

SULFIDE PHASE RELATIONS

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ABSTRACT

During the past twenty years, new methods have been developed and old procedures have been improved to permit systematic study of sulfide-type systems over large temperature and pressure ranges. The condensed systems containing the common sulfide-type minerals are now generally well known at temperatures above 250°C. The effects of high confining pressures on the phase relations have been investigated on a limited scale only, and kinetics of reactions are largely unknown.

Comparison of phase relations in known systems points up characteristic features pertaining to the types of compounds and their structures, solid solutions, stability ranges, and behavior under pressure. The melting relations, liquid solubilities, and immiscibilities displayed in binary systems permit general conclusions to be drawn about systems not yet investigated and provide a basis for classification of sulfide-type systems. Knowledge of the stable existence of compounds in synthetic systems often has made it possible to predict which compounds are likely to occur in nature. Subsequent search has led to the discovery of many of these compounds as minerals.

Applications of the synthetic systems have yielded information about the temperatures and pressures (partial and total) attained when ores formed. They have also demonstrated that sulfide-type minerals are not preserved as originally deposited but commonly reequilibrate, at widely differing rates, to temperatures below 200°C during periods of cooling or metamorphism. The fast rate of reequilibration is particularly well demonstrated in meteorites that have been exposed to shock. The sulfide assemblages in such bodies act as sensitive indicators of shocks that are too mild to be registered by minerals of other types.

The correlations commonly observed between ore types and host rocks indicate that improved understanding of the processes responsible for ore deposition can be gained through studies of systems containing ore, as well as rock components. Such investigations are only beginning but have already pointed to possible mechanisms of ore formation.

Future progress in the field of sulfide phase relations requires development of instrumentation so that partial and total vapor pressures over pertinent systems can be measured accurately and routinely. In order to understand and evaluate the reequilibration processes taking place in ores, the kinetics of systems whose phase equilibria are already known must be investigated systematically. New ideas and methods are needed to deal with sluggish reaction rates, so that sulfide systems can be explored below 250°C. The systems must be expanded to include all pertinent components participating in the ore-forming processes and as a consequence bridges must be built between the dry and wet approaches to the problems of ore formation.

INTRODUCTION

Sulfide- and arsenide-type systems have been studied for various reasons. Mineralogists have worked for more than a century to establish the compositions of the common minerals. Metallurgists, particularly since the turn of the century, have studied the high-temperature phase relations in such systems to derive methods for extraction of metals from ores. The development of reflected light microscopy and of methods for preparation of polished sections gave enormous impetus to the phase relation studies and provided geologists the opportunity to ponder the fine textures displayed in ores. Efforts to decipher the meanings of such textures produced considerable knowledge about the paragenesis of opaque minerals, but also, and perhaps more important, pointed up that a profound understanding of the processes operating during and after ore deposition must build on laboratory experimentation in which rigid control of pressure, temperature, and composition is possible.

A new dimension was gained in the understanding of phase relations when X-ray diffraction techniques became available, not only to identify compounds and minerals, but also to determine their crystal structures. Polished section microscopy and X-ray diffraction remain the two most important tools for identification of opaque phases in natural as well as synthetic systems.

EXPERIMENTAL METHODS

Spectacular advancements have been made, particularly during the last two decades, in the investigations of sulfide-type systems. This progress was made possible largely because of improvements in old research methods and developments of entirely new ones. Originally, open crucibles were used as reaction vessels. Heating resulted in considerable loss of volatile components and oxidation of the metals. Next, sealed silica glass tubes were used. The first tubes were large and unwieldy; the glass was of poor quality, and the volume in which vapor could form was many times larger than that of the condensed phases. Silica tubes are still being used, but have been gradually improved and are now well suited for modern research. These tubes are made of high purity silica glass, and a number of tube designs have been developed for varied types of experimentation (simple tubes, differential-thermal-analysis tubes, tubes in tubes, *etc.*). The materials to be investigated are weighed directly in the tubes, permitting composition control of better than 0.01 weight percent. Most of the silica tube experiments conducted so far have been of the so-called "quench type." The evacuated tubes are heated in muffle-type cylindrical furnaces with external dimensions of about 18" in length and 10" in diameter, and with a heating chamber of about 1" in diameter. The Nichrome windings are arranged to minimize the temperature gradient to less than 0.5°C over the tube length. At the termination of such experiments the silica tubes are plunged into cold water; cooling to room temperature is achieved in 3-5 seconds. Numerous differential-thermal-analysis (DTA) experiments have also been performed on sulfide materials. In these experiments, silica tubes with a thermocouple well are used. Experience has taught us that heating and cooling rates of 3°C/min give optimum effects, as recorded on the DTA charts. In addition, X-ray diffraction examinations of powdered materials at elevated temperatures have been performed

with the use of special silica tubes or capillaries as sample containers, with a wall thickness of 0.01 mm and outside diameter of 0.2–0.3 mm.

Silica tubes are rigid, and although the vapor volume can be minimized, it cannot be eliminated in closed reaction vessels made of this material. The pressure attained in such tubes is determined by the bulk composition of the reaction materials. Usually we know little more about the pressure than that it is lower than the pressure over pure solid or liquid sulfur at the same temperature. Some data on such pressures were obtained in the past by the Bodenstein-type silica spiral manometric method (Bodenstein, 1899), and more recently new data have been obtained by the electrom tarnishing method (Kordes and Rackow, 1952; Barton and Toulmin, 1964).

Methods have been developed also for experimentation under confining pressures exceeding those of the system, utilizing as reaction vessels ductile materials that will not react with sulfur (Kullerud and Yoder, 1959). Gold has been found to serve this purpose. Under confining pressures imposed by means of H₂O or argon gas in various types of pressure vessels (such as Tuttle or cold-seal vessels, or internally heated bombs), the gold tubes collapse around the condensed materials, and vapor space is effectively eliminated. Sulfide- and arsenide-type systems can now be investigated by quenching as well as by DTA experiments over wide temperature and pressure ranges, limited only by the pressure-temperature curve for the melting of gold.

New techniques have been developed for preparation of polished sections by utilizing cold setting plastics as mounting media. Good quality sections are now routinely prepared in a matter of minutes without application of high pressures or temperatures that might distort or destroy mineral structures. Upon termination of an experiment, the products can be identified by X-ray powder diffraction and in polished sections, and the next experiment can be prepared in 45 minutes to an hour. This represents an enormous saving of time, since previously the preparation of a polished section alone required at least 24 hours.

