SULFIDE PETROLOGY

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Abstract

The petrology of sulfide-rich rocks has the following special characteristics: (1) despite overall mineralogical variety, many ore deposits exhibit simple mineralogy at any single stage of mineralization; (2) the depositional pattern of many ores is such that even a single hand specimen may represent a complex series of superposed chemical systems; (3) sulfides are very susceptible to retrograde metamorphic processes. The interpretative study of sulfide-rich rocks, therefore, requires especially careful effort to reconstruct the history of the system.

Because many ore-forming systems tend to be open (in the sense of Korzhinskii, 1959) and to contian relatively simple phase assemblages for the number of components, quantitative knowledge of the compositions of phases is especially important in reducing the number of degrees of freedom so that the physical-chemical environment of ore formation may be evaluated. In general, the compositions of individual ore minerals reflect the activities of components in the environment more strongly than they do the simple effects of pressure and temperature on the minerals.

Aside from the presence of the major metals themselves, the two most important variables in determining sulfide mineral assemblages are activity of sulfur and temperature; total pressure ranks a poor third. An abundance of sulfidation-reduction reactions makes naturally occurring sulfide systems particularly amenable to thermodynamic quantification. The free-energy changes of univariant sulfidation-reduction equilibria are well represented as linear functions of temperature. The many experimentally determined invariant points help tie the grid of sulfidation reactions into a tightly knit package, whose internal consistency exceeds the accuracy of the individual measurements.

In spite of the widespread occurrence of its minerals, sulfur is a minor constituent of the crust compared to other redox-participating elements such as iron, carbon, hydrogen and oxygen; it is therefore these latter elements which ultimately exert the controlling influence on the activity of sulfur and thus on the mineralogy of the sulfides.

INTRODUCTION

The study of sulfide-rich rocks has always been properly considered as one facet of petrology; however, it is an aspect that is all too often ignored by the modern petrologist and has appeared almost solely within the realm of the economic geologist. My goal here is to broaden petrology, not to restrict economic geology.

Despite the presumptive title, this paper will not attempt to cover all aspects of sulfide petrology, for that would fill a thick volume. Instead, I shall consider briefly some of the problems and potentials in interpreting sulfide mineral assemblages. Supplementary material for this subject should include at least the topics covered in Geochemistry of Hydrothermal Ore Deposits edited by H. L. Barnes (1967) plus the articles by Gunnar Kullerud and Harold Helgeson in this volume. Despite excellent recent studies, such as those described in the Graton-Sales Volume (Ridge, 1968) or the work of Holland and coworkers at Providencia and Bluebell (Ohmoto and others, 1969, Sawkins, 1964), there has been, and remains, a profound deficiency in descriptive material relating to sulfide-rich rocks. In no instance of an appreciable degree of complexity are the mineral assemblages quantitatively understood. This lack is rapidly becoming the most serious barrier to additional progress.

Much of our effort in studying sulfide-rich rocks is directed toward understanding the petrogenesis of the sulfides, not merely their descriptive petrography. Therefore, we are not only concerned with what *is* but also with what *was*. We are especially interested in deducing the environmental parameters (temperature, pressure and

¹ Publication authorized by the Director, U.S. Geological Survey.

activities of all components) that prevailed when the deposit was forming, or was being modified from a still earlier form. Moreover, to evaluate the probability of various possible processes that may have operated on the rock, we would like to know the sequences of environments in time and space. Such are the goals, now let us consider some of the difficulties that have thusfar barred the way.

Complexity of the Problem of Interpreting Mineral Associations

The problem originates chiefly in the unraveling of a complex depositional pattern which may have been masked or erased by post-depositional processes. The initial goal of an investigation is then to recognize and characterize equilibrium mineral assemblages (groups of minerals that represent a current or former equilibrium state). This, however, is the most difficult and most neglected part of sulfide petrology.

First of all, with the exception of magmatic segregation, the processes of formation of most sulfide ores involve deposition from a dominantly aqueous fluid. There are many important deposits (such as those of the Mississippi Valley type, and many, if not most, of the geologically young deposits of the Cordilleran region of North and South America) which preserve a record of the mineral relationships at the time of formation. Minerals from such deposits frequently exhibit depositional detail in a bewildering array (see Fig. 1A thru D), an array marked principally by changes in chemistry but also by relatively minor changes in temperature. Sulfide ores tend to be depositories of the rarer elements; as a consequence of this and the chemical changes, the number of mineral species in a deposit as a whole can be large, sometimes much larger than would be permitted by the phase rule.



FIG. 1. Growth-zoned sphalerite from several localities. In each instance the area photographed is almost entirely sphalerite and represents less than 20 percent of the sphalerite paragenesis for that sample. The specimens are prepared as doubly polished sections from 0.05 to 0.5 mm thick. In general, color correlates with iron content ranging from 1 to 5 percent Fe in the darkest bands to <0.1 percent in the lightest ones. A. Piquette mine, Wisconsin. Width of photo is 3.3 mm. Transmitted light; B. OH vein, Creede, Colorado. Width of photo is 3.3 mm. Transmitted light; C. Leonard mine, Butte, Montana. Width of photo is 0.5 mm. Transmitted light; D. OH vein, Creede, Colorado. Width of photo is 3.3 mm. Transmitted light; C. Leonard mine, Butte, Montana. Width of photo is 0.5 mm. Reflected light. Photo shows nearly monotonous sphalerite with a few "blebs" of chalcopyrite. See Fig. 1F for the same field in transmitted light. This shows nearly colorless sphalerite with arborescent chalcopyrite preferentially replacing iron-rich zones in growth-banded pale yellow to brown sphalerite. The diffuse dark interface between the colorless and banded sphalerite is caused by disseminated fine chalcopyrite.

