

UNIVERSITY OF MANITOBA

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EXPERIMENTS ON THE TRANSPORTATION AND DEPOSITION OF SULFIDES
IN ALKALINE SULFIDE SOLUTIONS

BY

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I ABSTRACT

A short outline of the problem of the transport and precipitation of metallic sulfides in ore-bearing solutions is presented. Three modern theories are discussed, and experimental work supporting one of these is described. The conclusion is reached that the metallic sulfides are carried upward in hot solutions in the form of double sulfides with alkali sulfide, which are progressively broken down, precipitating the metallic sulfides. Under some conditions, colloidal sulfides result from the decomposition of the double sulfides, and these then may be coagulated in several ways. A combination of the double sulfide and colloidal sulfide theories of metallic sulfide transport and precipitation seems to explain the genesis of most of the common sulfide deposits.

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V INTRODUCTION

This investigation is an attempt to analyze critically the popular theories of the chemistry of sulfide precipitation in ore deposits and to add experimental evidence in favour of one of these theories which appears to the writer to be closest to the truth.

In that branch of geology now called economic geology, many theories of the deposition of sulfide ores have been presented. Frequently the only justification for a theory was that it was simple and fitted in well with the current philosophy of the subject. Very seldom was it subjected to reasoning based on known chemical facts and still more seldom to experiments that duplicated the postulated natural conditions. The complexity of the problem and its almost exclusively chemical nature have both discouraged field geologists from serious attempts to test the various theories and have led to a reaction whereby almost all the emphasis is now placed on structural controls rather than physico-chemical controls.

It will be generally agreed, however, that an understanding of the chemistry of the deposition of the sulfides is essential to the working out of many of the mining problems at present swept aside by variations of: "Gold is where you find it." There is apparently no reason why these problems cannot be solved. There is abundant chemical and physico-chemical data still untapped. There is much that can be done to test conflicting theories by the experimental duplication of natural conditions. He would be a poor petrologist who did not have some idea of how the igneous rocks were derived and how they were intruded. Likewise he would be a poor economic geologist who did not have at least a working hypothesis of how the sulfides were carried and precipitated.

The writer has set himself the task of digesting the current theories of sulfide deposition, chemical and physico-chemical data that have a bearing on this, and descriptions of naturally-occurring metallic sulfide deposits in the hope that out of this material, which was found to be very voluminous, might come an understanding both of the inconsistencies existing between theory and fact and of the direction in which research should be directed.

Part-time research during the sessions 1935-36 and 1936-37 at the University of Manitoba was a study of the properties of the metallic sulfides in colloidal form. Research during the fall and spring semesters, 1937-38, at the University of Wisconsin was a search of the geological and chemical literature and experimental investigation of the properties of the double sulfides of metals and sodium and of the colloidal metallic sulfides. Research during the session 1938-39 at the University of Manitoba was the completion of the work on double sulfides.

The description of the experimental work is preceded by a short history of the development of general ideas of ore deposition and a description of the three major theories of sulfide deposition. Following the description of the experimental work is a summary of the results and a general conclusion wherein a theory of metallic sulfide transport and precipitation, based mostly on the experimental results, is presented.

VI HISTORY OF THE THEORY OF ORE DEPOSITION

It has only been since the beginning of this century that the question of how the ore minerals are transported and deposited in nature has received anything like a serious objective study. Before the publication of the work of Posepny (1) in 1902, many theories were in vogue. Most of them had as foundation some variation of the lateral secretion hypothesis. The extreme theory of Sandberger was not accepted to any great extent, but in general, the idea was that meteoric water migrated downward, collected into trunk channels and rose upward in fissures. On warming up, or when warmed, they were solvents for the metallic sulfides, which they deposited later when cooling during ascension. There was also considerable support given to the theory that downward-percolating cold waters were responsible for solution and precipitation of the metallic sulfides.

After 1902, however, the theory that the ascension of hot solutions of magmatic origin was responsible for sulfide deposition began to gain support and soon supplanted other theories. The reason for the adoption of this theory was that it was practical. Other ore deposits could be found with its help. The very close association of batholithic domes and ore deposits over North America seemed to prove the magmatic theory.

Attention then began to centre on the method of transportation and deposition of the ore minerals. Two theories were presented. One stated that the rising solutions contained the sulfates of the metals, which were reduced to sulfides by organic matter with which the solutions came in contact (2). This fell into disfavour when it was demonstrated that organic compounds are

(1) Posepny, F: The Genesis of Ore Deposits, A.I.M.E., 1902.
 (2) Jenney, W.P.: The Chemistry of Ore Deposition. Ore Deposits, A.I.M.E., p. 305, 1913.

in general incapable of reducing sulfates to sulfides in water solution unless at very high temperatures. The other theory stated that the rising solutions contained enough free acid to depress the ionisation of hydrogen sulfide so that the metals, present as chlorides, could not precipitate as sulfides and that the gradual neutralization of the acid precipitated the metallic sulfides in an order dependent on how much of each metallic ion was in solution and on the solubility of each metallic sulfide. It can be demonstrated that this theory is untenable, yet to the present day it has many adherents.

Individual workers in the field, who used the evidence in ore deposits to formulate a theory of deposition rather than explaining a deposit by a preconceived idea, began to develop the hypothesis that sulfides were carried in the colloidal state. This received much support when the number of examples of colloform sulfides was realized. Opponents of the theory stated that it was not known for how long the sulfides were in the colloidal state before coagulation but all that is known is that just before precipitation they were in this form. This was a valid objection, and it will be seen that there are more specific objections to the theory of universal colloidal transportation and precipitation. These will be discussed later.

Recently, a new theory has entered the field and this postulates that the metallic sulfides are soluble in solutions of alkali sulfide from which they can be precipitated in a variety of ways. The novelty of this idea is more apparent than real, for Becker (1) presented it as early as 1888, but it has received very little support and even now its complexity is a deterrent to acceptance by geologists. Thus the three theories which seem to be receiving the most support today are the acid solution theory, or ionic sulfide theory,

(1) Becker, G.F.: Geology of the Quicksilver Deposits of the Pacific Slope, U.S.G.S. Mon 13, pp. 284, 368, 1888.

the double sulfide theory, and the colloidal sulfide theory. These will be separately discussed in more detail below.

VII PREVAILING THEORIES OF SULFIDE DEPOSITION

The Ionic Sulfide Theory

Metallic sulfides are slightly soluble in water and this fact has been used as a basis for the most generally prevailing theories of sulfide transport and deposition.

N.L. Bowen (1) has presented the most popular concept of this theory which is based to a large extent on the field work of the Geophysical Laboratory in Washington. According to this hypothesis, the metals are extracted from the magma chamber as chlorides by an acid solution containing H_2S or compounds that can produce it. The gradual neutralization of the acid by the wall-rock brings about the precipitation of the metallic sulfides.

The first objection to this theory is that the copper-iron sulfides and the sulfosalts cannot be synthesized in this manner. In fact it is the analytical method used in the separation of many of the common metals. This will be discussed more fully later.

The second objection is that the order of precipitation to be expected from chemical data on solubilities is almost identical with the order of deposition in nature, but reversed. That is, the most soluble sulfide precipitates first, and the most insoluble, last. It has been suggested that this reversal is due to the great difference in the initial concentration of the metals. That this will not bring about the desired reversal will be evident from the following discussion:

Consider the equation



(1) Bowen, N.L.: The Broader Story of Magmatic Differentiation. Ore Deposits of the Western States, p. 120, A.I.M.M.E., 1933.

where M is a divalent metal. Then, according to the Law of Mass Action,

$$\frac{[M^{++}] \times [S^{=}]}{[MS]} = K \quad \dots\dots\dots 1)$$

and

$$[M^{++}] \times [S^{=}] = K_{sp} \quad \dots\dots\dots 2) ,$$

since if the solid sulfide is in great abundance, its concentration may be said to be constant. It will be noticed that equations 1) and 2) are valid only when a state of equilibrium exists. If now two metallic sulfides are in equilibrium with the same solution,

$$[M_1^{++}] \times [S^{=}] = K_{sp1} \quad \dots\dots\dots 3)$$

$$[M_2^{++}] \times [S^{=}] = K_{sp2} \quad \dots\dots\dots 4)$$

and dividing equation 3) by equation 4),

$$\frac{[M_1^{++}]}{[M_2^{++}]} = \frac{K_{sp1}}{K_{sp2}} \quad \dots\dots\dots 5)$$

This means that if the solution is in equilibrium with two metallic sulfides (both of a divalent metal) then the metallic ions are present in a constant ratio (for any given temperature) and this ratio is the ratio of their solubility products. If the sulfide ion concentration increases, then metallic sulfides will precipitate, and the two will precipitate in this same ratio.

If now the initial ratio of the two metallic ions is such that the more soluble sulfide separates out first, then it will continue to do so until the ratio is that of their solubility products at that temperature, when both will precipitate out in that ratio until removed from the solution.

As an illustration, take the case of ZnS and PbS. In nature, ZnS precedes PbS in time of deposition and the precipitation of ZnS is usually nearly completed before the start of the PbS precipitation. Such a condition is impossible if the ionic sulfide theory of sulfide transport is true, since the latest data on sulfide solubility (1) give the solubility product for ZnS at 25°C as 1.15×10^{-26} , and for PbS, 7.00×10^{-30} . That is:

$$\frac{[\text{Zn}^{++}]}{[\text{Pb}^{++}]} = \frac{K_{sp\text{ZnS}}}{K_{sp\text{PbS}}} = \frac{1.15 \times 10^{-26}}{7.00 \times 10^{-30}} = 1.64 \times 10^3 = 1640,$$

which means that in order for ZnS to start to precipitate out before PbS, the ratio of Zn to Pb in the solution must be greater than 1640 to 1, and furthermore, when PbS starts to precipitate out, ZnS must precipitate out also, and in the ratio of 1640 to one of PbS. As noted above, this is not what takes place in nature.

It has been suggested that possibly the solubility products change a great deal with elevated temperatures and might even reverse. This was tested by Verhoogen (2) by means of thermodynamical methods, the results of which showed that the solubility products increase in general with

- (1) Ravitz, S.F.: The Solubilities and Free Energies of Some Metallic Sulfides. Jour. Phys. Chem., vol 40, pp. 61-70, 1936.
 (2) Verhoogen, J.: Solubility of Some Important Sulfides. Ec. Geol. 33, p. 34, 1938.

rising temperature, but the ratios between them remain fairly constant.

The ratio

$$\frac{[\text{Zn}^{++}]}{[\text{Pb}^{++}]}$$

at 100°C is 9.56×10^6 or 9,560,000, at 200°C, 6.92×10^8

or 692,000,000 and at 300°C, 1.59×10^{10} or 15,900,000,000. Since sphalerite and galena in general precipitate out of solution at a minimum temperature of 80°C (1) it will be seen that the ratio of zinc to lead required to be present in the solution to allow sphalerite to precipitate out before galena is very much greater than the ratio of zinc to lead mined in the world.

This line of argument may be extended to include the other metallic sulfides, so it appears impossible to reconcile the ionic sulfide theory, the data on solubilities and the natural order of precipitation.

The Double Sulfide Theory

Metallic sulfides form double sulfides with alkali sulfides and the reaction being reversible, this fact has been used to develop what will here be called the double sulfide theory of metallic sulfide solution and precipitation.

As above mentioned, Becker (2) presented a very plausible theory of the solution and precipitation of cinnabar in nature. He found that HgS is soluble in Na₂S solutions, forming double sulfides of various degrees of complexity and that it could be precipitated out again in various ways,

- (1) Newhouse, W.H.: Temperature of Formation of the Mississippi Valley Lead-Zinc Deposits. Ec. Geol. 23, p. 744, 1933.
 (2) Becker, G.F.: Op. cit.

one of which being merely dilution of the solutions. He found as well that some other metals, including gold, form such double sulfides with sodium, and presented the idea that in some kinds of sulfide deposits, this process of breakdown of double sulfides may be responsible for the deposition of the simple sulfides. This hypothesis did not receive the attention it merited and it has been only recently that experimental investigation of the hypothesis outlined have taken place. Freeman (1) proved that the common metallic sulfides form double sulfides on fusion with sodium sulfide, which, except for those of Hg, Sb and As, are decomposed by water, precipitating the metallic sulfide.

