Symposium
Problems of Postmagmatic
Ore Deposition.

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G. Kullerud has found (Kullerud - Yoder, this volume) that the cordierite which had been influenced by sulphur-bearing solutions was changed into sillimanite + pyrite + SO$_2$. It is of interest that these results may also be used for the explanation of the formation of the sillimanite-pyrite association in high-metamorphic series where the replacement of cordierite by sillimanite (with pyrite) can often be observed. It is evident that the sillimanite-pyrite association might even originate from other rock silicates (as for example, from biotite and garnet) because the replacement of these minerals by sillimanite is also frequent in high metamorphic series. This is to emphasize that the sillimanite-pyrite association in the high metamorphic rocks is not to be explained only by the single isochemic recrystallization of the primary sedimentary series but also by the metamorphic reactions in the late periods of the metamorphic and migmatisation processes when also sulphur-bearing solutions of magmatic or metatectic origin might be introduced.

SAWKINS F. J. (PRINCETON, U.S.A.)

Dr. Roedder reviewed many of the exciting avenues for research that are provided by the study of fluid inclusions in minerals. I would like to present some results of fluid inclusion studies made on the Providencia lead-zinc deposits in northern Mexico.

A generalized paragenetic diagram for the Providencia ore bodies is shown in figure 1; an attempt has been made to present the paragenetic data in a quantitative form. The bulk of the ore consists of massive sphalerite, galena, and pyrite deposited by replacement of the carbonate wallrocks. The later ore is vuggy and it is on this material that the bulk of the fluid inclusion studies have had to be concentrated.

Figures 1, 2 and 3 (on pl. I and II) demonstrate the zoning of sphalerite crystals found in Providencia ore bodies. It is within the framework of this zoning that the temperature and salinity data obtained from fluid inclusions have been plotted.

The temperature data obtained by homogenization studies of inclusions in sphalerite from Zinc West and Animas Ore Bodies are summarized in figures 2 and 3 respectively. Note the shape of the temperature curve and the lack of evidence for any temperature gradient over the vertical range encompassed by the data.
The results indicate that sphalerite, and presumably galena, precipitated continuously over the temperature interval from above 375°C to approximately 200°C. The shape of the temperature curve suggests that the ore solutions were gradually decreasing in temperature with time until the very final stage of hydrothermal activity.

![Diagram of mineral formation over fraction of hydrothermal mineralization](image)

Also present in the ore locally or in small amounts: Lime silicates, Muscovite, Chalcopyrite, Mn carbonates, Fluorite

Fig. 1. Generalized paragenesis diagram — Providencia ore bodies

when a decrease in the velocity of the solutions resulted in both a decrease in depositional temperatures and in the volume of sphalerite precipitated.

The results of salinity studies, made on the Roedder cooling stage and by observation of the solution of NaCl daughter minerals with increasing temperature, are shown in figures 4 and 5. Note that the vertical axis is now a measure of equivalent wt-% NaCl whereas the horizontal axis is still a paragenetic one.

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Fig. 2. Zinc West Ore Body - temperature results (sphalerite)
- □ Level 11, △ Levels 14, 15, ○ Levels 17, 18

Fig. 3. Animas Ore Body - temperature results (sphalerite)
- □ Levels 15, 16, 17, △ Levels 18, 19, 20, ○ Levels 21, 22
Fig. 4. Salinity data - Zinc West and Salaverna Ore Bodies
Zinc West: ○ sphalerite, △ calcite I, × quartz
Salaverna: ● sphalerite, ▲ calcite I

Fig. 5. Animas Ore Body - salinity results
○ sphalerite, × calcite, △ quartz
Although the data are not complete enough to permit a precise delineation of the salinity variations, several mechanisms can be invoked to explain these fluctuations in salinity.

1. Boiling within the hydrothermal column.
2. Incorporation of sedimentary salt by the rising hydrothermal solutions.
3. Mixing of juvenile, connate and meteoric waters of varying salinities.
4. Changes in the salinity of specific increments of hydrothermal solution at their source.

BODINE M. W., Jr. (PRINCETON, U.S.A.)

