

EQUILIBRIUM IN ORE DEPOSITS¹

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ABSTRACT

This paper discusses the terminology, concepts, and criteria involved in the recognition of equilibrium assemblages in ores, especially with reference to the determination of the physico-chemical environment of ore deposition. Equilibrium is attained much more rapidly in reactions between the depositing solution and the surfaces of crystals than in solid-state reactions; thus the solution acts as an equilibrating agent, while the sluggishness of the solid-state reactions may preserve some record of the ore-forming process. In general, the ease of studying phase relations in the laboratory is inversely related to the likelihood of the same minerals preserving their original compositions on cooling. Studies of ore minerals indicate that a wide range of departures from equilibrium can be recognized, and thus care must be taken to evaluate the effects of possible departures from equilibrium in terms of the precision of results desired.

INTRODUCTION

The application of laboratory phase-equilibrium studies to mineral deposits to obtain quantitative information on the physico-chemical environment of ore deposition has become increasingly popular in recent years. Most such applications rely either on the coexistence of two or more minerals or on the compositions of individual minerals in a given assemblage. The interpretation is usually based on the assumption of equilibrium among the minerals involved. In this paper we shall consider some of the problems in designating equilibrium assemblages in ores, for it appears that the recognition and selection of samples for meaningful analysis is at least as difficult as the laboratory determination of the equilibria with which the minerals are to be compared.

We shall first introduce some terminology and concepts, then consider reaction rates of interest to ore deposits, and end with a discussion of the application of equilibrium studies to the interpretation of ore-forming processes. This paper is oriented principally toward deciphering the conditions of initial mineral deposition. Most of our discussion is in terms of open space filling but the principles are also applicable to processes leading to replacement.

Most careful investigators have recognized the requirement of equilibrium in the application of experimental data to geologic situations, and thus many of the ideas incorporated into this paper are not original with us. We wish to thank Robin Brett, Eugene Roseboom, and Wayne Hall for reviewing the manuscript and to acknowledge discussions with many of our colleagues including Bruce Doe, Robert Fournier,

Irving Friedman, Verne Fryklund, Dick Holland, Gunnar Kullerud, Edwin Roedder, Paul Sims, Brian Skinner and E-an Zen, but we hasten to absolve them of responsibility for what follows.

CONCEPTS AND TERMINOLOGY

In this section we discuss equilibrium from two viewpoints: the thermodynamic and the observational. The thermodynamic approach is concerned with the analysis, on very general grounds, of the concepts of equilibrium and the description of any physical system. The observational approach deals with the reconstruction of past states of a system from observation of its present state.

Thermodynamic approach. In the following paragraphs we will discuss briefly various ramifications of the concept of equilibrium. More detailed, rigorous, and elegant treatments of these and related matters may be found in Guggenheim (1950), Prigogine and Defay (1954), Denbigh (1955) and Lewis and Randall (1961). We have not burdened this section with many specific examples because these will be found in succeeding sections.

a) Equilibrium

Equilibrium refers to a state from which a *system* has no spontaneous tendency to change. A *system* is that specific quantity of matter, or region of space, we choose to consider.

b) Types of equilibrium

We will discuss many types of equilibrium; these may be grouped in three different ways: (1) according to their relative stabilities, (2) according to the processes which give rise to each variety, (3) according to the degree to which equilibrium is attained.

A primary, and from a geological point of view most

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important, distinction to be drawn is between *true equilibrium*, in which there is no driving force tending to change the state of the system, and *false equilibrium*, in which a driving force exists but is unable to overcome some reluctance factor (e.g., friction) to produce a finite velocity of whatever process should occur (Prigogine and Defay, 1954, 40-41).

i) Grouping according to relative stabilities. The only geologically important types of equilibrium within this group are *stable* and *metastable equilibrium*.¹

A system in a state of stable equilibrium (or, in short, a stable system) is stable relative to all possible alternative states; there is no other state into which the system will transform spontaneously. A system in a state of metastable equilibrium is stable relative to all *adjacent* states and will return spontaneously to the metastable equilibrium state if displaced only a short way. It is, however, unstable relative to some *more distant* state or states; the system, if displaced sufficiently far from the metastable equilibrium state, will transform spontaneously to a more stable state. In the familiar mechanical analogy, a brick resting on one of its smaller faces is metastable relative to the stable state of resting on its largest face.²

ii) Grouping according to processes giving rise to equilibrium. The most important processes driving geological systems toward equilibrium are *thermal*, *mechanical*, and *chemical*.³ The criterion for thermal equilibrium is that the temperature be uniform throughout the system. For mechanical equilibrium, in the simplest case, pressure must be uniform throughout the system. At chemical equilibrium the chemical potential of each component is uniform throughout the system. Since it is relatively easy to choose geologic systems in which temperature and pressure are uniform, our principal concern will be chemical equilibrium and the factors affecting it.

No completely satisfactory theoretical treatment of *textural equilibrium* exists, though it is of considerable geologic interest. This concept is closely allied to the theory of interfacial stresses, and may be re-

¹ Other possible but geologically unimportant stability types of equilibria are *unstable* and *neutral* equilibrium. In the former, the system is not stable relative to at least one adjacent state; in the latter a finite range of contiguous states is all equally stable.

² The difference between metastable true equilibrium on the one hand and false equilibrium on the other is in most instances a matter of the scale on which the system is considered.

³ Except for special considerations, other types of processes such as those arising from magnetic, electrical or gravitational fields, may be, and are, neglected.

garded as a fine-scale modification of chemical and/or mechanical equilibrium. We regard a system as being in a state of textural equilibrium when the energetic contributions of the surfaces between phases are minimized; these contributions will depend on the size and shape of grains and perhaps on the compositions of the very thin regions adjacent to intergrain contacts. One would suppose that, other things being equal, the energetic contributions of the intergrain contact films should decrease as the area of contact decreases, leading ultimately to complete segregation of each phase into a single mass. It is not now clear whether the common occurrence in geological systems of even- but fine-grained fabrics reflects too small a driving force to produce a finite rate of recrystallization or whether unconsidered factors come into play to minimize the energy of the inter-grain surfaces in polygrain aggregates.

iii) Grouping according to degree of equilibrium. A system may be in complete or partial equilibrium. *Complete equilibrium* is equilibrium with respect to all processes considered in a particular analysis. The situation in which a system is in equilibrium with respect to at least one process and out of equilibrium with respect to any others is known as *partial equilibrium*. For example, a solution may be in equilibrium with barite in regard to the amounts of Ba^{2+} and SO_4^{2-} in the solution, but the sulfate may be out of equilibrium with the other sulfur-bearing ionic species in solution with respect to oxidation-reduction reactions. Partial equilibrium should not be confused with false equilibrium as defined earlier.