Steck, Slavin and Ralston (2) proved the existence of a transitory compound $\text{FeS} \cdot \text{Na}_2\text{S}$. Friedrich (3) proved the existence of $\text{Cu}_2\text{S} \cdot \text{Na}_2\text{S}$.

Gruner (4) showed that under the conditions of his experiments, Na_2S solutions dissolve As_2S_3 and Sb_2S_3 but not FeS and gold. The restricted nature of the experiments hardly justified his conclusion that sulfides other than those of Hg, Sb and As are not transported in nature as the double sulfides.

The work done on double sulfides shows that probably all the common metals may form such compounds with the alkalis and that they may be broken down again to the constituent sulfides.

One question remains to be answered by proponents of this theory of sulfide transport: are the metallic sulfides soluble in aqueous solutions of alkali sulfide and, if so, is the order of solubility similar to the order of deposition in nature? The fact that the sulfides of mercury,

- (1) Freeman, H.: Genesis of Sulfide Ores. Eng. & Min. J. 120, p. 973, 1925.
- (2) Steck, L.V., Slavin, M. and Ralston, O.C.: The System Sodium Sulfide-Ferrous Sulfide. J. Am. Chem. Soc. 51, pp. 3241-9, 1929.
- (3) Friedrich, K.: Metall u. Erz 11, pp. 79-88, pp. 160-7.
- (4) Gruner, J.W.: Solubility of Metallic Sulphides in Alkaline Sulphide Solutions. Ec. Geol. 23, p. 773, 1934.

antimony and arsenic, which are very soluble in solutions of alkali sulfide, are very often deposited subsequently to all the others, makes this not improbable.

The Colloidal Sulfide Theory

Metallic sulfides can be dispersed into colloidal form in several kinds of aqueous solutions and this fact has been much used as a basis of theories of sulfide transport and precipitation.

Clark and Menaul (1) found that the common sulfides can be dispersed in a mildly alkaline solution saturated with H_2S and can be precipitated out again by removal of the H_2S or by electrolytic coagulation.

Freeman (2) produced double sulfides of sodium and most of the common metals and noticed that when decomposed by water, they often formed fairly stable colloidal solutions. He suggested that some such process may take place in nature, giving rise to colloidal solutions of the sulfides, which would then be subjected to the ordinary processes of coagulation.

Stevens (3) studied the sols of iron sulfide and found that they were very stable in an alkaline sulfide solution.

Kania (4) formed sols of pyrite, chalcopyrite and sphalerite by fusing sodium sulfide with the appropriate metallic sulfide and then extracting the fusion with water. Colloidal solutions resulted, and these, on contact with calcareous and argillaceous material, deposited the sulfides, sometimes in crystalline form.

- (1) Clark, J.D. and Menaul, P.L.: Role of Colloidal Migration in Ore Deposits. *Ec. Geol.* 11, p. 37, 1916.
- (2) Freeman, H.: *Op. cit.*
- (3) Stevens, R.E.: Alteration of Pyrite to Pyrrhotite by Alkaline Sulfide Solutions. *Ec. Geol.* 28, p. 1, 1933.
- (4) Kania, J.E.A.: Origin of Pyritic Copper Deposits *Ec. Geol.* 31, p. 453, 1936.

While the work quoted does not exhaust the field, it represents the experimental accompaniment to this train of thought developed in recent years.

In sulfide ore deposits, colloform textures have been found, and this has been used as a criterion of colloidal deposition. Boydell (1) has given a good summary of the question up to 1924. Laskey (2) has described such textures existing in the copper ores at Kennecott, and Fischer (3), in some copper ores of the N.W. Colorado Plateau. The lead-zinc ores of S.W. Winconsin show textures that have been interpreted as being colloform.

In addition, it has been argued that deposition from the colloidal state need not result in colloform textures, and the experiments of Kania (4) and others seem to bear this out. This may very well be true, since crystals apparently perfect macroscopically are very imperfect microscopically (5) and if the discrete colloidal particles are single crystal units, these, as well as the separate ions may be used as the building-blocks of the larger crystal unit.

That colloids have been important in some sulfide deposits and that colloids may precipitate out in crystal form have been the basis for the current, though not widely accepted theory, that all sulfide deposits have resulted from the deposition of sulfides from the colloidal state. The validity of this hypothesis rests in great part on a demonstration that most of the metallic sulfides can pass through the high temperature zone in the colloidal condition and that the order of stability of the sulfides

- (1) Boydell, H.C.: The Role of Colloidal Solutions in the Formation of Mineral Deposits. I.M.M. London, 1924.
- (2) Laskey, S.G.: Colloidal origin of Some of the Kennecott Ore Minerals. Ec. Geol. 25, p. 737, 1930.
- (3) Fischer, R.P.: Peculiar Hydrothermal Copper-bearing Veins of the North-West Colorado Plateau, Ec. Geol. 31, p.571, 1936.
- (4) Kania, J.E.A.: Op. cit.
- (5) Buerger, M.J.: Lineage Structure of Crystals, Z.Krist 89, p. 195, 1934.

in this state in one of the postulated types of ore-bearing solutions coincides in part at least with the order of depositions as observed in sulfide deposits.

Kania (1) determined the order of stability of the sols of pyrite, chalcopyrite and sphalerite by determining which sol would coagulate the others. He found that in an alkaline sulfide solution the pyrite sol coagulated the chalcopyrite and the sphalerite sols. That is, a chalcopyrite or sphalerite sol passing over pyrite would tend to coagulate, with a certain amount of the pyrite dispersing. Chalcopyrite and sphalerite, according to this, would replace pyrite, which is often the paragenesis inferred from microscopic study of copper-bearing pyritic deposits. However, the order of deposition from a solution containing colloidal pyrite, chalcopyrite and sphalerite would be the reverse of that frequently observed in pyritic deposits, where pyrite is precipitated first and the other two later. The order of replacement based on relative colloidal stability for these three sulfides seems to fit the facts but not so the original order of deposition.

Another factor that must be considered is: if the sulfides are transported in the colloidal state, what was the course of events from the generation of the rest-magma to the formation of the colloidal sulfides? It seems unlikely that the sulfides were always in this state. According to the ionic sulfide theory, the metals were extracted as chlorides by an acid solution containing hydrogen sulfide and precipitated as sulfides on neutralization of the acid. The colloidal theory postulates that the sulfides as they appear were stabilized in colloidal form by the excess H_2S and then deposited in the order of their stability. According to the double

(1) Kania, J.E.A.: Op. cit.

sulfide theory, the metals were extracted as double sulfides of the metals and an alkali metal and precipitated by gradual breakdown of the double sulfides. As mentioned above, the sulfides as they appear would be stabilized in colloidal form by the excess alkali sulfide and would be precipitated in the order of their stability in such a solution.

The objections to the former theory are, first, that when sulfides are precipitated from a mixed solution of metallic chlorides, simple sulfides result rather than sulfides such as the copper-iron sulfides and the lead, copper and silver-arsenic, antimony and bismuth sulfosalts. This is the basis of the separation of the metals as sulfides in the analytical scheme, and appears to hold true up to 100°C. That is, if in a solution containing Ag^+ ion, As^{+++} ion, H^+ ion and S^{\equiv} ion, the concentration of the H^+ ion decreases, increasing the concentration of the S^{\equiv} ion to the point where the solubility product

$$\left[\text{Ag}^+ \right]^2 \times \left[\text{S}^{\equiv} \right] = K_{\text{spAg}_2\text{S}}$$

is exceeded, then some Ag_2S will precipitate out and not ruby silver, and ruby silver will not form from the Ag_2S precipitated no matter how long the solution containing arsenic is kept in contact with it. Since sulfosalts are so common in medium temperature deposits, this represents a serious difficulty in the way of this theory. The second objection is that the order of stability of metallic sulfide sols peptised by hydrogen sulfide in neutral or slightly alkaline solutions does not appear to be similar to the order of deposition. The order of dispersibility of various sulfides by means of H_2S in a slightly alkaline solution can be determined from the data given by Clark and Menaul (1). It shows no similarity to the general

(1) Clark and Menaul: Op. cit.

order of deposition.

As for the latter theory (the development of colloidal sulfides from the breakdown of double sulfides), the first objection (that complex sulfides cannot be formed in colloidal form from a true solution containing the components) is not valid, since sulfosalts such as ruby silver may be synthesized by keeping a solution of arsenic sulfide in alkaline sulfide in contact with silver sulfide (1), and Kania (2) found that when he fused chalcopyrite with sodium sulfide and decomposed the fusion with water, he obtained a colloidal solution of chalcopyrite, as evidenced by the crystals of chalcopyrite which grew on limestone from the solution at 95°C in eight days.

The second objection (that the order of stability of such sulfide sols is not the order of deposition found in nature) is valid and for the same reason as given for the former theory. For instance, pyrite, the sol of which was found to be so stable when peptised by sodium sulfide, is yet one of the first to separate from the ore-bearing solutions. However, it is found to be deposited over almost the entire range of temperature and pressure conditions, which may be explained by the great sol stability. The zone of first appearance of a metallic sulfide, which usually is near[®] the point of maximum precipitation of the sulfide, is the zone at which the sulfide begins to precipitate out of true solution, and all zones of deposition above this are due probably to coagulation of a sol generated at this first point.

The writer is of the opinion, then, that the colloidal theory of sulfide transport is not capable of application throughout the entire range of sulfide precipitation but that it does come into play to modify the

(1) see the experiments following.

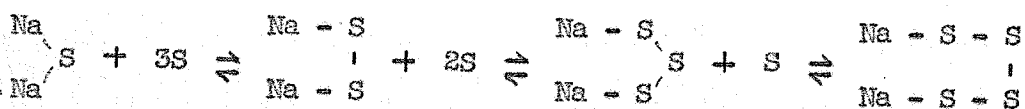
(2) Kania, J.E.A.: Op. cit.

order and amount of sulfides transported by some other method. There are at least two methods of sulfide transport in true solution, as described before, the ionic sulfide and the double sulfide methods. The former seems to be incapable of reconciling the chemical facts with the field facts, but what is known of the latter strongly suggests that this is possible. Accordingly, the experimental procedure of this investigation is directed toward the answer to the following question: are the properties of the double sulfides of the metals and alkali such that it may be in the double sulfide form that the metallic sulfides are transported in the ore-bearing solutions and if so, does their order of breakdown and their order of stability in the colloidal state explain the paragenesis and physical characteristics observed in sulfide ores ?

VIII EXPERIMENTAL INVESTIGATION AND RESULTS

Polysulfides and Double Sulfides

Sulfur is soluble in an aqueous solution or melt of sodium sulfide, forming unstable polysulfides which may be caused to liberate free sulfur again. The usual explanation of this phenomenon is that variable-length sulfur chains are formed, as follows:



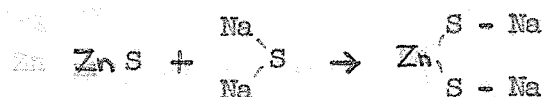
The length of the sulfur chains seems to have an upper limit at Na_2S_5 (1)

The reversibility of these reactions means that with sodium polysulfide in solution, there is a constant source of free sulfur present and the measure of the instability of the polysulfide is a measure of the concentration or activity of elemental sulfur in the solution. Thus if a metallic sulfide is soluble in a solution of alkali polysulfide and if the metal forms two sulfides, a higher and a lower, then when the solution becomes saturated with the metallic sulfide one of the two forms will appear depending on the sulfur concentration in the solution at the time. If the sulfur activity is below the sulfur vapour pressure of the higher sulfide at this temperature, the lower sulfide only will crystallize out, but if it is greater than this value, the higher sulfide will crystallize out. It follows that if an alkali polysulfide solution passes over the sulfide unstable in the solution it will tend to change it into the stable form.

