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CERTAIN ORE MINERALS

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## SOME SUGGESTIONS CONCERNING THE SEQUENCE OF CERTAIN ORE MINERALS

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### ABSTRACT

Phase diagrams for the ore minerals in the systems Cu-Fe-S, Fe-O-S, Cu-As-S, Pb-As-S and Pb-Sb-S are postulated, based on the observed sequence in various mining districts.

These diagrams strongly suggest the sequence of phases that appear in each of these systems and can be readily explained by assuming an increase in chemical potential of sulfur in the fluid mineralizing phase relative to that of the solid phases during the period when final adjustments in relations among the solid phases is taking place. The sequence of phases at a point in a vein and the sequence of introduction of components into a vein are not necessarily the same.

### INTRODUCTION

FEW attempts have been made to apply the Gibbs phase rule to sulfide mineral deposits, perhaps largely because sulfide mineral assemblages are so obviously disequilibrium assemblages. However disequilibrium assemblages of vein materials are most marked when examined on a gross scale, i.e. an entire vein or portions of a vein. Sufficiently small volumes of an ore deposit in many cases show apparent equilibrium assemblages of minerals. Examination of these small units of a mineral deposit, small even in terms of the scale of a microscope field, yields a picture of a succession of equilibrium conditions and it is the direction of change of this succession of equilibrium conditions that we wish to examine.

The Gibbs phase rule states that the maximum number of phases in a system equals the number of components plus two minus the number of degrees of freedom

$$p = c + 2 - f.$$

Goldschmidt, recognizing that most mineral assemblages must have formed over a considerable range of temperatures and pressures, noted that the number of degrees of freedom must be at least two, pressure and temperature. Thus he formulated the mineralogical phase rule

$$p = c.$$

Korzhinsky (8, 9) has discussed the application of the phase rule to open systems. Korzhinsky's rule states that the number of phases cannot exceed the number of fixed components. Thus, the various three-component systems we consider in this paper always contain sulfur as one of the components. Insofar as veins may be considered open systems with sulfur present in fluid

phase, the number of possible solid phases is reduced by one and only two mineral phases may be present in equilibrium. The triangular diagrams we present in this paper are therefore strictly applicable only to completely condensed systems, and show three possible solid phases in equilibrium. In open systems such as veins however, only two of these phases may be in equilibrium, with pressure and temperature varying and a sulfur rich fluid phase present. Thus we may assume that in typical cases our systems are always in disequilibrium, one of three minerals always being replaced by another.

The extent to which most sulfide deposits, on a gross scale, represent disequilibrium assemblages is immediately apparent. For example only three solid phases can be present in equilibrium in the condensed system Cu-Fe-S if pressure and temperature are variables, yet mineral assemblages that contain pyrite, marcasite, pyrrhotite, digenite, chalcocite, covellite, bornite, chalcopyrite, and others, are known; these assemblages have as many as five more phases than should be present in equilibrium.

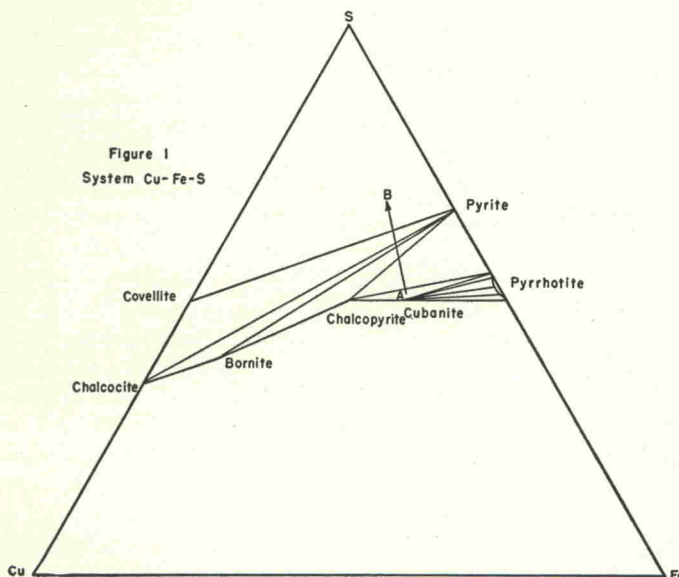
Although the number of solid phases in equilibrium at any given temperature, pressure, and composition in a three-component system is small, the identity of the solid phases may change in response to changes in the variables: temperature, pressure, and composition. Thus, during formation of a sulfide deposit, earlier-formed minerals are constantly being altered toward new compositions, i.e. replaced, in response to changes in the variables of the system. The replacement rarely, if ever, is complete and thus an ore deposit mirrors a history of changing conditions of equilibrium. The sequence of phases as indicated in hand specimens and under the microscope gives some indication of the direction of changing equilibrium conditions. It is these changing equilibrium conditions that we wish to examine.

