with the sulphide, all the water freed (1000 Km^3) is funneled through the small area of deposition, and all the sulphide is deposited as the solution passes by. Such a theory of genesis for a large sulphide orebody is certainly open to criticism.

Solubility is therefore a critical factor in the transportation of sulphides by hydrothermal solutions. This is evident from the following list, in which the volumes of source rock at 550°C required to produce given tonnages of Cu_2S have been calculated from Czamanske's solubility values and from apparent Cu_2S solubilities obtained in some of the present experiments, assuming the ideal conditions outlined above can be met:

Environment	Apparent Solubility (g/l)	Tons Cu_2S	Rock Volume
Water (Czamanske, 1959)	$3.5(10)^{-6}$	193	1,000 Km^3
Water (Expt. average)	$2.0(10)^{-4}$	11,000	' '
Artificial Sea Water	$2.4(10)^{-3}$	132,000	' '
NH_4Cl Solution	$1.1(10)^{-2}$	605,000	' '
H_2S-saturated Solution	$1.6(10)^{-2}$	880,000	' '
Na_2S or S (Expt. average)	$3.2(10)^{-2}$	1,760,000	' '

The last four solubilities yield attractive tonnages. The H_2S-saturated solution may be used as an example of an ore-forming solution; from it, 3.6 million tons of Cu_2S ore grading 4% copper can be produced from 200 Km^3 of source rock, and only 10 Km^3 of solution need pass through the depositional site if all the sulphide is precipitated.

The possibility that such ideal conditions may be obtained in natural environments should be considered briefly:

A. The temperature of 550°C is not considered to be unrealistic because high temperatures could have prevailed during deposition and the effects on wall rock, if any, could be erased by post-depositional metamorphism (Williams, 1955).

B. Concerning saturation, it is probable that near-equilibrium conditions exist in natural magmas, and therefore a water-rich differentiate would probably contain its maximum amount of sulphide, provided that the metallic components are available; they appear to be available in most basic igneous and mafic-rich sedimentary rocks.

C. The question of availability of water in magmas to provide hydrothermal solutions has long been debated. There is no question that magmas of different origin contain different proportions of free water (compare, for example, explosive and quiescent lavas) , therefore great variations in the volumes of hydrothermal fluids produced from different magmas would be expected. The 5% by volume used in these calculations is a possible water content which appears to be acceptable to most students concerned with the compositions of magmas (See Ingerson, 1954, and Buddington, 1959).

D. Large volumes of water cannot traverse rocks of low permeability. However, mineralization which is unmistakably epigenetic is invariably associated with fractures, fissures, or weakened zones in the host rocks; the effects of tectonic deformation are found everywhere in regions of widespread mineralization; and volcanism is always associated with crustal movement. Such evidence indicates that permeable channelways can exist in regions where igneous activity is taking place. Not only could large volumes of water move along such passages; they would also be focal points for the more volatile components of a confined magma.

E. Deposition of the sulphides is, beyond doubt, the most controversial subject related to the process of hydrothermal mineralization. The essential requirement is that the invading solutions must be out of equilibrium with their surroundings, otherwise no deposition will occur. The chances are infinitely high that the solutions would be out of equilibrium — chemically, physically, or both — at some point on their traverse, and at that point deposition will take place. The proportion of sulphides removed from the solutions, however, will be dictated by the degree of disequilibrium of the system and by the time allowed for approaching a state of equilibrium; time is necessary, for example, to effect replacement of minerals.

Geological structures must be favourable for the introduction of minerals into pre-existing rock bodies, whatever theory of transport is favoured. There must also be a source from which the minerals can be derived, and a chemical or physical potential must exist to cause movement. Magmas exist or are produced at one time or another in the earth's crust or sub-crust, and crystallization differentiation takes place when they cool in a confined space. Recent experimental studies by Schairer, Yoder, and others at the Geophysical Laboratory, Washington, support this theory. The final product of differentiation of a cooling, confined magma would contain the most volatile components, and according to studies in volcanic areas, water is the major component of this volatile fraction. Lindgren correctly named it a 'hydrothermal fluid'.