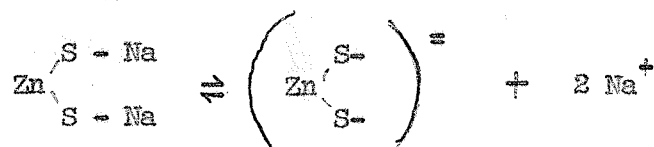
Double sulfides of the metals and an alkali metal may form double polysulfides similar to the alkali polysulfides. In preliminary experi-

(1) Mellor, J.W.: A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. II, p. 640, 1922

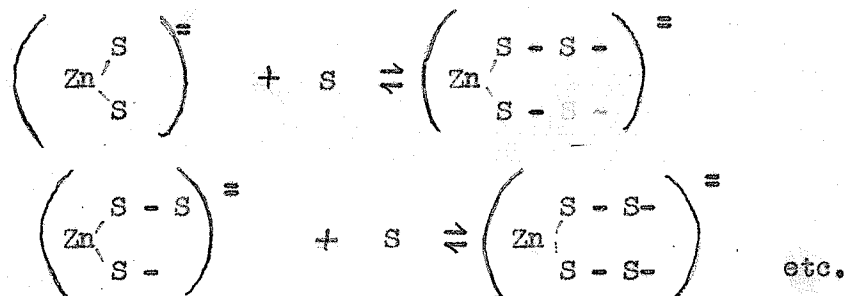
ments with double sulfides, it was found that if a mixture of Na_2S and ZnS in equimolecular ratio was heated, it sintered at a fairly low temperature and melted at a fairly high temperature. Freeman (1) gives the melting point of this compound as 620°C . If sulfur was added to the mixture, the melting point was lowered and a very large amount of sulfur could be dissolved in the melt. On cooling, the melt always seemed to be homogeneous. This behaviour is explained as follows: when the Na_2S and the ZnS were fused together, a double sulfide was formed, sodium thiozincate,



which ionised as follows:



The $(\text{ZnS}_2)^{=}$ ion, like the $(\text{S})^{=}$ ion, formed a polysulfide ion -

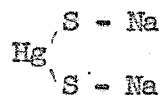


It was found that if a melt containing much sulfur is heated to a high temperature some sulfur boils away, preserving the analogy with the alkali polysulfides as far as reversibility goes.

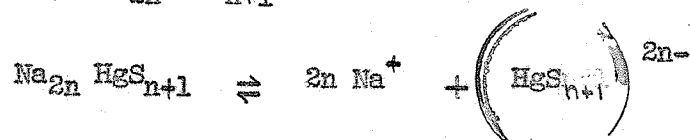
The formulae of a few double sulfides have been determined, as noted above, and in general they are simple, but in some cases, they are complex.

(1) Freeman, H.: Op. cit.

Becker (1) found that a compound $\text{HgS} \cdot \text{Na}_2\text{S}$ existed, but also proved the existence of compounds of the general form $\text{HgS} \cdot n \text{Na}_2\text{S}$, where n is 2, 3 and 4. The structural formula of the simple compound is likely



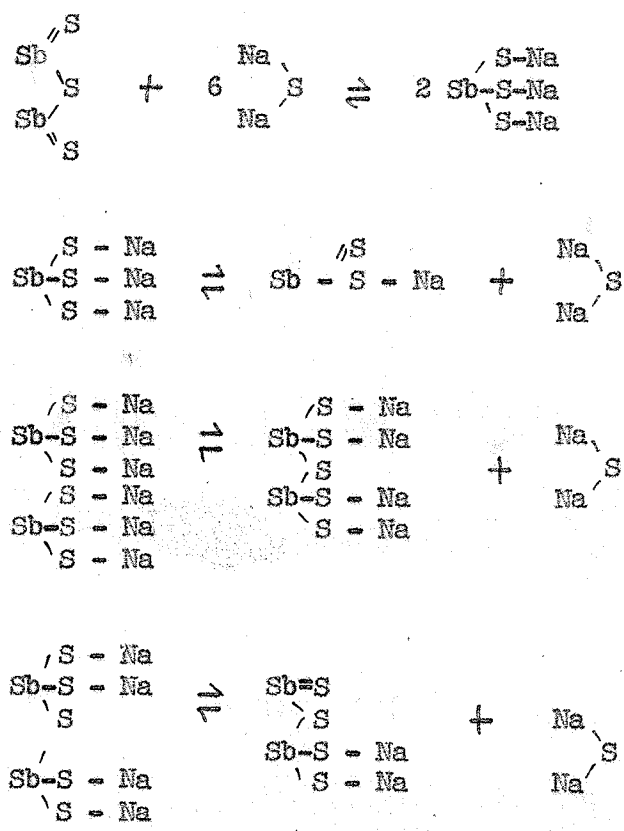
but it is difficult to prepare formulae for the others, using normal valencies. If coordination compounds exist in these cases, then they may be represented by $\text{Na}_{2n} \text{HgS}_{n+1}$, where $n = 1$ to 4, ionising as follows:



That is, a central mercury atom, surrounded by one to five sulfur atoms, the whole having a two to ten negative charge, surrounded by two to ten sodium positive ions. As far as the writer knows the double sulfides of mercury and sodium are exceptions in exhibiting coordination compounds.

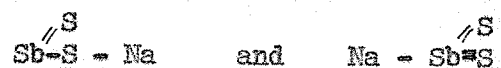
Another complexity possible in double sulfides is condensation with loss of some of the alkali sulfide. For instance, the following compounds of Na_2S and Sb_2S_3 are possible:

(1) Becker, G.F.: *Op. cit.*



which may all be included under the general formula $n \text{Sb}_2\text{S}_3 \cdot m \text{Na}_2\text{S}$, where the ratio $n : m$ is equal to or greater than 1:6.

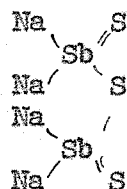
A third complication is that with the semi-metals, arsenic and antimony, two types of compounds can exist, those in which the sodium is attached to the sulfur which in turn is attached to the nonmetal, and those in which both the sodium and the sulfur are attached to the nonmetal. The two simplest representation of both types among the double sulfide of sodium and antimony are:



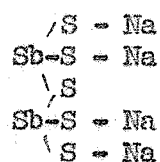
In solution, both give a $(\text{SbS}_2)^+$ ion and a Na^+ ion, and thus in reality

are identical since the negative charge of a complex ion cannot be said to reside nearer one of the constituent atoms than the others.

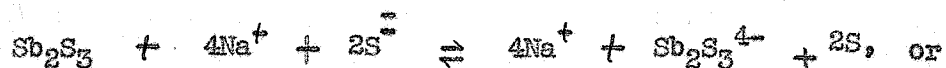
There is at least one grouping of the second type which is not identical with one of the first type. This is:



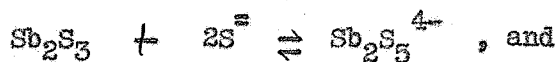
It will be noticed that a similar compound with the other grouping contains more sulfur:



The formation of the two compounds probably takes place as follows:



eliminating the 4Na^+ from each side of each equation,



That the latter equation takes place at temperatures up to 100°C is suggested by the following experiments. A solution of sodium polysulfide was prepared, saturated with sulfur at the boiling point of the

solution and then Sb_2S_3 was added. Immediately all the Sb_2S_3 was dissolved and a considerable amount of sulfur was precipitated. A solution of Na_2S was prepared and Sb_2S_3 was dissolved in it. Immediately the solution took on the yellow colour characteristic of sodium polysulfide solutions, showing that sulfur had been liberated and dissolved. At high temperatures and with a large excess of sulfur present, the first reaction may take place instead of the second, though no experimental evidence is available at present.

Arsenic sulfide reacts like antimony sulfide when added to alkaline sulfide solutions. The more the element resembles a nonmetal, the more likely is the second reaction to take place and vice versa. The very remarkable difference in the solubility of the sulfides of arsenic and antimony compared with the solubility of the sulfide of bismuth in an aqueous solution of alkali polysulfide may be explained in this manner, assuming that the double sulfide form, in which the semimetal acts as a nonmetal, is soluble, and the form, in which it acts as a metal, is insoluble in such a solution.

Chemical Experiments with the Sulfides

Iron Sulfides: Iron sulfide (commercial cast sticks) was fused with sodium sulfide (commercial flakes) in a pyrex test tube with a small amount of roll sulfur as flux. The cooled fusion mixture was a yellow or orange coloured homogeneous solid. When added to boiling water, it gradually dissolved, forming a dark green or greenish black solution. This solution is probably similar to that studied by Stevens (1) and is composed of iron

(1) Stevens, R.E.: Op. cit.

sulfide colloiddally dispersed.

It was found that as the amount of sulfur used in the fusion increased, the greener became the colloidal solution resulting from the extraction of the fusion by water and if very little sulfur was used, it was black. Also, if a greenish black sol was heated to boiling, it became black, returning to the original colour on cooling. In addition, if sulfur was boiled with a black sol in a sodium sulfide solution, it became green.

In order to find out the character of these sols, a deep green sol and a black sol were prepared, coagulated with calcium chloride solution, filtered, washed, dried and sealed separately in glass tubes. The green coagulum, now greenish black, was found to be non-magnetic, but the black coagulum, now a semi-metallic brownish black, was found to be magnetic. Both were analyzed by the X-ray powder diffraction method by Mr Lyons of the Department of Geology of the University of Wisconsin, but neither showed a recognizable pattern. The streak of pyrite is greenish black and that of pyrrhotite is a semi-metallic black and the coincidence of the magnetic properties and the increase in sulfur changing the black sol to the green, and vice versa, both suggest that the green sol is a pyrite sol and the black sol is a pyrrhotite sol. This is contrary to Stevens' (1) results, since he stated that both sols were of ferrous sulfide.

The amount of sulfur in the fusion mixture was increased to the maximum quantity possible. On cooling such a fusion, small crystals of what appeared to be pyrite were seen throughout the mass. On dissolving the fusion in water and decanting the green sol, a residue of small sparkling crystals was left in the beaker. These were removed and examined. Some were mounted in synthetic resin and polished. The majority of the crystals

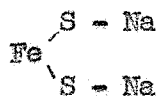
(1) Stevens, R.E.: Op. cit.

seemed to be cubes elongated in one direction and modified by the octahedral faces. The microscopic characteristics in reflected light were those of pyrite, though about 5% of the crystals were of marcasite showing polysynthetic twinning parallel to the elongation. The procedure was repeated using a larger fusion in a graphite crucible with slower cooling. Crystals of pyrite resulted, most of which were octahedrons. The maximum size was about 1.5 mm., but the crystal faces were not perfect.

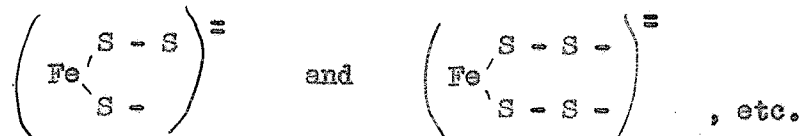
It was found to be impossible to grow pyrrhotite crystals in the same manner. No matter how much iron sulfide was added to the melt, none separated on cooling but all remained in the double sulfide complex. In a sense pyrrhotite may then be considered to be more soluble than pyrite in an alkali sulfide melt.

The stability of the green sol was found to be very great. A sol so concentrated that it was highly viscous remained stable for twenty-four hours and could be diluted to give a very stable sol. A fairly dilute sol was sealed with a small amount of air and a piece of recrystallized limestone in a glass tube and showed no signs of coagulation after one year in the laboratory.