Many observations have been made about the "usual sequence" of sulfide minerals. Gilbert (5) has observed that minerals appear in decreasing order of their relative hardness. Schürmann (11) noted a sequence of replacement among sulfides which was later shown to be approximately the inverse order of their solubility in water at room temperature. Bandy (1) has noted that the "normal" or "ideal" sequence is in approximate order of increasing proportions of cations to anions. Some aspects of sulfide sequence may be explored by aid of ternary diagrams of various condensed sulfide systems.

#### THE SYSTEM Cu-Fe-S

A great amount of detailed mineralogical information is available about relations between solid phases in the system Cu-Fe-S. Sales and Meyer (1949) postulate that at Butte ascending solutions react with iron-bearing minerals in the wall rock to form pyrite. Solutions thus depleted in sulfur then deposit chalcopyrite and bornite. Once the iron-bearing wall-rock minerals are converted to pyrite, the early chalcopyrite-bornite assemblage is replaced by the assemblage chalcocite and pyrite, which for a given copper-iron ratio is more sulfur-rich. The compositions of various solid phases in the condensed system Cu-Fe-S are plotted in Figure 1. We can draw various tie lines and erect a postulated ternary phase diagram.

Let us postulate that during the course of mineral deposition the partial pressure of sulfur increases, or some change takes place so that the relative chemical potential of sulfur at any one point in a vein increased with time. The expected mineralogical changes in the condensed system can be seen by the course of the arrow, Figure 1, from A to B. The assemblage stable at point A is cubanite, pyrrhotite, and chalcopyrite. As the sulfur potential increases along the path AB, the triangular field where pyrite, pyrrhotite and chalcopyrite are the stable phases is entered and cubanite disappears. With further change toward the S corner, the triangular field of pyrite, bornite, and chalcopyrite is entered and pyrrhotite disappears. The next phase to disappear is chalcopyrite as chalcocite appears. Bornite then disappears as covellite ap-



pears and even chalcocite will disappear if relative sulfur chemical potential is sufficiently high and sulfur content of the condensed system increases. We can now arrange the sulfides in the Cu-Fe-S system in a sequence based on the assumption of steadily increasing relative chemical potential of sulfur during mineral deposition. From early to late, stable phase assemblages are :

cubanite,\* pyrrhotite, chalcopyrite  
 pyrite, pyrrhotite, chalcopyrite  
 bornite, pyrite, chalcopyrite  
 chalcocite, bornite, pyrite  
 covellite, chalcocite, pyrite

\* Cubanite commonly, if not invariably, occurs intergrown with either chalcopyrite or pyrrhotite, presumably representing unmixing of a solid solution stable above 400 or 500°. The problem has been discussed by Borchert, Edwards and others. In ores presumably formed at lower temperatures, pyrrhotite and chalcopyrite occur together but cubanite is usually lacking.