Observational approach. We shall now consider some of the possible relations between coexisting minerals. To describe the relations between minerals as observed in the field, it is desirable to have some terms unencumbered by connotations of equilibrium. We shall follow the usage of Bartholomé (1958) and refer to those minerals occurring in direct contact with one another without the presence of an intermediate phase as an *assemblage*. If the minerals are believed to have been in equilibrium at some specific time the term *equilibrium assemblage* is applied. The term *association* will be used for minerals occurring together, the spatial and equilibrium relationships being unspecified.

Mineral associations have many possible complex relationships. It is most convenient to consider these in terms of idealized "end member" situations. Figure 1 (cases 1-4) illustrates the more important of these "end member" relations *at the time of deposition*.







	A	B	Description	Application of phase equilibrium
Relations at time of deposition	Case 1		<i>Equilibrium (simple)</i>	Ideal for use of phase equilibrium information
	Case 2		<i>Zoned equilibrium, superposition of several case 1 assemblages</i>	Use restricted to matched pairs of zones
	Case 3		B in <i>surface equilibrium</i> with A, B grew while A was nearly static	Useful under some circumstances
	Case 4		Synchronous deposition, but one or both metastable	Not useful if precision is required
Changes since deposition	Case 5		Equilibrium because of re-equilibration from any previous association	Gives conditions of re-equilibration
	Case 6		Internal homogenization of zoned equilibrium in one or both without mutual re-equilibration	Would give unreliable results

FIG. 1. Some possible relations between coexisting minerals.

It is assumed that the minerals have been preserved in unaltered (or reconstructable) condition.

a) Conditions at initial deposition

i) Case 1. The crystals formed in complete equilibrium with one another and with their environment, which was constant throughout crystal growth. The grains are therefore uniform throughout. Since the minerals have been preserved in unaltered condition, this case is ideal for the application of laboratory equilibrium studies to determine the physico-chemical environment in which the minerals formed. It should be clearly realized, however, that not all associations of homogeneous crystals fall into case 1 (note cases 5 and 6). We shall refer to this case as "*simple equilibrium*" when necessary to avoid ambiguity.

ii) Case 2. The crystals of A and B were deposited simultaneously from solutions whose character changed gradually or spasmodically during crystal growth. A given growth zone in A is matched by a correlative growth zone in B. The array is equivalent to a series of superposed equilibria of the type described in case 1 above. We shall refer to this relation as "*zoned equilibrium*." It is an especially useful variation of the partial equilibrium described previ-

ously; equilibrium is maintained between crystal surface and solution while solid state reactions within the crystal are in a state of false equilibrium.

iii) Case 3. This might be considered as a special variety of case 2 in which mineral A neither grew nor dissolved to an appreciable extent while mineral B was being deposited. As will be discussed more fully later, in many cases equilibration between crystals and solution is rapid. Therefore, the fact that mineral A neither grew nor was dissolved appreciably suggests that its surface was approximately in equilibrium with the fluid and so with mineral B throughout the growth of B. We thus have the unilateral situation wherein mineral B is in equilibrium with the surface of mineral A, but the bulk of mineral A is not necessarily in equilibrium with B. In this case we may refer to mineral B as being in *surficial equilibrium* with mineral A. To judge from the literature, this is an extremely common case and is potentially very useful (for example, see Sims and Barton, 1961).

iv) Case 4. This is synchronous or successive deposition but with one (or both) phases metastable. At present no reliable inference on the environment of ore deposition may be drawn from such relations

except that the rate of precipitation was too rapid for equilibrium to be attained.

b) *Postdepositional changes*

In the previous four cases we have assumed that the minerals were preserved in their original condition, but this assumption is frequently not valid. Two significant examples of postdepositional changes are described as cases 5 and 6 below and illustrated in Fig. 1.

i) Case 5. The minerals have re-equilibrated under conditions different from those obtaining at the time of deposition. This may be the result of failure to quench as the deposit cools or of a later metamorphic event. Although the end product may be difficult to distinguish from case 1, geologic evidence ranging from regional field relations to microscopic mineral textures may help make this distinction (see, for example, Sales and Meyer, 1951; Fryklund and Fletcher, 1956; and Skinner, 1958). Some minerals react much more readily than others; a special situation that is potentially very misleading is illustrated separately by case 6.

ii) Case 6. The minerals were originally associated in zoned equilibrium but during postdepositional history one or both of the crystals has homogenized. Although it is easy to visualize this possibility, its recognition in real ores requires detailed study. Suppose that crystals of galena and sphalerite coexist in zoned equilibrium as described in case 2 above. We know from laboratory studies (see Fig. 2) that diffusion rates of almost any kind are much higher in galena than in sphalerite. All vestiges of zoned equilibrium may be annealed out of the galena even though the coexisting sphalerite retains its original compositional banding.

iii) Exsolution. Although this phenomenon is part of case 5, it is more convenient to discuss it separately. True exsolution textures should present no difficulty for equilibrium studies provided that the state of the original single phase can be reconstructed. A major problem, of course, is distinguishing exsolution from replacement or simultaneous precipitation.

REACTION RATES AND ATTAINMENT OF EQUILIBRIUM

The purpose of this section is to note some of the experimental observations on reaction rates and to discuss in general terms the implications of the differences in rates to the interpretation of processes of ore genesis.

An extensive theoretical discussion of kinetics oriented toward metamorphic petrology has been pre-

sented by Fyfe and Verhoogen (1958) as part of GSA Memoir 73. We can add little to their treatment and will not discuss it at length. Their compilation of data summarizes most of the pertinent quantitative information on the kinetics of silicate equilibria and points up the fact that appropriate kinetic studies are scarce and that the problem of reaction rates is among the most challenging for the metamorphic petrologist and for the geologist in general. Garrels (1959) gives some very useful guides to the rates of geochemical reactions at low temperatures and has noted several examples of very important metastable equilibria under near-surface environments.

With very few exceptions, none of which are important to the present discussion, reaction rates increase with temperature. The rates of most reactions in the vicinity of room temperature increase by a factor of from 1.5 to 3 or 4 (and rarely more) for each 10° C. rise in temperature. The change in reaction rate with temperature at high temperatures is similar but less well defined (Figs. 2, 3).

Depending on the specific reaction, pressure may either increase or decrease reaction rates; unless a vapor phase is involved, however, the effect of pressure is small and is negligible compared to temperature for most reactions.