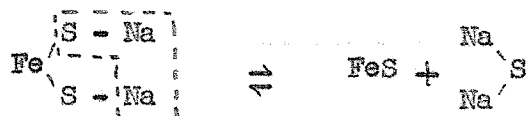
The reactions between sodium sulfide, iron sulfide and sulfur to give the double sulfide, pyrite crystals and the green and black sols are thought to be as follows: on fusing FeS and Na₂S, a double sulfide FeS. Na₂S results, probably having the structural formula



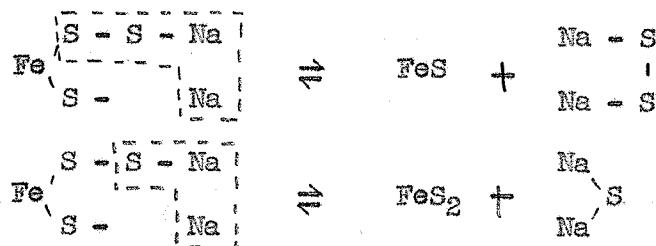
which in the melt ionises to $\left(\text{Fe} \begin{array}{l} \text{S-} \\ \text{S-} \end{array} \right)^{=}$ and 2Na^+ . The action of sulfur has the effect of creating a sulfur chain by addition, making a thioferrous ion of various degrees of complexity, such as



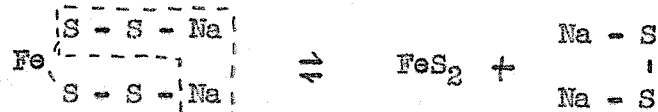
On cooling, the compounds Na_2FeS_2 , Na_2FeS_3 , Na_2FeS_4 , etc are present, and on decomposition with water, Na_2S and Na_2S_x are formed, with the iron holding one or two sulfur atoms. Decomposition of Na_2FeS_2 will yield only troilite or the black sol of FeS as follows:



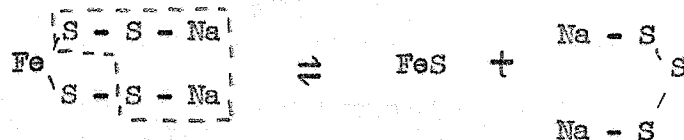
Decomposition of Na_2FeS_3 will yield green or black sols depending upon the method of breakdown, as follows:



Decomposition of Na_2FeS_4 will yield the green sol, as follows:



This is assuming that the sulfur chain for the sodium polysulfide is derived entirely from one sulfur chain of the double sulfide. Otherwise the black sol may be formed from this one as well, as follows:



No attempt was made to determine the formulae of the fusion mixtures in relation to the percentage of black to green sol resulting from their breakdown in water. The general result holds, however, that the longer the sulfur chains in the double sulfide, the more likely is pyrite rather than pyrrhotite to result from its breakdown.

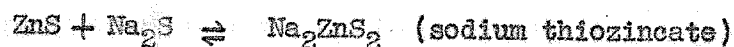
The conclusions reached from this work on the sulfides of iron are that in the absence of water, pyrite and pyrrhotite are soluble in a melt of sodium polysulfide forming double sulfides and double polysulfides, the solubility of the pyrite being greater at high than at low temperatures and always less than the solubility of pyrrhotite in the same type of melt. It also appears that sols of pyrite and pyrrhotite peptised by alkali sulfide and polysulfide are very stable. Especially is this true of the pyrite sol.

Zinc Sulfide: Zinc sulfide prepared from zinc nitrate was fused with sodium sulfide prepared from the pure crystals, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and the cooled fusion was dissolved in boiling water. A rather unstable colloidal solution of zinc sulfide resulted.

The fusion was repeated, but with the addition of sulfur. On decomposing the fusion in boiling water, a heavy powder resulted, which when washed and dried and examined microscopically was found to be composed of small hexagonal crystals. The hexagonal prism and hemihedral hexagonal pyramids were visible, and extinction was parallel to the C axis. This was evidently the hexagonal hemimorphic form of zinc sulfide, wurtzite. Many attempts were made to prepare the isometric modification, sphalerite, but these were unsuccessful. Although the temperature of formation (100°C)

and the alkalinity were both favourable for sphalerite formation according to the work of Allen, Crenshaw and Merwin (1), the speed of formation, which in this case is very great, must be more influential than the above in determining that the unstable form appears.

The equations covering the above reactions are probably of the general double sulfide form, as follows:



It is noteworthy that the decomposition of the polythio compound yielded crystals and the thio compound, a colloidal solution. The more sulfur used in the fusion, the larger the crystals and vice versa, through all gradations to a colloidal solution. This may be due either to the relative peptising power of sodium polysulfide and sodium sulfide derived from the breakdown of the complex compound or due to the slower decomposition of the double polythiosulfide.

Cadmium Sulfide: Amorphous cadmium sulfide was fused with sodium sulfide and sulfur and the fusion mixture, which was homogeneous, was decomposed in boiling water. A heavy scarlet powder resulted, which when washed, dried and mounted in balsam was found to be composed of small skeleton crystals. These crystals were made up of three bars set at right angles to each other, and of equal development. They had the elements of symmetry of the isometric system and were isotropic in plane-polarised light. They were assumed to be crystallites of the isometric form of cadmium sulfide, isomorphous with sphalerite.

(1) Allen, E.T.; Crenshaw, J.L., and Merwin, H.E.: The Sulfides of Zinc, Cadmium and Mercury. Am. J. Sci.(4), 34. p. 341. 1912.

Immediately after this experiment, some orange amorphous cadmium sulfide was heated to redness and then cooled. It was a lemon yellow color when cold and this powder was used in subsequent tests.

A repetition of the fusion described above was carried out and on dissolving in boiling water, a yellow powder resulted, which on examination was found to be composed of small crystals and crystallites having the elements of symmetry of the hexagonal hemimorphic class.

The experiment was repeated using freshly prepared amorphous cadmium sulfide, but again the yellow form was the result. Many trials were made, varying the proportions of the fusion mixture and guarding against contamination as much as possible of the boiling distilled water by the yellow form, but in every case, that was the form obtained.

An explanation that is not improbable is that the isometric form, which is the unstable form at this temperature, was precipitated in the absence of nuclei of the stable form, but this, when once prepared, so contaminated the air of the laboratory, and all solutions exposed to it, that all subsequent attempts to prepare the unstable form failed.

Cadmium sulfide, like zinc sulfide, is a fluorescent and phosphorescent compound and also like it, has no measurable heat of transformation of the one form into the other (1). Considerable research has been directed toward the solution of this problem, but from a review of the literature, there seem to be many contradictions and unexplained phenomena.

Lead Sulfide: Lead sulfide was fused with sodium sulfide and sulfur and the cooled fusion mixture was dissolved in boiling water. A heavy

(1) Allen, E.T., Crenshaw, J.L. and Merwin, H.E.: Op. cit.

dark grey powder was formed, which on microscopic examination was found to be composed of skeleton crystals of an opaque material having the lustre of galena. The elements of symmetry of the crystallites were those of the isometric system, and so they were concluded to be skeleton crystals of galena.

If only a small amount of sulfur was added to the fusion mixture the decomposition of the solidified fusion in boiling water yielded a rather unstable black colloidal solution, probably of galena.

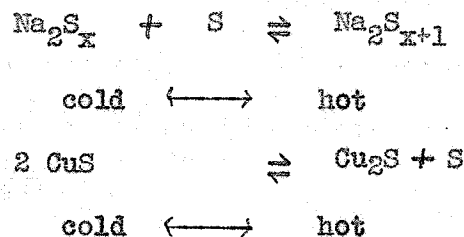
Copper Sulfides: Amorphous copper sulfide was fused with sodium sulfide and a very small amount of sulfur. The cooled fusion mixture was dissolved in boiling water, giving a stable brown colloidal solution. A similar fusion with a large amount of sulfur, when dissolved in boiling water, gave a green sol.

The former experiment was repeated, but adding a large amount of the fusion mixture to a small amount of water, and in small amounts at a time. Some of the material precipitated as a black powder, which under the microscope was seen to be made up of aggregates of small dendritic crystallites which were in turn made up of small cubic crystals. By its appearance, this was thought to be chalcocite.

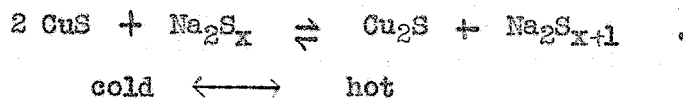
A similar procedure using the second fusion mixture yielded a number of flakes having a blue and purple colour by reflected light. This was thought to be covellite.

Similar relations were found to exist between the green and brown sols of copper sulfide as between the green and black sols of iron sulfide. On

boiling the green sol of copper sulfide in a solution of sodium sulfide, it turned brown and regained its original colour on cooling. A brown sol if boiled with a solution of sodium polysulfide turned green. This reversal of colour may be explained by the following equations:



so that

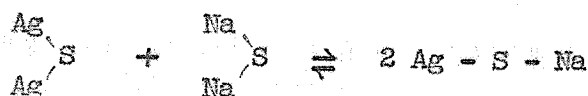


Whether chalcocite or covellite results from the decomposition of the double sulfide of copper sulfide and sodium sulfide depends, as in the case of iron sulfide, on the amount of sulfur dissolved in the fusion, or in other words, on the length of the sulfur chains in the double polysulfide. Thus it appears that the determining factors controlling which copper sulfide is precipitated by the decomposition of the double sulfide is the amount of sulfur in the polysulfide form in the double sulfide, and when once precipitated, the stability of one form or the other is dependent upon the sulfur concentration in the alkali polysulfide of the solution with which it is in contact.

Silver Sulfide: Silver sulfide was fused with sodium sulfide and sulfur and the cooled fusion mixture was dissolved in water. A black

precipitate and an unstable colloidal solution resulted and the black precipitate under the microscope was seen to be made up of dendritic crystallites composed of aggregates of cubic crystals of a black opaque substance. This was thought to be argentite.

The silver sulfide probably formed a double polysulfide with sodium sulfide and sulfur, which was broken down by water, as follows:



Mercury Sulfides: Black amorphous mercury sulfide was dissolved in a solution of sodium polysulfide and the solution was placed in an open pyrex test tube which was sealed in an unlined steel bomb. The bomb was heated to 300°C and kept about this temperature for twelve hours and then slowly cooled. On opening, no smell of H₂S was noticed and the solution was clear and colourless. At the bottom of the test tube rested a vermilion powder, which under the microscope was seen to be composed of euhedral crystals of cinnabar.

A solution of mercury sulfide in sodium polysulfide was prepared as before and then was diluted slowly with distilled water. After considerable dilution, but when it still had the yellow colour of the polysulfide, the solution began to turn a dark brownish black. This was found to be a colloidal solution of mercury sulfide and was quite stable. The sol was coagulated and was black when dry. This was probably metacinnabarite.

The solid coagulum was examined for metallic mercury but none was seen. Becker (1) reported that the dilution of a solution of mercury

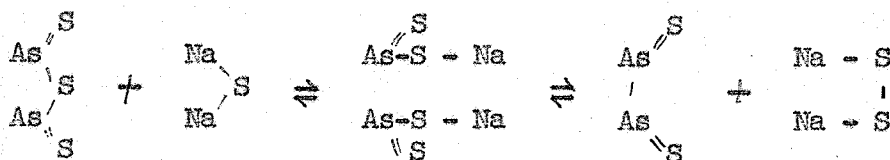
(1) Becker, G.F.: Op.cit.

sulfide in sodium sulfide precipitated metacinnabarite and some metallic mercury as well. Evidently if sodium polysulfide is used instead of the simple sulfide any mercury that appears is instantly converted to sulfide by the excess sulfur.

The reaction between sodium sulfide and mercury sulfide has been discussed before. The reaction that took place in the bomb at 300°C will be discussed later. Its effect is to remove sodium polysulfide, thus breaking down the double polysulfide and liberating mercury sulfide.