The last three groups represent the sequence found by Sales and Meyer at Butte; this is also the sequence of phases reported by mineragraphers for a large majority of ore deposits. Not all the groups of stable phases, of course, may be present in any one vein or mine. Pyrrhotite and cubanite are absent at Butte, and in many deposits the later stages, chalcocite and covellite, are not represented in the hypogene mineral suite. In many of the deposits, moreover, the evidence of extraction of sulfur by wall rock minerals is lacking, or at least has not been reported. We would like to suggest that this aspect of the Sales and Meyer story of Butte may not necessarily be an integral part of the general genetic picture. Characteristically, the sequence of phases that appear in the system Cu-Fe-S is one most readily explained by assuming increase with time of the relative chemical potential of sulfur. Early extraction of sulfur by conversion of iron-bearing wall minerals to pyrite will certainly permit a later relative increase in sulfur concentration of the solutions as the iron minerals in the wall rock become completely converted to sulfides. However, a steady relative increase of sulfur potential with time appears to take place even when there is no evidence of decreasing fixations of sulfur by the iron of the wall rocks. Reasons for such a possible increase will be discussed later in this paper.

The above examination of the phases in the Cu-Fe-S system points up a possibly unexpected relationship. The major sequence of phases, chalcopyrite followed by bornite, followed by chalcocite, takes place with increasing amount of sulfur in the bulk composition of all the solid phases but with actually decreasing amounts of sulfur in the copper bearing phases, for chalcopyrite contains more sulfur than bornite which in turn contains more sulfur than chalcocite. This part of the sequence thus fits both with Bandy's observation of decreasing sulfur to metal ratio with time and our thesis of sequence owing to steadily increasing sulfur chemical potential in the mineralizing fluids and consequent increase of sulfur with time in the condensed phases. Covellite, cubanite and pyrrhotite would be apparent exceptions in Bandy's scheme of sequence, but seem to fit in well as far as our hypothetical phase diagram is concerned.

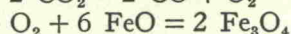
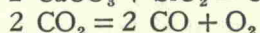
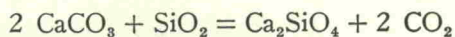
Our hypothetical phase diagram also explains Gilbert's generalization that bornite and pyrrhotite are incompatible. There are in the world many pyrrhotite-chalcopyrite deposits, such as Noranda (Quebec), Sherritt Gordon (Manitoba), Ducktown (Tennessee) and South Strafford (Vermont). In all of these bornite is absent or a rarity. Likewise hypogene chalcocite is virtually if not completely absent. On the other hand, deposits containing bornite, such as Butte and most of the porphyry copper deposits, contain no pyrrhotite.

#### THE SYSTEM Fe-O-S

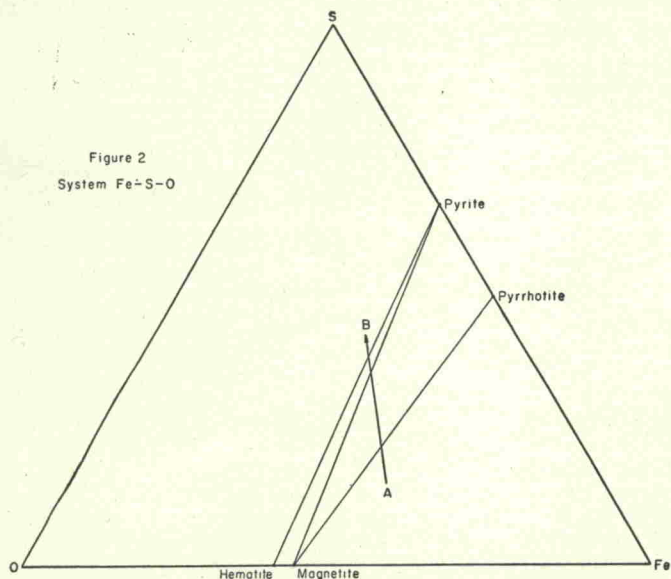
Hypogene solid phases in the system Fe-O-S are magnetite, hematite, pyrite, and pyrrhotite. Their genetic relations have been discussed extensively by Gilbert (4, 6) and by numerous other writers.