It is not easy to specify, operationally, just when a given reaction has reached equilibrium. The rates of many reactions depend on the concentrations of the reactants, and such reactions must approach equilibrium asymptotically. Thus, for many reactions under constant conditions, equilibrium is, in theory, never reached. This is another way of saying that no strictly reversible process can proceed to a finite extent in finite time. In the laboratory we speak of equilibrium being obtained when no further change is observed with time or when the "same" product is reached by diametrically opposite or very different paths. Thus the operational definition of attainment of equilibrium in the laboratory is controlled by our ability to observe the reaction, and we would recognize as "equilibrium" in most applications of experimental geology those reactions (depending on the particular system) which are between 90 and 99.9 per cent complete. Thus we use the parameter "time for equilibration" rather than the more rigorous term "rate of reaction" as the axis of abscissae in Figs. 2 and 3.

The degree of departure from equilibrium that can be tolerated in the geological application of chemical data depends on whether the purpose is to set broad

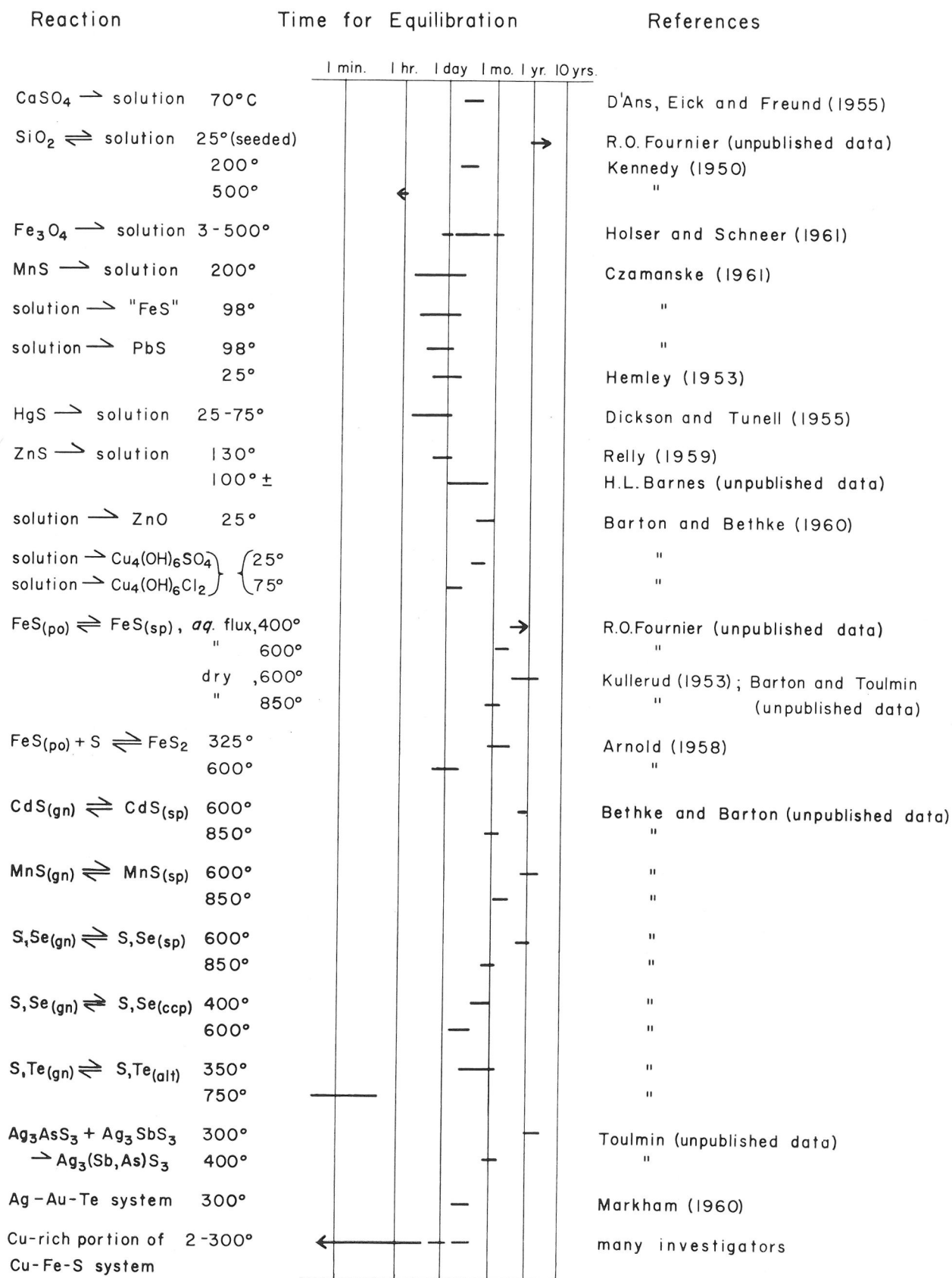


FIG. 2. Time for equilibration for some reactions of interest. The equations representing the reactions are abbreviated. Subscripts refer to phases in which the reacting component is in solid solution; po, pyrrhotite; sp, sphalerite; gn, galena; ccp, chalcopyrite; and alt, altaite. The solutions are of dominantly aqueous composition.

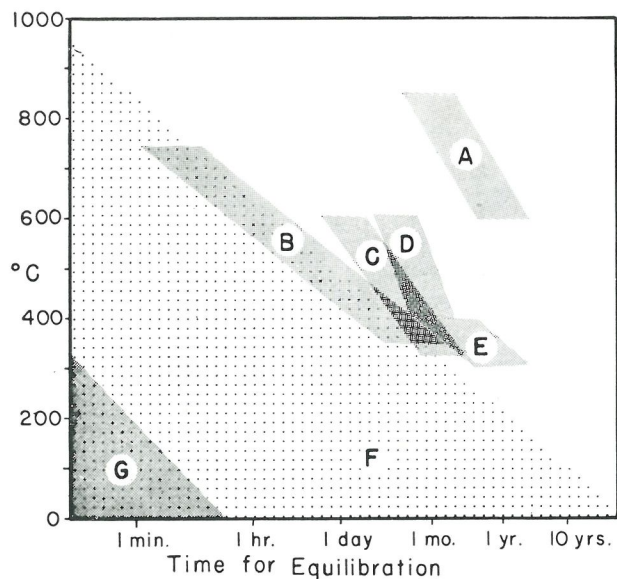


FIG. 3. Plot of time for equilibration against temperature for some of the data given in Fig. 2. A is the general curve for most solid-state reactions involving sphalerite. B is for the distribution of sulfur and tellurium between galena and altaite. C is for the equilibration of pyrite with pyrrhotite. D is for the distribution of selenium between galena and chalcopyrite. E is for equilibration between the ruby silvers. F is the general region within which lie most solution-crystal equilibria. G is the general region for most homogeneous reactions within the aqueous phase.

limits on the environment or to specify as precisely as possible the conditions under which a particular process operated. Thus, Barton (1957) and Krauskopf (1959), in estimating the general range of chemical environments of ore formation, were able to use data orders of magnitude less precise than those required by Sims and Barton (1961) in attempting to define the temperature and chemical potential of sulfur under which some deposits in the Central City District were formed. The most generally applied criteria of equilibrium in natural systems are based only on the presence or absence of particular minerals in particular associations. These criteria, however, do not guarantee the attainment of equilibrium with respect to the compositions of coexisting minerals. These considerations emphasize the importance of specifying the exact meaning of the unmodified term "equilibrium" in any particular context.