Arsenic Sulfide: Arsenic trisulfide was dissolved in sodium sulfide and the solution was placed in an open test tube in an unlined steel bomb which was sealed and heated to 300°C overnight. The solution had an orange substance in suspension and there were scarlet crusts at the bottom of the test tube. This material had the appearance of realgar.

The reactions during solution and precipitation may have been as follows:

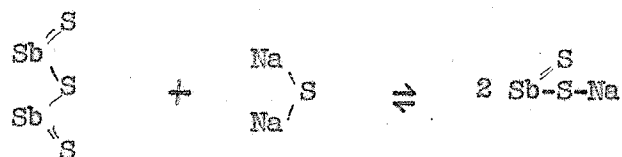


The reactions that took place in the bomb that removed the sodium polysulfide will be discussed later.

Antimony Sulfide: Red amorphous antimony sulfide was dissolved in sodium polysulfide, the solution was placed in an open test tube and this was sealed in an unlined steel bomb. The bomb was heated to 300°C for

twelve hours and then cooled. The solution was clear and colourless and needles of stibnite were clustered near the top of the test-tube, above the level of the solution. This was probably the level of the solution at 300°C.

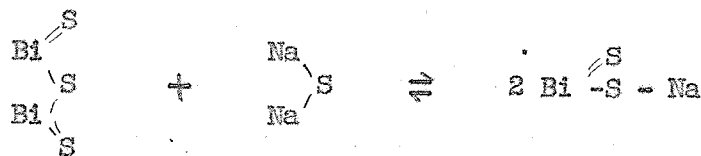
The solution and precipitation of the antimony sulfide probably took place according to the following reversible equation:



The reaction in the bomb destroyed the Na_2S , thus allowing the equilibrium to go completely to the left. This reaction will be discussed later.

Bismuth Sulfide: Amorphous bismuth sulfide was fused with sodium sulfide and sulfur. The cooled fusion mixture was not entirely homogeneous, as small equidimensional crystals of what appeared to be bismuthinite were scattered throughout the mass. The mixture was added to boiling water and a dark grey granular precipitate was thrown down. This was examined under the microscope and was seen to consist of two forms of bismuthinite, the small equidimensional crystals, with the edges rounded off, and skeleton crystals of isometric symmetry. The former crystallized while the melt was cooling and the latter when the double sulfide was decomposed by boiling water. Both had the same colour and lustre and appeared to be bismuthinite.

The formation and breakdown of the double sulfide may be expressed as follows:



Evidently bismuth sulfide differs from the sulfides of arsenic and antimony in its behaviour toward sodium polysulfide. Its solubility in melts of sodium polysulfide resembles that of pyrite rather than that of arsenic sulfide and antimony sulfide.

Molybdenum Sulfides: There are two common sulfides of molybdenum which behave differently toward sodium polysulfide. One is brown and is soluble in an aqueous solution of sodium polysulfide. The higher sulfide, molybdenite, is insoluble in such a solution and is not very soluble even in a melt of sodium polysulfide.

A mixture of molybdenum sulfides was prepared, dried and fused with sodium sulfide and a very small amount of sulfur. The cooled fusion mixture was completely soluble in boiling water. A similar mixture of molybdenum sulfides was fused with sodium sulfide and a large amount of sulfur. The fusion mixture was broken up and flakes of molybdenite were seen. The pieces were added to boiling water and a considerable amount of silvery flakes was precipitated. These were washed, dried and examined. They exhibited the properties of molybdenite.

The marked difference in the solubility of the two sulfides of molybdenum in a melt of sodium polysulfide is noteworthy, and will be discussed more fully later.

Copper-Iron Sulfide: A mixture of amorphous sulfides of copper and iron in which the ratio of copper to iron was one to one was prepared. This was fused with sodium sulfide and a small amount of sulfur, cooled and added to boiling water. A black colloidal solution and a flocculent precipitate were produced.

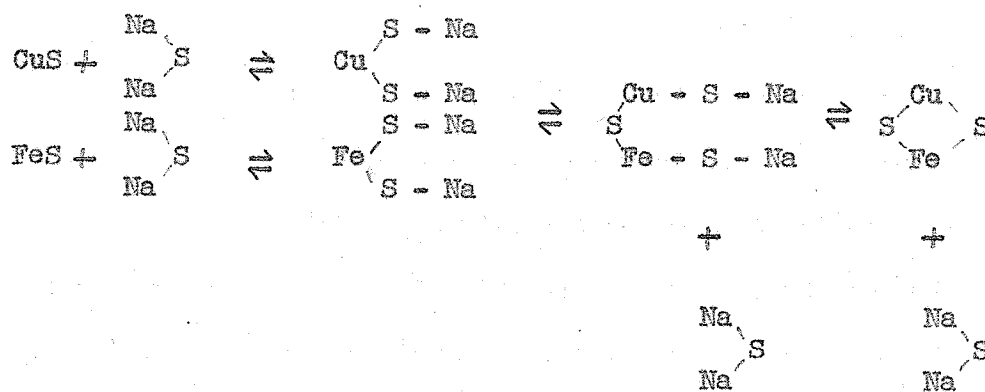
The same procedure was repeated using a little more sulfur. The result was mostly colloidal and flocculent but some snowflake-like crystallites of pyrrhotite and a few blue flakes of covellite were seen.

The same procedure was repeated using a large amount of sulfur. The result was a greenish colloidal solution and greenish black flocculent material with some blue flakes of covellite.

It seemed that the first trial gave a mixture of FeS and Cu_2S , the second a mixture of FeS and CuS, and the third a mixture of FeS_2 and CuS. Though not definitely determined, it seems unlikely that chalcopyrite was formed in any of the trials.

In order to decompose the double sulfide by water at a high temperature, the fusion mixture was placed in an open test tube in an unlined steel bomb containing some water. The bomb was heated to 300° for twelve hours, cooled and opened. The double sulfide was decomposed to a golden yellow colour. This was washed free of alkali sulfide, mounted in resin, polished and examined by the reflecting microscope. The mineral looked like chalcopyrite and the etch tests confirmed this.

The formation of the double sulfide and its breakdown to chalcopyrite may be represented by the following equations:



Sulfosalts: Pyrargyrite ($3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$) was chosen as a representative of this group because of its ease of identification.

Silver sulfide was sealed up in a pyrex glass tube with a solution of antimony sulfide in sodium polysulfide. The tube was sealed up in a bomb and heated to 300° for thirty-eight hours, cooled and opened. Well-shaped crystals had grown from the silver sulfide, and when embedded in resin, polished and examined by reflected light were proved to be pyrargyrite.

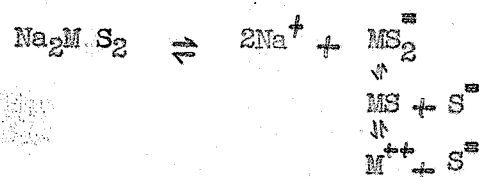
Thus simple sulfides in contact with solutions of the semi-metal sulfides in alkaline polysulfide are not stable (under at least some conditions of temperature and concentration of the solutions), and form sulfosalts. This fact is of great importance in the development of a theory of sulfide transport and deposition, and will be discussed later.

The Order of Solubility of Metallic Sulfides in Solution of Sodium

Sulfide: As has been shown, the sulfides of mercury, arsenic, antimony and one of molybdenum are quite soluble in aqueous solutions of sodium sulfide and polysulfides. Up to 100°C the other metallic sulfides are quite insoluble, though the ease of dispersal of some of these into the

colloidal form has occasionally been mistaken for true solubility. It has also been shown, however, that the other metallic sulfides are soluble in a melt of sodium polysulfide, and it remains to be determined whether or not they are soluble in an aqueous solution of sodium sulfide or polysulfide at elevated temperatures.

Assuming that the preceding theory of double sulfide formation is true, then neglecting minor reactions such as hydrolysis of ions, the following equilibrium will be set up in a solution containing a double sulfide of a divalent metal and sodium:



Thus the greater the ionisation of the simple sulfide MS into the ions M^{++} and S^{\equiv} , the smaller will be the amount of the ion MS_2^{\equiv} . Taking two metallic sulfides of greatly different solubilities in water it would be expected that the more soluble one would be less soluble in a sodium sulfide solution, whereas the less soluble one would be more soluble in such a solution. This, for instance, is true of zinc sulfide and mercury sulfide. It is not known, however, if the order of solubility of the metallic sulfides in solutions of sodium sulfide is the exact reverse of the order of solubility in water.

The method of determining the order of solubility of the metallic sulfides in aqueous solutions of sodium sulfide which was used in this investigation is dissolving two metallic sulfides at a high temperature, cooling, and examining the relationship between the two crystalline sul-

fides, the well-known criteria of order of crystallization being used to determine which was the more soluble, or the last to crystallize.

The difficulties involved in this study are that at high temperatures very high pressures result from the vapour or gas pressure of the water and the gas pressure of the H_2S that is evolved, and as sodium polysulfide is an extremely corrosive substance at elevated temperatures, the solution must be enclosed in a substance not attacked. Graphite, being unattacked by sodium polysulfide in dry melts, was used to contain the solution and an alloy steel bomb was used to support the graphite container. A cross-section sketch of the bomb and graphite liner is shown in fig. 1.

The bomb was made of a chromium-nickel-molybdenum alloy steel (1) and the gasket, of hardened sheet copper. The graphite double lining was machined from Acheson graphite electrode rods (2).

The method of sealing the solution within the bomb was as follows: the solution was placed in the inner graphite cup, and the bomb, containing the other graphite cup, was inverted and placed over it. The bomb was then turned upright and the packing rim was filled with a paste of iron powder and water. The copper gasket, the bomb head and the thrust ring were placed in position. The bomb head cover was screwed down to the limit and then was turned back a fraction of a turn. The bomb head cover bolts were then turned down in the following order:

1
5 7
3 4
8 6
2

- (1) Supplied by the Atlas Steel Company, S.P.S. 245, machined from rolled annealed stock and then heat treated by cooling in oil from $1500^{\circ}C$ and drawing from $950^{\circ}C$.
- (2) Supplied by the Canadian National Carbon Company, Grade AGX.

The furnace was made of a piece of brick pipe wound with Chromel A resistance wire and insulated with asbestos cement. The temperature was measured by means of a platinum - platinum-iridium thermocouple in a hard glass test tube inserted in the thermometer well of the bomb.

The assumption was made that the passage from subcritical to supercritical conditions in the solvent has little significance in regard to the solubility of any of the solutes as long as the density of the solvent remains constant while passing through the critical interval (1). This may be accomplished by having the volume of solution such that when at a temperature just under the critical it will completely fill the container. The volume of the inner graphite cup is 52.3 cc and the volume of water at room temperature that will fill this at the critical temperature is 21.7 cc. The effect of solutes on this relation was neglected.

The solutions that were used contained two metallic chlorides, sodium sulfide, sulfur and water. The ratio of the molecular amounts of the metals present was made equal, but the ratio of mols of sodium sulfide to metallic chlorides had to be adjusted so that at the high temperature all the metallic sulfides were dissolved. The ratio of sulfur to sodium sulfide was adjusted in some cases so that the desired metallic sulfide crystallized out. For instance, in determining which of chalcocite (Cu_2S) or argentite (Ag_2S) is more soluble in sodium sulfide, the sulfur concentration must be low enough so that covellite (CuS) does not precipitate out and also high enough so that native silver (Ag) does not precipitate out on cooling.