The use of minor-element analyses of single hydrothermally precipitated phases to define the concentration ratios present in the parent solutions has been reviewed in the pre-Symposium Supplementary Volume by Bodine-Holland-Bortesik. Similar data have been used by Tischendorf in the pre-Symposium Volume in his study of the strontium sulfate content in barites. This discussion will present some of the minor-element data obtained from calcites from the lead-zinc-silver deposit Providencia,

Fig. 1. Manganese content vs. strontium content of calcites from the Zinc West Mine, Providencia district, Mexico. The path defined by the heavy borders and arrows illustrates the trend of compositions throughout the several successive calcite generations. After Holland (unpublished data)
Mexico, where several calcite generations were deposited following the major sulfide mineralization as discussed by Sawkins.

The fractionation of an element between calcite and the parent solution is defined by the distribution coefficient $K^x_{++}$, where the ratio of the minor element to calcium concentration in the solid phase is equal to the product of the distribution coefficient and the ratio of the minor element to calcium concentration in the fluid phase:

$$\frac{m_{x^{++}}}{m_{Ca^{++}} + c} = K^x_{++} \cdot \frac{m_{x^{++}}}{m_{Ca^{++}} + a q}$$

where $x^{++}$ is represented either by Mn or Sr ion. In this discussion we will look at both the distribution of manganese and strontium. Sawkins in the previous discussion reviewed the temperature criteria for the Providencia district and these show a thermal environment of 300—350°C for the Providencia’s calcites. At such temperatures the distribution coefficients for manganese and strontium in calcites $K^C_{Mo}$ and $K^C_{Sr}$ are 2.0 and 0.2 respectively. Preliminary trace-element studies in the calcite generations by Holland and others show variations in the calcite compositions from one
to seven weight per cent manganese and 50—600 ppm strontium. Such data would indicate variations in the cation ratios for the parent solution of 0.01—0.1 for the Mn/Ca ratio in the solution and $5 \times 10^{-4} - 1 \times 10^{-3}$ for the Sr/Ca ratio.

From a study of zoned crystals, Holland has shown that the changes in manganese and strontium content as a function of time follow a remarkably regular path. Figure 1 illustrates a diagram of calcite composition from the Zinc West ore body. The originally low Mn content increases with a constant low Sr content. This is followed by a gradual decrease of Mn content approaching the initial low value and is accompanied by an increase in the Sr content. Later calcite deposition contains little Mn but yields a gradual decrease in the Sr content. A similar, although less well-defined, path has been noted for paragenetically equivalent calcite sequence from the Animas Mine as shown in figure 2. This would tend to indicate that during the growth of these calcites, the concentration ratios, Mn/Ca and Sr/Ca within the hydrothermal fluid changed uniformly throughout the district as a function of time.

ROEDDER E. (WASHINGTON, U.S.A.)

Both primary and secondary inclusions of relatively pure liquid carbon dioxide have been found in the olivine crystals from olivine nodules in a number of basalts. This unusual and unexpected discovery indicates that CO$_2$ may be a major constituent of the earliest exhalations from deep-seated basalt magmas, and hence equilibria involving CO$_2$ should be considered in discussions of gas transport mechanisms. The appearance of these inclusions, the methods needed for their detection and analysis, and some of the physicochemical consequences of their occurrence will be given.

YPMA P. J. M. (LEIDEN, NETHERLANDS)