Hydrothermal magnetite and hematite in appreciable quantity are found almost exclusively in high temperature limestone environments. Probably the

formation of metasomatic calcium silicates frees  $\text{CO}_2$ , which at the relatively high temperature of these deposits, partially dissociates and oxidizes the iron in the hydrothermal solutions. The reactions are summarized by the equations:



Magnetite,  $\text{Fe}_3\text{O}_4$ , is extremely insoluble, and will precipitate readily so that the various reactions continue to run. The CO escapes upward with the partially spent hydrothermal solution.



The relationships between the phases in the system Fe-O-S suggest that in the vast majority of cases early silicates are followed by magnetite with pyrrhotite, followed by later hematite and pyrite. In this system, hematite and pyrrhotite seem to be incompatible species. The postulated diagram, Figure 2, appears to explain fairly well the observed relationships. Again, the sequence of phases indicates a steadily increasing amount of sulfur in the condensed system. Our phase diagram suggests that the stable groups are pyrite-magnetite-pyrrhotite and hematite-pyrite-magnetite.

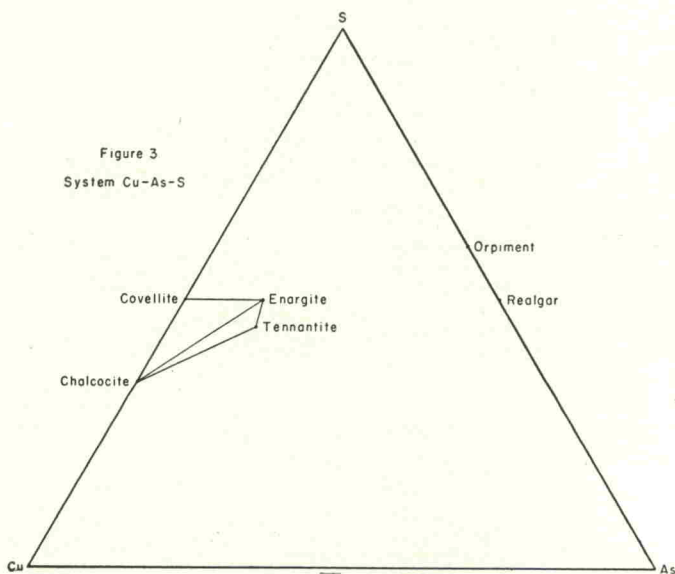
#### THE SYSTEM Cu-As-S

The solid phases in the system Cu-As-S are shown in Figure 3. The relations between enargite and tennantite have been studied in numerous ore deposits as well as experimentally.

Sales and Meyer have shown that at Butte, tennantite is followed by

enargite at about the time chalcocite and bornite are followed by chalcocite and pyrite. Enargite is displaced from tennantite almost directly toward the sulfur corner of the triangular diagram and Sales and Meyer have interpreted the shift from tennantite to enargite as a result of increasing sulfur concentration in the solution. Gaines (3) has shown experimentally that enargite crystallizes from hydrothermal solutions at higher partial pressures of sulfur, and tennantite forms from the same solutions at lower partial pressures of sulfur.

On the As-S side of the three component system, the phases realgar and orpiment are of interest. Here also, orpiment seems to be the later of the two phases. It occurs in many cases as veins cutting realgar and as late alteration crusts on realgar. In many deposits, the relations of these two phases are, however, not unequivocal.



#### THE SYSTEM Pb-As-S

The sequence of phases in the systems discussed so far appears to be explainable on the assumption that the volatile component, S, increases in relative chemical potential with time at a given point in a vein, thus causing relative amounts of sulfur in the various condensed systems to increase.