The present experiments have shown that the apparent solubility of Cu_2S in high temperature aqueous solutions is much higher than has been previously accepted. If geological conditions are favourable for the introduction of similar natural fluids into the crustal rocks, there is no reason to doubt that orebodies of Cu-S or Cu-Fe-S minerals can be deposited from hydrothermal solutions.

Surface Migration

The lack of hydrous minerals within and about a few major sulphide orebodies has caused much dissention as to the sulphides having a hydrothermal origin, and, among those geologists most directly associated with these deposits, the sulphide 'magma' theory is widely accepted. High temperatures are required to melt the common sulphides, however, and in many cases there is not only a lack of high temperature metamorphic effects in the enclosing rocks, but also much apparent geothermometric evidence that sub-liquidus temperatures existed during emplacement of the sulphides. Such indications of lower temperatures may not be reliable, but assuming they are, the question arises as to how the sulphides were transported.

Experiments carried out in this study have shown that in excess sulphur environments chalcocite, digenite, and bornite become mobile at temperatures far below their melting points, and move readily as thin films along surfaces and grain boundaries or through narrow passages under the influence of temperature and concentration gradients. The mobile layers of the sulphides evidently have a low surface tension, which facilitates migration. Provided that there is a concentrated source of these sulphides, that sulphur is abundant, that the gradients are maintained, and that passages exist, Cu-Fe-S orebodies could form by this process of surface migration; moreover, emplacement could take place very rapidly.

Water apparently plays no part in the process of surface mobilization of these sulphides, therefore surface migration can take place in completely 'dry' environments. The more refractory sulphides such as pyrite, pyrrhotite, and pentlandite did not move as readily in similar environments, however, and it is evident that a higher energy source must be invoked if a similar theory of transport for them is to be proposed.

A sulphur-rich magma is the most likely source for those sulphide deposits of low water content and frequently basic silicate affiliations. Such a magma may have been produced by partial differentiation of a plutonic basic magma, by anatexis of deeply buried sulphide-bearing sediments or, as proposed by Brown (1950), by tapping of an abyssal sulphide-rich layer of primeval origin.

Injection of Sulphide 'Melts'

The sulphide 'magma' theory also incorporates the idea that differential forces act upon a sulphide-rich melt and inject it into the confining rock. There is sufficient geologic evidence to support the theory of injection of silicate magmas into crustal rocks, but for the same reasons that the sulphide magma theory is treated with suspicion, so does a theory of mass injection of sulphides meet with disfavour.

Some of the present experiments have shown that high-copper sulphides move readily at sub-liquidus temperatures in excess sulphur environments without the benefit of directive forces. Other experiments in which differential pressures were applied revealed that in similar environments these sulphides flowed easily by plastic deformation to fill any available openings. It requires no great leap of the imagination to apply such experimental evidence to natural sulphide systems.

SUMMARY AND CONCLUSIONS

A series of 25 experiments was carried out to:

(a) test the solubilities of some copper sulphides in different hydrothermal solutions in an open system, under moderately high temperature-pressure conditions, in order to compare the effectiveness of the solutions as transporting media. The products of deposition and replacement at both high and low temperatures were also examined;

(b) examine the features of surface mobilization of sulphides in high-sulphur aqueous and non-aqueous environments, determine the cause of activation, and measure the rate of movement of the mobile products formed;

(c) test the response of the sulphides to deforming forces in both high-and low-sulphur aqueous environments.

An open system was used in the hydrothermal experiments, so that rates of transport of sulphides, rather than absolute solubilities, could be compared for the different solutions. Two pressure vessels connected in series with a hydraulic pump and metering valve permitted flow of solutions through the experimental system at a desired rate. The vessels were independently heated so that the temperatures of the 'source' vessel containing the sulphides and the 'depositional' vessel containing rock materials could be regulated at will.