I would like to comment on the papers presented by Mr. Ingerson, Mr. Holland and Mr. Roedder, as they refer to the use of fluid inclusions as samples of ore-bearing solutions. In cases of homogeneous entrapment the mode of homogenization provides an indication as to the nature of the ore-bearing solutions, either gaseous, fluid or liquid, depending on the behaviour of the liquid-vapour boundary of the inclusions on heating. Smith and Little (1959) have drawn attention to the possibility of non-homogeneous entrapment. Because of widely diverging homogenization temperatures and different modes of homogenization in one crystal, they concluded to crystallization under boiling conditions, by which process liquid and vapour in different ratios were trapped by the growing crystal. I will not deny the possibility of crystallization under boiling conditions, but this will not count for all cases of heterogeneous entrapment, as will be shown in the following example.
Artificial crystals grown from a thermostatically controlled saturated salt solution often show small irregularities in the form of less transparent bands. These bands appear to consist of inclusions mostly filled with brine, occasionally, however also with air. The growth of these crystals took place in the interval of 60—30°C in an open vessel. The banding is due to irregularities of the thermostatic control, resulting in resorption or an increased rate of crystallization. The occurrence of large air bubbles is particularly interesting, since during the growth process no air bubbles can be observed in the brine. Apparently the sudden disturbance of equilibrium (if we may refer to the slow and even crystal growth as close to the state of equilibrium) brought about the exsolution of air, whereby the irregular surface of the crystal provided nuclei for the exsolution of air.

We thus have a clear example of heterogeneous entrapment from a largely homogeneous solution. One may expect this phenomenon also to occur in nature. Different filling degrees of inclusions in deposits of the 150—250°C temperature range may be explained in this way.

HOLLAND H. D. (PRINCETON, U.S.A.)

Professor Barnes suggested in his lecture that transport of zinc and of some other heavy metals takes place in the form of bisulfide complexes. That transport in this form is possible has been shown by Professor Barnes’ beautiful experiments, but the application of this concept to ore deposits encounters serious difficulties. The very high concentration of bisulfide ion, ca. 1 molar, that must be present to transport zinc in sufficiently high concentrations to produce ore deposits has never been found in primary fluid inclusions. Instead, the sulfur content of these fluids is small, between $10^{-2}$ to $10^{-3}$ molar, and the sulfur is apparently present almost exclusively as sulfate ions, not as bisulfide ions.

This observation casts grave doubt on the significance of Barnes’ experiments for the transport of heavy metals in ore-forming fluids, and it seems worthwhile to cast about for an alternative explanation. Some recent measurements at Princeton of the solubility of sphalerite at 80°C in aqueous solutions of NaCl in equilibrium with a vapor phase consisting of $\text{H}_2\text{S}$ and $\text{H}_2\text{O}$ by N. W. H. Inners (1963) suggest such an alternative, at least for epithermal deposits. H. Inners has shown that the solubility of sphalerite first decreases with increasing pH, then remains constant, and finally increases with increasing pH. Solubilities which are “geologically interesting” can be reached in the presence of large bisulfide ion concentrations — the Barnes region — or at quite small concentrations of reduced sulfur. I would like to propose that the second method of reaching sufficiently high zinc concentrations may be of considerable geological importance, as it is in agreement both with the present data on the composition of fluids in fluid inclusions and with the mineralogy of epithermal deposits. Precipitation of sphalerite can be produced by the reduction of sulfate ions, or by the admixture of $\text{H}_2\text{S}$ or of solutions containing $\text{HS}^-$ and $\text{S}^\text{2-}$. The reduction
of sulfate at low temperatures by bacteria is a well-known phenomenon, and sulfate reduction by H₂, CO, and CH₄ takes place quite rapidly in the laboratory above 225°C.

It seems entirely too early to settle on a single mechanism of ore metal transport in epithermal solutions at this time, and I do not feel that Barnes’ mechanism should be rejected, but I believe that we should keep in mind that his mechanism does have shortcomings, and that at least one feasible alternative is available.

GUNDLACH H. (HANNOVER, G.F.R.)

Prof. Barnes gave us in his diagram of the sulphur anions only the following as stable: HSO₄⁻ (bisulphate), SO₄²⁻ (sulphate), HS⁻ (bisulphide) and S⁻ (sulphide), in addition also H₂S (hydrogen-sulphide) and S₈ (sulphur as liquid).

In chemistry further sulphur anions are known, representing medium valences of sulphur between —2 (sulphide) and +6 (sulphate) some of which are also forming complexes with metals. The best known of these are the complexes of thiosulphate with silver used in photography.