A new tool, which so far has not been used very much in the study of sulfide-type phase equilibria, but which holds considerable promise for future research, is the electron probe. Analyses of coexisting phases in synthetic assemblages produced in one experiment can give exact compositions which we now must determine by making dozens of runs. Theoretically the electron probe makes it possible to determine quenchable phase relations in a condensed system at a given temperature by one analysis of each of the coexisting phases in each univariant field. In other words, an isotherm can be outlined by as many experiments as there are univariant fields in the system.

CLASSIFICATION OF BINARY SYSTEMS

Sulfide-type systems are generally assumed to involve selenides and tellurides in addition to sulfides. Arsenide-type systems are assumed to involve not only arsenides but also antimonides and bismuthides. When we consider melting relations and the behavior of compounds in binary sulfide, selenide, telluride, arsenide, antimonide, and bismuthide systems, however, it becomes apparent that the above assumptions are not generally valid. A compilation of available experimental data on melting relations in about 180 pertinent binary systems was presented by Kullerud (1970). A considerably compressed version of the original tabulation is given in Figure 1. Here each of the IVA, IIIA, IIB, IB, VIII, VIIB, and VIB groups of elements is allotted one line in the first vertical column, whereas in the original table one line was given to each of most elements in each group. The staggered horizontal

row lists sulfur, selenium, tellurium, arsenic, antimony, and bismuth in that order. The elements included in the VA group listing are As, Sb, and Bi; those of IVA are Ge, Sn, and Pb; those of IIIA are Al, In, and Tl; those of IIB are Zn, Cd, Hg; those of IB are Cu, Ag, and Au; those of group VIII are Ni, Pd, Co, and Fe; that of group VIIB is Mn; and those of VIB are Cr, Mo, and W.

In each of the S-Se, S-Te, and Se-Te systems homogeneous liquid exists above the liquidus over its entire length. Congruently melting compounds do not exist in these systems. All the other sulfide and selenide systems contain liquid-immiscibility fields and at least one, or a maximum of two, congruently melting compounds. The arsenide and antimonide systems, in contrast, do not contain liquid-immiscibility fields; their liquids are homogeneous across the individual binary systems. A number of these systems contain no congruently melting compounds, some contain one, some two, and some three. It is interesting that the S-As, S-Sb, S-Bi, and Se-As, Se-Sb, and Se-Bi systems behave as sulfide-type, not as arsenide-type systems. In Figure 1 it is noted, from the heavy lines separating the systems that contain immiscible liquid fields from those that contain homogeneous liquids, that the telluride systems in general behave like arsenide systems. The only exceptions are offered by the IIIA and IB group elements. Bismuthide systems are noted to behave generally as arsenide systems, although a number of exceptions exist.

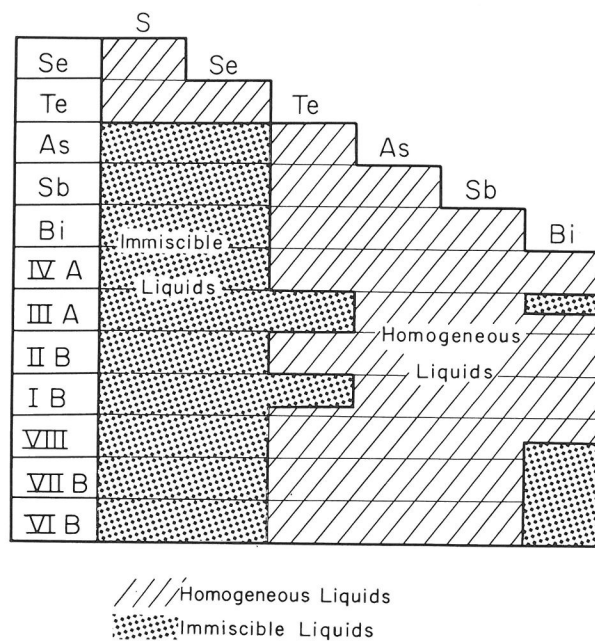


FIG. 1. Schematic presentation of melting relations in binary sulfide, selenide, telluride, arsenide, antimonide, and bismuthide systems. All sulfide and selenide systems, with the exception of S-Se, S-Te, and Se-Te, contain at least one, and a maximum of two, fields of liquid immiscibility. Arsenide and antimonide systems do not contain such fields. Almost all telluride and most bismuthide systems are of the arsenide type.

Figure 1 shows that the telluride systems cannot be classified as of the sulfide type. Most binary telluride systems are of the arsenide type. Of the telluride systems represented in ores, only those involving copper and silver are of the sulfide type. We must, therefore, if we are to classify systems from the melting behaviors, limit ourselves to sulfides and selenides with the term sulfide-type systems.

In the following we shall confine our discussion to sulfide systems, although it will apply to selenide systems as well. These systems can be subdivided into three types. About one half of the systems on which information exists contain two liquid-immiscibility fields, as seen in Figure 2. Here one liquid-immiscibility field occurs in the composition region between the metal and a sulfide phase and another between the sulfide phase and sulfur. Usually these systems contain one congruently melting compound, but some may contain two. Examples of this type, which we will refer to as type 1, are provided by Sb from group VA; Ge, Sn, and Pb from IVA; Tl from IIIA; Zn, Cd, and Hg from IIB; Cu and Ag from IB; Mn from VIIB; and Cr from VIB.

The second type, shown in Figure 3, features a eutectic between the metal and the sulfide phases and a liquid-immiscibility field between the sulfide phase and sulfur. Again one or two congruently melting compounds may exist, the systems with one such compound being the more common. Examples of type 2 are provided by Bi from group IA; and Ni, Co, and Fe from group VIII.

The third type, shown in Figure 4, features a liquid-immiscibility field between the metal and the sulfide phases and a eutectic between the sulfide phase and sulfur.

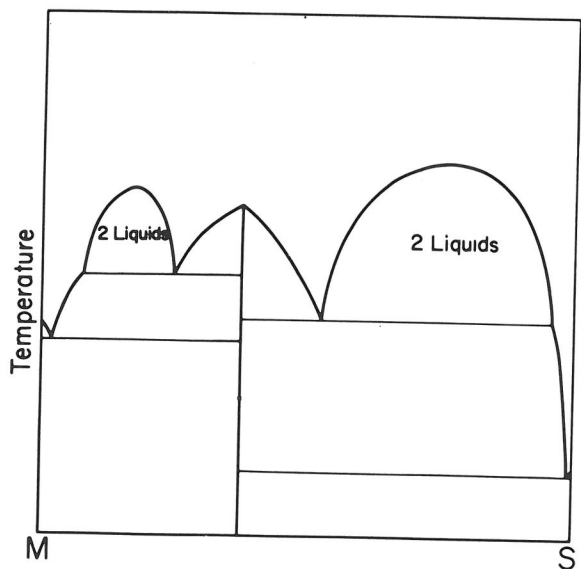


FIG. 2. Melting relations in type-1 binary sulfide or selenide systems are characterized by one liquid immiscibility field in the composition range between metal (M) and a congruently melting compound and by a second liquid immiscibility field in the region between the compound and sulfur or selenium.