However, detailed study inevitably reduces the mineralogical complexity to the extent that for any *single stage of mineralization* (representing an interval of deposition during which there was no discernable chemical or physical change) there are usually far too few, rather than too many, phases for the number of components. In the terminology of Korzhinskii (1959), the system tends to be "open" with respect to many components.

Over the years a considerable body of observational data on the textural interrelationships of sulfides has accumulated (for example, see Bastin, 1950, or Edwards, 1947, or Ramdohr, 1960.) It is certain that ore textures present much information, but it is equally certain that there are few areas of scientific endeavor that are more subject to misinterpretation than the study of ore textures. The interpretation of ore textures is the most maligned, most difficult, and most important aspect of the study of these rocks. As an example of the difficulty in recognizing features, consider the standard polished section (Fig. 1E) showing, in reflected light, a uniform field of sphalerite with a few blebs of chalcopyrite to one side. One might pass a hundred such fields without comment except, perhaps, to wonder inconclusively whether the chalcopyrite had grown with, exsolved from, replaced, or been replaced by, the sphalerite. The same field of view illuminated with transmitted light (Fig. 1F) shows colorless sphalerite with chalcopyrite replacing banded yellow sphalerite, a feature that would never have been recognized in a normal examination of the polished section. How many times have supposedly definitive studies overlooked such essential detail?

The second major aspect of the problem is the intervention of postdepositional processes.¹ For example, many sulfide deposits have been oxidized and subjected to supergene enrichment. This is a readily discernable process which, while it may mask the nature of the original deposit, does not often lead the observer astray. In contrast, there is metamorphism, a process which has been overlooked and misinterpreted by literally generations of geologists. The rates of reaction for sulfides vary widely,

¹ In 1963 Barton, Bethke, and Toulmin presented an extensive review and discussion entitled "Equilibrium in Ore Deposits"; since then several additional significant studies have been made. Craig, Naldrett and Kullerud (1968) have summarized extensive experimentation in the Cu-Ni-Fe-S system at the Geophysical Laboratory concluding that the initial crystallization of Sudburytype ores was as a copper- and nickel-bearing pyrrhotite solid solution and that a large amount of subsolidus reequilibration was required to produce the presently observed assemblages. Brett (1964) critically examined exsolution reactions in the Cu-Fe-S system. Stanton (1964) and Stanton and Gorman (1968) investigated the rate of approach toward textural equilibrium of strained sphalerite, galena and chalcopyrite; their results are most interesting and their conclusions in basic agreement with those of the author. Inexplicably, the rapid textural equilibration that they found for sphalerite is seemingly inconsistent with the sluggish rates of chemical equilibration observed by Barton and Toulmin (1966).



FIG. 2. Time for equilibration for various minerals as functions of temperature.

but in general they are much higher than for silicates or oxides (see Fig. 2). As a consequence, some sulfide minerals such as argentite or chalcopyrite may react internally to homogenize initial compositional zoning or reactions may occur between some sulfides while adjacent, more refractory sulfides (such as sphalerite or pyrite) or silicates remain unaltered. Such changes could occur during deposition, in which case the compositional zoning of crystals would be destroyed as fast as it tried to form, during cooling following deposition, or during subsequent events such as regional or contact metamorphism.

Sulfides as a group will be among the first minerals to exhibit very low grade metamorphic effects, and they may well react so completely as to erase all of the fine-scale record of their heritage, even when the country rocks show little evidence of metamorphism. The older literature is heavily populated with interpretations of bedded and massive sulfide deposits in terms of the nearly complete replacement of pre-existing sedimentary rocks by sulfide minerals. There are without doubt such things as true replacement deposits (mantos, sulfide-bearing contact skarns, replacement veins, etc.) yet many recent investigators, Anderson (1969), Kinkle (1966), or Stanton (1966), have concluded that the conformable portions of such deposits as Mount Isa, Broken Hill, Sullivan, Ducktown, Rio Tinto, Rammelsberg, and many others may have originated as low temperature hydrothermal or even sedimentary deposits at, or near, the sea floor. They were subsequently buried and, in most cases, isochemically metamorphosed to mineral assemblages and textures that differ from the original ones. It is also probable that metamorphosed ores have cooled slowly enough from the conditions of the metamorphic maximum for extensive retrograde reactions to occur among the sulfides so that the presently observed rock is several stages removed from its

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initial state. As an example of such reactions, Yund and Kullerud (1966) have shown that above 334°C chalcopyrite+pyrrhotite react to yield pyrite+the high temperature polymorph of cubanite. Many sulfide ores contain the low-temperature pyrrhotite+chalcopyrite assemblage, but few, if any, show cubanite+pyrite even though the associated silicate rocks may indicate temperatures well in excess of 334°C. Such retrograde phenomena are so common in sulfides that one must either find evidence¹ for the lack of prograde or retrograde metamorphic reactions or reconstruct the original state before proceeding on to the task of interpreting the mineral association in terms of the environment of initial ore deposition. For some deposits this may mean simply that the sulfide mineral assemblage can tell us nothing at all about the environment of initial ore deposition.

Having discussed some of the field-related problems concerning mineral assemblages, let us now turn to the interpretation of mineral assemblages within the context of laboratory-acquired data on mineral stabilities.

THERMODYNAMIC APPROACH TO PHASE DIAGRAMS

In contrast to chemical engineering, where pilot plant experiments can successfully evaluate unknown parameters, much of experimental geology is afflicted with the youcan't-have-your-cake-and-eat-it-too syndrome. Rocks represent many-component, many-condition chemical systems; but in the laboratory only one or two independent variables may be studied simultaneously. Moreover, individual experiments that last for more than a few months, or at most a few years, are frowned on by impatient experimentalists, administrators, fund providers, and even the custodial staff. Therefore, one must experiment under conditions that are not identical to the much more leisurely geologic processes, and we must extrapolate our experimental work: from simple systems to complex ones, and from high temperature to low. Fortunately, the basis for extrapolation is firmly based in thermodynamics.