Reaction rates in homogeneous systems (those containing only a single phase) are amenable to quantitative study. Most reactions of interest to the geologist, however, are heterogeneous (involving two or more phases) and involve so many variables that quantitative treatment of their kinetics is seldom even attempted. Because the overall rate of a reaction that

involves several steps is governed by the rate of the slowest step, kinetic studies of appropriate simple reactions may be applied to complex geologic processes.

Reactions in homogeneous aqueous solution. Most reactions between molecules and ions in solution (such as: $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$, $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$, and $\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$) are rapid even at room temperature, and equilibrium is quickly attained. A few such reactions, as pointed out by Garrels (1959), may be very sluggish; important examples are the inertness of sulfate ion to changes in redox potential and the slow rate of formation and decomposition of some polymerized aqueous species such as the molybdates.

Reactions in the solid state. Solid-state reactions are generally much slower than those in aqueous solution, but there is a tremendous variation in geologically important solid-state reactions, as indicated in Figure 2.

Aside from difficulties of nucleation, solid-state reaction rates are controlled principally by solid-state diffusion, which in turn is related to such things as bond strength and structural defects. High bond strength tends to be associated with hardness, brittleness, high melting point (if congruent or nearly so) and low vapor pressure. In support of this line of reasoning, we may note that sphalerite, arsenopyrite, pyrite, alabandite, Fe-Co-Ni arsenides, hematite, and magnetite are much more sluggish in their solid-state reactions than are galena, chalcopyrite, most sulfosalts, argentite, electrum, chalcocite, and pyrrhotite. The effects of structural defects are hard to evaluate, but it is obvious that gross-defect structures such as those of pyrrhotite, bornite, or tetrahedrite may favor more rapid diffusion than would be possible if the phases were "stoichiometric." Defects of lesser magnitude, such as those of semiconductors or phosphors, are possibly important, but not enough is known about the role of such defects in minerals to generalize at present.

The broad generalizations about relative reaction rates noted above and semiquantified in Figs. 2 and 3 must be tempered by a careful appraisal of the geologic environment and history of the mineral assemblage considered. Even the normally fickle minerals such as galena or tetrahedrite may yield valuable clues regarding equilibrium conditions during deposition for some deposits formed at low temperature. Conversely, even the sulfides considered most likely to have preserved the record of their origin may not

have done so if subjected to extreme conditions.

Bartholomé (1958) has summarized the work of many previous investigators, demonstrating the fact that equilibration between chalcopyrite, bornite, chalcocite, digenite, and copper takes place so rapidly, even at relatively low temperatures, that the compositions and textures of the minerals record only their most recent history. He also emphasizes the frequent observations that reactions involving chalcopyrite are slower than the rest and that those involving the nucleation of pyrite are very much slower than other reactions in the Cu-Fe-S system. The commonly observed tendency for ores representing the copper-rich portion of the Cu-Fe-S system to violate the mineralogical phase rule is usually attributed to the inertness of pyrite.

The rapid reaction rates suggested by the data in Figs. 2 and 3 present an incompletely resolved problem—why isn't re-equilibration in ores almost universal? For example, synthetic pyrrhotite "equilibrates" with pyrite in a few weeks at temperatures as low as 300° C. regardless of whether the starting material is (1) stoichiometric FeS+pyrite or (2) a very iron-deficient pyrrhotite. Yet studies of natural pyrrhotites often reveal pyrrhotite compositions consistent only with temperatures higher than 300° C.; why didn't the pyrrhotite continuously change its composition as the ore cooled from its high temperature of formation? Edwards' (1954) answer to this question is that ores cool extremely rapidly by the mechanism of being injected into "cold" country rock. Barton and Toulmin (1961) have proposed that other probable cooling mechanisms (especially the throttling of high pressure-temperature solutions into cool ground water) may be adequate to explain rapid cooling. They further suggest that effective "quenching" of some ore deposits may be accomplished during the waning phases of mineralization by the entrance of cool ground water into the region previously occupied by high temperature ore solutions. The mechanisms they propose would produce much more rapid cooling than would heat flow through the wall rock. Nevertheless, there remain deposits to which none of these "rapid-cooling" explanations can apply. As an example, the Nairne pyrite deposit described by Skinner (1958) is a regionally metamorphosed sedimentary sequence containing significant amounts of pyrite and pyrrhotite. Skinner determined the composition of the pyrrhotite, which is consistent with an equilibration temperature of about 300° C. (Toulmin and Barton, 1962). It is very difficult to explain how this

pyrrhotite was effectively quenched since the entire metamorphic sequence must have taken many thousands of years to cool.

The problem of re-equilibration has also been considered in detail by Kullerud (1959) and Lyon (1959). Laboratory work by Kullerud showed that synthetic FeS-rich sphalerite exsolved more rapidly at 500° C. than did natural sphalerite of similar iron content from Broken Hill. He attributed this behavior to the inhibiting effect of other elements (Cd, Mn, etc.) in the natural material. Similarly, we have observed that a per cent or so of each of a dozen minor elements appeared to inhibit reaction in the Cu-Fe-Zn-Pb-S system at 600° C. While these observations suggest another possible solution to the problem, other as yet undetermined factors must also be important in retarding solid-state reactions in sulfides, for many workers (*e.g.*, Lyon, 1959) have gotten at least partial reaction in short-term heating experiments on natural materials at geologically reasonable temperatures.

Most geothermometers involving phase equilibria must be regarded as providing only minimum temperatures of ore formation, unless it can be shown that subsequent processes have not erased the earlier record. For example, a zoned crystal offers evidence that complete re-equilibration of that crystal has not occurred. The use of exsolution relationships as quantitative geothermometers is extremely hazardous because of the many unevaluated complexities concerning the equilibrium phase relations and the rates of reaction, nucleation and recrystallization. In particular, part or all of the exsolved material may migrate completely out of the host grain, making reconstruction of the original state of the grain difficult, if not impossible. The presence of exsolution lamellae, however, does not guarantee that some additional material has not migrated completely out of the grain. The results of an extended study on the problem of exsolution textures are being prepared for publication by Robin Brett at the Geophysical Laboratory, and we shall not dwell on this problem.

