REPORT ON S.E.G. SYMPOSIUM ON THE CHEMISTRY OF THE ORE-FORMING FLUIDS
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EDWIN ROEDDER

INTRODUCTION

During the week of August 31–September 4, 1964, a group of 46 scientists\(^1\) from a variety of fields met to report on those portions of their recent and current research that were pertinent to the study of the chemistry of the ore-forming fluids, to exchange data and information on experimental techniques, and to discuss the most favorable directions for future research. The meeting was under the aegis of the Society of Economic Geologists, and was made possible by a grant from the National Science Foundation covering travel and living expenses of the participants. The meeting was one of a series proposed some years ago by R. M. Garrels in his report to the Society as Chairman of the Research Committee. All arrangements for the meeting were made by an Organizing Committee, set up in 1962, consisting of H. L. Barnes, E. N. Cameron, H. D. Holland, C. Meyer, and E. Roedder (Chairman). The Committee profited, however, by many suggestions from a number of individuals. The meeting was held on the campus of Princeton University, Princeton, N. J.

Attendance at the meeting was limited severely by several considerations, only one of which was financial. Although it was obvious that many geologists not only could profit from attendance, but could also contribute to the meeting, it was felt that the informal atmosphere engendered by a small group would promote a freedom of expression that would be impossible in a larger one. The major goal of the meeting was to encourage and guide further research in the field through the free interchange of ideas among active workers. The Organizing Committee was therefore instructed to extend invitations on this basis. In addition to those from the U. S. A., eight of the participants were from five countries overseas and from Canada.

A series of ten technical sessions was set up, in a time sequence designed to cover the major facets of the subject with as much continuity as possible. These sessions were as follows:

1. Mineral stability and phase assemblages: their application to ore-forming temperatures and pressures.
3. High-temperature solution chemistry of sulfides.

\(^1\) Names and addresses are listed at the end of this report.
5. High-temperature solution chemistry of silicates and the generation of ore fluids.
6. Hydrothermal fluids as deduced from wallrock alteration; the thermal regime.
7. Hydrothermal fluids as deduced from fluid inclusions and hot springs.
8. Hydrothermal fluids as deduced from isotopic studies.
9–10. Hydrothermal fluids as deduced from mine studies, zoning, etc.

Each three-hour session consisted of three or four semi-formal presentations, plus some short talks, with considerable informal discussion during and after each. The remainder of each day was available for informal discussions and relaxation.

In order to encourage informality at the meetings, and free discussion of unpublished and incomplete work, no direct publication was planned, other than this summary of the highlights. Large portions of the contributions either have been or will be published in articles by the participants. The main purpose of this summary is to report to the general membership of the Society the trends in thought on these subjects, as brought out in the symposium, and to call attention to the pertinent research activity, both published and publication pending, in the numerous disciplines involved. A book dealing with the same general subject as the symposium is now in preparation, but is being handled as a completely separate entity.

1. MINERAL STABILITY AND PHASE ASSEMBLAGES: THEIR APPLICATION TO ORE-FORMING TEMPERATURES AND Pressures

P. B. Barton, Jr., discussed the significance of recent experimental studies on sulfide systems to the problem of establishing the environment of ore deposition. The major variables controlling sulfide mineralogy are temperature and the fugacity of sulfur; total pressure is of minor significance.

The carefully determined thermochemical properties and phase relations of the important system Fe-S provide a firm basis for understanding other, more complex, sulfide systems. For example, an extensive study of the system Fe-Zn-S shows that the present use of the iron content of sphalerite as a geothermometer is not warranted. However, the iron content of sphalerite has a great deal of potential as a thermometer when, and if, proper calibration is obtained at low temperatures and at known activities of FeS.

A diagram having temperature and fugacity of sulfur as its coordinates is a very useful mode of representation of the geologically significant aspects of sulfide phase equilibria. Numerous mineralogically important sulfidation equilibria (e.g., pyrrhotite + S₂ = pyrite; chalcopyrite + S₂ = pyrite + bornite; fayalite + S₂ = magnetite + quartz + pyrrhotite; or silver + S₂ = argentite) form a grid on such a diagram; the array is analogous to Bowen's petrogenetic grid. The probability of assemblages such as silver + argentite, or digenite + covellite, or tennantite + enargite actually controlling (or buffering) the sulfur fugacity in a real ore fluid is remote, because the quantities of any of these potential buffers are usually small relative to the amount of
ore fluid that may consume or supply sulfur. Some pyrite + pyrrhotite ores might be an exception to this generalization.

Calculations based on measurements with sphalerite, galena, chalcopyrite, and pyrrhotite suggest that substitutional solid solutions are much more nearly ideal in their thermochemical properties than are defect solid solutions.

Many different thermometers are possible in ore mineral assemblages, and the distribution of trace elements between coexisting phases may eventually provide a number of them for cross-checking, but there are serious problems in sampling, analysis, and calibration that must be solved before they will have maximum utility.

R. Yund discussed his experimental work on stable assemblages in the system Cu-Fe-S at temperatures of 500° C and lower. There are many invariant points in this system that may be of geological significance. He has found three different modifications of cubanite, one of which may be the “chalcopyrrhotite” found in nature. Heating experiments also confirmed that some natural “valleriitites” are apparently a mixture of a chalcopyrite-like polymorph and magnesium-aluminum hydroxide on a submicroscopic scale.

Yund feels that an intensive effort should be made to extend sulfide experimental studies down into the geologically more significant but experimentally very difficult lower temperature ranges. Thus a one-year run showed that chalcocite and pyrite, a very common natural assemblage, is not a valid equilibrium pair at 100° C. The so-called “X-bornite,” frequently found in low-temperature environments such as the uranium and redbed copper ores, has about one-half of 1 percent excess sulfur, and presents some very interesting phenomena upon heating to 20° to 200° C for periods up to one month. It is not known whether it is a polymorphic form of bornite or a separate phase of different composition. It is formed only at low temperatures. Yund also reported on low-temperature work at Brown University on the system silver-copper (with A. Thompson) and on the distribution of Zn-65 between galena and pyrite (with B. Giletti). Equilibrium was very slow in both cases.

On the other end of the temperature scale, R. Brett noted that post-ore dikes at Broken Hill, Australia, are cut by veinlets of Fe-Pb sulfides, and so he and G. Kullerud made some studies of the system Fe-Pb-S. First melting in this system occurred at 717° C. With added components such as ZnS, it thus appears possible to obtain such a rheomorphic sulfide melt at < 700° C.

B. J. Skinner discussed various factors controlling the kinetics of solid state reactions in sulfides. Inasmuch as we must be able to specify the state and composition of sulfide minerals at their time of formation in order to use sulfide phase equilibria to decipher the physico-chemical environment of ore deposition, kinetic studies will be at least as important to an understanding of ore formation as equilibrium studies.

Quenching rates for sulfides must be much faster than for carbonates and silicates. Within the sulfides it is a general rule that the higher the metal/sulfur ratio, the more metallic the properties of the sulfides, and the faster the solid state reaction rates. Thus, pyrrhotite reactions are faster than pyrite, and chalcocite reactions are faster than digenite, which in turn are faster than those for covellite. The reaction velocities for metal sulfides may also be
roughly tied to the bonding and coordination between metal and sulfur, and to the position of the metals on the periodic table.

The lower reaction rates found in the compounds with lowest metal/sulfur ratios means that the most easily quenched compounds are also those with the lowest temperatures of maximum stability. For example, pyrite, FeS$_2$, which is easily quenched breaks down to pyrrhotite, Fe$_{1-x}$S, plus liquid sulfur at 742° C. Pyrrhotite reacts much more rapidly than pyrite and hence has undesirable quenching properties. The sulfides found in high temperature environments are therefore those least likely to remain unreactive as the rock or ore deposit cools. It is highly improbable, for instance, that any sulfides formed at magmatic temperatures will quench, unchanged, to room temperature, and it is probable that few natural sulfide assemblages may be quenched, unchanged, from above about 300° C. Recognition of these effects is important not only for geothermometry and paragenetic studies, but also for designing and interpreting high-temperature sulfide solubility studies.