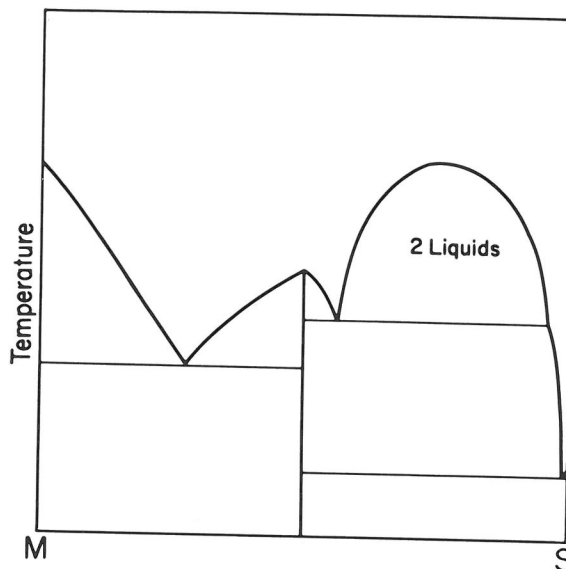


FIG. 3. Melting relations in type-2 binary sulfide or selenide systems are characterized by the appearance of a eutectic in the region between metal (M) and a congruently melting compound and by a liquid immiscibility field in the region between the compound and sulfur or selenium.

Examples of type 3 are provided by As from group VA and apparently by Al from group IIIA.

The compiled data do not convey the impression of orderly grouping of one versus two liquid-immiscibility field systems. A rigid classification is premature, mainly because we lack knowledge of melting relations in the sulfur-rich portions of many systems. Recently methods

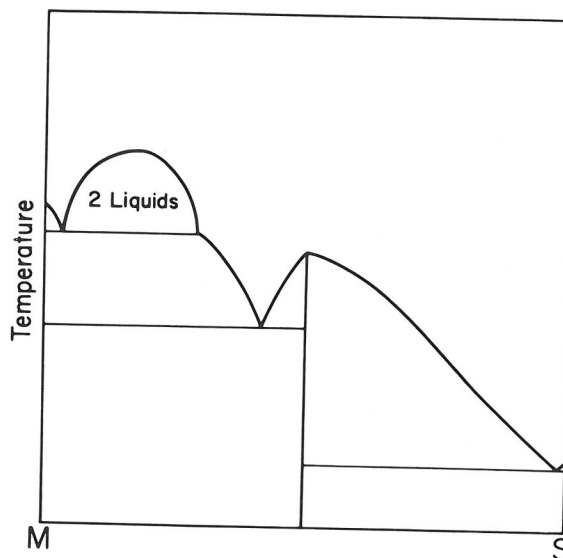


FIG. 4. Melting relations in type-3 (perhaps nonexistent) binary sulfide or selenide systems are characterized by the appearance of a liquid immiscibility field in the region between the metal (M) and a congruently melting compound and by a eutectic in the region between the compound and sulfur or selenium.

have been devised to yield this kind of information, but only the sulfur-rich portions of mineralogically important systems have been investigated so far. Additional studies of remaining sulfide systems can only increase the number of systems containing two fields of liquid immiscibility.

It is interesting to note that those systems that contain a true compound¹ also contain two fields of liquid immiscibility. In these systems one liquid-immiscibility field occurs on the metal side of the true compound and one on the sulfur side.

Perhaps the empirical rule, emerging from the compiled data and to which no exception is known, that all binary metal-sulfur systems contain one or two fields of liquid immiscibility, may be expanded. The extended rule would include the statement that when a true compound occurs in a binary metal-sulfur system, fields of liquid immiscibility exist on the metal side as well as on the sulfur side of the compound. It does *not* follow that a compound is "true" if liquid-immiscibility fields occur on both its metal and sulfur sides.

The metal-sulfur systems without exception each contain one or two congruently melting compounds. Classification of these systems based on the number of such compounds does not appear feasible at this stage.

CONDENSED SYSTEMS

Most of the binary, many of the ternary, and a few of the quaternary condensed systems containing the common sulfide-type minerals have been investigated in some fashion from liquidus temperatures to about 250°C. In addition, a considerable number of telluride, arsenide, antimonide, and bismuthide systems, and some important sulfosalt systems have been investigated. These systems, with the exceptions already discussed, do not behave like sulfide systems, however, and for that reason will not be discussed here.

At temperatures approaching liquidus, reaction rates are rapid and the phase relations are simple. Equilibrium may be achieved in a matter of minutes in most systems. At lower temperatures the phase relations generally become more complicated, owing to the appearance, or sometimes disappearance, of phases. At the same time reaction rates become sluggish and the establishment of equilibrium, even at 500°C, may require years.

The degree of knowledge that we have acquired of phase relations in mineralogical sulfide systems is generally a function of factors such as:

1. The frequency of occurrence in nature of the system's phases and/or of their economic importance. For instance, since pyrite and pyrrhotite are the most common sulfides, the iron-sulfur system has been studied more than any other sulfide system.

2. The upper temperature limit of about 1250°C of existing experimental procedures. The melting relations of

¹ That is, a compound that melts at an invariant temperature to a liquid of the same composition as the solid in the presence of a vapor that has the same composition as the solid and liquid.

many important systems, such as zinc-sulfur and molybdenum-sulfur, cannot be systematically investigated because of this limitation.

3. Sluggish reaction rates at low temperatures. The phase relations in many important systems, such as the iron-sulfur system below 300°C and the iron-zinc-sulfur system below 600°C, remain relatively unknown because of this factor.

Binary systems. Some of the pertinent binary sulfide systems are listed in Table 1. The temperature range over which the phase relations are known is indicated in columns 2 and 5. The letter *L* refers to liquidus temperatures. Columns 3 and 6 list the type, as defined above, to which each system belongs.

From a mineralogical point of view, the most important binary system is that involving iron and sulfur. Table 1 shows that in this type-2 system the phase relations are known from liquidus temperatures to 300°C. Thus information is available on the relations between the common mineral pyrite and the hexagonal high-temperature pyrrhotite phase (Arnold, 1962) and on the thermal stability of monoclinic pyrrhotite (Taylor, 1969). This system is complicated below 300°C. Because of slow reaction rates at low temperature, phase equilibrium studies have not been very successful in determining the stability fields of minerals such as mackinawite (Fe_{1+x}S , where $x \leq 0.07$), greigite and smythite, which reportedly are Fe_3S_4 polymorphs, marcasite, or the numerous superstructures of hexagonal and monoclinic pyrrhotites.