Solution-crystal equilibrium. In general, equilibration between crystals and aqueous solution is rapid relative to the time involved for ore-forming processes. With few exceptions crystal-solution reaction rates are intermediate between those of homogeneous reactions in aqueous solutions and solid-state reactions (Figs. 2, 3).

a) Growth of crystals. Crystal growth is conveniently discussed in terms of the degree of supersaturation in the medium from which the crystal grows. We

shall begin by considering crystal growth under near-reversible conditions, and then proceed to consider growth under conditions progressively further removed from equilibrium. Equilibrium may be maintained as long as crystal nucleation and growth keep pace with the changes causing precipitation in the solution. Failure of crystal-solution equilibration to keep up with changes in solution may lead to appreciable amounts of supersaturation and this, in turn, may allow metastable precipitates to form. Some supersaturation is needed for primary nucleation, and solutions of some substances can become highly supersaturated. As an extreme example, solutions supersaturated with respect to quartz by about 2000 per cent can be maintained for years at 25° C. Highly supersaturated solutions are not necessary for crystal growth, however, for crystals can grow from very slightly supersaturated solutions. The importance of spiral dislocations of crystal growth (Frank, 1949), in fact, lies in the mechanism they provide for avoiding the nucleation of successive layers. Thus it is possible that crystals may grow from almost imperceptibly supersaturated solutions (*i.e.*, at "equilibrium") provided that a seed is present. The seed may be a crystal of the same mineral or a crystal of some other phase whose surficial atomic configuration is similar to that of the crystallizing phase. It is probable that, other things being equal, the rate of crystal growth will be roughly proportional to the degree of supersaturation.

Details of the history of crystal growth are more readily obtained for transparent than for opaque minerals, and for this reason much of the evidence we cite comes from observations of sphalerite. Our conclusions are compatible with the much smaller amount of observational data on fluorite, quartz, barite, and carbonates.

Study of polished "thick sections" of sphalerite from a variety of localities reveals sharp and delicate color banding (reflecting principally variation in iron content) that preserves the growth history of the crystals in minute detail (Fig. 4). Analyses of individual color bands of such sphalerite from Creede, Colorado, show that compositional differences as small as a few hundredths of a per cent Fe in iron-poor sphalerite (<1 weight per cent Fe) may be distinguished readily by color differences (Figs. 4A and 4B). The growing crystal's ability to respond quickly (relative to the rate of crystal growth) to apparently subtle changes in the environment is thus a strong argument that crystal-solution equilibrium was nearly attained for these growth bands.

We shall now consider briefly some of the processes taking place at the surface of a growing crystal of variable composition. Various investigators have treated the surface layer(s) of a growing crystal as a "phase" distinct from either the depositing solution or the interior of the crystal. The composition of the surface "phase" will be controlled by the equilibrium between it and the solution. Surface "phases" of different crystal forms may be distinct from one another, so that different ions are selectively taken up by certain forms. On the other hand, the equivalent structural sites in the interior of the crystal should have equal probability of containing a given atom. Thus, in order for the interior of the crystal to reflect the composition of the depositing fluid there must be equilibrium between the interior and surface "phases." This equilibrium is apparently frequently attained, but visible hour-glass features are common enough in minerals to cast suspicion on all crystals whose habit during growth includes more than a single form. In the absence of pertinent experimental data, we suspect that the elements that are more

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FIG. 4. Photographs of polished thick sections (1–2 mm thick) of sphalerite. Transmitted light. Spots are opaque or fluid inclusions in the sphalerite or air bubbles in the epoxy resin used to cement the specimen to a glass slide. The black lines are cleavages.

A. Delicate growth banding in sphalerite; note sharp color differences between bands and uniformity of individual bands. Specimen from Creede, Colorado.

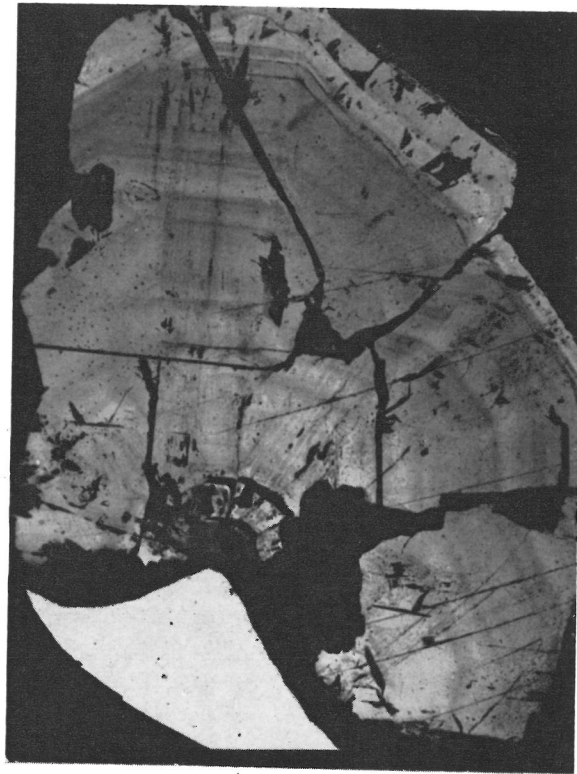
B. Delicate growth banding in sphalerite. Interpreted as near-equilibrium crystal growth (except for the very earliest patchy sphalerite just above the point of the white area at the lower left). The white area at the lower left is the mold left by the complete removal by hydrothermal leaching of an octahedral fluorite crystal. Specimen from Creede, Colorado.

C. Finely banded (not very prominent) early light sphalerite growing around a core of wallrock (black). A later, darker generation of sphalerite contains growth bands showing very patchy distribution of iron within the same growth zone, obviously a disequilibrium feature. The latest sphalerite is a discontinuous light marginal growth band which has been partially leached away. A surface of strong hydrothermal leaching (shown as a dark line of fluid and opaque inclusions generally paralleling, but in detail crosscutting, growth banding in the inner light sphalerite) is preserved in the inner light sphalerite generation 2 or 3 mm below the darker growth band. Specimen from Creede, Colorado. Temperature of formation from fluid inclusions on the order of 200–250° C. (Roedder, 1960).

D. Portion of sphalerite crystal showing very irregular coloration which is at least partly controlled by twinning (the "ENE striking" straight lines). The growth zones are very difficultly visible as color bands crudely concentric about a center somewhere off the photo to the right. Specimen probably from the Joplin area.