The results obtained from the dynamic hydrothermal experiments show that the solubilities of chalcocite and bornite in water under the conditions used are much greater than has been indicated by free energy data. The apparent solubilities increase upon addition of soluble salts to the solutions, and are highest in solutions which contain sulphur, in either the elemental or ionic state. No replacement of rock materials placed in the depositional vessel was effected.

Mobilization of the surface atoms of chalcocite and bornite is effected readily when elemental sulphur is present in Cu-S and Cu-Fe-S systems held at temperatures of 550°C. Sulphur appears to lower the lattice disordering temperature, and consequently the surface tension, to the point where a thin layer of the sulphides can become mobile and migrate across surfaces or penetrate narrow passages under the influence of temperature of concentration gradients. Water apparently plays no part in the process of surface mobilization, therefore migration occurs equally rapidly in either aqueous or non-aqueous environments. The rate of migration of chalcocite across surfaces in 'dry' environments was approximately one centimeter per 24 hours.

Chalcocite, covellite, and bornite moved readily to fill available openings when differential forces were applied to them in high-sulphur atmospheres. The movement was apparently achieved by plastic deformation, as resistance to the deforming forces was evident. The sulphides only fractured in low-sulphur atmospheres.

The conclusions reached from this experimental investigation are as follows:

(1) Hydrothermal fluids which contain sulphur are capable

of transporting considerable quantities of copper sulphides in solution, and could easily form large copper sulphide orebodies if geologic conditions favour the deposition of sulphides from solution. Solutions low in sulphur are less able to form sulphide orebodies because of the much lower solubility of sulphides in them.

(2) Copper sulphides in high-sulphur environments can migrate readily across foreign surfaces under the influence of temperature or concentration gradients. This process of surface migration, which takes place in non-aqueous atmospheres at temperatures well below the melting points of the sulphides, may be an extremely important natural means of transport of sulphide minerals from one point to another.

(3) If a concentrated sulphide mass having a high sulphur content is subjected to natural differential pressures, the sulphides will move at sub-liquidus temperatures into areas of low pressure. The more refractory sulphide phases would move less readily, and may even become segregated from the more mobile phases to produce a zoned orebody.

No single theory of ore genesis can explain all the diverse features of mineral deposits, and frequently may fail to explain important features in even a single deposit. In the writer's opinion it is necessary to recognize the possibility that several processes of mineralization could have been active throughout the history of an ore deposit, and it is therefore a question not of favouring a single theory of emplacement, but of determining which process was the most dominant in producing the deposit. In this study both the hydrothermal and magmatic theories of ore transport and deposition have received impressive experimental support.

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OUTLINE OF EXPERIMENTS

1. HYDROTHERMAL GROUP - LOW SULPHUR

Expt.	Purpose of Experiment	Content of Bombs		Environment	Temperatures (°C)		Pressure (psi)	Length of Run (Hours)	Vol. Liquid Passed (ml.)	Remarks
		B.1	B.2		B.1	B.2				
A	Solubility and ions tests	Chalcocite, Pyrrhotite in contact	Peridotite	Distilled Water	510	210-160	15,000	14	- - -	B.1 leaked, no transfer to B.2
B	Repeat of A	Chalcocite, Pyrrhotite in contact	Peridotite	Distilled Water	520	200-160	16,500	48	1250	Rapid feed into B.1 caused 3 leakages
C	Migration and Solubility tests effect of CO_2 on deposition	Chalcocite, Pyrrhotite, separated by Alundum filter	Peridotite Pyrrhotite Calcite	Distilled Water	620	200-140	16,000	72	1250	Two leakages at entry end, B.1
D	To test effect of saline waters on solubility	Chalcocite, Pyrrhotite separated by filter, Pyrite in contact with Pyrrhotite	Calcite Pyrrhotite Peridotite	Artificial sea water; less sulphate	620	200-140	16,000	10	150	Lines blocked, terminating experiment
E	Testing solubility in chloride solutions	Chalcocite	Diabase Calcite	1.0 M NH_4CL solution	550	(1) 220-150 (2) 350-250	15,500	5	70	Nickel sealing washers substituted for copper. B.1 reversed to avoid leakage
F	Total transport of copper, and radicals tests	Chalcocite, Filter at exit end	Calcite Pyrrhotite Diabase	Distilled Water	550	210-130	15,500	48	850	- - - - -
G	Total copper transport, radicals tests, identity of mobile Cu mineral	Chalcocite	-------	Distilled Water	550	- - -	15,500	15	350	B.2 not used
H	Total transport and radicals tests, check of minerals identification	Chalcocite	Quartz	Tap Water	550	180-110	15,500	26	900	- - - - -
I	To test movement of Bornite	Bornite	Quartz	Tap Water	550	180-110	15,500	10.5	240	Lines blocked