The widespread occurrence of cation-disordered structures—structures with a fixed sulfur lattice but completely disordered cations—explains many of the extensive composition fields and rapid reaction rates found in the Cu, Fe and Ag sulfides. Existence of cation-disordered states, with correspondingly high diffusion rates, suggests an explanation of why so few Cu-Fe sulfide minerals are found with compositional zoning. Furthermore, it suggests the possibility that cation zoning may be obliterated at temperatures and rates different from those for anion zoning, for example, zoning of sulfur isotopes. Thus, a study of homogenization rates in such minerals as galena, chalcopyrite, and bornite could lead to estimates of maximum time-temperature heat treatments for minerals after their formation.

2. HIGH-TEMPERATURE SOLUTION CHEMISTRY: COMPLEXING AND STABILITY

E. U. Franch gave a considerable body of experimental data that he and his students and colleagues have obtained on hydrothermal systems at high temperatures, and pressures up to 8,000 atm., including data on the viscosity and dielectric constant for water. The ingenious experimental techniques used permitted obtaining spectrophotometric data, as well as electrical conductivity. Spectrophotometry, with sapphire windows at up to 500° C and 3,500 atm., permitted among other results, the identification of cobalt and nickel complexes in solution. One of the goals of this work was to determine the dissociation constants of water and of a variety of solutes in aqueous solutions. The dissociation of pure water seems to increase both with temperature and density; shockwave experiments by S. D. Hamann, of Sidney, permit determinations at densities as high as 1.7 g/cm$^3$. The conductivity from actual dissociation of the water itself at high temperatures and pressures is sufficient to overshadow the effects of trace contamination that interfere at lower temperatures. The two-phase region in the system CO$_2$-H$_2$O has been determined up to 3,500 atm. The critical curve is interrupted. The upper branch starts from T$_c$ (H$_2$O) at 374° C, proceeds to a minimum temperature of 270° C, and turns
again to higher temperatures. Dissociation at high temperatures in homogeneous mixtures in the system \( \text{CO}_2-\text{H}_2\text{O} \) was found to be negligible, and HCl was found to be a weaker electrolyte than KCl under these conditions. Some data have also been obtained on dissociation in CaCl\(_2\) solutions.

N. I. Khitarov discussed several dynamic studies made in his laboratory concerning the mechanisms of transport of metals in hydrothermal systems. The frequent close association of molybdenite and quartz in nature suggested the possibility of a siliconolybic acid complex as an ore-transport mechanism. Experimental runs made at temperatures up to 450\(^\circ\) C and pressures up to 500 atm. showed that the siliconolybydate ion is stable (i.e., soluble) under these conditions. It will react with the calcium of marble or from plagioclase in granite to precipitate powellite, and with dissolved H\(_2\)S in excess of 0.01 mole per liter to precipitate molybdenite.

Another line of investigation discussed by Khitarov dealt with the transport of lead. He tabulated some analyses of water leaches from natural galena crystals containing inclusions. The amount of lead found in one of these solutions was 0.15 percent of the original galena sample. Synthetic solutions and deep oil-well waters simulating these inclusions (high calcium) were found to dissolve as much as 120 ppm of PbS at room temperature. Other dynamic experiments showed very high solubility of lead chloride in water and steam at temperatures up to 370\(^\circ\) C, and up to 600 ppm of Pb was dissolved from galena by a 0.25N NaCl–HCl solution containing 5–7 ppm H\(_2\)S, at pH 4 and 350\(^\circ\) C. At 100 ppm H\(_2\)S, only 30 ppm Pb was dissolved.

Khitarov feels that both the experimental data and the occurrence of lead with silica show that the presence of water in the magma apparently is sufficient to prevent lead retention in silicate melts in amounts greater than we find by analysis of the average lead content of granitic rocks. He pointed out, however, that there is an enormous unexplored area in the study of such processes, and that the important task consists of the selection of the most significant portions. For this purpose, he feels that working models of such processes must be set up, in accord with the geological data, to guide the general topical investigations.

J. W. Cobble discussed his efforts to obtain, by both theoretical and experimental procedures, reliable values for the thermodynamic functions and stabilities of ions at elevated temperatures. One of the important parameters is the entropy of the ion. The entropy of the ion at higher temperatures can be predicted theoretically, and thus leads to estimates of the heat capacity for a wide variety of species (J. Am. Chem. Soc., v. 86, p. 5377–5404, 1964).

Cobble used estimated and measured heat capacities to predict the high-temperature dissociation constants for water and H\(_2\)S. The second dissociation constant for H\(_2\)S has a large positive heat capacity and hence will cross the first dissociation constant, eliminating the HS\(^-\) ion above this point. Cobble is determining thermodynamic data on solutions up to 300\(^\circ\) C, using a high-pressure twin thermistor titanium calorimeter. He is also making calculations of activity coefficients from high-temperature experimental solubility data.
3. HIGH TEMPERATURE SOLUTION CHEMISTRY OF SULFIDES

H. C. Helgeson discussed recent data on the chemical composition of the brines encountered in geothermal steam exploration near the Salton Sea, California. The brines contain up to 27 percent dissolved solids, primarily composed of NaCl, CaCl₂, and KCl in the mole ratio of 5.4/1.6/1. The concentrations (molalities) of Ag, Cu, Pb, and Zn are 2.5 x 10⁻⁴m, 1 x 10⁻⁴m, 4.2 x 10⁻⁴m, and 9.4 x 10⁻⁵m, respectively. ΣCO₂ ranges from 1.5 x 10⁻⁴m to 1.1 x 10⁻³m, ΣS = 1.3 x 10⁻³m, ΣH = ~ 3 x 10⁻²m, and ΣAg, Cu, Pb, Zn, Fe = 5 x 10⁻⁴m. These data were derived from material balance calculations based on measurements of brine and steam flow-rates and non-condensable fractions together with a large number of brine, gas, and steam condensate analyses; they therefore represent concentrations in the formation fluid at depth. It is particularly interesting to note that the total heavy-metal concentration is 38 times that of total sulfur.

Helgeson believes these parameters, particularly the high chloride with low ΣS, are indicative of the nature of hydrothermal ore-forming solutions in general, and that the geothermal brines reflect the importance of pore solutions in buried sediments as a source of hydrothermal fluids. He pointed out that the K/(Na + K) mole ratio found requires a temperature of 390° C to fit Orville's data for albite and orthoclase in mutual equilibrium with NaCl-KCl-H₂O solutions (as opposed to the measured reservoir temperature of 340° C). The Na/H and K/H mole ratios are consistent with Hemley's kaolinite stability field; however, chlorite and epidote are the predominant alteration minerals in the reservoir rocks, with kaolinite virtually absent. Pyrite is the only abundant sulfide. The lead concentration in the fluid agrees with that predicted by Helgeson's calculations for the system PbS-NaCl-HCl-H₂O.

He emphasized the profound effect of complexing on sulfide solubilities as a function of temperature, pressure, and composition. He considers that the molecular species HCl plays a key role in high-temperature chloride-rich hydrothermal solutions, where it serves as a hydrogen ion scavenger and a common ion link between chloride and non-chloride species. He considers it likely that most sulfides will exhibit solubility reversals as a function of temperature in chloride-rich, low-sulfur solutions, unless ΣH is low. As a consequence of the high degree of formation achieved by HCl, he feels that any metal ion complex involving the hydrogen ion cannot be a significant contributor to sulfide solubilities in most chloride-rich hydrothermal solutions at elevated temperatures.

In sulfur-rich solutions, in spite of a high chloride concentration, solubility reversals generally would not be expected to occur except to the extent that the maximum in the log K(T) curve for H₂S(sq) is reflected in the solubilities with temperature (e.g., Dickson's experimental results for HgS). Hydrogen sulfide complexing of the metals may be important under some conditions, and in a more alkaline, sulfur-rich environment below 500° C, where HS⁻ is more stable than H₂S, bisulfide complexing may contribute significantly to sulfide solubilities (e.g., Barnes' experimental data). However, Helgeson believes chloride-rich solutions with low ΣS to be more geologically realistic than their sulfur-rich counterparts.
Helgeson pointed out that the high degree of formation of the molecular species NaCl in chloride-rich solutions above \( \sim 200^\circ \text{C} \) causes a striking decrease in ionic strength and consequent redistribution of species and change in ion activities with increasing temperature. Thus the formation of simple sulfide and 1:1 chloride complexes are favored above \( \sim 200^\circ \text{C} \). The fact that the molecular species NaCl and HCl become important only above \( \sim 200^\circ \text{C} \) suggests that the chemical controls and mechanisms of ore deposition in low-temperature deposits are quite different from those operating at higher temperatures, providing the basis for a discontinuous classification of ore deposits into epithermal, mesothermal, and hypothermal categories.