1 cm
A



1 cm
B



1 cm
C



1 cm
D

likely to show strong fractionation between various crystal forms are those which are minor components because of stereochemical factors rather than solely because of geochemical abundance. Components capable of extensive solid solution are presumably similar to the host in terms of crystal chemistry and thus fractionation between forms may not be as pronounced. Sphalerites from many localities, particularly but not exclusively those from Mississippi Valley type deposits, often show a very patchy incorporation of pigmenting components (probably iron) within individual growth bands (Figs. 4C and especially 4D). The surface of a single face of the growing crystal appears not to have been in equilibrium even with itself and thus the solution from which it crystallized cannot have been in equilibrium with the whole surface. Obviously, we cannot use such a crystal for purposes that depend critically on the composition of the crystal.

At Creede, growth zones of such patchy sphalerite alternate with zones of the delicately banded sphalerite described earlier (see figure 4C). Therefore we infer that the conditions of crystal growth alternated between near equilibrium and considerable supersaturation.

Even higher supersaturation may lead to the development of many new nuclei, with the result that growth of individual crystals is inhibited. Extreme supersaturation may yield colloidal precipitates which, judging from the literature, are not uncommon, especially in low-temperature deposits.

One feature of solution-crystal equilibrium presents difficulty in practical applications. As mentioned above, "equilibrium" crystal growth tends to produce large crystals with few intercrystal contacts. Thus the crystals most likely to have grown in equilibrium with the same solution are apt to show few textural criteria of it. A possible way to "prove" simultaneous deposition and equilibrium, based on the distribution of trace elements between coexisting phases, has been suggested by Bethke and Barton (1959), but as should be clear from the preceding pages, many problems remain.

b) Hydrothermal leaching. The partial or complete re-solution of hydrothermal minerals by later hydrothermal solutions has occurred in many ore deposits. It is perhaps most frequently recognized in connection with replacement, wherein the replaced mineral (or some of its constituents) is redissolved either before or during deposition of the later mineral. Leaching without immediate replacement is also common, though to judge from the literature its

recognition is not so widespread. Several examples (from the literature) of hydrothermal leaching of ore minerals are cited later in this paper; our observations (Bethke *et al.* 1960) at Creede, Colorado, seem to be typical. Examination of doubly polished slabs of individual sphalerite crystals reveals repeated "solution unconformities," which round and corrode previous crystal forms; later deposition usually reconstructs the earlier forms. As pointed out previously (Barton, 1959) hydrothermal leaching of well crystallized materials demonstrates that hydrothermal environments contain solutions capable of dissolving sulfide minerals; thus it is not necessary to resort to colloids or other mechanisms involving metastability in order to explain ore transport. In the Creede deposit the leaching surfaces are associated with delicately banded sphalerite and never with the patchy sphalerite (see Fig. 4C), even though both types of sphalerite are present (in different growth zones) in the same crystal. The leaching thus supports the contention that the finely banded material was deposited under quasi-equilibrium conditions, the concentration of sphalerite in solution varying just above and below the solubility of sphalerite.

If the surfaces of crystals are in "equilibrium" with the solution surrounding them, the composition of the solution will be buffered at the saturation level for the various minerals in contact with it. Thus the concept of surficial equilibrium mentioned earlier is applicable, and we may be able to make use of equilibrium relations that are not obviously applicable from the simple examination of ore textures (Sims and Barton, 1961).

Summary of reaction rates. The discussion in the preceding sections implies that, in considering the initial equilibrium and the requirements for its preservation, the geologically important types of reactions are crystal-solution and solid-state reactions. For a given system there appear to be broad, frequently poorly defined limits to the conditions under which its phase relations will be capable of furnishing quantitative information on the environment of deposition. On one hand there is an upper "temperature-time" limit above which the original mineral assemblage reacts internally or with its environment to provide a new assemblage that does not preserve a complete record of the initial deposition; on the other hand there is a lower "temperature-rate of deposition" limit below which there is such a departure from equilibrium during deposition that calculations in-

volving the equilibrium assumption are not meaningful. Useful equilibrium studies must therefore deal with assemblages falling between these limits. It is possible that under some circumstances (high solid-state reaction rates combined with sluggish solution-crystal equilibration) the upper and lower limits may effectively overlap, as in the case of colloidal Cu-Fe sulfide deposits. Such an assemblage may provide a better indication of present than of past temperatures. Minerals having high bond strengths (sphalerite, pyrite, iron oxides, arsenopyrite, etc.) are much more likely to preserve the record of their history than others in which the rates of solid-state diffusion are large (chalcocite, digenite, bornite, chalcopyrite, galena, etc.). In general, the ease of studying phase relations in the laboratory (by DTA, x-ray heating camera, short-term phase-equilibrium investigations) is inversely related to the reliability of applying them to mineral assemblages in the field.

APPLICATION TO THE STUDY OF ORE DEPOSITS

Deposition of a simple zoned ore body. It is of interest to consider the emplacement of a hypothetical ore body in light of the foregoing discussion of equilibrium behavior.

To show more clearly the general solubility relations in an ore-forming process, let us consider a hypothetical and greatly simplified vein system. Figure 5 is an attempt to construct a model showing some of the salient features as they pertain to this discussion. The diagram is for a steady-state model which, unrealistically, does not change with time. The diagram shows solubility or concentration plotted against the ensemble of temperature, pressure, and composition variables that affect the solubility of minerals. This horizontal coordinate is plotted simply as distance from the source, but it must be remembered that many factors may affect the shape of the curves. For each crystalline phase, two curves are drawn: a solid line representing the concentration of the substance in the solution; and a line of "o's" representing its solubility in the solution. Dashed segments of the concentration curves represent metastable conditions. The actual construction of the curves in Fig. 5 is arbitrary, and the curves are meant only as illustrations of general principles.

As the solution leaves its source, in this case supposed to be of granitic composition, it is probably in surficial equilibrium with the minerals of the granite. As it passes outward the solution goes through various changes in physicochemical environment, the

net result generally being to decrease the solubilities of the various compounds present in solution. The solution was originally saturated with quartz, and thus as it moves outward quartz is deposited. Near the source, only quartz is at the saturation level, and a barren quartz vein results; further along, however, the solubility of pyrite drops until it reaches the concentration of FeS_2 in the solution and pyrite begins to deposit with the quartz. In a like manner, sphalerite and galena may be deposited successively to form pyrite-quartz, pyrite-quartz-sphalerite, and finally pyrite-quartz-sphalerite-galena veins. The solution may never become saturated in some phases, e.g., halite, and thus halite does not occur as a mineral in this model even though the concentration of NaCl in the ore fluid may be very high.