The lead-sulfur system is well known from liquidus temperatures to about 100°C (Kullerud, 1969a). This type-1 system contains only one compound, PbS, equivalent to its only reported mineral, galena. In the Zn-S system, probably also of type 1, one compound, ZnS, is reported to occur in two polymorphic forms. Cubic ZnS, sphalerite, is stable at temperatures below 1020°C, and hexagonal ZnS, wurtzite, above 1020°C (Allen, Crenshaw,

TABLE 1. SOME MINERALOGICALLY IMPORTANT BINARY SULFIDE SYSTEMS, THE TEMPERATURE RANGES OVER WHICH THEIR PHASE RELATIONS ARE WELL KNOWN, AND THEIR CLASSIFICATION BY TYPES AS DEFINED IN TEXT

1.	2.	3.	4.	5.	6.
System	Temperature °C	Classification	System	Temperature °C	Classification
Fe-S	L-300	2	Sb-S	L-150	1
Pb-S	L-100	1	Bi-S	L-150	2
Zn-S	1100-200	1	Ni-S	L-200	2
Cu-S	L-150	1	Sn-S	L-200	1
Ag-S	L-100	1	Mn-S	L-800	1
Hg-S	L-100	1	Cd-S	L-800	1
Mo-S	1100-600	?	Cr-S	1200-600	1
As-S	L-150	3(?)	Co-S	1000-500	2

L refers to liquidus temperatures.

and Merwin, 1912). Wurtzite occurs in many localities where temperatures near 1000°C were never attained. Recent experiments indicate that sphalerite and wurtzite may have slightly differing metal-to-sulfur ratios and therefore may not be polymorphs (Shalimova, Morozova, and Soldatov, 1963; Shalimova and Morozova, 1965; Barnes and Scott, 1966). In the type-1 copper-sulfur system the liquidus relations and the behavior of the chalcocite (Cu_2S)-digenite (Cu_9S_5) solid solution are known above about 400°C (Kullerud and Yund, 1960). Below 435°C the solid solution is intersected by a solvus. We have incomplete knowledge of the behavior of this solvus (Roseboom, 1966) and of the stability fields of at least two minerals, djurleite ($\text{Cu}_{1.96}\text{S}$) and anilite (Cu_7S_4), occurring in the Cu_2S - Cu_9S_5 composition region (Morimoto and Koto, 1970). The stability fields of covellite (CuS) (Kullerud, 1965*a*) and of blue-remaining covellite (Cu_{1+x}S) (Moh, 1964) have been investigated. The silver-sulfur system is also of type 1. It contains only one compound, Ag_2S , which exists in three polymorphic forms (Kracek, 1946). The mineral acanthite is the natural analogue of the low-temperature monoclinic polymorph. The much discussed mineral argentite displays the morphology of the intermediate-temperature, cubic Ag_2S polymorph but gives the acanthite X-ray powder diffraction pattern (Ramsdell, 1943). Argentite then obviously crystallized in the temperature region where cubic Ag_2S is stable and developed the morphology of this form. On cooling, it inverted to the monoclinic polymorph.

The mercury-sulfur system is of type 1 (Kullerud, 1965*b*). It contains only one compound, HgS , which melts congruently at 825°C and occurs in two polymorphic forms: cinnabar, which is stable below 345°C, and meta-cinnabar, which is stable above this temperature.

Two compounds are known in the molybdenum-sulfur system. These are Mo_2S_3 and MoS_2 . Mo_2S_3 has monoclinic crystal structure and is stable between 610°C and its melting point at about 1300°C (Morimoto and Kullerud, 1962). It does not have a mineral equivalent. The MoS_2 compound is stable below about 1350°C; it reportedly occurs in two polymorphic forms. One of these is hexagonal and is represented in nature by the common mineral molybdenite. The other is rhombohedral and reportedly is associated with molybdenite in certain localities (Takeuchi and Nowacki, 1964). Heating of the rhombohedral form at 1000°C produces hexagonal MoS_2 , indicating that a polymorphic relationship does exist (Wildervanck and Jelinek, 1964). Coexistence of the two forms in ores indicates that if they are polymorphs they are not in equilibrium with each other because equilibrium coexistence would demand a difference in composition. Amorphous material of or near MoS_2 composition occurs in a number of low-temperature localities. This material, commonly referred to as "jordisite," crystallizes to hexagonal MoS_2 on heating. Much work remains to be done on the Mo - S system. This work is hampered because determination of liquidus relations requires temperatures so high that

silica tubes cannot be used. At temperatures below 600°C, reaction rates are exceedingly sluggish.

The system arsenic-sulfur is represented in nature by the minerals realgar (AsS) and orpiment (As_2S_3). The AsS compound occurs in two polymorphic forms and melts at 306°C. The low-temperature form, stable below 244°C, has monoclinic crystal structure, and is the synthetic analogue of realgar. The high-temperature form has unknown crystal structure. The As_2S_3 compound has monoclinic symmetry and melts congruently at 316°C (Roland, 1966). The formation of glasses as a result of cooling of liquids below solidus temperatures sets this system apart from those mentioned above and is of considerable theoretical and technical interest. Barton (1969) has shown that a field of liquid immiscibility exists above 797°C in the arsenic-rich portion of the system. A second field of liquid immiscibility may exist in the S - AsS portion of the system. Experimental evidence of such a field is lacking. Formation of glass on cooling of charges in this composition region hampers determination of equilibrium phase relations. Based on existing information, this system should be classified as type 3. This is the only known example of type 3. I believe that future investigations will demonstrate that this system is actually of type 1.

Only one antimony sulfide, stibnite (Sb_2S_3), occurs in nature, and only one compound, Sb_2S_3 , is known in the type-1 Sb - S system. Similarly Bi_2S_3 , equivalent to the mineral bismuthinite, is the only compound in the type-2 Bi - S system.

The type-2 system nickel-sulfur contains the compounds Ni_3S_2 , Ni_7S_6 , NiS , Ni_3S_4 , and NiS_2 , all of which occur as minerals. The stability fields have been determined for all these phases (Kullerud and Yund, 1962). The crystal structures of the minerals correspond to those displayed at low temperatures by the synthetic compounds.