Helgeson presented provisional thermodynamic data for silver chloride complexes \( (\text{AgCl})_n \) where \( n = 1, 2, 3, 4 \) up to \( 350^\circ \text{C} \), predicted from solubility data and electrostatic approximations of \( \log K(T) \). He is continuing his computer calculations of sulfide solubilities in hydrothermal solutions and is currently working on the system PbS-AgS-NaCl-HCl-CO_3-S-H_2O-(KAlSi_3O_8-KAlSi_3O_10(OH))_. He has developed predictive equations to calculate the necessary thermodynamic parameters and has worked out computer programs to handle as many as ten components at elevated temperatures. He hopes to define the interaction of complexes in hydrothermal solutions more completely and to further relate them to congruent and incongruent precipitation of sulfides, hydrothermal leaching, zoning, paragenesis, and rock alteration processes.

H. L. Barnes disagreed strongly with the importance that Helgeson placed on chloride complexes and that Cloke (see next entry) placed on polysulfide complexes. For ore transport, he thinks that even 5 ppm ore metal in solution is insignificant and inadequate. He presented experimental evidence that the solubilities of ZnS, CuS, FeS_2, Ag_2S, and PbS in pure H_2S solutions over a wide range of temperature and pH were usually \(<1 \text{ ppm} \). He also presented experimental results that he felt proved that chloride complexes were geologically not even as important as carbonate or fluoride complexes for Zn above about 400\(^\circ\) C. He found that the solubility of ZnS in bisulfide solutions is actually depressed by the addition of 3N NH_4Cl or NaCl up to 200\(^\circ\) C, and he feels that polysulfide complexes are geologically unrealistic as they require a very high pH to form, and are known to be unstable both experimentally and thermodynamically.

Barnes then showed that measurements in bisulfide solutions (up to 10 molal) gave very adequate solubilities (up to 4,000 ppm) as bisulfide complexes of ZnS, CuS, CuS, CdS, PbS, HgS, and Ag_2S. At temperatures above roughly 300\(^\circ\) C, simple sulfide complexes of higher solubility, such as HgS_2^2-, are more probable in nearly neutral ore solutions. In bisulfide solutions the solubility of FeS_2 was only at the analytical background (\( \sim 0.1 \text{ ppm} \)). A variety of carbon-bearing sulfur species may help in this respect, and some do occur naturally. He feels that sulfate is sufficiently low in ore fluids that it may be ignored.

G. K. Csanyeske gave a brief report on some experimental studies on the solubility of galena in strong chloride brines resembling those found in inclusions in Mississippi Valley deposits, with added CO_2 and H_2S, at tem-
temperatures in the range of 100°-200° C. Although as much as 400 ppm lead would dissolve in these fluids at pH 2.5, only 0.2 to 2 ppm was soluble in the more reasonable range of pH 5-7 (all measured at room temperature). Thus Czamanske feels chloride complexes are not adequate for lead transport at these temperatures.

P. L. Cloke first described some dynamic experiments on the apparent solubility of galena and covellite. A solution of 10 percent NaCl, 0.24 molar in HCl, passed over galena at 200° C and 1,000 psi, transported lead equivalent to 1.5 g/l, and the true solubility is assumed to be greater. Covellite yielded no solubility (<1 ppm Cu) under these conditions, but yielded 0.8 g/l at 400° C and 6,000 psi.

Cloke expects a mixture of polysulfide ions at the intersection of the fields of SO₄²⁻, HS⁻, and elemental S on the Eh-pH diagram for sulfur species, and feels polysulfide may be present in ore fluids in amounts about equal to sulfate. Most present evidence indicates a very small field of dominance for polysulfide, too small to be geologically significant. However, some evidence suggests that the field might increase in size at higher temperatures so that any polysulfide formed, e.g. from the reaction of H₂S and SO₄, would remain stable. He showed that bisulfide and sulfate did not react at high temperatures, but that once formed, polysulfides can exist for at least 24 hours in neutral solution at 400° C. There is enough error in the heat capacity data to allow for a significant increase in the polysulfide field, particularly when it is remembered that heat capacities for polysulfides are based only on a 5° temperature interval (25° C to 30° C). It is well known that liquid sulfur changes from mostly ring to mostly chain structure in the temperature interval 30° C to 190° C, but there are no data to indicate whether polysulfides, also having chain structures, likewise increase in stability with temperature. More experimental work is needed before any definitive statements can be made regarding the possible presence of polysulfides in ore solutions.

Polysulfide solutions will dissolve sulfides of Cu, Ag, As, Sb, Bi, Sn, and Zn. Probably gold and galena will also dissolve, but several experiments failed to produce detectable solution of pyrite. The concentration of polysulfide necessary to achieve geologically significant solubility depends critically on the concentration of metal in the ore fluids. With 10⁻⁴ gm/l (Krauskopf) to 10⁻⁶ gm/l (Garrels) the total sulfur concentration may be as low as 10⁻⁸ to 10⁻⁶ molar. Once the metal is in solution as a polysulfide anionic complex, precipitation could occur in many ways. Oxidation by ferric compounds, reduction by graphite, increase of pH by limestone or alteration of silicates, decrease of pH by acid waters, loss of sulfur by pyritization of wall rocks, dilution by ground water, and decrease of temperature or pressure would all cause precipitation. Cloke believes that the reason polysulfides are not found in fluid inclusions, if they were ever present, is that they disproportionate on cooling to form sulfate and bisulfide.

F. W. Dickson described a bomb having a sintered, porous Teflon filter that he has set up for determinations of solubility up to 300°, in systems where precipitation on quenching may cause difficulty. He has work in progress on a variety of hydrothermal systems involving HgS, Sb₂S₃, As₂S₃, SiO₂, Na₂S,
and CaSO₄. The solubilities of cinnabar, stibnite, and orpiment in Na₂S–H₂O solutions increase as a function of temperature over most of the temperature range, and decrease as a function of pressure over the entire range of experimental pressures. Preliminary data on the mutual solubilities of quartz and cinnabar at 200° C and 500 bars show that both phases dissolve appreciably (0.25 wt. percent HgS and 0.40 wt. percent SiO₂ in 1.86 percent Na₂S solution).

4. HIGH TEMPERATURE SOLUTION CHEMISTRY OF CARBONATES AND SILICATES

H. D. Holland first reviewed some work by N. W. Hinners, in reply to Barnes. Hinners showed that at 80° C the solubility of sphalerite in aqueous solutions in equilibrium with a vapor phase containing about 0.5 atm. H₂S first decreases with increasing pH, then remains nearly constant, and finally increases again. The decrease in sphalerite solubility at low pH values can be explained readily in terms of the "acid solubility" of ZnS. In the pH-insensitive region zinc must be present largely in neutral complexes of the type ZnS·(H₂S)ₙ where n is probably 2 or 3. At higher pH values the dominant zinc species is singly charged and probably has the formula ZnS·HS⁻·(H₂S)ₘ where m is either 1 or 2. Addition of NaCl increases the zinc concentration of solutions in equilibrium with sphalerite. The effect is largest in the low-pH region, and smallest in the intermediate-pH region. At a pH of 2 the zinc concentration in 3-molar NaCl is about 100 times greater than in a NaCl-free solution. At a pH of 7 the concentration of zinc (10 ppm) in a 3-molar NaCl solution is about 10 times greater than in a NaCl-free solution. Most of the NaCl-effect in the pH range between 5 and 7 is simply due to the effect of ionic strength on the activity coefficient of the zinc complex in solution. It seems likely that the temperature of formation of much of the sphalerite in mid-continent type lead-zinc deposits was somewhat above 80° C and in the pH range 5 to 7. The effect of NaCl on zinc transport in the fluids responsible for these deposits would be negligible only if comparable concentrations of bisulfide ion were present. There is, at present, little evidence in favor of such a hypothesis.