In some environments, particularly at low temperatures, the physicochemical environment may change more rapidly than the solution can adjust its composition; the resulting supersaturation may permit the formation of metastable phases. This possibility is illustrated for silica and pyrite. It is a common observation that quartz veins may pass laterally (or vertically) into chalcedony veins even though the associated sulfides may not take on a colloidal aspect. In the case of pyrite, some sluggishness in nucleation (corresponding to a supersaturation of only a few per cent) has been sketched for the point of initial precipitation. Thus pyrite enters the mineral assemblage of the vein much less abruptly than do sphalerite and galena, as shown in the bottom part of Fig. 5. In actual ores, the variations of the loci of deposition with time, and possible momentary supersaturation prior to nucleation and crystal growth, would tend to smooth out the abrupt appearance of minerals in the zoning pattern.

The model given in Fig. 5 makes it easy to visualize at least two ways in which an ore body may become zoned. The incoming solutions may reach saturation in different minerals at different places (as indicated by the intersections of the curves for solubility (circles) and concentration (solid lines) for each of the various minerals), or the slopes of the saturation curves may vary for a given mineral as well as from one mineral to another.

Although the relative amounts of phases deposited are indicated in the lower part of Fig. 5, the absolute amounts are indeterminate and will vary across the diagram. The shapes of the solubility curves are arbitrarily chosen to obtain a zoned ore body; but, in defense of the model, it must be realized that ores are most likely to be deposited in regions where the

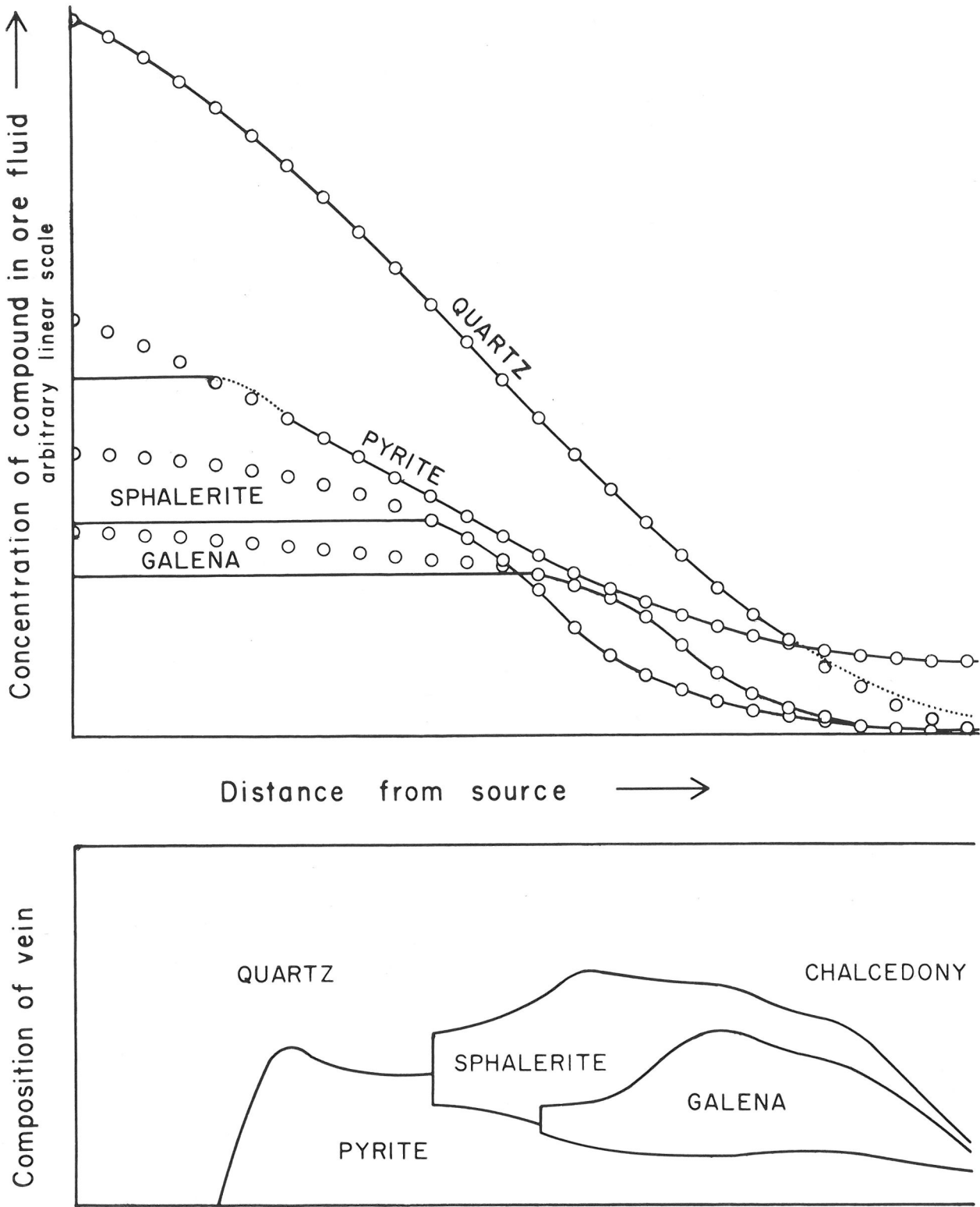


Fig. 5. Schematic diagram for the deposition of an ore body.

Upper part: Solubility vs distance diagram

Solubility indicated by circles; concentration by solid lines; supersaturation by dotted lines.

Lower part: Character of ore body deposited in the model, showing relative proportions of minerals deposited

solubility changes most rapidly. The shapes of the solubility curves will be controlled by such complex processes as throttling, mixing with ground water, and other factors affecting the chemistry of the ore fluid; these are beyond the scope of the present discussion.

Mineralogical bottoming of ore. Let us now consider how hydrothermal leaching might operate in the model ore-forming system just described; we may as well confess at the outset our intention to develop a criterion for the impending bottoming of an ore body.

The position of a zoned Zn-Pb ore body is evident from Fig. 5. The incoming solution at the bottom of the incipient ore body (on the left side of the diagram) is just reaching saturation with sphalerite, and sphalerite is depositing from there to the end of the model. If for some reason the region of undersaturation with respect to sphalerite should shift into the region where sphalerite had previously been deposited, the sphalerite there would be leached. Such encroachment of the region of undersaturation on the region of saturation would be expected to occur most commonly near the lower limit of the range of sphalerite deposition. Thus observation of increasing amounts of leaching in the lower part of an ore body would be a criterion for the impending bottoming of the ore body.