As before mentioned, the fullungsgrad or degree of filling above the critical temperature was kept high, and though equilibrium in the complex reaction between sodium polysulfide and water is reached, there is no pro-

(1) Ingerson, E.: Relation of Critical and Supercritical Phenomena of Solutions to Geologic Processes. Ec. Geol. 29, p.454, 1934.

gressive loss of any of the reactants or products, so that, as an approximation, the order of solubility may be taken as that in a solution of the composition placed in the bomb. Actually the composition will be lower in sodium sulfide and sulfur and will contain hydrogen sulfide, sodium hydrogen sulfide and some sodium sulfate which it did not have at the beginning, and while this may affect the solubilities of each of the metallic sulfides in the solution, it is assumed here that it will not affect to any degree the relative solubilities of the two metallic sulfides.

Experiment No 1.: The following were placed in the bomb: $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 8.249 grams; S, 1.096 grams; CuCl , 0.552 grams; AgCl , 0.799 grams; H_2O , 15.5 cc. The bomb was sealed, heated to 410°C in three hours and cooled to 30°C in seventeen hours. Much H_2S escaped when the bomb was opened. The crystalline mass at the bottom of the graphite cup was washed, transferred to a watch-glass and dried. Crystals were also noticed lining the inner graphite cup where the solution had been in contact with it.

The crystals on the side of the graphite cup appeared to be of chalcocite. The free crystals were of chalcocite, but with many bunches of fine wire silver, and a few sheafs of wire copper. No argentite was seen. In polished section, chalcocite and metallic silver were identified.

Evidently there had been considerable recrystallization of the cuprous sulfide, but the sulfur concentration, at least during the last stages of the cooling, had been such that metallic silver and not argentite was stable in the solution. The presence of some metallic copper indicates that had the solution contained less sulfur, chalcocite also would have been unstable and given place to metallic copper.

No conclusions could be drawn as to whether chalcocite or argentite

was more soluble in the solution used.

Experiment No 2.: The above procedure was repeated using the following amounts of the components: $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, 8.241 grams; S, 3.598 grams; CuCl , 0.216 grams; AgCl , 0.312 grams; H_2O , 15 cc.

Crystals on the side of the inner graphite cup were identified as chalcocite. The free crystals were mostly of chalcocite, with some argentite and there were many bundles of wire silver. The relationship between the chalcocite, argentite and silver is shown in fig. 2, and was interpreted to mean that the argentite crystallized out after the chalcocite, and was subsequently altered to wire silver. It was concluded that chalcocite is less soluble in the solution used and crystallizes out before argentite.

It is also evident from this and the preceding experiment that if reducing alkaline solutions are in contact with chalcocite and argentite, the latter is the first to be reduced to the metal.

Experiment No 3.: The following were placed in the bomb: $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, 8.588 grams; S, 3.974 grams; CuCl , 0.203 grams; PbCl_2 , 0.570 grams; H_2O , 15 cc. The bomb was heated to 415° in three hours and cooled to 20°C in twenty hours. H_2S escaped on opening. The crystals were washed and dried. Some crystals were seen on the inside of the inner graphite cup.

The crystals on the inside of the graphite cup were of chalcocite and galena, but arranged in a definite manner. For 2.2 cm from the rim of the cup, the crystals were mostly of chalcocite, but above this they were of galena to 2.4 cm from the rim. Some galena crystals were also seen in the upper part of the chalcocite zone. The zoning of the crystals probably was due to crystallization on the walls of the container at different

temperatures, hence at different levels of the solution. Thus galena crystallized out first, followed by chalcocite, as the solution cooled.

The relationship of galena and chalcocite in the free crystals in polished section is nearly that of having mutual boundaries, but the galena is often enclosed completely in chalcocite, and never the reverse.

See fig. 3.

It was concluded that galena is less soluble in the solution used and crystallizes out before chalcocite.

Experiment No 4.: The following were placed in the bomb: $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 25.212 grams; S, 11.023 grams; PbCl_2 , 0.529 grams; ZnCl_2 , 0.259 grams. The bomb was sealed, heated to 415° in three hours and cooled to 25° in nineteen hours. H_2S escaped on opening. Crystals of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and sulfur were seen at the bottom of the graphite cup and crystal faces of what looked like galena were seen on both surfaces of the inner graphite cup and on the inner surface of the outer graphite cup. The crystalline mass was washed with water to remove the sodium sulfide and then, after drying, with carbon disulfide to remove the sulfur.

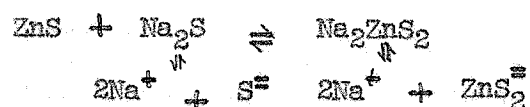
The inner surface of the inner graphite cup was washed as above and examined. Cubical and nearly cubical crystals of galena were seen adhering to the graphite, and also small yellow crystals of sphalerite.

The free crystals were examined after embedding in bakelite and polishing. Galena and sphalerite were identified but no conclusions as to which crystallized first were reached. They seemed to be separate free crystals.

The crystals were mounted in balsam and examined under the petrographic microscope. Sphalerite was identified from its isometric outlines

and isotropic character between crossed nicols. Small crystals of galena were occasionally seen growing out from crystals of sphalerite, as shown in fig. 4. This was considered sufficient evidence to state that under the conditions of the experiment, sphalerite is less soluble than galena in solutions of sodium polysulfide.

The results of this experiment are of interest due to the fact that, as pointed out previously, sphalerite nearly everywhere precedes galena in time of deposition. It may be argued that the concentration of sodium polysulfide used is much greater than any that occurs in nature. This is doubtless true, but the relative solubilities of the two is the same in such solutions no matter what the concentration, as may be seen from the following:



$$\frac{[\text{ZnS}_2^{2-}]}{[\text{ZnS}] \times [\text{S}^{2-}]} = K$$

$$\frac{[\text{ZnS}_2^{2-}]}{[\text{S}^{2-}]} = K_{\text{ZnS}}$$

(The concentration of ZnS may be considered in great excess and hence constant).

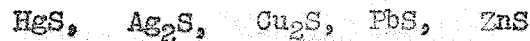
$$\frac{[\text{ZnS}_2]}{[\text{PbS}_2]} = \frac{K_{\text{ZnS}}}{K_{\text{PbS}}} = K_t$$

(The two sulfides are in contact with the same solution).

Thus at any one temperature, the ratio of the amount of ZnS to the amount of PbS taken into solution is constant, no matter what the concentration of sodium sulfide.

It was pointed out previously that the ratio $\frac{[\text{Zn}^{++}]}{[\text{Pb}^{++}]}$ is greater than one in the presence of sulfide ion. This fact was used to argue against the ionic sulfide theory. If the ratio $\frac{[\text{ZnS}_2]}{[\text{PbS}_2]}$ is less than one, as stated above, the same logic can be used to prove that these two sulfides may be carried in and precipitated from, the double sulfide form in ore-depositing solutions.

From the foregoing experiments it was concluded that in solutions of sodium polysulfide, silver sulfide is more soluble than cuprous sulfide, cuprous sulfide is more soluble than lead sulfide and lead sulfide is more soluble than zinc sulfide. From the earlier experiments on the metallic sulfides, it is evident that mercury sulfide is much more soluble than any of these four sulfides. Thus the known order of solubility, starting with the most soluble, is:



Since no essential difference exists between dry melts and aqueous solutions of sodium polysulfide except that in the former greater concentrations of sodium polysulfide and higher temperatures are possible, it is likely that the order of solubility of metallic sulfides in both types of

solutions is the same. In dry melts, pyrite, bismuthinite and molybdenite are more insoluble than all the other sulfides. In aqueous solutions cinnabar, realgar, stibnite and a sulfide of molybdenum are more soluble than the other sulfides. The sulfides of the intermediate group, sphalerite, greenockite, galena, chalcocite and argentite, are very soluble in dry melts of sodium polysulfide but just moderately soluble in aqueous solutions of the same at high temperatures. Thus the order of solubility of the simple metallic sulfides in solutions of sodium polysulfide, starting with the most insoluble, is:

molybdenite	sphalerite, galena, chalcocite, argentite	cinnabar
bismuthinite	pyrrhotite	realgar
pyrite	greenockite	stibnite
		and molybdenum sulfide

Except for the very soluble molybdenum sulfide, this order is very similar to the order of deposition of the simple sulfides in nature. Arsenic and antimony sulfides are sometimes removed completely from the solution by the precipitation of sulfosalts, and probably the soluble molybdenum sulfide is removed in every case in this way. The evidence for this is that in oxidized lead ores, there often is found the lead molybdate, $Pb Mo O_4$, and the molybdenum must have been released during the oxidation of some complex sulfide containing it, and a molybdenum sulfide is not known in low-temperature deposits which commonly contain cinnabar, realgar and stibnite.

The order of solubility of the metallic sulfides in solutions of sodium polysulfide and the order of natural deposition being so similar can hardly be a coincidence and this is deemed to be further evidence

that the natural ore-bearing solutions are solutions of the metallic sulfides in alkaline polysulfide.

The Order of Stability of the Sulfide Sols

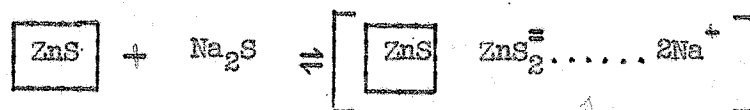
It was found that colloidal solutions of the metallic sulfides peptised by sodium sulfide are very easy to prepare. A method that gave fairly stable sols was as follows: a few drops of a solution of the chloride or sulfate of the metal were added to a large volume of a dilute solution of sodium sulfide while shaking or stirring rapidly. The resultant colloidal solution was usually transparent, showed no opalescence and remained stable for some time.

In preliminary experiments it was seen that for any one metallic sulfide, there was a concentration of sodium sulfide that acted as peptiser to the maximum degree, and experiments were carried out to see if this optimum concentration was the same for each sulfide. Colloidal solutions of iron sulfide were prepared using various concentrations of a stock solution of sodium sulfide prepared from the hydrated crystals. The various sols were corked and placed in order and were compared over a period of a few days to see which was the most stable. The stages noticed before coagulation were: (1) decrease in transparency, (2) some flocculent material, the rest colloidal, (3) all flocculated, but easily dispersed again on shaking, and (4) all flocculated and not easily dispersed on shaking. Using these as progressive stages, it was seen that among the sols of iron sulfide there exists a maximally stable sol, with stability nearly symmetrically decreasing away on each side of this,

toward a lower and a higher concentration of sodium sulfide.

The same was seen in the case of the sols of copper, zinc, lead, silver and mercury sulfides, though the maximum was not in the same place in each case, the maximum for iron sulfide being exhibited in a solution more concentrated than for any of the others, and for mercury sulfide, in one more dilute than any of the others, and for the rest somewhere between the two.

Since all these metallic sulfides form double sulfides with sodium sulfide, it may be that each particle of sulfide is stabilized by a double layer consisting of an ionised double sulfide, as follows:



The more soluble a metallic sulfide is in a sodium sulfide solution, the more difficult will it be to prepare a colloidal solution using it as peptiser. The more soluble it is, the faster will recrystallization to larger units take place and thus the less stable will be the colloidal solution. Thus if the sodium sulfide concentration is too great, the colloidal solution of the metallic sulfide will be unstable due to recrystallization and grouping of units, while if it is too small, the colloidal solution will be unstable due to inability to form enough of the double sulfide at the boundaries of the sulfide particles to form the protective double layer. A maximum stability at one sodium sulfide concentration should be exhibited, and the experimental evidence seems to bear this out. In addition this concentration of sodium sulfide to give maximum stability of a metallic sulfide sol should vary with the

metal of the sulfide. A sulfide more soluble than another in sodium sulfide should show its maximum in a more dilute solution of sodium sulfide. This appears to be the case among the sulfides studied. Mercury sulfide is the most soluble in sodium sulfide solutions and is peptised to the colloidal state by sodium sulfide solutions more dilute than can be used for, say, iron sulfide. The experimental method was not deemed sufficiently accurate to determine the exact order of maximum stability among the other metallic sulfide sols, but probably it is the same as the order of solubility in sodium sulfide solutions.