We shall begin by separating possible variables into relatively unimportant ones which we shall subsequently neglect and important ones which we shall discuss. We can dispense with electrical, magnetic, and gravitational fields for, despite the fact that they may all occur in natural environments, their magnitudes are far too small to influence mineralogical equilibria measureably.

Next let us consider pressure, and it is not so easy to write off. Each cubic centimeter of volume change in a reaction corresponds to a pressure coefficient of 0.0239 cal/bar; that is, for a pressure change of 1500 bars a reaction with a ΔV of 2 cc will have its equilibrium shifted by $2 \times 1500 \times 0.0239 = 71.7$ cal. Volume changes for reactions between condensed phases are usually small but may range up to 2 or 3 cc/g atom, amounting to changes in the free energy of reaction of several tens of cal/kbar. Most

¹ Some criteria for doing this are suggested by Barton, Bethke, and Toulmin (1963).

ore deposits that were formed at depths greater than 5 or 10 km,² and perhaps many that were formed at shallower depths, will likely be cooled so slowly that the initial record will be completely erased, thereby making any initial state calculations of moot value. Therefore, neglecting pressure will not usually result in an uncertainty of greater than about a hundred calories/g atom in the free energy for a reaction of significance of sulfide petrogenesis. This uncertainty should be compared to the 100 to 1000 cal (or more) uncertainty in standard free energies. Of course, if one is dealing with sulfides in the mantle or lower crust, pressure will be much more important.

Two further concerns in evaluating the role of pressure are thermal expansion and compressibility. Skinner's (1966) compilation of thermal expansion data for sulfides shows average volume increases of 1 or 2 percent (a few tenths of a cc) from room temperature to 400° C; moreover, thermal expansions on opposite sides of a reaction tend to compensate. Of even less importance is compressibility, for Birch's (1966) compilation shows that a pressure increase of 2 kbar achieves only 0.2 to 1 percent volume decrease.

A summary of measured univariant P-T curves where vapor is not present (Fig. 3) shows very little effect of pressure on the equilibrium temperature. In summary, phase relations of sulfides are relatively insensitive to pressures of the magnitude found in the upper crust, and most phase relations have much more promise as thermometers than barometers.³

The remaining variables of state are temperature and composition, both of which are very important. Composition can be an awkward variable and we, therefore, find it convenient to discuss the variation in phase assemblages for fixed compositions. Another parameter which is particu-

² A hydrostatic load gives about a maximum of about 10 km/kbar; lithostatic gives about 3.5 km/kbar.

⁸ For possible exceptions see Scott and Barnes (1969) and Clark (1960)



FIG. 3. Depth-temperature plot for vapor-free univariant equilibria. Depth coordinate also shows pressure in kbar. Data are from various sources as cited by Barton and Skinner (1967).

larly useful is the activity of a component common to several phases. In the case of the sulfides we find that the activity of sulfur serves as a unifying variable with which to compare different bulk compositions.

The convenient standard state for sulfur is the ideal diatomic gas, S2, at a fugacity of one atmosphere and at the temperature of consideration. This state is used even though it is physically unattainable (due to the condensation of solid or liquid sulfur) below 614°C (the point at which $Ps_2=1$ atm). The activity of S_2 , a_{S_2} , is thus numerically equal to the partial pressure of S2 in atmospheres, but bear in mind that the presence or absence of a gas phase is inconsequential. The S2 gas standard state is convenient because curves for sulfidation reactions are not required to bend arbitrarily at the melting, transition, and boiling points of sulfur as would be the case if the standard state for sulfur were chosen, in the conventional manner, as the stable form at one atmosphere at the temperature of interest. Compilations of data in the literature frequently use the latter standard state, so some extra care in calculation is warranted.

One of the most useful ways to present sulfidation data is by plotting reactions so as to generate a metallogenetic grid, the coordinates of which are temperature and activity of S_2 . As will be discussed below, there is a sensibly linear relationship between the free energy change, ΔG , and temperature for many sulfide reactions. Because ΔG $=-RT\ln K$ where T is in degrees Kelvin and K is the equilibrium constant, and because most sulfidation reactions can be written so that all of the reactants and products except for S₂ are in their standard state, it follows that $\log a_{S_2}$ is a sensibly linear function of 1/T. (See Barton and Toulmin, (1964) and Barton and Skinner, (1967) for further discussion). Figure 4 shows a series of such sulfidation curves for several metals. Many other such curves are compiled by Barton and Skinner (1967) and by Richardson and Jeffes (1952).

The general tendency for ΔG versus T, or log a_{S_2} versus 1/T, curves to be linear has been pointed out by many, including Richardson and Jeffes (1948) and Kubaschewski,



FIG. 4. Log a_{S_2} -temperature grid showing typical sulfidation reactions.



FIG. 5. Plot against temperature of differences in standard free energies of formation between the tabulated values of Robie and Waldbaum (1968) and linear equations fit to the same data.

Evans and Alcock (1967, p. 30). A linear curve implies constant values for the enthalpy and entropy changes for the reaction, a relationship that is generally recognized not to be rigorously true, even though it may well be valid. There is little to be gained in work with sulfides by applying a highly precise deviation from a straight line when the absolute position of the line is uncertain by at least several hundred calories (see Kubaschewski, Evans, and Alcock, 1967, p. 29). The principal source of uncertainty is the heat of reaction; this is because mineral sulfides are so refractory, and tend to yield such poorly characterized solution products that satisfactory heats of solution are difficult to obtain. Also, many sulfidation reactions are too sluggish to obtain heats of reaction directly. The best approach for sulfides appears to be to measure the equilibrium constant of formation (which gives ΔG°) of a phase at high temperature and then to extrapolate to other temperatures using heat content data, plus an evaluation of activities if solid solutions are involved. An alternative of measuring $\log a_{\rm S_2}$ as a function of temperature and simply extrapolating the curve is subject to error because the temperature range of measurement is often too limited to obtain an adequate control on slope; however, this method does have the advantage of automatically including at least an approximate correction for solid solution between phases in the reaction. As examples of the minimal departure from linearity for sulfidation reactions (and for solid-solid reactions as they can be constructed by adding sulfidation reactions) I have have fitted linear least squares curves to the data for several sulfides from the compilation of Robie and Waldbaum (1968) who used a rigorous computation method involving the enthalpy at 289°K and hightemperature heat content measurements. The departure of the points from the linear function is too small to show on ΔG versus T plot, and I have therefore used a plot of ΔG linear- ΔG rigorous versus T for comparison (Fig. 5). The departures are mostly less than 100 cal/g atom. In view of the uncertainty in the positions of the equilibria