Let us compare the leaching in the model described above with several recent descriptions of hydrothermal corrosion of ores. Lacy and Hosmer (1956) describe the hydrothermal leaching of barite, tetrahedrite, galena, sphalerite, pyrite, chalcopyrite and carbonates in several Peruvian mines; the almost complete leaching was generally *below* known ore on the same structure. Turneure (1960) notes the hydrothermal corrosion of pyrrhotite, leaving pyrite boxworks, in the central zones of some Bolivian tin-silver deposits. Sims and Barton (1961) found hydrothermal leaching of sphalerite near the zinc-poor core of the symmetrically zoned Central City district in Colorado. We have recognized several periods of leaching of sphalerite and galena at Creede, Colorado. The intensity of leaching increases with depth and is at a maximum at the bottom of the present workings. We therefore conclude that detailed study of hydrothermal leaching may in some cases provide the mining geologist with another tool to bring to bear on the problem of the continuation of ore with depth.

It is not necessary that the solubility of minerals in a hydrothermal solution decrease outward from the source; it may remain nearly constant, or increase, or

fluctuate. For example, because of the rapid changes in the density of water as temperature changes at constant pressure in the P-T region just above the critical point, the solubility of quartz (and by analogy, most other minerals) increases as the temperature drops in the interval from 600 to 400° C. Further, because of complex chemical reactions within the ore fluid and between the ore fluid and its environment, solubilities could behave in almost infinitely varied ways. Some minerals, *e.g.*, calcite and anhydrite, have a negative thermal coefficient of solubility in simple aqueous solutions and might well be leached by solutions that had been saturated with them at higher temperatures.

Determination of the physicochemical environment of ore formation. Knowledge of the physicochemical conditions under which an ore deposit formed is obviously a prerequisite to reliable inference of the ore-forming process. For this reason, much of the laboratory effort in sulfide studies has been devoted to measuring those properties of minerals that may indicate the temperature, pressure, and chemical environment at the time the minerals formed. To apply these studies to mineral deposits, however, we must have some criteria by which to evaluate the degree of attainment of equilibrium. In developing these criteria, we must carefully distinguish the indications of equilibrium at the time of initial deposition from those of postdepositional equilibration (or re-equilibration). Concordant "readings" by several independent methods constitute the best available evidence for equilibrium in an assemblage, though by itself the concordance gives no indication whether the conditions of equilibrium refer to the time of initial deposition. Textural or structural evidence may permit the possibility of postdepositional re-equilibration to be evaluated—euhedral, zoned crystals in a vuggy, banded vein, for example, are unlikely to have re-equilibrated.

In contrast to the foregoing "positive" lines of evidence, most criteria for equilibrium are negative: they amount to the absence of evidence for disequilibrium. Thus if an assemblage does not violate the phase rule, or if a mineral does not show compositional variation in a single association, we infer that the minerals under study are (or were) in equilibrium. Again we must rely on textural and structural evidence to decide *when* the equilibrium occurred.

Complete attainment of equilibrium is rarely, if ever, demonstrable, so we should also consider the extent to which departures from equilibrium may be evaluated, and tolerated, in the interpretation of ore

deposits. Obviously, a growth-zoned sphalerite (Fig. 4) is not in equilibrium even with itself, and yet each zone may represent a fleeting set of equilibrium conditions during the formation of the deposit. Growth-zoning on a very fine scale, which we have observed in sphalerites from many deposits of the open-space filling type, suggests that the crystal responded to minor fluctuations in physicochemical conditions during ore formation, and also indicates that complete re-equilibration of the crystal has not occurred after deposition. Provided (1) that the range of composition in the zoned crystal is not too great, and (2) that we have reason to believe that the solution was in contact with the minerals required for a useful assemblage, we may be able to set broad limits on the temperature, pressure, and chemical activities at deposition from the bulk composition of the zoned crystal. Of course, much more detailed information, including the important feature of the sequence of changing conditions, could be obtained if it were feasible to analyze the crystal zone by zone, as by use of an electron micro-probe.

We should re-emphasize at this point the important distinction between equilibrium in the sense of compatibility of phases (basis of the concept of mineral facies) and equilibrium in the sense of compatibility of mineral composition (basis of quantitative geothermometry, etc.).

If the available evidence against disequilibrium is only that the number of minerals in an association or assemblage does not exceed that allowed by the phase rule, we can, in general, infer only broad limits to the conditions of deposition. Here again, textural and

structural observations are often significant. If in a specimen composed largely of pyrrhotite, magnetite, and hematite, for example, we observed that pyrite was restricted to thin bands separating grains of pyrrhotite from grains of hematite, we might infer that the association had formed under conditions where the assemblage pyrrhotite-magnetite-hematite was stable and had later partially reacted internally under conditions permitting the alternative assemblages, pyrite-magnetite-hematite and pyrrhotite-pyrite-magnetite. In the light of Barnes and Kullerud's (1961) demonstration that the reaction of pyrite and magnetite to form hematite and pyrrhotite takes place above about 675° C., we could interpret our observations to mean that the deposit had formed above 675° C. and that partial re-equilibration had occurred as the deposit cooled below 675° C. Obviously, the principles we have illustrated with reference to temperature changes may equally well be applied to changes of pressure or of chemical parameters.

In conclusion, there may be a close enough approach to equilibrium between crystals and the depositing solution for various equilibrium systems to be applied to interpretation of the physico-chemical processes and environment of ore deposition. However, successive stages of mineralization and possible subsequent processes of metamorphism of the ore may tend to mask or destroy the record of initial mineral deposition. Even the most careful laboratory equilibrium studies and the most precise analytical data thus are of little use without detailed knowledge of the paragenetic relations among the minerals.

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DISCUSSION

G. DEICHA (Paris): Le fait de retrouver dans les minerais sulfures des effets d'un déséquilibre cristallo-génétique manifeste (*Bull. Trim. Inform. B.R.G.M.*, Paris, **47**, 1, 1960), vient renforcer les conclusions analogues qui fournit souvent l'étude des gangues: des observations au microscope électronique, poursuivies en collaboration avec M. Cl. SELLA (C.N.R.S., Bellevue), montrent en particulier que l'abondance des lacunes de cristallisation et des pores intergranulaires (*C. R. Acad. Sci.*, Paris, **253**, 1774, 1961), est très variable dans le quartz tant stérile que métallifère (Mine de Saint-Véran, dans les Alpes françaises, par exemple).

P. M. BETHKE (Washington): Our observations of fluid inclusions

in sphalerite are consistent with your broader generalizations.

G. W. LEO (Washington): Insofar as it is necessary for you to determine precise compositions of distinct zones in zoned crystals, what is the technique you use for such determinations, especially in the case of small crystals and/or their compositional zones?

P. M. BETHKE (Washington): Thus far all of our analyses have been on relatively coarse grained material from which several milligrams could be separated from each zone by hand picking. Presumably the electron micro-probe would be very satisfactory for those elements within its range.