The System-Alkali Polysulfide, Water

During the experimental work on double sulfides it was found that a reaction takes place between sodium polysulfide and water, forming oxy-salts and hydrogen sulfide. This reaction has been commented upon by several investigators, but has not been studied to the extent that the equilibrium constant at various temperatures has been found.

A solution of sodium polysulfide was sealed up in a glass tube, heated in a bomb to about 300°C for twelve hours, cooled and opened. The solution effervesced and much H_2S was evolved. The solution was nearly colourless and microchemical tests for the ions SO_4^{\equiv} and S^{\equiv} were positive, and for the ions SO_3^{\equiv} and $\text{S}_2\text{O}_3^{\equiv}$ negative. Evidently a reaction involving an equilibrium between H_2S , H_2O , Na_2S_x , NaHS and Na_2SO_4 , with possibly minor amounts of Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and H_2S_x exists in the solution. As a qualitative test of the reversibility of the reaction, a considerable amount of Na_2SO_4 was placed in the Na_2S_2 solution and the same procedure

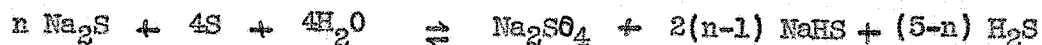
was repeated. The solution filled 50% of the tube and the rest was air. After cooling it was seen that some sulfur had separated and that the solution was a faint yellow colour and contained no more than traces of the ions SO_3^{\equiv} and $\text{S}_2\text{O}_3^{\equiv}$. The total SO_4^{\equiv} concentration at the end of the test was found by precipitation with barium. The data and calculations are given below:

Weight of Na_2S	0.2841 grams
Weight of S	0.4725 "
Weight of Na_2SO_4	0.6209 "
Weight of H_2O	7.6187 "
Temperature of heating	320°C
Time of heating	20 hours

(The sulfate in 3 cc. of the solution at the end of the test was precipitated as BaSO_4).

Weight of BaSO_4 in 3 cc. of solution	- 0.0704 g
Weight of Na_2SO_4 " " " "	- 0.0429 g
Weight of Na_2SO_4 in 7.6187 cc. of solution	- 0.3268 g
Weight of Na_2SO_4 destroyed by the reaction	0.2941 g

It is evident that the reaction can be reversed by excess of one of the products, so it is probably in the nature of a true reversible equation. It is difficult to balance such an equation, but put into a general form, it is:



If $n = 1$, this becomes



The importance of this reaction in the theory of ore deposition is that if the double sulfide theory is true, then the action of water on double sulfides and polysulfides at elevated temperatures must be considered, as this must influence the stability of the double compounds. In other

words, if the metallic sulfides are carried as double sulfides in an aqueous solution, then some such reaction as given above will control the amount of alkali sulfide present, which will in turn determine the amount of metallic sulfide which can be carried. Loss of H_2S , driving the reaction to the right necessitates the alteration of more alkali sulfide to sulfate, thus causing the breakdown of more double sulfide to precipitate more metallic sulfide. Removal of the sulfate ion would have a similar effect.

It was this reaction, with a subsequent loss of H_2S that caused the breakdown of the double sulfides of mercury, arsenic and antimony to precipitate cinnabar, realgar and stibnite in the experiments described in the early part of this chapter. In a closed system, however, once a state of equilibrium has been reached, temperature will be the determining factor controlling solution and precipitation of metallic sulfides since it will influence both the stability of double sulfides and the shift of the equilibrium. In a system from which H_2S can escape, the rate of escape, since it determines the course of the equilibrium, will be the controlling factor in the precipitation of the metallic sulfides.

It will be noticed that a shift of the equilibrium to the right means a change from a solution richer in sulfur to one poorer in sulfur. It thus would determine which of two sulfides of a metal would precipitate out at any one point.

IX CONCLUSIONS

The ionic sulfide theory of sulfide transportation and deposition does not seem capable of reconciling the chemical data and the field facts. The colloidal sulfide theory is a good explanation of some phases of replacement and deposition but claims of universal applicability are unsound. The double sulfide theory appears to be able to explain most of the features of sulfide deposition, and combined with the colloidal sulfide theory, is thought to be a reasonable explanation of how the ore deposits were emplaced.

It is well established that metallic sulfides form with sodium sulfide double sulfides which may break down again to the constituent sulfides. Sodium sulfide and double sulfides can dissolve sulfur to form polysulfides. This also is a reversible reaction.

The double polysulfide of iron and sodium forms pyrite or pyrrhotite on decomposition depending on the sulfur concentration in the polysulfide form in the double compound and in the solution in contact with the iron sulfide. The sols of iron sulfide, both pyrite and pyrrhotite, are very stable in solutions of sodium sulfide and polysulfide. Pyrite appears to be less soluble than pyrrhotite in a melt of sodium polysulfide.

Double sulfides and polysulfides of zinc, cadmium, lead, copper, silver, mercury, arsenic, antimony, bismuth, and molybdenum were prepared and gave, on decomposition, sols or crystals of wurtzite, greenockite, β cadmium sulfide, galena, chalcocite, covellite, argentite, cinnabar, metacinnabarite, realgar, stibnite, bismuthinite, and molybdenite.

Triple sulfides of copper, iron and sodium were prepared and when in the correct proportions and decomposed, formed crystalline chalcopyrite.

A representative member of the sulfosalt group, pyrargyrite, was synthesized by keeping a solution of the double sulfide of antimony and sodium in contact with silver sulfide at an elevated temperature.

It was then proved that the double sulfides of some of the metals and sodium are stable in the presence of water at high temperatures and that the metallic sulfides crystallize out on cooling. In the case of lead and zinc sulfides, the former is more soluble in solutions of sodium polysulfide, precipitating out as crystals of galena later than the corresponding crystals of sphalerite. That this is also the order of deposition found in natural deposits of these two sulfides is put forward as a point in favour of the double sulfide theory. The order of solubility of the sulfides of silver, copper, lead, zinc and mercury in solutions of sodium polysulfide is, starting with the most soluble:



Dilute sodium sulfide and polysulfide solutions were found to be very good peptisers for the metallic sulfides in the colloidal state and they exhibit this property to a maximum degree at one definite concentration. This optimum concentration of sodium sulfide as peptiser is different for each of the sulfides, being more concentrated for a sulfide less soluble in sodium sulfide solutions and less concentrated for one more soluble.

It was found that an equilibrium exists between sodium polysulfide, sodium hydrogen sulfide, sodium sulfate, sulfur, hydrogen sulfide and water. Decrease in pressure, decrease in concentration of hydrogen sulfide and sulfate ion and probably decrease in temperature all decrease the polysulfide concentration.

The theory of sulfide deposition that seemed to follow from this work

is briefly as follows. The ore-bearing solutions leaving the magma chamber as the aqueous residue of the crystallization of the igneous mass carry the metallic sulfides as complex double polysulfides of the metal and an alkali metal. After leaving the chamber, the solutions are subjected to decrease in pressure, lowering of temperature and a loss of some constituents due to reaction with the wall-rock. Due to any or all of these changes, the double sulfides become unstable and break down progressively, precipitating the simple metallic sulfides in a definite order. Complex metallic sulfides such as chalcopyrite and the sulfosalts precipitate out when one of the components (copper sulfide in the former case and arsenic and antimony sulfide in the latter) are more soluble than the other component, which has usually precipitated out in the simple forms a short time previously. That is, the complex metallic sulfides crystallize out later than one of the components and before the other. Native metals precipitate out instead of the sulfides when the sulfur concentration becomes low. Lowering of the sulfur concentration can be brought about by the formation of pyrite from iron minerals in the wall-rock at high temperatures, the oxidation of sulfide ion to sulfate ion by ferric minerals at relatively low temperatures and the loss of hydrogen sulfide driving the oxidation-reduction of sulfur by water to the oxidation side. This last reaction takes place under low-pressure conditions and necessitates an increase of the sulfate concentration in the solutions to compensate for the loss of hydrogen sulfide. Thus the effect of the solutions on the wall-rock at high temperature will be that of pyritisation, at medium temperature - reduction and at low temperature-sulfatisation. The simple order of precipitation of the metallic sulfides from solution may be profoundly altered by the peptisation of minerals already formed

into the colloidal state, from which they may coagulate in a different order. However, no mineral can separate out from the colloidal state if it is not stable in the solution carrying it, and changes take place in the composition of the sol particle as changes take place in the solution with which it is in contact.