Holland then discussed work in his laboratory on the solubility of carbonates in hydrothermal systems. The solubility of calcite in CO₂–H₂O solutions at a given temperature increases with increasing CO₂ pressure, and at a given CO₂ pressure, decreases with increasing temperature between 25° and 300° C. The addition of small amounts of NaCl increases the solubility of calcite, but at 100° C the solubility of calcite passes through a maximum near a NaCl concentration of 2 molar. The solubility maximum becomes less pronounced toward higher temperatures. Calcite precipitation in hydrothermal systems due to loss of CO₂ pressure by boiling is certainly possible, but it seems likely that reactions within the solutions which affect the pH, and reactions with wall rocks, are more commonly the cause of calcite precipitation from hydrothermal solutions.

M. Bodine discussed experimental studies he made in Holland's laboratory on trace elements in carbonates. These studies were made because the composition of the carbonates presumably reflects the composition of the ore fluids,
and were done by using homogeneous reactions in which the slow, time-
dependent thermal decomposition of various organic compounds in solution in
the bomb adds controlled amounts of CO₂ to the reactants at the temperature of
the run. The distribution of manganese between liquid and solid (precip-
itating carbonate) was found to be strongly in favor of the solid. The distribu-
tion coefficient at a given temperature remains constant regardless of the
amount precipitated, using the Doerner-Hoskins relationship, indicating that
surface equilibrium but not solid homogeneity is achieved. The coefficients
found varied from about 2.5 at 300° to about 17 at room temperature, but con-
siderable scatter was found, possibly due to inhomogeneous precipitates.

P. Orville discussed several studies of equilibria between water solutions
and feldspars. In reactions between alkali feldspars and alkali chloride solu-
tions, a ten-fold change in total solution concentration (at constant Na/K ra-
tio) did not affect the equilibria, but pressure did cause a shift. Reactions of
plagioclase (plus quartz) with Na–Ca chloride solutions at 700° C showed
a strong fractionation of calcium in favor of the solid phase. Reversible equi-
lbrium is achieved in two weeks. Several portions of the plagioclase series
showed ideal behavior, but there appear to be some discontinuities. Such
studies have many possible applications, ranging from a better understanding
of the chemistry of aqueous salt solutions to a knowledge of subsolidus relations
in feldspars, in addition to the more obvious uses for geologic thermometry and
barometry, or for relating natural ore fluids or inclusion fluids to a given min-
eral assemblage.

5. HIGH-TEMPERATURE SOLUTION CHEMISTRY OF SILICATES AND THE
GENERATION OFORE FLUIDS

K. B. Krausköpf discussed the available evidence for the immediate and
ultimate source for the ore metals, and the various processes whereby they are
concentrated. The association of certain types of ores with certain mafic
igneous rocks is very specific, but the associations with granitic rocks are much
more variable. Although they are ambiguous, there are a number of lines of
evidence for association of some ores with granitic rocks. These include: geo-
graphic association of ore deposits and such rocks; zoning related to them; asso-
ciation of specific elements with specific rock types; high content in the
igneous rock of the same element as in the associated ore deposit (e.g., Sn); age
determinations on ore and rock; and experimental evidence that the process of
concentration is feasible. As to ultimate source, any concentration process
may well be superimposed on a previous concentration process (e.g., what
would happen if a Kupferschiefer were assimilated by a granite?). Volcanic
processes provide a variety of possible concentration mechanisms, and incipient
metamorphism of rocks or older ore deposits is a very reasonable possibility.
Although nonigneous processes may be useful for some types of deposits, such
as ground-water migration for the sedimentary uranium-vanadium deposits,
many sedimentary processes are apparently inadequate. Heating of ground
waters may help, but this adds considerable ambiguity as to the source of the
water.
In discussion of this paper B. Doe showed that the lead isotope data do not
provide anything to contradict the concept of lateral secretion for the origin of
the Mississippi Valley lead-zinc deposits. In the Butte area, they indicate the
source to be old, with a low U/Pb ratio.

C. W. Burnham described a number of the experimental studies undertaken
at his laboratory on the solubility of water in silicate melts, and its effects on
phase equilibria and rate processes. When the water pressure approximately
equals the total pressure, a nepheline melt was found to contain about twice as
much water by weight as an albite melt, and this, in turn, had somewhat more
water than a basaltic melt at the same temperature. At 10,000 atm H$_2$O pres-
sure, the beginning of melting was about the same for basalt, granite, and peg-
matite, with large differences appearing mainly at lower pressures. The crys-
tallization of primary muscovite in high-alumina granites, and of spinel in ba-
salt at high oxygen fugacities, greatly expands the melting intervals of these
rocks. The amount of water dissolved in most melts was found to be a
straight-line function of the square root of the fugacity of water, and hy-
drous granite melts were found to be highly ionized. The miscibility gap in
the granite-water system is very large, and a continuous range of melts ap-
ppears feasible only in high-alkali compositions at very high water pressures.

G. M. Anderson discussed the significance of some of the experimental sili-
cate-water studies in terms of geological processes. The distribution of water
in a melt is affected by both temperature and pressure gradients, but these
effects are probably not as great as previously thought. Thus the Soret effect
does not appear to be important because of the low-temperature dependence of
the solubility of water in silicate melts. The effect of pressure gradients on
water content in undersaturated melts has been recalculated and found to be
less than that given by Goranson. Anderson summarized available solubility
data for quartz and feldspars in aqueous solutions and presented some recent
data on aqueous phase compositions in equilibrium with a pegmatite at mag-
matic temperatures and pressures. Up to 9 weight percent of solids dissolves
in the aqueous phase at 10 kilobars and 650° C. In concentrated alkali chlor-
ride solutions, appreciable gold or platinum (from the containers) is dissolved
in the vapor phase (perhaps 0.1 weight percent) at 600° C and higher.

A. J. Ellis summarized the extensive work that he and his colleagues have
done toward understanding both the mechanics and the chemistry of actual hy-
drothermal fluids that occur in geothermal steam areas such as Wairakei, New
Zealand. These studies indicate the large extent of the Wairakei system,
which covers at least 20 square miles, to depths of more than 4,000 feet, and
hence is much greater than the surface activity would suggest. The total nat-
ural inflow and outflow is very small relative to the volume of hot water pre-
sent, and even the 0.3 km$^3$ of hot water pulled out has apparently not affected
the compositions of the drillhole discharges noticeably. The lifetime of such
systems may be as much as a million years. The work of Steiner has shown
the alteration sequence, from the surface down, to be montmorillonite, mor-
denite, wairakite, albite, adularia, and hydromica. The isotopic composition of
the hot water reflects that of the local ground waters, but the circulation is suffi-
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iciently slow to permit the waters to lie essentially on the boiling curve. The gases present—mainly CO₂ but also some H₂S, N₂, NH₃, CH₄, and even ethane (from buried organic matter)—occur in very small amounts, but still control such equilibria as magnetite vs. pyrite. There are very small amounts of heavy metals in these waters—only 10⁻³ to 10⁻⁴ that of the Salton Sea brines. Ellis has done extensive experimental work on determination of dissociation constants, and their pressure and temperature dependence, as well as solubility studies. He finds that the polythionates generally decompose in water at 200° C to form H₂S and sulfate. The solubility of CaCO₃ in Wairakei water was higher than in an equivalent NaCl solution, presumably due to silica in solution. He also reported some very interesting results of leaching rocks with pure water at temperatures of 300°–600° C. By this method he could obtain a classical “magmatic” water, with up to 500 ppm of salts (mainly NaCl), and containing significant amounts of B, Li, Rb, and Cs. The Na/K ratios obtained agreed with Wairakei waters and with Orville’s data. Heavy metals such as arsenic were extracted from pumice, and he could take much of the copper out of a basalt at 600° C (see next entry).