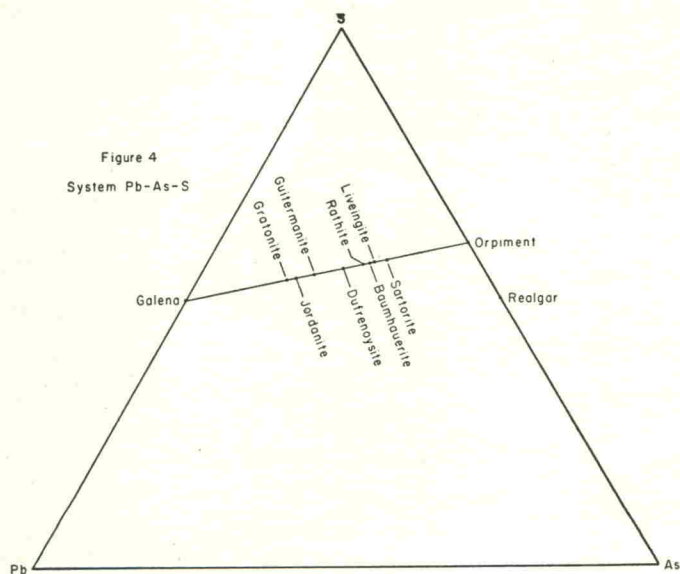
It is of interest, therefore, to examine the more volatile compounds of sulfur whose behavior might be expected to parallel that of sulfur. These compounds are  $As_2S_3$  and  $Sb_2S_3$ .

With the exception of realgar and native arsenic, the compositions of all the minerals in the system Pb-As-S lie on a straight line between that of galena and that of orpiment. All the minerals are rare and many of them are re-

ported only at Binnenthal in Switzerland. The phases reported in this system are:

	PbS	As <sub>2</sub> S <sub>3</sub>
Orpiment	0	1
Sartorite	1	1
Liveingite	5	4
Baumhauerite	4	3
Rathite	3	2
Dufrenoyite	2	1
Guitermanite	3	1
Jordanite	4	1
Gratonite	9	2
Galena	1	0

The compositions of these minerals are plotted on the triangular diagram in Figure 4. The sequence of deposition at Binnenthal, according to Boder



(2), is in order of progressive increase in the  $As_2S_3$  content. Jordanite is replaced by dufrenoyite and by baumhauerite; rathite by baumhauerite, by sartorite and by realgar. Galena in this district is rare and is commonly associated with jordanite. The sequence of phases can, of course, be readily explained by assuming that the arsenic behaves in a manner somewhat similar to sulfur in that its relative chemical potential increases also with time at a given point in a vein.