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FIG. 6. Free energies of mixing for several sulfosalts. The data for the Cu, Ag, and Pb compounds are from Hall (1967) and do not necessarily represent all of the phases stable on a given join.

there appears little reason to abandon the linear curves. However, reactions involving aqueous species are usually pronounced exceptions to the above-defended linear ΔG versus T generalization.

The sulfidation reactions as written are univariant: that is, in the presence of a gas phase the number of condensed phases equals the number of components. Either temperature or pressure, but not both, may be varied arbitrarily. If we replace gas pressure by a_{S_2} , we still have a univariant curve (providing the role of total pressure is negligible, as noted earlier). The intersections of univariant curves give rise to invariant points, the positions of which can be calculated easily (see Barton and Skinner, 1967). Because the intersections of sulfidation curves tend to be very shallow, it is obvious that an error of several hundred calories (or of a few tenths of a log unit a_{S_n}) would shift individual curves and hence the calculated temperature of an invariant point by many degrees. Conversely, an experimentally determined invariant point provides a valuable triangulation station that aids in the refinement of the locations of all of the univariant curves emanating from the invariant point.

There are few data for sulfosalt phases, and those that are available do not always correspond to recognized minerals. Obviously a great deal of work is yet to be done before sulfosalts will be well distinguished thermodynamically. Figure 6 shows the free energy of formation of several sulfosalts *from the simple sulfide components* (data from Hall (1967) and Barton, unpubl.). Note the expanded scale. It is evident that a given sulfosalt is not a great deal more stable than any of several alternative configurations representing the same bulk composition. Therefore, one should not be too surprised to find that relatively small changes in temperature, pressure and composition might rather strongly modify the configuration of sulfosalt fields in phase diagrams. For the same reason, calculation of sulfosalt phase diagrams from independent thermochemical information would require unreasonably precise data. Sulfosalts are similar to most silicates in that they are commonly intermediate phases along joins between simple compounds. Natural sulfosalt assemblages potentially may contain far more precise thermochemical information than experimental data now available; the analogous situation for silicate assemblages has been pointed out by Garrels (1957).

Having generated a grid of sulfidation reactions, we are able to locate certain assemblages relative to the temperature— a_{S_2} environment. For example, a hematite+galena assemblage must have formed in the upper shaded field in Figure 7, and a pyrrhotite+bismuthinite assemblage somewhere in the lower field.¹ Many more such limited assemblages might be devised, but as we noted earlier, mineral assemblages rarely, if ever, consist of a number of phases in excess of the number of components; therefore, univariant or invariant conditions are not often defined by the available phase assemblage. Consequently, phase assemblages cannot be expected to furnish either unique temperatures or a_{S_2} values or any other condition or state, for the conditions of mineral equilibration. In order to reduce the number of degrees of freedom further, and thereby to be able to solve for temperature, a_{S_2} , and the activities of all other components at the time of mineral equilibration, we must consider the compositions, not merely the identities, of the phases. This will be the topic for much of the remainder of this paper, but first we need to mention buffers and indicators, a subject also discussed by Barton and Skinner (1967).

A sulfide-bearing assemblage that constitutes the reactants and products for one of the isobarically univariant curves shown in Figure 7 can be considered as either an S_2 buffer or an S_2 indicator. In the role of a buffer the assemblage performs the function of either providing or consuming sulfur, at constant temperature, as needed to maintain a constant value for a_{S_2} . As an indicator the assemblage merely records the passing of the environment from one side of the univariant curve to the other, the mineral array being preserved only because the later assemblage effectively armors the earlier one and thus prevents its complete destruction. In ores, this phenomenon is commonly observed as partial replacement of one mineral (or mineral assemblage) by another. The distinction between buffers and indicators is one of scale rather than principle, because the indicator reaction generates its own microenvironment within which it functions as a buffer, without controlling the chemistry of the larger body.

¹ An attempt to define mineral facies in terms of a_{S_2} and temperature would be of dubious value because a_{S_2} can be highly variable, within a single hand specimen, or even within the same crystal.

Buffers and indicators may be of either the "fixed point" or the "sliding scale" type. A fixed-point buffer (or indicator) exists when the number of phases equals the number of independent components, that is, under divariant conditions. At constant temperature and pressure it defines the activity of each component at a precisely determined level. An example might be pyrite which in the unary system FeS_2 controls a_{FeS_2} at unity; to the extent that pyrite is a stoichiometric phase, the a_{S_2} and a_{FeS} values are not fixed, however, and they may vary widely, though not independently. Another example is the assemblage pyrite+magnetite+hematite which controls the activities of all possible components in the Fe-S-O system, i.e., a_{FeS} is controlled through the reaction $FeS_2\!+\!3Fe_3O_4\!=\!4Fe_2O_3$ +2FeS. This and several other fixed-point-type reactions that control a_{FeS} in the presence of pyrite are shown in Figure 8. A sliding scale buffer or indicator also defines the activity of a component, but the level at which the activity is defined is a function of the composition of the buffer. The buffering (or, more probably, indicating) of a_{FeS} by the (Zn, Fe)S solid solution is an example, and Figure 8 shows this quantitatively within the framework of the fixed-point-type reactions. The ionic buffers commonly used in aqueous chemistry are of the sliding scale type. In contrast to the fixed buffers which are divariant (=isobarically univariant), the sliding scale buffers are at least trivariant and must have their variance reduced by specification of the composition of phases. Each time the concentration of a component in a phase of variable composition is specified, the variance of the system is reduced by one. Because a major goal is to reconstruct the environment at the time of equilibration, we wish to reduce the variance as much as possible, hence the emphasis on composition of minerals.