6. HYDROTHERMAL FLUIDS AS DEDUCED FROM WALL-ROCK ALTERATION; THE THERMAL REGIME

K. H. Wedepohl gave a short report on the leaching of basalts (investigated mineralogically by Sigvaldason) in Iceland by two hot springs, one alkaline (pH 9.5) and the other acid (pH 1.5). The basalts are decomposed in zones a few meters wide around the source. The original rock contained 14 percent Fe₂O₃ (total Fe), 90 ppm Zn, and about 180 ppm Cu. On the basis of TiO₂ as an assumed inert reference material, the alkaline water reduced both Zn and Cu to 80 ppm, and reduced the iron to 8 percent Fe₂O₃. The acid water reduced the iron to less than 0.5 percent Fe₂O₃, and Zn and Cu to less than 10 ppm.

P. Toulmin, 3rd, discussed the factors affecting the thermal regime in any hydrothermal process. The possible heating effects, including hydrothermal alteration and precipitation, are generally rather minor, except perhaps in tectites. The cooling effects are: (1) conduction of the walls; (2) hydrothermal leaching; (3) reversible expansion; (4) irreversible expansion; and (5) mixing with surface water. Calculations by S. P. Clark, Jr. (Yale University) have shown that the effects of conduction into cooler walls are negligible, so that the vertical gradient in the vein is < 1°/km, by any geologically reasonable flow velocity over geologically short times (months or a few years). Hydrothermal leaching, the reverse of precipitation, is generally insignificant in thermal effects. Adiabatic (reversible) expansion would be effective only if long vertical distances were involved. Throttled (irreversible) expansion has considerable possibilities in the high-temperature range, and in the two-phase region, but depending upon the geothermobar followed may cause either heating or cooling. Cooling by throttling would be expected to cause rapid dumping of dissolved material in disequilibrium textures, and this dumping should tend to eliminate the throttle by physical plugging. Ground water will
ultimately move in on the hot zones, and by virtue of rapid convective overturn, may telescope temperature ranges of deposition or quench in high-temperature assemblages.

Toulmin also described a new geothermometer that appears to be promising, based on already known thermodynamic data pertinent to the reaction: biotite + sulfur → alkali feldspar + magnetite (or hematite) + pyrrhotite (or pyrite) + H₂O. Calibration runs are in progress.

J. J. Hemley discussed a variety of experimental hydrothermal studies he has made to clarify understanding of the chemistry of wall rock alteration. His work has concentrated on compositional parameters in the aqueous phase and their control on the formation of alteration minerals and patterns along chemical and P–T gradients in the host rock. Such studies of the aqueous chemistry provide the necessary tie, heretofore lacking, between research on sulfide and alteration mineral genesis, and their interrelationship in the formation of ore deposits. Hemley has been concerned with more accurately extending the curves for feldspar and mica alteration to lower temperatures, and also to higher P–T conditions. The mixed Na–K system is also being investigated, as well as the role of variable silica activity. Experimental phase diagrams showing silica concentration as a function of alkali ion/H⁺ ratios indicate that silica activity is extremely significant. For example, high silica activity lowers the pyrophyllite field and decreases the size of the mica field. The reaction diagrams also indicate the improbability of stabilization of K-feldspar with kaolinite by very high silica activities under hydrothermal conditions, as pyrophyllite or montmorillonite formation is favored. This is in disagreement with Fournier (next entry). Hemley also found that the solubilities of silica phases (quartz, cristobalite, and gel) at 300° C and 15,000 psi show little variability at pH 1 and at neutrality, as a function of change in NaCl or KCl concentration from 0.5 to 4 molar. Work is being done in equivalent systems with sulfate instead of chloride, to understand the occurrence of alunite.

Hemley pointed out the great need for more laboratory-field studies on other types of alteration. The present work is aimed primarily at granodiorite base-metal deposits, but very little has been done on alteration types such as those of the Mother Lode gold or various Canadian Shield deposits.

R. O. Fournier discussed the significance of the alteration sequence he has found around the veins at Ely, Nevada, in comparison with the sequences found by R. Sales and C. Meyer at Butte, Montana, and by F. Gonzales Bonorino in the Front Range, Colorado. The alteration at Ely has been confused in the past by failure to distinguish between the high-temperature (deuterite) alteration to the northeast, and the lower-temperature hydrothermal activity to the southwest. By careful distinction between the alteration of alkali feldspar and of plagioclase, Fournier was able to determine that between the kaolinite and the sericite-quartz zones at Ely is a zone in which first K-feldspar, and then K-feldspar and muscovite, occupy the plagioclase sites (on approaching the vein). He believes this is a consequence of a high concentration of silica in wall rock pore solutions, formed by alteration processes. At the time and place of release of silica by the decomposition of plagioclase, quartz does not precipitate and the activity of silica in solution may become large enough for silica gel
to form. The resulting metastable high-silica activity depresses the muscovite field and permits the assemblage kaolinite + K-feldspar at temperatures below about 250° to 300° C at 1,000 bars pressure. Above these temperatures, at high silica activities, pyrophyllite would form rather than kaolinite. A supersaturated silica solution is a transient condition. Where quartz precipitates, generally near veins, the concentration of silica in solution decreases, and kaolinite and K-feldspar react to give muscovite and quartz.

7. HYDROTHERMAL FLUIDS AS DEDUCED FROM FLUID INCLUSIONS AND HOT SPRINGS

E. Roedder discussed the significance of data from fluid inclusions in ore-fluid research. Although many of the data are only qualitative or semiquantitative at best, and there are numerous sources of ambiguity, fluid inclusions provide a large amount of valuable information on the ore fluids, much of it impossible to obtain any other way. One of the major problems in any inclusion study is to determine the origin of the inclusions—primary, pseudosecondary, or secondary. Only a comparatively small percentage of all inclusions can be proven to be primary, but there are many different mechanisms of inclusion formation that leave evidence permitting such a determination. Inclusion shape is an exceedingly poor criterion for mode of origin, as most inclusions now have considerably different shapes than when originally trapped.

When adequate safeguards are followed, geologic thermometry by fluid inclusions is among the most accurate methods, and certainly is the most generally applicable. Although leakage occurs, a number of independent lines of evidence seem to preclude its being a common feature. Inclusions provide the only data we have on the density of the ore fluids, an important parameter in evaluating the mechanics of mixing with ground waters. Considerable compositional data regarding fluid inclusions in the minerals of ore deposits can be determined by a variety of methods, many of which require little more than a microscope. With few exceptions, the concentration of total sulfur is low, and H₂S is exceedingly rare. The newer analytical techniques, including neutron activation, atomic absorption spectrometry, and mass spectrometry (for both isotopes and gases), are yielding important new data, but the major problem in such work still is the selection and extraction of truly significant samples to analyze.

Evidence of the existence of two immiscible fluids at the time of trapping is surprisingly common. The second fluid (in addition to water solution) may be supercritical CO₂, organic fluids, or steam (i.e., boiling). Evidence was also presented for the separation of, and hence saturation with respect to, immiscible globules of a dense, highly saline (≈ 50 percent NaCl), water-rich phase from granitic magmas at Ascension Island, and for the separation of immiscible globules of dense, supercritical CO₂ during the formation, at considerable depths, of the minerals of the olivine nodules so common in alkaline basalts throughout the world.

D. E. White discussed the occurrence, chemistry, and source of thermal and mineral waters associated with mercury and base metal deposits. He believes
there are fundamental differences in composition between the fluids forming
these two types of deposits. Those of mercury deposits are more dilute than
sea water, and are relatively high in total CO₂, B, NH₃, and hydrocarbons, and
low in Ca and Cl. The waters of base metal deposits, in contrast, typically
have 3 to 10 times the salinity of sea water, with Na, Ca, and Cl as over-
whelmingly dominant constituents.

From this study, White concludes that several different mechanisms may
account for mercury transport. No strong evidence is found for transport in
alkaline (high pH) solutions high in sulfide. Mechanisms that can operate in
nearly neutral solutions of only modest sulfide content are indicated by the hy-
drothermal alteration mineral assemblages as well as the pH values of the
presently associated waters. One mechanism is thermal instability of HgS,
either in the presence or absence of vapor at temperatures above about 150° C.
Complexes involving bisulfide, organic compounds, and ammonia, are all pos-
sibilities that should be considered. Ammonia is a prominent constituent of
the waters, and buddingtonite, the ammonium feldspar recently described by
Erd et al. (1964), is now known from three mercury deposits. In the Cymric
oil field, metallic mercury is precipitated from petroleum, and Hg is relatively
high in the waters and gases. Organic or some nonsulfur-bearing inorganic
complexing is indicated, as these fluids lack sulfur. In discussion of this point
F. W. Dickson pointed out that those waters that are depositing mercury must
be different from those that can transport it, and that sulfide probably was
involved.