Three compounds— SnS , Sn_2S_3 , and SnS_2 —occur in the type-1 tin-sulfur system, which has recently been studied by Moh (1969). The low-temperature form of SnS is orthorhombic, and its mineral equivalent is called herzenbergite. The high-temperature polymorph, stable between 600°C and its congruent melting point at 880°C, has unknown crystal structure. The Sn_2S_3 compound melts incongruently at 760°C. It reportedly exists in four polymorphic forms, of which the low-temperature orthorhombic form, stable below about 670°C, corresponds to the mineral ottemannite. The SnS_2 compound melts congruently at 865°C. It exists in two polymorphic forms, of which the low-temperature hexagonal form, stable below 691°C, corresponds to the mineral berndtite.

The compounds in the manganese-sulfur type-1 system are MnS and MnS_2 . MnS , which melts at 1610°C, exists in three polymorphic forms (Hansen and Anderko, 1958). The low-temperature green cubic form is equivalent to the mineral alabandite. MnS_2 , which has a natural analogue in the mineral hauerite, has pyrite structure and melts incongruently below 404°C (Kullerud, 1964). This system is very inadequately known.

TABLE 2. SOME MINERALOGICALLY IMPORTANT TERNARY SULFIDE SYSTEMS AND THE TEMPERATURE RANGE OVER WHICH THEIR PHASE RELATIONS HAVE BEEN INVESTIGATED

System	Temperature, °C
Cu-Fe-S	L-200
Zn-Fe-S	1000-600
Pb-Fe-S	750-300
Ni-Fe-S	L-400
Mo-Fe-S	1000-500

L refers to liquidus temperatures.

The cadmium-sulfur system contains one compound, CdS, which melts congruently at 1475°C. Two minerals are reported to have CdS composition. These are greenockite, which has hexagonal wurtzite structure, and hawleyite, which has cubic sphalerite structure. The hexagonal form is apparently the low-temperature polymorph (Rittner and Schulman, 1943), but the relationship between these two forms is far from resolved. By comparison with the ZnS modifications, which are isostructural with those of CdS, it is noted that whereas cubic ZnS is stable at low temperature and hexagonal ZnS at high temperature, hexagonal CdS is stable at low temperature and cubic CdS at high temperature.

Minerals of the type-1 chromium-sulfur system have not been reported in terrestrial occurrences but have been found in certain meteorites (El Goresy and Kullerud, 1969). A number of phases exist in this system. $\text{Cr}_{1.03}\text{S}$, which is monoclinic, is stable below about 570°C; Cr_{1-x}S , which is hexagonal, melts congruently at about 1650°C; $\text{Cr}_{2.1}\text{S}_3$, which is stable below about 1100°C and which at low temperatures may include Cr_3S_4 composition, occurs in a high-temperature rhombohedral and a low-temperature monoclinic form. CrS , Cr_2S_3 , and Cr_3S_4 have been reported as minerals; the last, the only one named, is called brezinaite (Bunch and Fuchs, 1969). The type-2 cobalt-sulfur system contains five compounds: Co_4S_3 , which is stable between 932° and 788°C; Co_9S_8 , which has the cubic pentlandite structure and is stable below 833°C; Co_{1-x}S , which is hexagonal, melts congruently at 1182°C (Curlook and Pidgeon, 1953), and decomposes to Co_9S_8 and Co_3S_4 at 464°C (Rosenqvist, 1954); Co_3S_4 , which has cubic spinel structure and is stable below 660°C; CoS_2 , which has pyrite structure and is stable below about 1000°C (Kullerud, unpub. research). Of these compounds, only Co_3S_4 and CoS_2 have mineral equivalents—linneaitite and cattierite.

Ternary systems. The ternary sulfide systems most commonly represented in nature are those which, in addition to iron and sulfur, contain as a third component one of the common metals such as Cu, Zn, Pb, Ni, or Mo. Some of these systems are listed in Table 2. The second column indicates the temperature range over which the systems have been investigated in the laboratory.

The copper-iron-sulfur system contains the common minerals chalcopyrite and bornite, and the less common

phases cubanite and idaite. Experimental studies have outlined the stability fields and phase relations among these minerals and have shown that certain minerals, such as valleriite, which previously were regarded as copper-iron sulfides, do not belong in the ternary system (Yund and Kullerud, 1966).

The iron-zinc-sulfur system contains no reported ternary compounds, but a very extensive solid solution of iron monosulfide in ZnS is demonstrated in nature as well as in experiments (Kullerud, 1953; Barton and Toulmin, 1966). It is conceivable that in the future we will find that a solvus (or solvi) intersects the FeS-ZnS solid solution field at relatively low temperatures. Thus, one or more ternary compounds may exist on the FeS-ZnS join at low temperatures. Such a relationship would explain many seemingly contradictory experimental results, certain zoning patterns, and mineral assemblages involving iron and zinc sulfides.

The phase relations between galena and the iron sulfides have been investigated (Brett and Kullerud, 1967). Ternary compounds do not occur in the iron-lead-sulfur system, and ternary solid solution fields are very narrow indeed. A homogeneous ternary sulfide liquid exists above 716°C.

The nickel-iron-sulfur system contains the important mineral pentlandite ($[\text{Fe,Ni}]_9\text{S}_8$) and the less important minerals violarite (FeNi_2S_4) and bravoite ($[\text{Fe,Ni}]_2\text{S}_2$). The stability fields of these minerals and their phase relations have been determined (Kullerud, 1963a; Clark and Kullerud, 1963; Craig, 1968). In the condensed system, pentlandite is stable only below 610°C, where it forms in a solid state reaction between a pyrrhotite and a Ni_3S_2 -type phase and thus is not a typical magmatic mineral, as earlier interpreted.

The molybdenum-iron-sulfur system contains one reported ternary mineral, femolite ($\text{Mo}_5\text{FeS}_{11}$) (Skvortsova *et al.*, 1964), which has not been synthesized. The only ternary synthetic phase is $\text{FeMo}_4\text{S}_{5.5}$, which is stable from above 1000°C to 535°C (B. Grover, G. Kullerud, and G. H. Moh, manuscript in preparation). A homogeneous, ternary, sulfur-rich sulfide liquid exists in the system above 726°C (Kullerud, 1967a).

Quaternary systems. Very few quaternary systems containing sulfur and three common metals have been investigated in detail, although fragmentary information exists, particularly about the melting relations in many such systems. Two pertinent systems, Cu-Fe-Ni-S (Craig and Kullerud, 1969) and Cu-Fe-Pb-S (Craig and Kullerud, 1967), have been investigated from liquidus temperatures to about 400°C. Quaternary compounds have not been encountered in any of these systems. The copper-iron-nickel-sulfur system includes more than 99 percent of the sulfide minerals occurring in magmatic deposits of the Sudbury type. Knowledge of the system over a large temperature range enables us to follow the path of crystallization of homogeneous sulfide liquids of pertinent compo-

sition to form a homogeneous pyrrhotite-type phase, which on continued cooling exsolves chalcopyrite and pentlandite. The developments of the typical sulfide mineral assemblages of the Sudbury-type ores thus can be convincingly demonstrated.