General Factors Influencing the Compositions of Minerals

The equation relating the composition, X, of a phase to the activity, a, of a component is



 $X = a/\gamma$

FIG. 7. Log a_{S_2} -temperature grid showing limited fields for hematite+pyrite+galena and pyrrhotite+bismuthinite assemblages.



FIG. 8. Log $a_{\rm Fe8}$ -temperature grid with superposed sulfidation equilibria of the sort $MS_x+{\rm Fe8}=MS_{x-1}+{\rm Fe8}_2$. The composition of sphalerite that would coexist with these assemblages is indicated.

where composition is expressed as a mole fraction and γ is the activity coefficient.

The relation of these quantities to chemical potential is

 $\mu - \mu^{\circ} = RT \ln (X \cdot \gamma)$

In dealing with mineral solid solutions there are two obvious choices for standard state of the solute. The first is the pure solute component *in a crystal structure identical to the solvent*. Such a state may or may not be physically attainable, but such a choice is very convenient for describing and theorizing about the properties of a solid solution. However, in comparing the uptake of a component into several different phases, each of which has a different structure, this first choice becomes awkward in that the comparable activities must be related through the chemical potentials of the individual standard states, *i.e.*

$$\mu^{\circ}_{1} - \mu^{\circ}_{2} = \operatorname{RT} \ln \frac{a_{2}}{a_{1}}$$

The second choice is to use a single standard state for a given component regardless of the nature of the solid solution. This alternative will be used in this paper because it makes clearer the discussion of the distribution of trace elements between coexisting phases.

Choice of components. The proper recognition of components is essential when dealing with solid solutions in sulfides. Although we commonly refer to the "cadmium" or "iron" content of a sphalerite, the solid solutions for our purpose lie on the ZnS-CdS and ZnS-FeS joins, and it is a_{CdS} and a_{FeS} , not a_{Cd} or a_{Fe} , that is important here. However, such simple one-for-one substitution does not create either conceptual or operational difficulties.

A particularly troublesome situation in minerals is presented by coupled substitution, the condition in which a pair of ions of different charge, e.g., Ag^+ and Sb^{3+} , substitute for two ions in the host phase, e.g. 2 Pb²⁺, in such a way as to maintain the charge balance. Because minerals are so often compositionally complex at the trace level, the activities of components participating in coupled substitution are so involved in the total array of multiple-charge substitution that quantification is virtually worthless. As an example, what kind of components could usefully be extracted from a galena composition in which the substitution is of the form

(Ag, Cu, Tl) (As, Sb, Bi, Ga, In) S₂ for 2 PbS?

Factors controlling the activity and activity coefficient. In considering the uptake of a minor component by a growing crystal it is convenient to separate the two factors of the equation,

$$X = a/\gamma$$

The activity, a, deals with the chemical environment imposed on the growing crystal by its surroundings, most specifically by the fluid phase from which crystallization may be occurring. In order of importance, the activity is a function of the composition, temperature and pressure of the environment. All of these factors are external to anything going on within the crystal. The activity can be locally buffered, as described previously; or it may be controlled remotely, as $a_{\rm NiS}$ might be controlled through the interaction of H₂S-bearing fluids with nickel-bearing silicates far removed from the site of deposition. Whether or not a component is buffered locally determines whether it is termed "inert" or "perfectly mobile" following the terminology of Korzhinskii (1959).

The activity coefficient, γ , is determined solely by the temperature, composition, and pressure of the growing crystal itself. The solvent in a dilute solid solution obeys Raoult's Law in that the activity of the solvent component is equal to its mole fraction. The compositional range over which "dilute" behavior is maintained varies from system to system, but in general, the greater the degree of solid solution, the greater the range of "dilute" behavior. The compositional range of Raoult's Law also tends to be much wider for simple substitutional solid solutions, such as (Zn, Fe)S, than for omission type solid solutions such as Fe_{1-x}S or Cu_{1+x}Fe_{1+x}S₂.

The Gibbs-Duhem relationship requires that so long as the solvent obeys Raoult's Law, the activity of the solute is proportional to its mole fraction. However, the proportionality constant (=activity coefficient) is generally not unity. Previous arguments regarding the minimal role of pressure apply here also and we shall probably be safe in assuming that the influence of pressure is negligibly small. The role of composition is not so minor, but it appears to be small so long as coupled substitution is excluded. The effect of temperature on activity coefficients is variable, but not of large magnitude.

Summarizing available data, variations in composition and temperature can produce effects of up to one order of magnitude, and rarely more, on the *activity coefficient*. In contrast, the *activities* of many components may vary by not just one log unit, but by many! For example, Figure 8 shows the variation of a_{FeS} over a range of 6 log units while being in equilibrium with either pyrite or pyrrhotite. The series of mineral assemblages along the univariant curves superposed on the diagram show that natural environments do indeed span most of this range. The figure also shows how the composition of sphalerite will vary over the $a_{\rm FeS}$ -temperature range covered by the diagram.

For components such as SnS, MnS, or In_2S_3 that seldom appear as major constituents of ore minerals the variation in activity may be even greater than that for FeS.

Thus the range in variability of activity is drastically greater than that for the activity coefficient, and it is obvious that the concentration of a nonessential constituent in a mineral is influenced far more strongly by a than by γ . It is, therefore, futile to try to use the trace component composition of a single phase (such as the silver content of galena or the mercury content of sphalerite) to try to define some parameter such as the temperature of mineral deposition unless the activity of that component is somehow fixed.