In discussing the Na–Ca–Cl brines associated with base metal deposits, in-
cluding data from fluid inclusions and the Salton Sea geothermal brines, White
suggested that the waters may normally be slightly acid and deficient in sulfur,
dependent upon some other source of sulfur for efficient formation of an ore
deposit. Chloride complexes are probably much more important than sul-
fide complexes. These brines may form by at least three mechanisms: (1) as
late-stage magmatic products, with deuteric albition of plagioclase supply-
ing the Ca; (2) as connate waters; Na–Ca–Cl brines are the dominant type of
interstitial water in deep pre-Tertiary sedimentary basins throughout the world,
evidently forming by means of membrane filtration and complex diagenetic re-
actions; and (3) as circulating meteoric waters that dissolve evaporites and
then react with rocks in a geothermal environment. Present evidence sug-
gests that the Salton Sea geothermal brines probably formed by the third
mechanism. The exceedingly low sulfur content of these waters may be due
in part to loss of H₂S to a through-streaming vapor phase. The associated
sediments are now undergoing low-grade metamorphism and hydrothermal
alteration, permitting establishment of some limits on conditions of formation
of chlorite, epidote, and other minerals. A comprehensive study by Harmon
Craig (Univ. California, San Diego) and White of the hydrogen and oxygen
isotopes in many hot spring waters, including the Salton Sea brines, indicates
that local surface waters are the dominant source by far; the oxygen of the
thermal waters becomes enriched in O¹⁸ through exchange with the oxygen
of the rocks.
R. N. Clayton discussed oxygen isotopic equilibria between minerals and aqueous solutions, and mentioned results of a cooperative study of the Salton Sea area with White. From this work it appears that the oxygen of the rocks has become lighter by about 10 per mil, and the waters have become heavier by a similar amount, indicating that roughly equal masses of water and rock are involved. Both silicate and carbonate portions of the rocks have exchanged oxygen with the waters, and available data indicate that these isotopic reactions may have achieved thermal equilibrium in the deeper and hotter parts of the geothermal field.

B. Doe reported on lead isotope studies he has made, and on strontium isotope studies by C. Hedge, both of which indicated that very little if any of the lead and strontium in the Salton Sea brines could have come from a magmatic source such as the associated rhyolitic domes. The lead is of J-type, but not as anomalous as the Mississippi Valley leads.

W. E. Hall discussed briefly the work that he has done in collaboration with I. Friedman on the Mississippi Valley fluorspar-zinc deposits. Starting with a careful study of vug mineral parageneses in southern Illinois, chemical and isotopic analyses of fluid inclusions indicate the original ore fluids to have been connate waters, mobilized by a convection system established perhaps with heat from a buried intrusion beneath a nearby cryptovolcanic structure, Hicks Dome. During the sequence of ore deposition, however, there apparently was an influx of isotopically much lighter waters, possibly of magmatic origin, and at the end stages of deposition the connate brines appear to have been flushed out by fresh, meteoric waters.

8. HYDROTHERMAL STUDIES AS DEDUCED FROM ISOTOPIC STUDIES

I. Friedman discussed C\(^{18}\)/C\(^{12}\) and O\(^{18}\)/O\(^{16}\) studies of limestones adjoining ore bodies in the Mississippi Valley lead-zinc deposits. The two ratios vary with distance from ore, but the C\(^{18}\)/C\(^{12}\) is not always in the same direction. He also reported similar studies made in his laboratory on samples from Providencia, Mexico, by R. Rye. Here the several generations of calcite show a reasonably consistent and parallel decrease in both C\(^{18}\)/C\(^{12}\) and O\(^{18}\)/O\(^{16}\), from unaltered limestones to those calcite crystals formed at the highest temperature. This change in carbon, incidentally, requires considerable amounts of carbon in the ore fluids.

Friedman also discussed the significance of his work with R. Clayton and Donald L. Graf on the deuterium and O\(^{18}\) contents of “connate” waters. From this it appears that all old seawater has been lost, and that present-day connate waters are modified meteoric water, and not modified seawater. Deuterium values show little change and no relation to salinity, but oxygen values show a strong correlation with salinity; presumably the well-known slow increase in chloride content with time is paralleled by gradual equilibration of the oxygen in the waters with the heavier oxygen in the rocks, even at low temperatures, plus possible fractionation during membrane filtration.

M. L. Jensen reported on the work that he and his students have done in attempting to correlate basic geologic knowledge with sulfur isotopic analyses.
(S\textsuperscript{82}/S\textsuperscript{84}) of ore deposits throughout the world. In addition, he interpreted their results in light of laboratory experiments on sulfur-reducing and sulfur-oxidizing anaerobic bacteria, and measurements of isotopic fractionation on volcanic and fumarolic fluids from Japan, Hawaii, and Yellowstone.

Magmatic hydrothermal sulfides (e.g., from all Cordilleran intrusives studied) exhibit a very narrow spread in δ S\textsuperscript{84} values at zero per mil, as do most sulfides that are intimately associated with intrusive bodies. This is suggestive of an upper mantle source for the sulfur of this primordial composition. Sulfides associated with intrusives in New Brunswick, some intrusives in the Alps, specific Canadian shield intrusives, and certain Rhodesian igneous bodies also exhibit narrow spreads in their δ S\textsuperscript{84} values, but almost always show great enrichment in the S\textsuperscript{84} isotope. Jensen infers that this is a result of the homogenization, at granitization temperatures, of sulfur derived predominantly by reduction of sulfates in the preexisting crustal rocks.

Red-bed copper deposits, sandstone-type uranium deposits, Mt. Isa sulfide deposits, and some of the Rhodesian copperbelt and Katanga deposits exhibit δ S\textsuperscript{84} values of sufficient spread to be suggestive of a bacterial origin for the sulfur. Such sulfur need not be syngenetic in origin, as it may have formed in the sediments epigenetically, as in the sandstone-type uranium deposits.

Jensen suggested that sulfate-reducing bacteria existing in organic matter in sediments or bioherms could have produced the effective reductant, hydrogen sulfide, that may help explain the concentration of zinc and lead in deposits of the Mississippi Valley type. In such areas connate waters contain abundant sulfate, which, even at temperatures slightly above 100° C, can only be reduced in nature by sulfate-reducing anaerobes. Certain sulfate-reducing thermophilic anaerobes, such as Clostridium nigrificans, may still be viable in water at such temperatures, when under lithostatic pressure. The δ S\textsuperscript{84} composition of the sulfur in sulfides of Mississippi Valley type deposits is suggestive of such processes.

Metamorphism will tend to homogenize the highly variable δ S\textsuperscript{84} values of sulfides containing biogenically formed sulfur. Sulfides from Balmat, N. Y., are highly enriched in S\textsuperscript{84}, but only exhibit about a 15 per mil spread. High-rank metamorphism may have reduced the presupposed greater spread by limited mixing and homogenization. Specific Rhodesian copperbelt sulfide deposits that exhibit δ S\textsuperscript{84} spreads that seem low for biogenically produced sulfides may also be the result of lower-rank metamorphism plus preferential loss through mobilization of S\textsuperscript{82}. In contrast, preferential mobilization in magmatic hydrothermal processes generally results in residual enrichments of only a few per mil in S\textsuperscript{84}.

Finally, Jensen reported that he is now performing δ O\textsuperscript{18} studies on quartz, oxide, and silicate minerals that coexist with the sulfur-bearing minerals on which δ S\textsuperscript{84} values have been obtained.

H. P. Taylor, Jr., detailed some of the experimental results he and his colleagues have obtained on oxygen isotope fractionation between fluids and various minerals. Such studies may permit: (1) the recognition of disequilibrium assemblages; (2) geothermometry; (3) establishing the extent of exchange between fluids and preexisting rocks; and (4) determination of
the source of ore fluids (if exchange reactions do not take place). He has established the sequence of fractionations for 13 major rock-forming minerals from the highest O\textsuperscript{18} (quartz) to the lowest (magnetite), and finds this sequence to be identical in both igneous and high-temperature metamorphic rocks. The most satisfactory mineral pair provides a thermometer (yielding the temperature at which the equilibrium was frozen in), which can be accurate to ±10° to 15°C with present mass spectrometry.