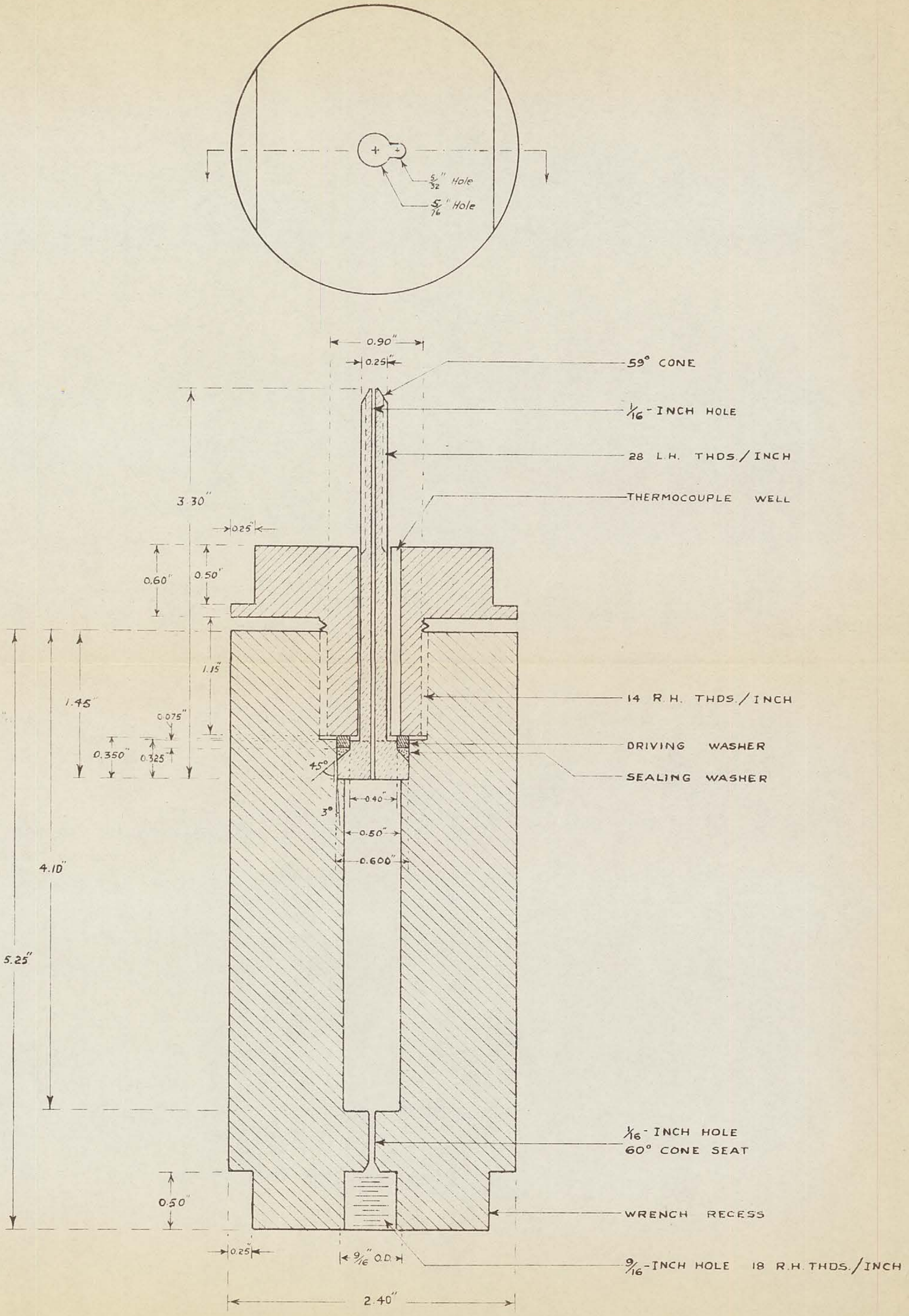
OUTLINE OF EXPERIMENTS

Expt.	Purpose of Experiment	Content of Bombs B.1	Content of Bombs B.2	Environment	Temperatures (°C) B.1	Temperatures (°C) B.2	Pressure (psi)	Length of Run (Hours)	Vol. Liquid Passed (ml.)	Remarks
2.	HYDROTHERMAL GROUP - EXCESS SULPHUR									
J	To test movement of materials under high sulphur pressures	Chalcocite	Quartz	Sulphur, Distilled Water	550	350-200	15,000	3	Nil	Line blocked. No transfer Cooled slowly
K	Repeat of J	Chalcocite	Quartz Diabase	Sulphur, Distilled Water	550	500-450	15,000	6	24	Slow flow rate. Line blocked
L	Equilibrium conditions studies, solubilities. Replacing rock minerals	Chalcocite Peridotite	Quartz Peridotite	Sulphur, Distilled Water	550	300-190	15,000	96	10	Intermittent bleed-off every 24 hours
P	To check transportation as double sulphides or complexes	Chalcocite	Calcite, Peridotite Pyrrhotite	1.0 M Na_2S solution	550	285-230	15,500	12	200	Lines blocked. B.1 corroded
V	To test mobility in H_2S atmosphere	Chalcocite Bornite	Quartz Chlorite Schist Pyrrhotite	H_2S gas, Distilled Water	550	300-250	300	27	100	H_2O introduced intermittently Pressure equals bottle pressure
3.	LOW PRESSURE SYSTEMS - EXCESS SULPHUR									
M	To test mobility in dry Cu-S system	Glass Tube	Chalcocite	Sulphur	550		Atmospheric Pressure	40	Nil	Thermocouple reacted. Temp. increased to 650°C for 10 hours Electrical resistance 1 Megohm
W	Repeat of M Cu-Fe-Ni-S System	Glass Tube	Chalcocite, Bornite, Pentlandite, Chalcopyrite	Sulphur	650		Atmospheric Pressure	72	Nil	- - - - - -
U_A	Comparison of mobilities of minerals and their phases. Cu-Fe-S System	Single Bomb	Bornite, Marcasite	Sulphur	580		Sulphur V.P. 77 psi	18	Nil	Registered pressure high Bomb not evacuated
U_B	As U_A Cu-Fe-Ni-S System	Single Bomb	Bornite, Pentlandite	Sulphur	550		Sulphur V.P. 56 psi	19	Nil	As U_A
U_C	As U_B	Single Bomb	Chalcocite, Pentlandite	Sulphur	550		Sulphur V.P. 56 psi	19	Nil	As U_A