Galena occurs with copper-iron sulfides in numerous localities, and the investigation of the copper-iron-lead-sulfur system has delineated the stability fields where galena can coexist with minerals such as chalcopyrite, bornite, cubanite, and idaite. A homogeneous sulfide liquid, rich in Pb and Cu, occurs in this system to temperatures near 500°C. Such liquids are of particular interest to economic geologists because they indicate a possible enrichment process for copper and lead in certain ores.

Very few if any ores exist that do not contain major components in addition to copper, iron, lead, and sulfur. The most common such additional component is zinc. The five-component system Cu-Fe-Pb-Zn-S includes a very high percentage of the sulfide minerals of many ores, and knowledge of this system would add much to our understanding of mineral assemblages in such ores. Progress on this complex system is hampered by the difficulties presently encountered in the Fe-Zn-S system.

PRESSURE EFFECTS

In condensed systems very small changes in pressure commonly have a great effect on the stability of minerals and mineral assemblages. For instance, in the condensed iron-sulfur system, pyrite is stable to about 580°C when the sulfur pressure is 1 mm of mercury and to 690°C at 1 bar of sulfur pressure (Allen and Lombard, 1917). Thus an increase in pressure of 1 bar increases its stability by more than 100°C.

When the vapor phase over such systems is eliminated by confining pressures transmitted through the walls of ductile reaction vessels, the systems become relatively insensitive to pressure variations. For instance, pyrite is stable to about 745°C at a confining pressure of 20 bars and only to 770°C at 2000 bars (Kullerud and Yoder, 1959).

Our knowledge of the effect of high confining pressures on sulfide phase equilibria is very sketchy and fragmentary. No one system has been systematically investigated at a selected high pressure. Some information does exist, however, on the behavior of certain minerals and compounds over considerable pressure ranges. As a general rule it appears that pressure complicates phase relations, inasmuch as numerous phases that do not occur in the condensed systems become stable at high confining pressures.

Extensive solid solutions are common among phases in condensed sulfide systems. When these solid solutions are exposed to confining pressures, the positions of the solvi shift to decrease the size of the solid solution fields. This rule of decrease in solid solution among coexisting phases with increasing pressure has no documented exceptions.

The effect of pressure is generally small, less than 1 mole percent per kbar.

In the iron-sulfur system a eutectic exists in the Fe-FeS composition region at 988°C and 31 weight percent S. Pressure does not measurably influence the temperature of appearance of liquid, but the liquid composition becomes enriched in iron and reaches 73.5 weight percent Fe at 30 kbar (Brett and Bell, 1969). This increase of iron in the liquid phase is in accordance with the general observation that pressure tends to change the liquid composition in the direction of the component that has the higher melting temperature. Stoichiometric FeS has the simple NiAs structure above 139°C and a NiAs superstructure ($a = \sqrt{3}A$, $c = 2C$) below this temperature. The inversion is very rapid and is readily detected by DTA. Under confining pressures in the range from 10 to 20 kbar, the temperature of this inversion decreases markedly and occurs at 95°C at 20 kbar (Kullerud, Bell, and England, 1965). Thus a negative ΔV is demonstrated over a large P - T range. However, X-ray powder diffraction data, obtained above and below the inversion temperature, indicate a positive ΔV for the inversion in the condensed system (Taylor, 1969). Thus, the P - T curve has positive slope at low pressures and negative slope at high pressures. These experimental results indicate that a new nonquenchable FeS polymorph exists over a large P - T region.

The composition of pyrrhotite in equilibrium with pyrite is not measurably influenced by pressures of 1 and 2 kbar (Arnold, 1962). The upper stability curve of pyrite has been investigated to 5 kbar and has a positive slope of about 14°C per kbar (Kullerud and Yoder, 1959).

The NaCl-type structure of galena becomes distorted at high pressures and yields to give orthorhombic symmetry (Bridgman, 1940; Takahashi, Bassett, and Weaver, 1964). Heating of PbS and sulfur mixtures at high pressures reportedly produces PbS₂ (T. Bååk, pers. commun.).

Ag₂S and a considerable number of other minerals and compounds which possess the acanthite-type structure at 25°C and atmospheric pressure have high-pressure polymorphs (Bridgman, 1937; Bell and Kullerud, 1970). Cu₂S has a high-pressure tetragonal polymorph (Skinner, Boyd, and England, 1964). The covellite upper stability curve has been determined to 10 kbar (Kullerud, 1965*a*; Kullerud, Bell, and England, 1968). It has a positive slope of about 9°C per kbar. CuS₂ with pyrite structure has been synthesized at 30 kbar and temperatures in excess of 550°C (Munzón, 1966).

A study of the upper stability curve of polydymite (Ni₃S₄) revealed that the spinel structure is stable only to a few hundred bars pressure. Apparently all M₃S₄ compounds with the spinel structure invert to a hexagonal or monoclinic form under pressure, as indicated in principle in Figure 5 (Kullerud, 1969*b*). This inversion has been observed in numerous minerals and compounds—such as linneite (Co₃S₄), violarite (FeNi₂S₄), and daubréelite (FeCr₂S₄)—and may be exemplified by the greigite-smythite relations in Fe₃S₄.

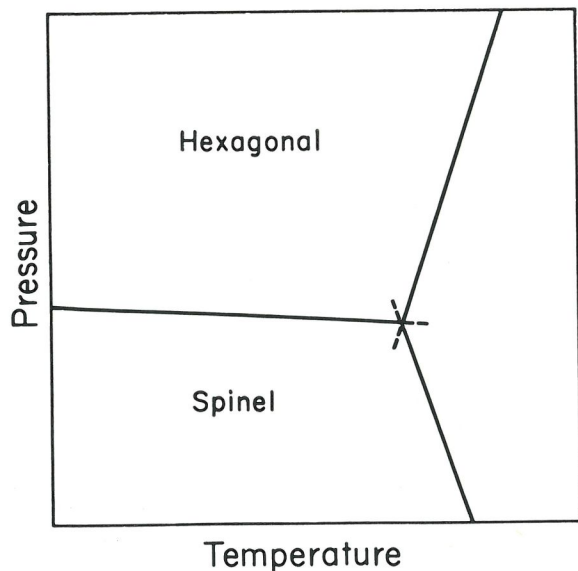


FIG. 5. Pressure-temperature plot showing schematically the behavior of sulfide (and selenide) compounds containing metal and sulfur (or Se) in the 3:4 atomic ratio. At low pressures and temperatures these compounds have spinel structure. At high pressures they are hexagonal (or monoclinic), and at high temperatures they decompose (e.g. Ni_3S_4 , Co_3S_4), melt, or invert to a third polymorphic form (e.g. FeCr_2S_4).