The exchange between fluid and crystal may be exceedingly fast. Thus albite exchanged alkali with a KCl solution and came to within 90 or 95 percent of equilibrium with respect to oxygen isotope exchange in 5 minutes at 700°C. The conversion of kaolinite + KCl to muscovite exchanges all oxygen. On alteration of granites, as at Butte, the residual quartz was unaffected even where the feldspar has been completely exchanged. Such studies may thus permit the identification of the source of some minerals in alteration zones; with additional controls it may be possible to determine the relative volumes of solid and liquid. Taylor has discovered what appears to be a pervasive hydrothermal homogenization of oxygen isotopes across metamorphic rock types in New England. He finds also that very large areas of rocks in the Adirondacks of New York have developed considerable variations in O\textsuperscript{18}, probably because of exchange with large volumes of water during metamorphism.

W. F. Stawson discussed the work he and Russell have done on lead isotopes in ore deposits. These are found to be generally either uniform, with only very small variations, or variable, with about two orders of magnitude greater variation. Practically all the uniform deposits fit a relatively simple growth curve; concordant deposits show concordant leads. The lead for such deposits must come from a source that has overall uniform ratios for U/Pb, Th/Pb, and Th/U. Several possibilities are presented: the lead can come from a homogeneous subcrust or mantle, from the homogenization of large blocks (continental size) of the crust, or from a heterogeneous source that has frequent mixing. Arguments were presented which supported the first possibility and rejected the third. The Sr, S, and Pb isotopes in oceanic basalts show a homogeneous source and hence a homogeneous mantle, and it is possible that mantle lead is still migrating into the crust, via single or multistage processes.

9. and 10. HYDROTHERMAL FLUIDS AS DEDUCED FROM MINE STUDIES, ZONING, ETC.

K. H. Wedepohl discussed the similarities and differences between the Permian Kupferschiefer and the Devonian Rammelsberg deposits, and their possible origins. The major portion of the ore at Rammelsberg (Goslar, Germany) occurs in two lenses of very limited, local occurrence, whereas the Kupferschiefer is a 1-foot bed traceable across Europe for 1,500 km. Both ores show very fine grain size and strong evidence of concordant ore beds having vertical (stratigraphic) compositional and mineralogical zoning that is uniform over large distances in the Kupferschiefer. Both are Pb-Zn-Cu
deposits in bituminous shales that are free of any evidence of metamorphism or hydrothermal alteration. The Kupferschiefer is, with few exceptions, carbonate bearing. On the basis of paleogeographic evidence, sedimentation rates, and the possible concentrations of ore metals in the sea water, Wedepohl proposes formation of ore concentrations in the Kupferschiefer in near-shore basins about 300 meters deep or less, bacterial reduction of sulfate producing $\text{H}_2\text{S}$ in the bottom water, and perhaps yearly overturn (exchange) of water, for 10,000–50,000 years. The metals presumably were introduced in higher-than-normal sea water concentration by redbed-type weathering of the adjacent landmass.

Similar reasoning does not fit the Rammelsberg deposit, and Wedepohl agrees with Kraume, the geologist at the mine, in assuming submarine hot-springs as the local source for the metals there. In comparison with the Kupferschiefer, the Rammelsberg ore lenses contain large amounts of barite. The vertical sequence of zones rich in quartz, pyrite, chalcopyrite, sphalerite, galena, and barite reflects changes with time, in the composition of these springs or in the precipitating conditions.

John F. Hunt described some of the extensive field and laboratory work being done by Anaconda geologists at the porphyry copper deposit at El Salvador, Chile. Systematic copper and iron sulfide assemblages are present in the disseminated primary ores. These disseminated sulfide assemblages are zoned both horizontally and vertically. Specific primary oxide, silicate, and sulfate phases are associated with definite sulfide assemblages at given locations within the zonal pattern.

Primary sulfate is present at El Salvador as anhydrite. The importance of sulfate is emphasized by the fact that sulfur as anhydrite may equal or exceed sulfide sulfur in certain zones at El Salvador, and equal as much as 15 percent by volume in some rocks. Supergene waters have in many places hydrated the anhydrite to gypsum and then dissolved the gypsum completely. These secondary waters thus converted originally dense impervious rocks, impregnated with anhydrite, to porous and incompetent rocks. Supergene enrichment has not yet been found in the anhydrite or sulfate zone.

W. S. Burbank briefly described some very unusual pipelike ore deposits in the San Juan Mountains, Colorado. The sequence of formation appears to have been the intrusion of igneous pipes at a depth of 3,000–4,000 feet, and then the entrance of hot fluids that were throttled into the brecciated ground in and around the pipes. These fluids dissolved much rock, leaving many large caves and tubes, up to tens of feet in size, particularly at the top of the pipes. Much of this dissolved material was apparently redeposited above to form large, rather impervious siliceous caps. Later fluids formed replacement base metal ores in the length of the pipe and locally deposited enargite-stromeyerite-galena ores as open-space filling below the cap. The ore now contains some gypsum that may have been anhydrite originally, but many gypsum veinlets in the wall rocks are probably the result of the extensive supergene oxidation of pyritized rocks.

W. S. White briefly described the environment of deposition of the Michigan native copper deposits. Stoiber and Davidson have shown that the
POROUS BASALT FLOW TOPS, POSSIBLY CONTAINING AS MUCH AS 400 PPM COPPER ORIGINALLY, HAVE BEEN ALTERED, WITH INCREASES IN SiO₂, Fe, Na, H₂O, AND Cu, AND LOSSES IN Al, Mg, AND Ca. UNCORRECTED FLUID-INCLUSION TEMPERATURES IN QUARTZ ARE 300° C OR MORE. THE GEOMETRY OF THE LAKE SUPERIOR BASIN INDICATES THAT THE LAVA FLOWS EXTEND DOWN DIP TO DEPTHS IN THE RANGE OF 30,000–50,000 FEET. AT THESE DEPTHS AND PRESSURES, CRUSHING AND INCIPENT METAMORPHISM OF THE LAVAS SEEM INEVITABLE, AS DOES THE DRIVING-OUT OF HOT WATER THAT HAS PARTICIPATED IN THIS METAMORPHISM, PERHAPS LEACHING COPPER. LEACHING EXPERIMENTS, SUCH AS THOSE BEGUN BY ELLIS, COULD TEST THESE INFERENCES.

B. J. SKINNER SUGGESTED THAT THE LARGE PURE MASSES OF STROMEYERITE REPORTED TO OCCUR IN CERTAIN MINES IN THE SAN JUAN MOUNTAINS, COLORADO, MUST HAVE CRYSTALLIZED BELOW 93° C. BELOW 93° C STROMEYERITE HAS A NARROW COMPOSITION RANGE, BUT ABOVE 93° C IT INVERTS TO A CATION-DISCORDERED STRUCTURE WITH A VERY WIDE COMPOSITION RANGE. IT WOULD BE FORTUITOUS FOR A LARGE MASS OF THE HIGH-TEMPERATURE FORM TO HAVE JUST THE RIGHT COMPOSITION TO YIELD PURE STROMEYERITE ON QUENCHING. A SIMILAR ARGUMENT, THOUGH NOT QUITE SO COMPPELLING, MAY BE USED FOR THE OCCURRENCE OF PURE MASSES OF LOW DIGENITE.

PURE MASSES OF α-DOMEYKITE (Cu₅As) ARE KNOWN TO OCCUR IN THE MICHIGAN COPPER DISTRICT AND A NUMBER OF OTHER LOCALITIES, AND IT IS SUGGESTED THAT THESE MUST ALL HAVE FORMED BELOW 115° C. ABOVE 115° C, α-DOMEYKITE BREAKS DOWN TO A MIXTURE OF ALGODONITE (Cu₉₋ₓAs) AND β-DOMEYKITE (Cu₉ₓ₋ₓAs). AGAIN, IT WOULD BE UNLIKELY TO GET MIXTURES OF THE HIGH-TEMPERATURE ASSEMBLAGES IN JUST THE RIGHT PROPORTION TO GET PURE α-DOMEYKITE ON COOLING.