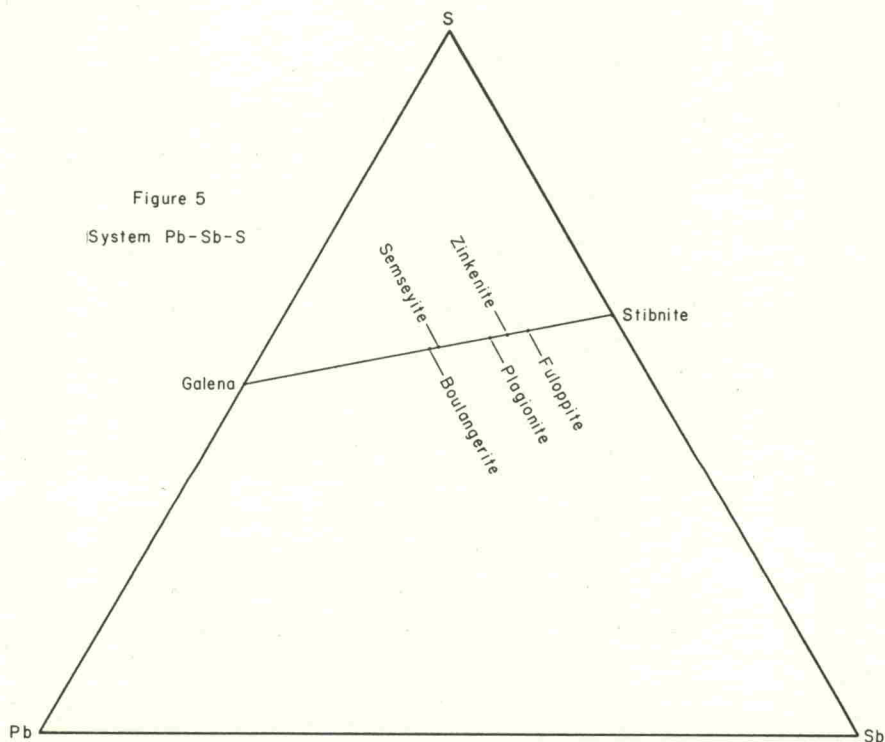
#### THE SYSTEM Pb-Sb-S

A large number of phases occur in the system Pb-Sb-S. All of the compositions except that of native antimony, fall on a straight line between that

of galena and stibnite and are shown in Figure 5. The various phases are:

	PbS	Sb <sub>2</sub> S <sub>3</sub>
Galena	1	0
Boulangerite	5	2
Semseyite	9	4
Plagionite	5	4
Zinkenite	1	1
Fuloppite	3	4
Stibnite	0	1

The detailed genetic relations of these minerals are not known. However, in several localities boulangerite follows galena and is followed by stibnite.



Available evidence strongly suggests thus that the relative chemical potential of  $Sb_2S_3$  in the ore-forming fluid increases with time as does that of  $As_2S_3$  and S.

#### DISSOCIATION OF SOLID PHASES

In summary, then, the three-component systems examined to date show a rather striking trend. The relative chemical potential of the more volatile component of the solid phases apparently increases in the ore-forming fluid with time during ore deposition at any fixed point in a vein and successively

later phase assemblages are enriched more and more in sulfur, antimony sulfide, or arsenic sulfide as the case may be.

We perhaps may clarify these relations by considering the equilibrium between a volatile and a solid. Let us take, for example, the compounds  $\text{CuS}$  and  $\text{Cu}_2\text{S}$ . The relation between dissociation pressure and temperature for these two phases is shown in Figure 6. Curve A in Figure 6 is the dissociation sulfur vapor pressure of  $\text{CuS}$ . Curve B is the dissociation sulfur vapor pressure of  $\text{Cu}_2\text{S}$ . The graph shows the partial pressure of sulfur vapor plotted versus temperature. The stability fields of chalcocite, covellite and metallic copper are shown. Along curve A, the chemical potential of sulfur in

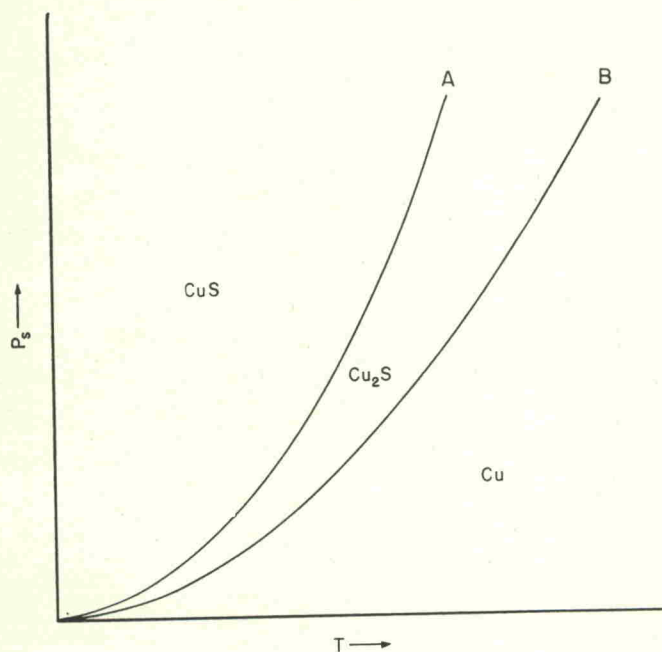


Figure 6

the vapor phase plus the chemical potential of chalcocite is the same as that of covellite, whereas along curve B, metallic copper and sulfur vapor are in equilibrium with chalcocite. Were there copper sulfides containing more sulfur than covellite, their boundary curves would, of course, be farther to the left than that of covellite diagram. As the relative sulfur chemical potential is raised, we progress from the field where metallic copper is stable to the field where chalcocite is stable and on to the field where covellite is stable.