Chalcopyrite in ores believed to have been deposited at elevated temperatures often displays inversion twinning, which originated when this phase transformed on cooling from a cubic to a tetragonal crystal structure. This inversion takes place at about 550°C in the condensed system (Yund and Kullerud, 1966). Under pressure the inversion temperature is lowered markedly and is as low as 400°C at 40 kbar (Kullerud, Bell, and England, 1965).

The upper stability curve for pentlandite, which originates at 610°C in the condensed system, has a negative slope. At 25 kbar pentlandite is stable only below 400°C (Bell, England, and Kullerud, 1964).

SULFIDE-ROCK SYSTEMS

Knowledge of pertinent sulfide systems has provided background for studies of certain complex systems involving the ore components as well as those of typical associated rocks. It has been found by observation in nature (Skinner and Peck, 1969), as well as by experiments (Kullerud and Yoder, 1968), that copper-nickel-iron sulfide liquids are immiscible with noritic type silicate liquids and that the solubility of the sulfide liquid in the silicate liquid is very limited. Such studies also clarify the ubiquitous coexistence of magnetite with Sudbury-type sulfide assemblages and demonstrate how the silicate-magnetite assemblages buffer the metal:sulfur ratio of the ores (Naldrett and Kullerud, 1967). Similar liquid immiscibility fields have been shown to exist between iron-lead sulfide liquids and granitic liquids (Kullerud and Yoder, 1968).

A beginning understanding of the possible reactions that

may be responsible for sulfide ore formation not only in magmatic rocks but also in metamorphic and sedimentary rocks has been achieved through preliminary experiments on sulfide-silicate, sulfide-oxide, and sulfide-carbonate systems at subsolidus temperatures (Kullerud, 1967b).

APPLICATIONS OF PHASE RELATIONS TO MINERALS

Geologists have been motivated to perform studies on phase relations in mineral systems by the belief that applications of laboratory findings can promote an understanding of mineral associations and textures as they appear in ores. The studies on synthetic systems produced many sulfide phases that were not known as minerals. Search for the mineral equivalents in appropriate localities has led to the establishment of a number of new mineral species. Examples are provided by the $\text{Cu}_{1.96}\text{S}$ compound, which was named djurleite when found in ores (Roseboom, 1962; Morimoto, 1962), the Sn_2S_3 and SnS_2 minerals ottemannite and berndtite (Moh, 1969), the Ni_7S_8 mineral godlevskite (Kulagov, Evstigneeva, and Yushko-Zakharova, 1969), the Cu_5FeS_6 mineral idaite (Frenzel, 1959), the mineral called α -bornite (Yund and Kullerud, 1966), and many others.

The studies of thermal and compositional stabilities of minerals and mineral assemblages yielded a number of results that were contrary to existing theories of ore deposition. For instance, the finding that pyrite melts incongruently and under no circumstance can crystallize directly from a liquid near pyrite in composition (Kullerud and Yoder, 1959) stood in opposition to the old theory of magmatic deposition of this mineral. The finding that pyrrhotite is stable over a large temperature range and that its occurrence in ores is largely determined by sulfur fugacity seemingly opposed the old idea that pyrrhotite is a high-temperature mineral. The finding that pentlandite in most ores is produced through an exsolution process from a pyrrhotite-type phase similarly opposed the old interpretation of pentlandite deposition directly from a magma (Kullerud, 1963b; Naldrett, Craig, and Kullerud, 1967).

The laboratory studies also demonstrated that certain compounds, whether synthesized early or late in a series of experiments, always form euhedral crystals. The textures produced in such experiments can readily be interpreted to indicate that the euhedral crystals formed first. An example of this is provided when presynthesized pyrrhotite is heated with a small amount of sulfur. Pyrite will grow in euhedral crystals in a groundmass of pyrrhotite. Some of the time-honored criteria used for interpretation of the sequence of mineral formation in ores indicate that pyrite was earlier in this sequence than pyrrhotite.

During the initial stages of application of experimentally determined systems to ores, some assumptions were made that in retrospect were rather naive and clearly not valid. One such assumption was that equilibrium existed between coexisting phases when they were deposited and that these equilibrium assemblages were quenched when

the ores cooled and remained unchanged through geological time. This assumption was convenient for the application of synthetic phase equilibrium diagrams. Application demonstrated, however, that sulfide mineral assemblages are not quenched and preserved in ores but change and reequilibrate extensively during cooling or metamorphism. Evidence of such reequilibration is now so plentiful that it cannot all be listed. It suffices to give a few examples from typical mineral assemblages found in the Sudbury ores. These ores crystallized at temperatures near 1000°C (Naldrett and Kullerud, 1967). The ores presently consist of pentlandite, which is stable below 610°C; chalcopyrite of CuFeS_2 composition, which can exist only below about 200°C; superstructure-type hexagonal and monoclinic pyrrhotites, stable well below 200°C; and pyrite-pentlandite assemblages, stable only below 200°C.

However, there is also evidence to indicate that reequilibration was not effective to temperatures presently existing in the ores. Pyrrhotite and pyrite, which commonly coexist, did not react to form greigite or smythite.

Careful study of each mineral and mineral pair shows that they respond in various degrees to changes in temperature and pressure. The degree of adjustment depends on a large number of factors, such as rate of cooling, type of metamorphism, bulk composition and mineral type, trace elements, time, presence or absence of solutions, and grain sizes. It is clear that in closed ore systems in which the present mineral assemblages represent the bulk composition of the ore deposited originally, pertinent phase equilibrium diagrams can be used to decipher the path of reequilibration. This has been done successfully for the Sudbury ores (Naldrett and Kullerud, 1967). Use of these diagrams can inform us about the relative rates of reequilibration of existing phases but not about absolute rates. Most ore systems were not closed, and losses or gains of volatile components like sulfur or oxygen may have changed their mineralogy significantly since original deposition occurred. Attempts to decipher the equilibration processes for such ores through use of the phase equilibrium diagrams dictated by present mineralogy would be doomed to failure.

The applications have taught us that solid solutions among sulfide minerals are not suited for purposes of geological thermometry. In theory the principle of such thermometers is sound, but in practice the ores do not cooperate.