It is possible that some geochemical reason might prevail to limit variability in a. For example, there are no feasible geochemical processes for effectively separating Zn from Cd; therefore, the Cd/Zn ratio is relatively uniform in base metal deposits and the a_{Cds} in sphaleritedepositing environments rarely varies by more than an order of magnitude (which is still far too large a variation for useful thermometry.)

Now let us consider the uptake of a component which is not observed as a separate entity in nature, and in fact, need not even have a stable existence as a pure phase.

The entrance of gold into a simple sulfide such as galena might be an example. Based on only the most preliminary sort of experimental data, let us consider the gold content of galena in equilibrium with free gold. Gold might enter as the un-ionized metal atom in interstitial positions, or it might be present as a gold sulfide component, e.g., Au₂S, AuAuS₂, or Au₂S₃ none of which is known as a compound stable relative to gold plus sulfur. Very preliminary experiments (Barton, unpubl.) show that gold enters galena only in the presence of excess sulfur (the quantitative relationship is still obscure) and that silver decreases and bismuth increases the solubility of gold in galena. Therefore, the gold is probably present, at least in part, as the Au₂S component whose solubility is increased by the coupled substitution of AuBiS2 (analogous to the enhanced solubility of argentite in galena by the substitution of AgBiS₂, Van Hook, 1960). The reaction $4Au + S_2 = 2Au_2S$ must lie in the metastable region beyond the reach of pure sulfur vapor as shown schematically in Figure 9. From the stoichiometry of the reaction we can contour the log $a_{\rm S2}$ versus T grid in terms of $a_{Au_{2}S}$. If the activity coefficient for Au₂S in galena were known as a function of temperature we could contour the diagram in terms of gold content of gold-saturated galena. Granted that this part of the discussion is purely schematic, it nevertheless illustrates two points: (1) As temperature changes, the behavior of a component in a saturated solid solution is not simple; it

may decrease on cooling as would be the case along the pyrite+pyrrhotite curve, or it might increase on cooling as along the sulfur condensation curve. The difference between some roasting and free-milling gold ores might well be the effective sulfur buffer system that functioned during the post-depositional history of the ore. Of course, other gold-bearing solid solutions (such as pyrite or arsenopyrite) may not behave as does galena, but the principles should be similar. (2) It is entirely possible to work satisfactorily with components which may not be seen as minerals. The copper content of pyrite might be expected to have a similar dependency on as2 provided that the copper-rich pyrite lies on the FeS2-CuS2 join.1 A further extension of the discussion of the behavior of a component in solid solution is that of the distribution of a component between two or more phases as discussed below.

If we consider the equations for the same component in two different phases and then divide one expression by the other, *i.e.*,

$$\frac{X_1}{X_2} = \frac{a_1/\gamma_1}{a_2/\gamma_2} = \frac{\gamma_2}{\gamma_1} = D$$

the activity terms cancel out and the distribution coefficient, D, is equal to the inverse ratio of the activity coefficients. The activity coefficients are functions of the temperature, pressure and composition of the host phase, but we have noted already that the role of pressure is minor. Two typical isotherms, (P. M. Bethke and Barton unpubl. data), for the distribution of CdS between sphalerite and galena are shown in Figure 10. So long as we are dealing with dilute solid solutions the deviation of the activity coefficients from a constant value should be trivial, and temperature alone exerts a significant control on the

¹ The studies of copper-rich pyrite by Frenzel and Ottemann (1967), Einaudi (1968), and Shimazaki (1969) demonstrate the possible significance of this example.



FIG. 9. Hypothetical log a_{S_2} -temperature grid suggesting the wide range of variability of a_{Au_2S} in equilibrium with native gold.





distribution coefficients. The method appears to provide promising geothermometers, but the difficulty of finding and separating for analysis samples that were deposited in mutual equilibrium presents a serious problem for successful application, as is evident from consideration of the highly complex ore textures shown in Figure 1. The distribution of sulfides of monovalent and trivalent metals between coexisting sulfides of divalent metals, for example, Ag₂S, Tl₂S, In₂S₃, or Sb₂S₃ between sphalerite and galena, will be extremely difficult to quantify in such a way as to be useful because they inherently become involved in coupled substitutions.

THE SULFIDATION STATE OF NATURAL ENVIRONMENTS

The metallogenic grid of sulfidation reactions shown in Figure 11 covers a large range of sulfur activities, and some



FIG. 11. Log a_{S_2} -temperature grid showing the region of principal ore-forming environments.

deposits may have sufficient mineralogical variation to be represented by one-third or more of the total as2 range. As noted earlier the sulfide-forming environments usually do not buffer themselves on a given sulfidation curve. Instead the sulfides seem to precipitate under arbitrary conditions that may either vary systematically or apparently irregularly, showing that the solid phases being precipitated do not buffer a_{S_2} , but function as indicators of a_{S_2} in the depositing solution, and that the solutions themselves are not of constant composition. Something determines the as, of solutions; if not the local precipitates, then what? The source of ore fluids is responsible for the initial state of the fluids, and, although the specific volume of rock responsible for a given ore fluid cannot often be identified, much less examined, the following observation is pertinent. Neither igneous nor metasomatic metamorphic rocks commonly have sulfide assemblages that alone would control a_{s_0} ; instead the buffer systems appear to be such as:

 (1) 2FeS+8FeSiO₃ (in pyroxene)+2Fe₃O₄ =8Fe₂SiO₄ (in olivine)+S₂
(2) 6FeS+8KAlSi₃O₈ (in feldspar)+8H₂O+6Fe₃O₄ =8KFe₃AlSi₃O₁₀(OH)₂ (in biotite)+3S₂
(3) 4FeCO₃+5FeS₂=3Fe₃O₄+4C+5S₂

Reactions such as these involve rock-forming minerals that are available in huge quantities relative to ore deposits. The activities of several of the components in the above reactions are not fixed because they are part of solid solutions functioning as solid state buffers.