The equations of the dissociation curves A and B are simple. They are given by the Clausius-Clapeyron equation  $dp/dt = \Delta H/T\Delta V$ . In the region of modest to high temperatures and relatively low sulfur-vapor pressures, the ideal gas law may be substituted. Neglecting the volume of the solid phases

and substituting  $V = RT/p$ , we have

$$\begin{aligned} dp/dt &= p\Delta H/RT^2 \\ \ln p &= \Delta H/RT + C. \end{aligned} \quad \text{by integration}$$

In this equation  $\Delta H$  is, of course, the heat of dissociation and  $R$  is the gas constant. Thus the partial pressure of sulfur in equilibrium with a sulfide reaches zero only at a temperature of absolute zero on the Kelvin scale.

The sequence of phases in the three-component systems discussed earlier in this paper suggested strongly that each successive phase or phase assemblage was steadily enriched in the more volatile component. The history of the

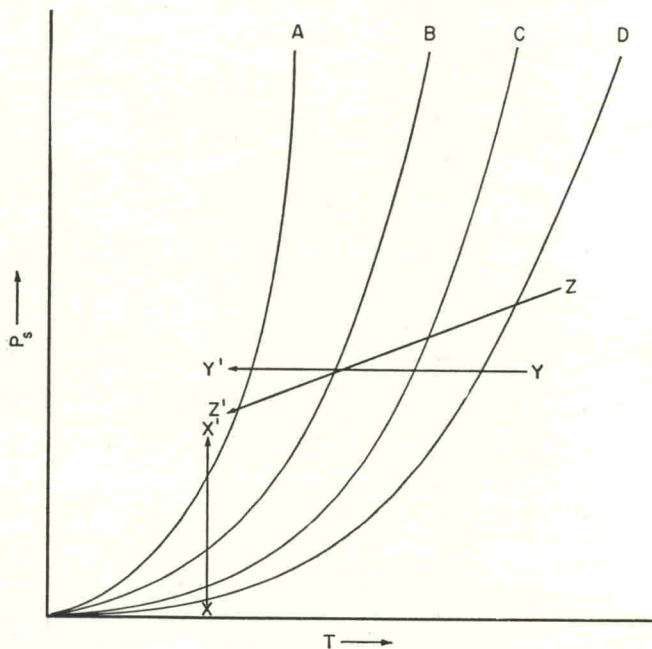


Figure 7

ore-forming fluid may thus be indicated on a  $PT$  plane such as Figure 7. In Figure 7, the curves A, B, C, and D represent curves of the dissociation pressures of various solid phases or phase assemblages. The partial pressure of the volatile component, S,  $As_2S_3$  or  $Sb_2S_3$  in the systems earlier described, is plotted versus temperature. It is immediately apparent that the transition from phase D to C to B to A, in equilibrium with the ore-forming fluid, can take place with the composition, temperature and partial pressure of sulfur in the fluid changing along a great variety of paths. Three possible paths, all with the same sequence of phases, are shown in Figure 7. These paths are indicated by  $XX'$ , and  $YY'$  and  $ZZ'$ .

Thus, the path of the ore fluid might be  $XX'$ , a path where temperature

remains constant or rises and the partial pressure of the volatile component of the ore mineral increases with time. This is the path postulated by Sales and Meyer for Butte. However, alternative paths, such as YY' or ZZ', will give the same phase assemblages and sequence of phases. In path YY', partial pressure of the volatile remains constant and temperature steadily declines. In the case ZZ', partial pressure of the volatile component declines as temperature declines.