Experimentally determined stability curves of individual minerals and mineral assemblages delineate the pressure-temperature fields within which these phases formed in ores. The fugacity of sulfur over a number of sulfide assemblages has been determined at various temperatures. Considerable knowledge exists on the partial and total pressures and temperatures attained when many ores were deposited.

Applications of determined phase relations to mineral assemblages demonstrate that incompatible mineral assemblages are more common in shocked meteorites than in

terrestrial ores. Because of the fast rate of reaction in sulfide systems at elevated temperatures and pressures, the sulfide minerals respond to shocks that are too mild to be recorded by silicates or oxides. The sulfides, therefore, may be used as sensitive indicators of shock.

FUTURE DEVELOPMENTS

The mineralogist's dream of being able to specify the conditions attained during and after ore deposition by use of phase relations determined in the laboratory has not come true as yet. Although the initial hurdles blocking progress in research have been cleared and substantial knowledge has been gained on sulfide systems, much work remains to be done in the future. Some of this work involves more or less routine explorations of phase equilibria in additional two-, three-, and four-component systems that are represented in ores. Some of the studies that clearly should be performed have been hampered because required methods and equipment have not been developed. Most of the work that must be done has been clearly outlined for us, however, as a result of applications to ores of the systems that have already been studied.

Such applications have not only demonstrated shortcomings in laboratory research efforts but have also pointed up entirely new areas for rewarding future investigations.

Reequilibration among minerals during cooling and metamorphism of ores demonstrates the need for systematic studies of the kinetics of pertinent systems, as well as of the low-temperature phase relations of many systems whose behaviors at elevated temperatures already are well known.

The kinetic studies must be performed on closed systems whose phase equilibrium relations are known as well as on systems whose compositions can be gradually changed in controlled experiments. It is hoped that studies of this kind will decipher the history of the ores, will reproduce and explain some of the many fine textures observed in polished sections, and will provide new criteria for derivation of paragenetic sequences. Applications of such results to data obtainable from ores by modern polished section microscopy and new microanalytical techniques may lead to a breakthrough in our understanding of mineral enrichment processes.

The exploration of low-temperature phase relations in most dry sulfide systems is hampered by sluggish reaction rates. We need new methods capable of yielding equilibrium data at least down to 100°C in a matter of days or weeks. Studies on alloys have indicated one such method. Metallurgists have found that addition of certain elements in the parts-per-million concentration range to some simple systems will increase reaction rates by as much as 9 orders of magnitude, whereas addition of other elements will retard reaction rates several orders of magnitude. Such small amounts of selected additives do not measurably influence the phase equilibrium relations in sulfide systems. Selected trace elements may, therefore, be em-

ployed to increase reaction rates for achievement of equilibrium at low temperatures in short periods of time in certain systems. Other trace elements may be used to decrease reaction rates in other systems and thus make it possible to quench individual phases or assemblages that are nonquenchable in the pure systems.

Reaction rates in some systems are considerably increased when the sulfides are submerged in a liquid produced from a mixture of low-melting chlorides. This method should be explored more fully. Precipitation of sulfides from aqueous solutions may be one of the best approaches to unravelling low-temperature phase relations. The aqueous systems contain many major components in addition to those present in the dry systems, however, and the correlations between the two are commonly not clear. Experimental comparison of the dry and wet systems can be obtained by investigations of both at a given temperature sufficiently high for achievement of equilibrium. If the phase relations in the dry system can be inferred from data obtained in the wet system at a temperature where equilibrium is attainable in both, then the wet system may also serve to produce equilibrium data for the dry system at low temperatures.

The limited number of high-pressure experiments performed so far on sulfides has shown that all sulfides, with the possible exception of those having the pyrite structures, have high-pressure polymorphs. Many of these forms, stable at pressures below 10–12 kbar, must have once existed in ores; others, stable at much higher pressures, may presently exist in the earth's interior. Systematic high-pressure studies on sulfide minerals may cause us to revise our views on ore deposits as well as on the structure of the earth.

The recent emphasis on meteorite mineralogy has led to the discovery of about twenty-five new opaque minerals, most of which are sulfides. These sulfides not only occur in systems that have not been investigated but some of them represent entirely new mineral types. Djerfisherite, $K_3(Cu,Na)(Fe,Ni)_{12}S_{14}$, as an example, represents a type that contains K and Na as well as the customary heavy elements. In addition, probe analyses of meteorite minerals have demonstrated existence of sulfide solid solutions containing large percentages of elements like Ca, Mg, Cr, and Ti, which are not chalcophile under terrestrial conditions. The meteorite studies, and most recently the moon studies, have pointed to a considerable number of new sulfide systems, for example Fe-Ti-S, that should be investigated.

As demonstrated by variation in mineralogy and chemistry, equilibrium commonly cannot have existed between mineral assemblages found physically separated in ores, although minerals that were in physical contact with one another may at some time have formed individual equilibrium assemblages. Some or all of these assemblages, however, may have existed in equilibrium with a common homogeneous gas, vapor, or liquid phase. The fugacity of sulfur in this phase, therefore, determined the degree of "sulfidation" of each assemblage. For this reason it is often useful to express phase relations in terms of fugacity versus composition or fugacity versus temperature, or in similar types of diagrams. In order to do so we must obtain far more data on the fugacity of sulfur over common univariant assemblages at temperatures ranging from about 25° to 1000°C. Valuable data have been obtained by silica spiral manometric methods, by which total vapor pressures over the systems are obtained; by the electrum tarnishing methods, which produce data on sulfur alone provided other volatiles are not present; and by dew-point methods. These methods do not readily produce data of required precision at high and low temperatures, nor do they inform us about the relative concentrations of the numerous sulfur species in the vapor phase. Perhaps mass spectrometric methods can give us such data in the future.

Investigations of reactions between rocks and sulfides have just begun, and so far we have studied mainly the effects of pure sulfur on silicate and carbonate minerals and rocks. This type of research must be expanded to involve sulfur in various vapor species from H_2S to SO_2 .

Much systematic work remains to be done to clarify the behaviors of sulfides over a wide range of confining pressures. We have been successful in developing equipment for differential thermal analysis at high pressures and have found that many sulfides possess high-pressure polymorphs that cannot be preserved to normal pressures and temperatures. It is necessary, therefore, that we develop equipment for obtaining precise X-ray powder diffraction data on sulfide materials at high pressures and temperatures.

Knowledge of phase relations in synthetic sulfide systems is increasing at a steady rate. Application of this knowledge to ores is lagging behind, and the gap is widening. Real progress in the understanding of why, when, and where ores form depends to a large extent on integration of laboratory and field efforts, and we must apply ourselves increasingly to this end in the future.

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