OUTLINE OF EXPERIMENTS

4. DIFFERENTIAL PRESSURE EXPERIMENTS

Expt.	Purpose of Experiment	Apparatus	Content of Vessels	Environment	Temperature (°C)	Pressure (psi)	Length of Run (Hours)	Remarks
N	To force movement of Cu_2S by differential pressure. Peristaltic force	2-part Capsule within Bomb	Chalcocite at collapsible end. Non-collapsible end empty	Sulphur	550	7,500	4	Capsule collapsed. No apparent leakage
O	Repeat of N	As N	As N	Sulphur	550	10,000	30	Capsule collapsed. Water within, indicating leakage at late stage
Q	Repeat of N Directive force	Differential Pressure Bomb	Chalcocite at dynamic end. Quartz, Peridotite at static end	Sulphur	550	10,000 Confining	2	Bomb released at 550°C. Cooled slowly under jack pressure
R	Repeat of Q Pentlandite added	As Q	Chalcocite, Pentlandite at moving end. Quartz, Peridotite at static end	Sulphur	550	5,000 Confining	2	Bomb released. Cooled slowly under jack pressure
S	Repeat of R	As Q. Male plug lengthened	As R	Sulphur	550	500 Confining	4	No leaks
T	To test mobilization in low-sulphur environment	As S	As R Nephrite substituted for Quartz	Distilled Water	550	500 Confining	18	No leaks