In all three cases, XX', YY', ZZ', the volatile component will be extracted from the system due to reactions between earlier solid phases and the ore fluid as each of the curves D, C, B, or A is crossed. Thus, the path of the solution will tend to be offset down slope as each boundary curve is crossed.

It is apparent from Figure 7 that the relations in the three-component systems discussed in this paper lend neither support nor do they disprove the thesis that an apparent mineral sequence at a point in a vein is established during an ascending temperature scale. Indeed, the path of the ore fluid that seems most reasonable to the present author is that of ZZ' where declining temperature goes hand in hand with declining sulfur partial pressure. This may well put the final imprint on the ore mineral assemblage and give the sequence we observe at any one point. It must be kept clearly in mind that the sequence of phases that we observe in a hand specimen or under the microscope is not necessarily the sequence in which the components were introduced, but rather represents in part the imprint of the final stages of re-adjustment of the phases as temperature declines and the partial pressure of the various volatile components in equilibrium with the phases decreases. In this respect the behavior of silicates cannot be contrasted too sharply with the behavior of sulfides. Solid diffusion in magmatic silicates is sufficiently slow to be almost non-existent and late stage adjustments among silicate phases is in general trival, though formation of hydrates completely analogous to the reactions among sulfides discussed in this paper is locally important. Solid diffusion in the sulfides, on the other hand, is extremely important and takes place most readily. All workers who have heated sulfide assemblages under experimental conditions can attest to this. Thus, the sequence of phases observed among sulfides represents the relations finally frozen into the mineral assemblage and may have no particularly close bearing on the order of introduction of the components to a given point in the vein. For these reasons the sequence at any one point in a vein system might be expected to be reasonably similar to the succession of zones upward and outward along a vein away from a center of deposition, although the quantities of the phases would be expected to range widely.

#### AUTHORSHIP AND ACKNOWLEDGMENTS

The suggested phase relationships are based largely on diagrams prepared by McKinstry in 1952; since then similar diagrams for these and other systems have been prepared by students in the Laboratory of Mining Geology, Harvard University. The discussion of their significance in terms of physical chemistry is largely by Kennedy.

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## REFERENCES

1. Bandy, M. C., 1940, A theory of mineral sequence in hypogene ore deposits: *ECON. GEOL.*, v. 35, p. 359-381, 546-570.
2. Boder, Henri, 1934, Beiträge zur Kenntnis der Gestein und Minerallagerstätten des Binnenthals: *Schweizer Min. pet. Mitt.*, v. 14, p. 309.
3. Gaines, R. V., 1952, Ph.D. thesis, Harvard University.
4. Gilbert, Geoffrey, 1925, Some magnetite-ilmenite relations: *ECON. GEOL.*, v. 20, p. 587-590.
5. —, 1924, The relation of hardness to the sequence of the ore minerals: *ECON. GEOL.*, v. 19, p. 668-673.
- , 1925, Antipathy of bornite and pyrrhotite: *ECON. GEOL.*, v. 20, p. 364-370.
6. —, 1926, Significance of hematite in certain ore deposits: *ECON. GEOL.*, v. 21, p. 560-577.
7. Goldschmidt, V. M., 1911, Die Kontaktmetamorphose im Kristianiagebiet: *Kristiania Vidensk. Skr.*, I. Math.-Nature, Kl. 11, p. 123.
8. Korzhinsky, D. S., 1936, Mobility and inertness of components in metasomatism: *Akad. Nauk S.S.S.R. Sec. Geol.* 1, p. 35-60.
9. —, 1950, Phase rule and geochemical mobility of elements: 18th Internal Geol. Cong. (Great Britain) Rept. pt. 2, p. 50-65.
10. Sales, R. H., and Meyer, C., 1949, Results from preliminary studies of vein formation at Butte, Montana: *ECON. GEOL.*, v. 44, p. 465-484.
11. Schürmann, C., 1888, Ueber die verwandtschaft der Schwermetalle zum Schwefel: *Liebigs Annalen*, v. 249, p. 326-350.