There are many geologically feasible reactions which may be written as buffers of S_2 , but simply buffering S_2 is not enough. This is because the dominant sulfur bearing species is not S₂; S₂ is only a convenience in calculation. The major, low- to medium-temperature aqueous species are H₂S, (K, Na, H)SO₄⁻, and possibly others, as discussed by Helgeson (1969). Because these species can be participants in redox reactions, the relative proportions of other components that may also participate in redox reactions, *i.e.*, CO₂, CH₄, H₂, Fe²⁺, etc., are very important, especially because these other components may individually or collectively be present in excess of sulfur. Even further complexities exist, for the dominant sulfur-bearing species are involved in hydrolysis and base exchange equilibria (for example, $3H_2S+KSO_4^-+2H^+=2S_2+K^+$ $+4H_2O$). This means that at the source, in route, and at the site of deposition there are diverse types of reactions ranging from magmatic crystallization (or metamorphic or diagenetic recrystallization), to wallrock alteration, mixing of fluids from different sources, and ore and gangue precipitation which can play important roles in determining the activities of S2 and of other components as well. The complexities of these processes are appreciated (see, for example, Meyer and Hemley, 1967) but not quantitatively understood as yet, although significant strides in this direction have been taken by Holland (1965) and especially Helgeson and others (1970) and Helgeson (1970).

The "main line" sulfidation state of the most ore deposits tends to run from the pyrrhotite field at high temperature well into the pyrite field at low temperatures, as suggested in Figure 11. The reason, of course, is the general position of the multiple equilibria of the sort just discussed. There is considerable variation within this trend, and an understanding of the specific reasons for a given pattern is a major goal of current research.

Low sulfidation states. Except for the near-surface, oxidizing environment where a_{S_2} is decreased through the formation of sulfates, extremely low sulfidation states (near the iron-pyrrhotite curve) are rare. Three principal types of occurrence are worth mentioning: (1) In meteorites, or perhaps in deep mantle material, the bulk chemistry is such that there is not enough oxygen and sulfur to use up all of the metals; this is not the situation with most crustal rocks. (2) Reaction with organic materials may reduce the oxygen activity and lead to the reduction of a_{S_2} through reactions such as:

$$S_2 + 2H_2O + C = CO_2 + 2H_2S$$

(3) The instability of wustite $(Fe_{1-x}O)$ relative to magnetite+iron coupled with the paucity of silica to react with FeO to form ferrous silicates under the conditions of serpentinization of some peridotite bodies yields iron which can be sufficiently abundant to use up any available sulfur:

$$80Mg_{1.8}Fe_{0.2}SiO_4 + 104H_2O + S_2$$

 $= 24 Mg(OH)_2 + 2Fe + 2FeS + 4Fe_3O_4 + 40 Mg_3Si_2O_5(OH)_4$

Such chemistry might well be responsible for the generation of highly reduced, high pH solutions that would be favorable for the generation of mercury deposits.

High sulfidation states. Very high sulfidation states, approaching the native sulfur field, are also rare. These occur principally in five situations, none of which concern "normal" hydrothermal environments: (1) Volcanic sublimates frequently contain native sulfur derived from the rapid cooling of tenuous vapors containing free sulfur generated at least in part by the reaction SO₂+2H₂S $=2H_2O+3/2$ S₂; (2) The oxidation and acidification of H₂S-bearing, hot spring waters often produce free sulfur; (3) The partial oxidation of sulfide ores may yield native sulfur; (4) The biogenic reduction of sulfate often produces native sulfur and associated high sulfidation state sulfides (e.g. hauerite, MnS_2). (5) The heating to high temperatures of sulfide assemblages which had previously formed at low to moderate temperature can produce a high sulfidation state. For example, a basalt dike intruded into a pyrite vein will certainly break down the pyrite adjacent to it; whether the sulfur escapes outward to produce a more sulfur-rich halo (as by converting chalcopyrite to bornite+pyrite) or moves into the dike as it cools to sulfidize iron-bearing silicates, depends on local fracturing and other factors beyond the scope of this paper.

SULFIDE PETROLOGY

I wish to reemphasize that, despite the essential nonexistence of a molecular sulfur species in the ore forming environment, the activity of sulfur, specifically a_{S_2} , is extremely useful because it relates different sulfide assemblages to a common variable that exerts a significant control over sulfide mineralogy.

GOALS OF CURRENT RESEARCH

Because difficulty in dealing experimentally with multicomponent systems requires us to extrapolate from simple to complex systems, and because we must extrapolate downward in temperature from the conditions under which meaningful experiments can be carried out, the methods of thermodynamics are particularly attractive. In addition to the acquisition of a reservoir of data on end-member compounds, a thorough understanding of the thermodynamic behavior of solid solutions is essential. The most convenient line of thermochemical study appears to be the examination of sulfidation reactions, bearing in mind that any thermodynamic study requires a firm understanding of the phase equilibria before the results can be interpreted.

Our knowledge of specific mineral relationships is woefully inadequate. We need field studies in which the understanding of mineral paragenesis is pushed to the ultimate, far beyond the usual simple bar diagram. Finally, the most important requirement of sulfide petrology is to integrate the studies of sulfides with those of all other phases occurring in rocks and to view the sulfides in terms of the whole petrologic environment.