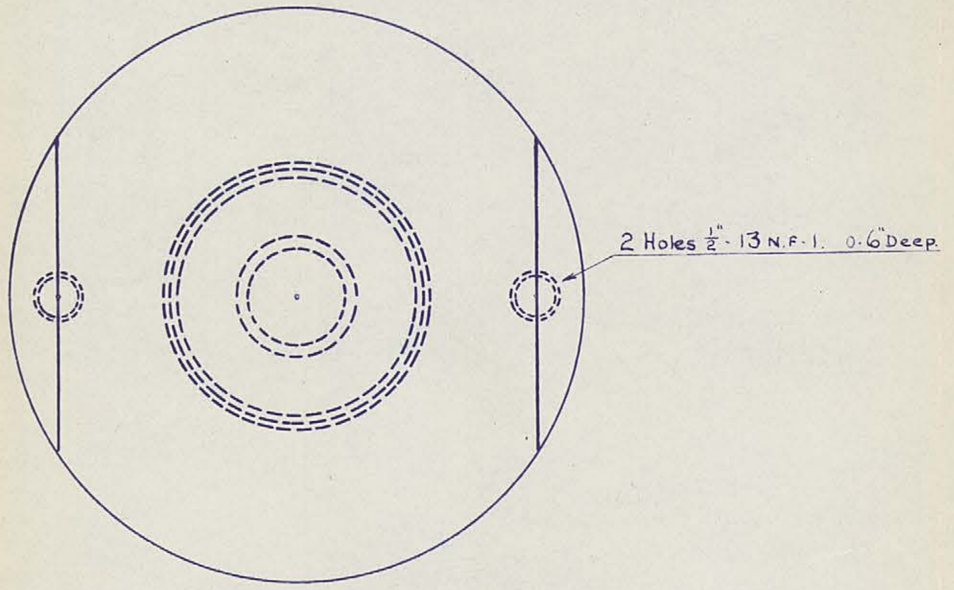
HIGH PRESSURE VESSEL

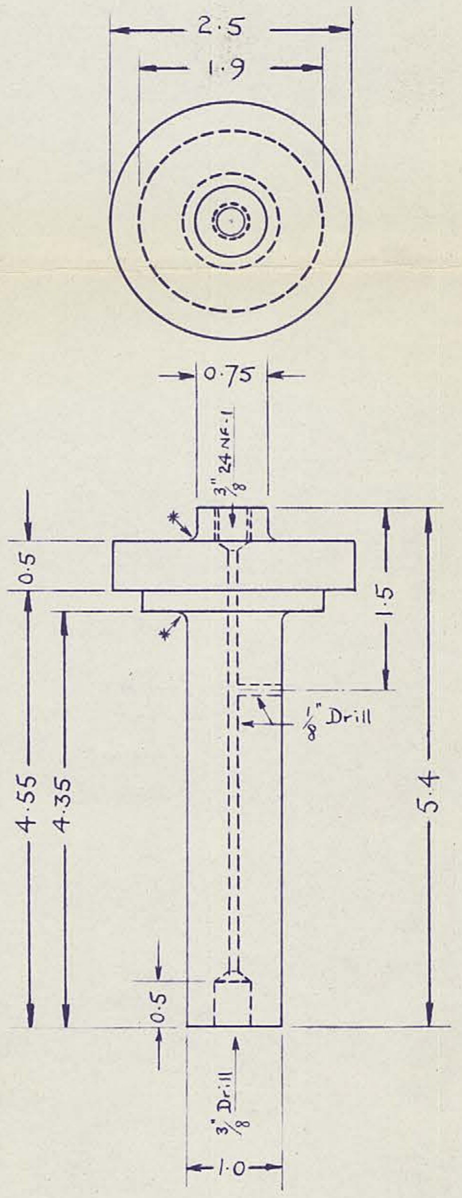
ASSEMBLY DRAWING

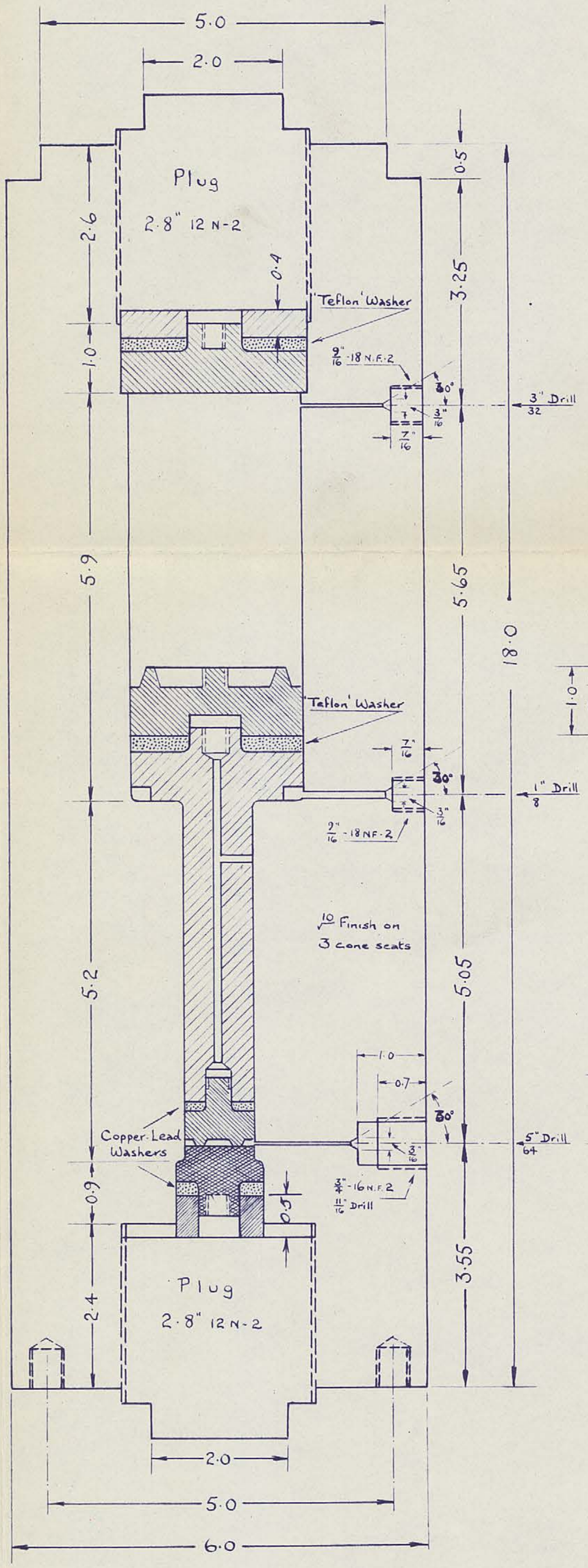