U. PETERSEN DESCRIBED THE WIDE VARIETY OF MINERAL DEPOSITS FOUND IN THE CENTRAL PERUVIAN MINERAL BELT, A REGION 100 × 500 KM, NORTHEAST OF LIMA, PERU. THESE VARY FROM QUARTZ-MOLYBDENITE VEINS IN GRANITE, THROUGH CONTACT METASOMATIC AND HYDROTHERMAL VEIN DEPOSITS, TO REDBED-TYPE COPPER DEPOSITS, ALL PRESUMABLY EPIGENETIC, AND ALL ARRANGED IN COMPOSITIONALLY DISTINCT NORTH-WEST-SOUTHEAST TRENDING BELTS PARALLEL WITH THE GRAIN OF THE COUNTRY. ABOUT HALF OF THESE DEPOSITS HAVE A DIRECT RELATION TO IGNEOUS BODIES, ABOUT A THIRD SHOW AN OBSCURE RELATION, AND THE REST (MAINLY REDBED COPPER DEPOSITS) SHOW NONE. THE IGNEOUS ROCKS RANGE FROM GRANITE TO DIORITE AND THEIR FINE-GRAINED AND PORPHYRITIC EQUIVALENTS, WITH QUARTZ-MONZONITE PREDOMINATING IN THE LARGER DISTRICTS. IN ADDITION, THERE IS A STRONG SPATIAL RELATION OF ORE DEPOSITS TO REGIONAL HIGH-ANGLE COMPRESSIVE FAULTS. SULFUR ISOTOPES FROM ORE OF THE MAJOR DEPOSITS FALL WITHIN THE NARROW RANGE OF S³² VALUES CHARACTERISTIC OF MAGMATIC-HYDROTHERMAL DEPOSITS.

PETERSEN ALSO DISCUSSED THE PARTICULARLY WELL DEVELOPED ZONING OF THESE ORE BODIES, WHICH IS BOTH DISTRICT-WIDE AND IN THE INDIVIDUAL DEPOSITS, PIPES, AND VEINS OF THE DISTRICTS. THIS ZONING IS CHIEFLY COMPOSITIONAL FROM A HIGH-S, -CU, AND -AS ZONE, GRADING THROUGH Zn AND Pb ZONES INTO A LOW-S ASSEMBLAGE, HIGH IN Ag AND SH. SUPERIMPOSED ON THE ZONING ARE STRONG LITHOLOGIC CONTROLS THAT ACTED BOTH STRUCTURALLY AND CHEMICALLY. EXAMPLES OF CHEMICAL CONTROLS ARE PROVIDED BY THE RELATIVE ABSENCE OF ORE IN CLEAN SANDSTONE FORMATIONS, THE PREDOMINANCE OF Pb-Zn IN LIMESTONE COUNTRY ROCK AND THE INFLUENCE ON MINERALOGY OF VARIOUS ROCK TYPES. FINALLY PETERSEN MENTIONED OBSERVATIONS
pertaining to relations between paragenesis and zoning due to advancing and receding depositional fronts.

K. C. Dunham reported on the status of the Cornish tin district, where a drilling program is underway and two mines are operating. The ore veins are subparallel, cut a zone of granitic stocks that are probably joined together below, and also postdate a series of quartz porphyry dikes locally called elvans. The veins are zoned from tin at depth to copper above, but any particular vein shows repeated stages of fracturing and deposition. Tourmaline has crystallized from the magmatic stage through to the late stages, where it replaces biotite, and the large contact aureoles (up to 4 miles wide) may have 5 percent tourmaline. One of the tin veins bottoms in a 5-meter red microcline-quartz graphic pegmatite, with some late tin and tungsten, but little wallrock alteration. Higher up, the veins show extensive tourmalinization and some pockets of intense greisenzonation. A chlorite zone occurs beyond the tourmaline, and in two of the 5 stocks, economically valuable kaolin has been worked to at least a depth of 800 feet (with the present water table at 50 feet).

Dunham also described the Northern Pennine orefield. This shows very strong zoning about two main centers, from a core of low-temperature pyrrhotite with chalcopyrite, through an intermediate zone with fluorite, galena and sphalerite, to a peripheral zone with barite and/or witherite. F. J. Sawkins’ work on fluid inclusions indicates temperatures ranging from 220° C near the center down to a near-surface temperature for the barite. The centers lie over buried granite stocks which predate the ore; the center recently investigated by boring is itself mineralized. Mineralization is believed to have been due to hot fluids that rose, through fractures, in the older granite and spread out in the gently domed later sediments above. Mixing with strong connate brines in the sediments is a possibility, for brines with as much as 1,300 ppm barium remain trapped in the sediments. Solution of Permian evaporites might have contributed, but this is doubtful.

C. Meyer discussed some of the features of Butte, Montana, that have come out of an intensive, long-term study of the district. There was continuous fracturing throughout the mineralization period, and later. The veins are strongly zoned mineralogically, vertically and horizontally, with the core of the district high in Cu, an intermediate Cu and Zn zone, and a peripheral Zn and Mn zone. Near the geographical center of the district is a zone in which quartz-molybdenite veinlets are important. This zone tops just above the 2,800 level and slopes outward at about 45°, though it may flatten below the 3,800 level. The veinlets generally have little alteration adjacent to them, and they are always cut by the major copper- and zinc-rich veins and their sericitic and argillic alteration zones.

Within the molybdenite zone on deep levels, some structurally early, fluorite-bearing, quartz molybdenite veinlets are enveloped in 1-inch to 3-inch dark-colored alteration envelopes having the assemblage K-feldspar, biotite, muscovite. Anhydrite is present in both veinlets and altered wall rock, along with pyrite, chalcopyrite, magnetite, and hematite.
Meyer also described some experimental solubility studies on sphalerite crystals, by the weight-loss method, at 2,000 atm. and temperatures up to 600° C. The presence of quartz and muscovite in the charge, in addition to KCl (i.e., buffering by the K-feldspar-mica-quartz reaction curve described by Hemley) increased the weight loss from the sphalerite crystal approximately tenfold over the loss in a plain KCl solution, to about 1 gram ZnS/1,000 g solution at 350° C, and 14 grams at 600° C. K-feldspar was formed by dehydrolysis of the muscovite. The metal and hydrogen ion species in solution are not known.

P. M. Bethke discussed some of the results that he and his colleagues have obtained on a detailed study of the OH vein, a small ore body at Creede, Colorado, and which, in principle, may well be applicable elsewhere. The OH vein was formed as a simple fracture filling, at a depth or perhaps 500–1,000 feet to the top of the ore body. The vuggy ore has many large crystals of sphalerite that are strongly zoned. Careful study of a large number of doubly polished plates cut from crystals collected throughout the ore body established that these zones could be correlated to yield a “sphalerite stratigraphy,” the grosser features of which can be traced throughout the mine. Studies of fluid inclusion compositions and homogenization temperatures, and the balance of the paragenesis could be tied in with this stratigraphy. “Disconformities,” representing intervals of hydrothermal leaching, are common, and indicate near-equilibrium, noncolloidal transport. They may also indicate the bottoming of the ore deposit, as fluids that are actively dissolving sphalerite cannot have gone far through a sphalerite-encrusted vein, unless the reason for the increased solubility lies in a progressively changing parameter, such as loss of gases. These finely zoned crystals record fluctuations in the composition of the depositing fluid, and provide excellent evidence against later equilibration. More rapid crystallization results in the deposition of unequal amounts of iron and other elements on the different growing crystal faces, and hence, may yield gross differences in the composition of samples taken from materials that were deposited simultaneously. Sphalerites formed at very low temperatures, such as the Mississippi Valley ores, have almost no recognizable zoning, but show instead an irregular splotchy pattern of coloration. Although most of the color zoning in the Creede sphalerites reflects variation in iron content of several orders of magnitude, other “trace” elements should be studied similarly, and indeed other minerals should be checked for such zoning. The complexities of the paragenesis, in time and space, disclosed by the study of this “simple” deposit, if present but unnoticed in other mineral deposits, may account for some of the difficulties in interpreting the data obtained from them.

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