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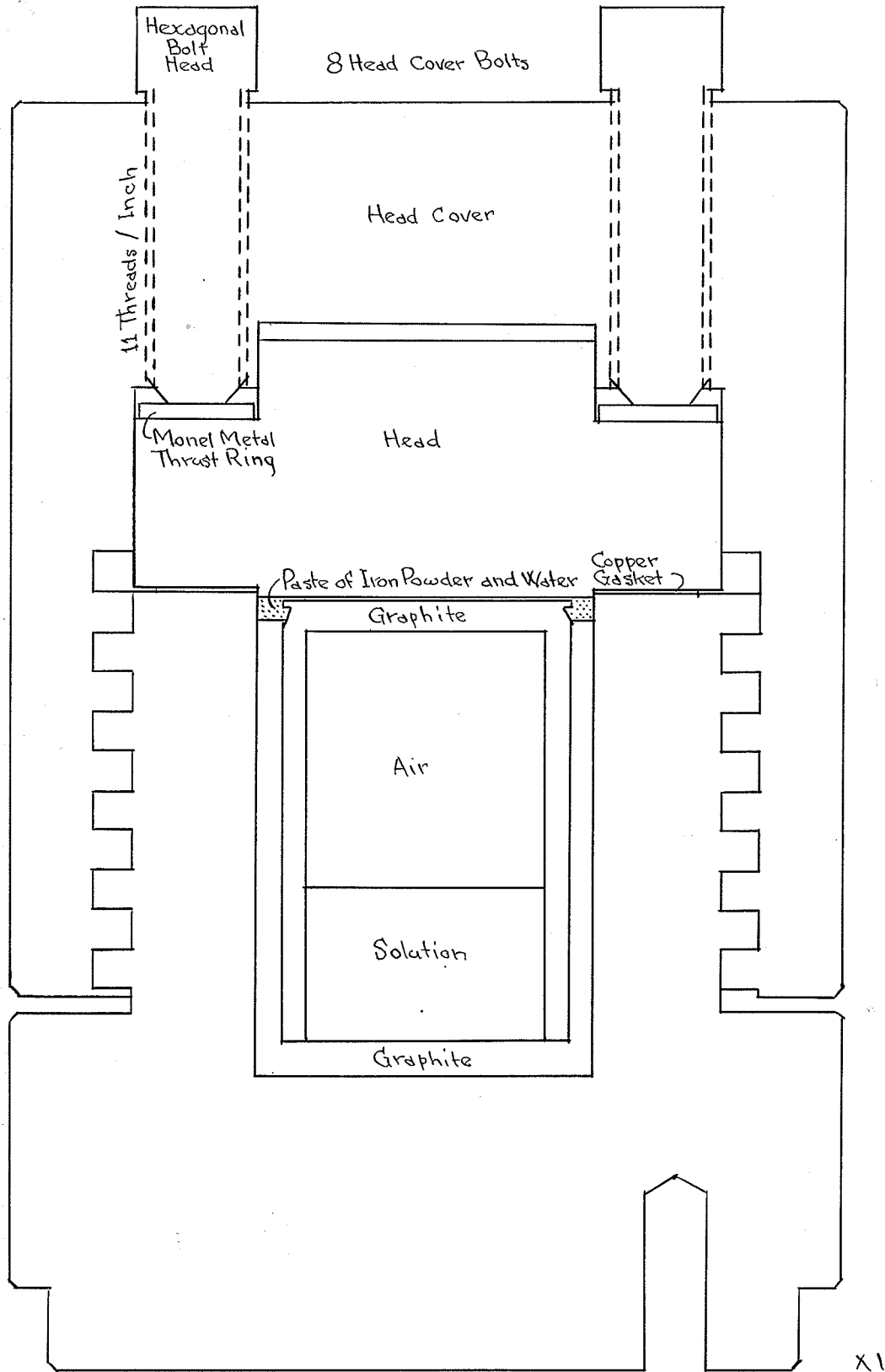
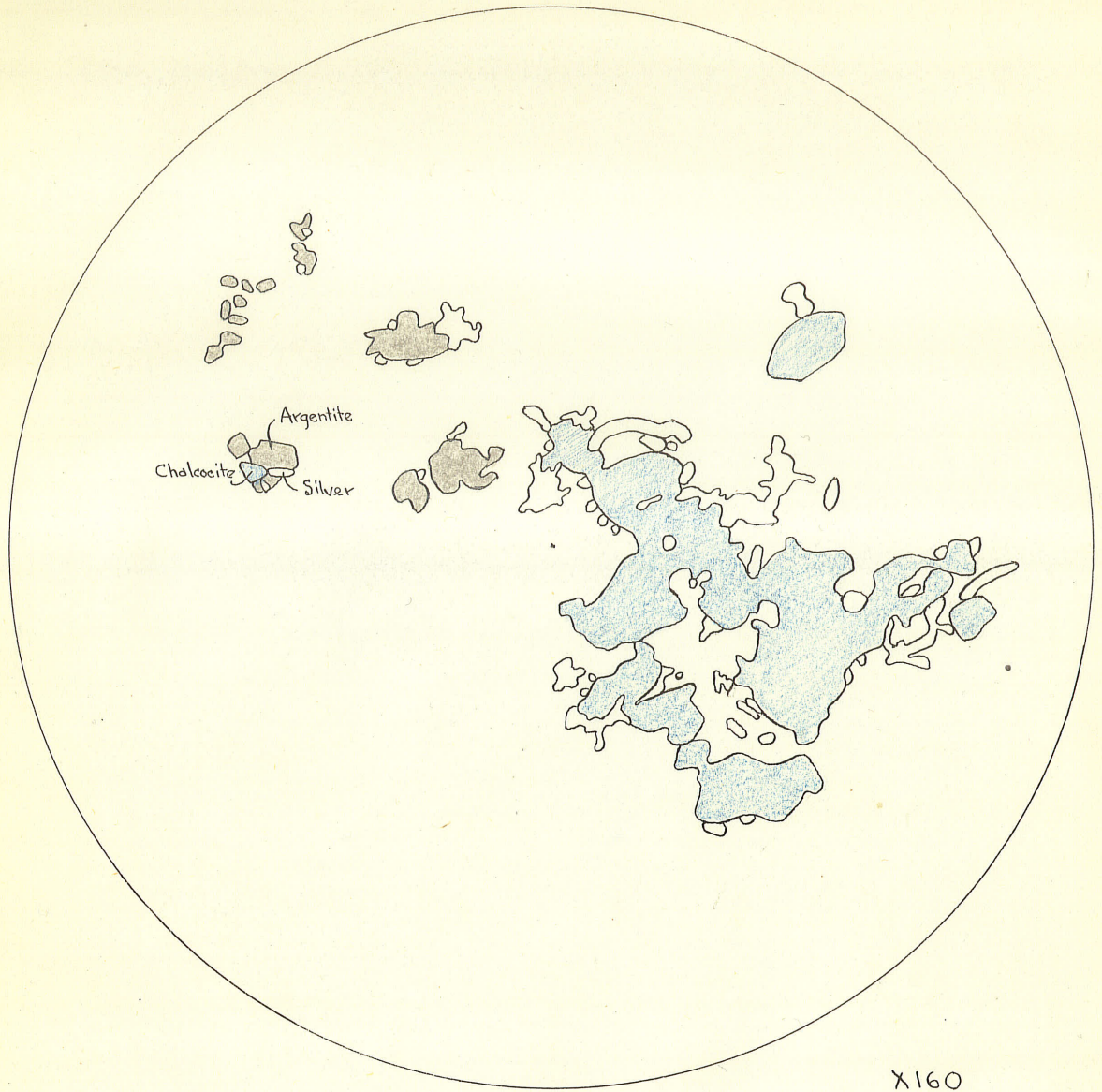


Figure 1 .



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Figure 2 .

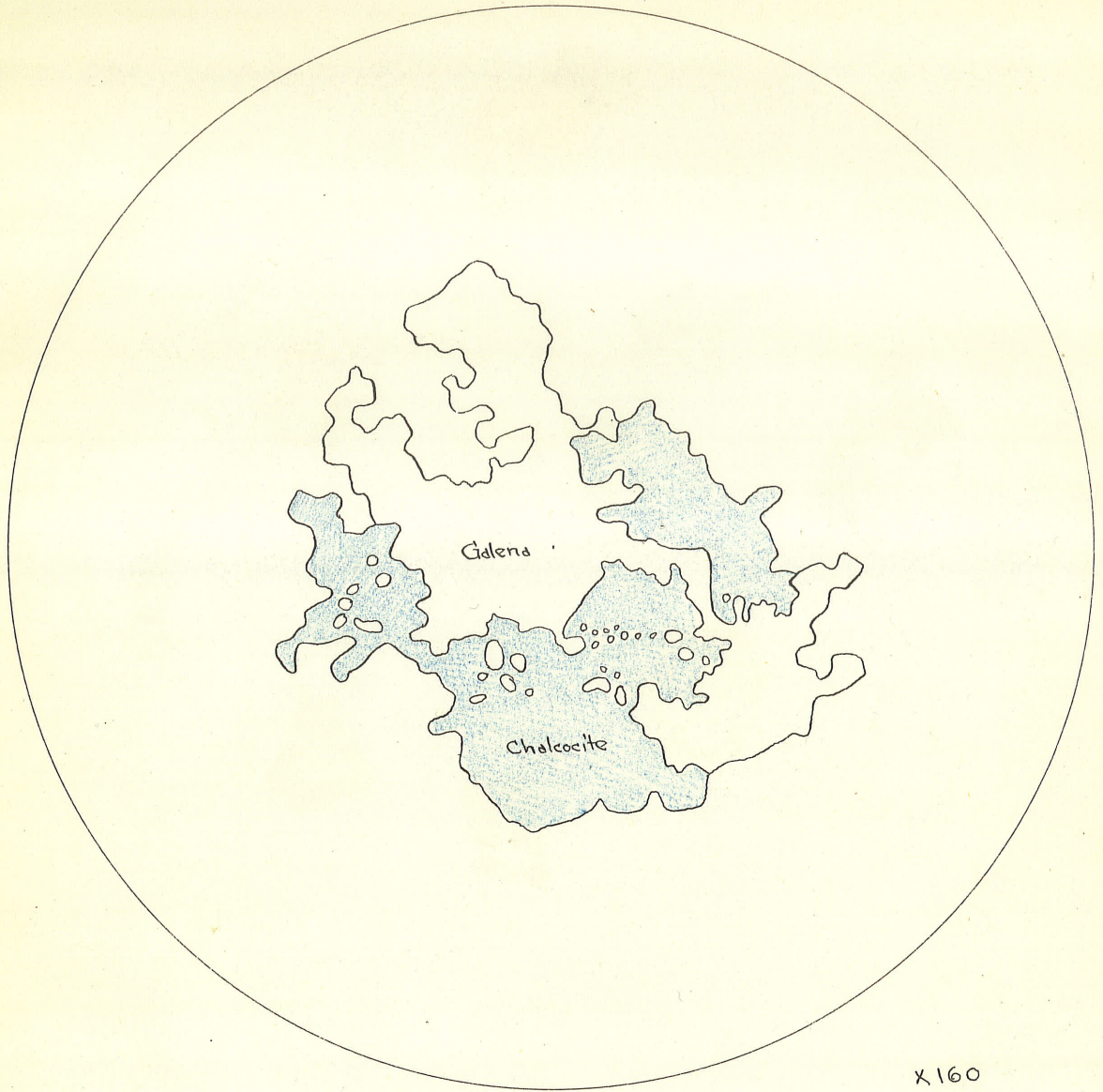


Figure 3 .

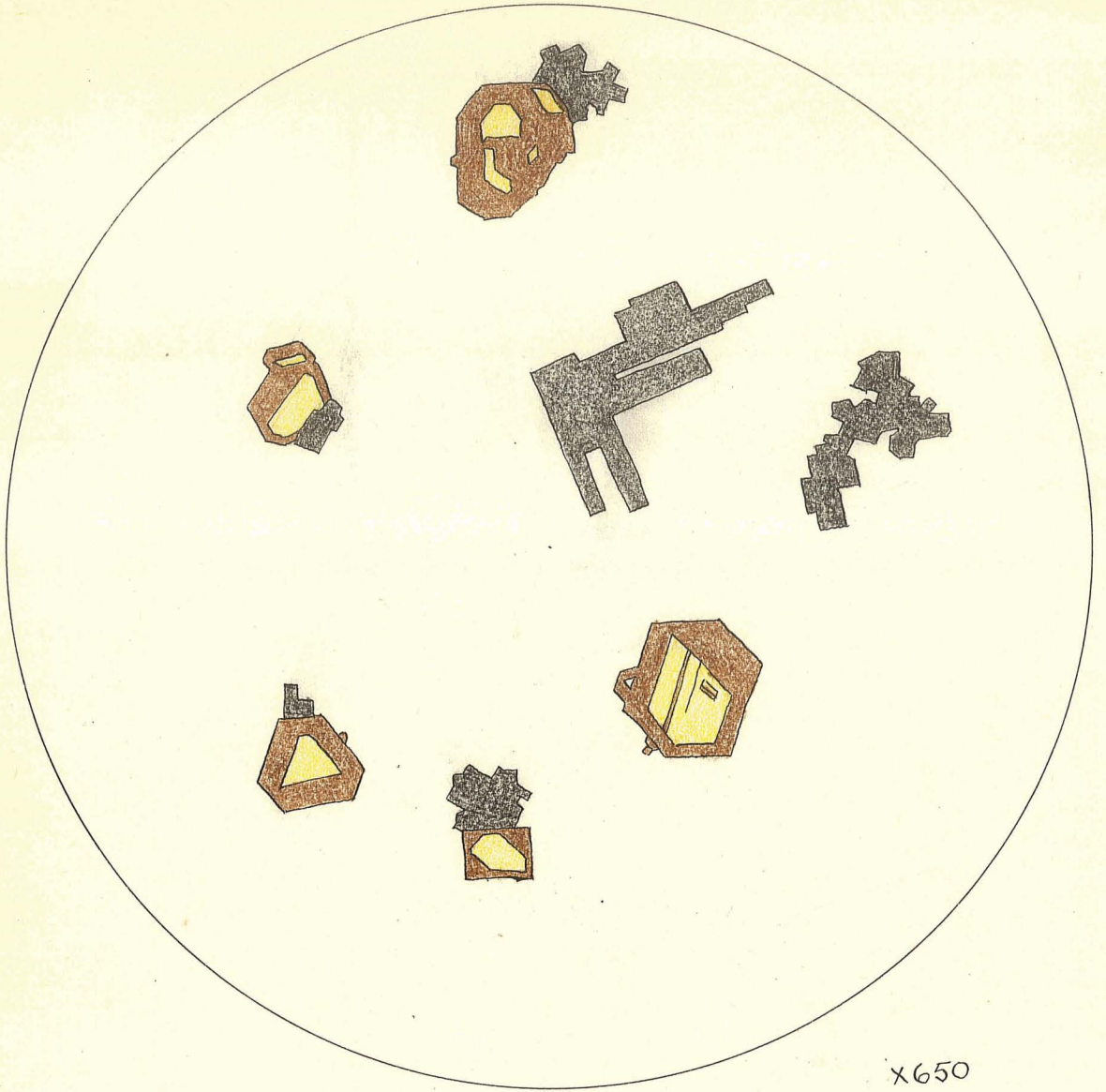


Figure 4.