FULL SCALE

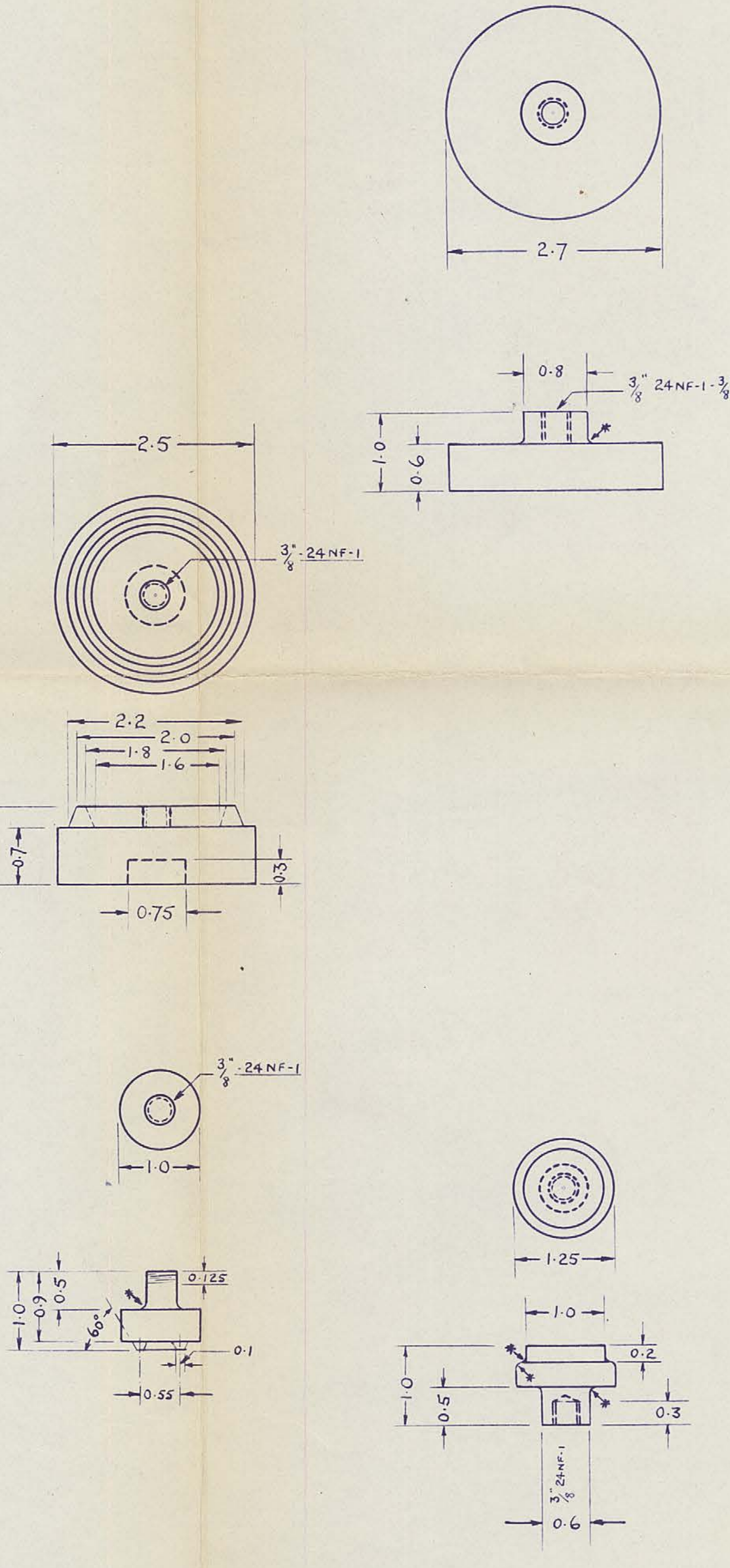
October, 1957

J.A. SOLES









Note:
All mating parts i.e. Intensifier bore, piston components and seals, are to have 'Class 3' fits and 0.000001" finish.

* = 1/16" Radius

Steel: Heat treated **431** s.s.

PRESSURE INTENSIFIER

Scale - Half-Size

Mar. '59

J.A.S. & R.V.O.