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References

- ANDERSON, C. A. (1969) Massive sulfide deposits and volcanism. Econ. Geol. 64, 129-146.
- BARNES, H. L. ed. (1967) Geochemistry of Hydrothermal Ore Deposits. Holt, Rinehart and Winston, Inc., New York. 670 p.
- BARTON, P. B., JR., P. M. BETHKE, AND P. TOULMIN III (1963) Equilibrium in ore deposits. *Mineral. Soc. Amer. Spec. Pap.* 1, 171–185.
- ——, AND B. J. SKINNER (1967) Sulfide mineral stabilities, In Barnes, H. L. (ed.,) *Geochemistry of Hydrothermal Ore Deposits*, Holt, Rinehart and Winston, New York.
- , AND P. TOULMIN III (1964) The electrum-tarnish method for the determination of the fugacity of sulfur in laboratory sulfide systems. *Geochim. Cosmochim. Acta* 28, 619–640.
- _____, AND _____ (1966) Phase relations involving sphalerite in the Fe-Zn-S system. *Econ. Geol.* **61**, 815–849.
- BASTIN, E. S. (1950) Interpretation of ore textures. Geol. Soc. Amer. Mem. 45.
- BIRCH, F. (1966) Compressibility-elastic constants. Geol. Soc. Amer. Mem. 97, 97-173.
- BRETT, P. R. (1964) Experimental data from the system Cu-Fe-S and their bearing on exsolution textures in ores. *Econ. Geol.* 59, 1241-1269.
- CLARK, L. A. (1960) Arsenopyrite As:S ratio as a possible geobarometer (Abstr.). Geol. Soc. Amer. Bull. 71, 1844.
- CRAIG, J. R., A. J. NALDRETT, AND G. KULLERUD (1968) Succession of mineral assemblages in pyrrhotite-rich Ni-Cu ores. Carnegie Inst. Wash. Year Book 66, 431–434.
- EDWARDS, A. B. (1947) Textures of the ore minerals and their significance. Australasian Inst. Min. Metall., Melbourne, 185 p.
- EINAUDI, M. T. (1968) Copper zoning in pyrite from Cerro de Pasco, Peru. Amer. Mineral 53, 1748-1752.
- FRENZEL, G., AND J. OTTEMANN (1967) Eine sulfidparagenese mit Kupferhaltigem Zonarpyrit von Nukudamu Fiji. Mineralium Deposita 1, 307–316.
- GARRELS, R. M. (1957) Some free energy values from geologic relations. Amer. Mineral. 42, 780-791.
- HALL, H. T. (1967) Application of thermochemical data to problems of ore deposition (Disc.). Econ. Geol. 62, 1108.
- HELGESON, H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Amer. J. Sci. 267, 729-804
- -----, T. H. BROWN, A. Nigrini, AND T. A. Jones (1970) Calcula-

- tion of mass transfer in geochemical processes involving aqueous solutions. *Geochim. Cosmochim. Acta*, **34**, in press.
- HOLLAND, H. D. (1965) Some applications of thermochemical data to problems of ore deposits. II, Mineral assemblages and the composition of ore-forming fluids. *Econ. Geol.* **60**, 1101–1166.
- KINKLE, A. R., JR. (1966) Massive pyritic deposits related to volcanism, and possible methods of emplacement. *Econ. Geol.* **61**, 673–694.
- KORZHINSKII, D. S. (1959) *Physiochemical basis of the analysis of* of the paragenesis of minerals. [English transl.] Consultants Bureau, New York. 142p.
- KUBASCHEWSKI, O., E. L. EVANS AND C. B. ALCOCK (1967) Metallurgical Thermochemistry, 4th Ed. Pergamon Press, New York. 426 p.
- MEYER, C., AND J. J. HEMLEY (1967) Wall rock alteration In H. L. Barnes, (ed.) *Geochemistry of Hydrothermal Ore Deposits*, Holt, Rinehart and Winston, New York. 167–235.
- OHMOTO, H., M. BORCSIK AND H. D. HOLLAND (1969) Chemistry and origin of hydrothermal fluids at the Bluebell mine, British Columbia. Abstr. Progr. *Geol. Soc. Amer.* Part 7, 165.
- RAMDOHR, P. (1960) Die Erzmineralien und ihre Verwachsungen. Akademie-Verlag, Berlin. 1089 p.
- RICHARDSON, R. D., AND J. H. E. JEFFES (1948) The thermodynamics of substances of interest in iron and steel making; I. Oxides. J. Iron Steel Inst. 160, 261–270.
- —, AND —— (1952) The thermodynamics of substances of interest in iron and steel making; III. Sulfides. J. Iron Steel Inst. 171, 165–175.
- RIDGE, J. D., (ed.) (1968) Ore Deposits of the United States, 1933– 1967—The Graton-Sales Volume. 2 vol. AIME, New York, 1880 p.
- ROBIE, R. A., AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. U. S. Geol. Surv. Bull. 1259.
- SAWKINS, F. J. (1964) Lead-zinc ore deposition in the light of fluid inclusion studies, Providencia mine, Zacatecas, Mexico. *Econ. Geol.* 59, 883-919.
- SCOTT, S. D., AND H. L. BARNES (1969) Sphalerite geobarometry. Abst. Prog. Geol. Soc. Amer. Part 7, 202-203.
- SHIMAZAKI, H. (1969) Synthesis of a copper-iron disulfide phase (abstr.). Can. Mineral. 10, 146.

SKINNER, B. J. (1966) Thermal expansion. Geol. Soc. Amer. Mem. 97, 75-96.

 STANTON, R. L. (1964) Mineral interfaces in stratiform ores. Trans. Inst. Mining Met. Sec. B, 74, 45-79.
(1966) Compositions of stratiform ores as evidence of de-

(1966) Compositions of stratiform ores as evidence of depositional processes. *Trans. Inst. Mining Met. Sec. B*, **75**, 75–84.
AND H. GORMAN (1968) A phenomenological study of grain

boundary migration in some common sulfides. Econ. Geol. 63, 907-923.

- Van Hook, H. J. (1960) The ternary system Ag₂S-Bi₂S₃-PbS. *Econ. Geol.* 55, 759–788.
- YUND, R. A., AND G. KULLERUD (1966) Thermal stability of assemblages in the Cu-Fe-S system. J. Petrology 7, 454-488.