These medium valences of sulphur are not stable in solutions. For a long time they exist only in equilibrium with the above-mentioned stable anions, that is along the boundaries between the stability ranges in the diagram given by Prof. Barnes. Garrels and Naeser (1958) calculated the maximum equilibrium concentrations of these anions, thiosulphate and different polythionates at a given total sulphur concentration.

In spite of these results the anions mentioned above were found in nature in much higher concentrations, viz. up to now in springs being connected with young volcanic activity: in 1911 and in 1940 in New Zealand and in 1923 in the United States, Lassen Peak. In volcanic areas, the existence of these compounds in waters is easily to be understood.

Last year I had the opportunity to investigate some sulphur-containing springs in Greece, which were closely related to sedimentary strata. In these springs, too, ound polythionates and thiosulphates in concentrations, being several ranges of order higher than the maximum equilibrium concentrations calculated by Garrels and Naeser:

\[ \text{S}_2\text{O}_3^{2-} \quad 0.02 - 0.05 \text{ me/l} \text{ against about } 10^{-3} \text{ me/l maximum, in equilibrium,} \]
\[ \text{S}_4\text{O}_6^{2-} \quad 0 - 0.02 \text{ me/l against about } 10^{-17} \text{ me/l, maximum in equilibrium,} \]
\[ \text{S}_4\text{O}_6^{4-} \quad 0 - 0.03 \text{ me/l against unknown equilibrium concentration.} \]

The conclusion is that these compounds decompose only very slowly in order to reach equilibrium, if the solution concerned — in this case by reaching the surface — is getting under new physico-chemical conditions.

In the case of changes of the oxidation-reduction potential of the sulphur-containing metal-bearing solution, therefore we have to regard the existence, at least
temporary, of these sulphur-oxygen-anions. Discussing the transport and especially
the precipitation of metals we have to consider their (probable selective) ability
of forming metal complexes.

Of course, this is valid for low-temperature solutions only; at higher tempera-
tures these sulphur-oxygen-anions are unstable, because the equilibria are then
reached too quickly.

BARNES H. L. (UNIVERSITY PARK, U.S.A.)

Response to Dr. Holland (A) and to Dr. Gundlach (B)

(A) 1. Although the high solubility of metallic chlorides or sulfates offers an easy
mechanism for transport, this method is not geologically compatible. For example,
transport by complex ions is necessary to produce zoning — transportation by simple
sulfates and deposition by reduction to sulfides must give a sequence of precipitation
the same as the sulfide oxidation potentials and not the same as commonly observed
zoning.

2. Furthermore, the vertical distribution of minerals such as pyrrhotite and
pyrite demonstrates that the oxidation state of ores decreases with increasing depth.
The process of transport in the form of sulfates requires oxidizing conditions during
transport followed by reduction to sulfides. This sequence is opposite to that observed
in many vein deposits.

3. The high sulfate content of fluid inclusions is certainly expected if either
H₂ or H₂S leak to any extent from the inclusion at any time. The easy passage of H₂
through steel and most materials particularly at high temperatures is well known.
For this reason, we can not use fluid inclusions as indications of oxidation state but
rather as indications of density, cation ratios, temperatures, and so forth, assuming
of course, that the inclusion fluid was not a portion of corroding fluid instead of a
depositing fluid.

4. Stoichiometrically, it is unlikely that sufficient reducing agents are available
for reduction of the quantities of sulfates needed for sulfide ore deposition:

\[ \text{SO}_4^{2-} + 4\text{H}_2(\text{g}) \rightarrow \text{HS}^- + \text{OH}^- + 3\text{H}_2\text{O} \]

Using probably our most powerful reducing agent, hydrogen, four moles of hydrogen
are needed per mole of deposited sulfide!

5. The textures of ores precipitated by contact of either a chloride or sulfate
solution of the metals with a sulfide-forming environment must be considerably
different from those of normal ores. The solubility products of the sulfides are so
extremely small that all metals would most probably be deposited simultaneously
in a fine-grained mass, producing neither equilibrium assemblages, paragenetic
sequences, large crystals or replacement textures.

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6. In addition, in a paper presented last year at the Annual Meeting of the Geological Society of America, I presented data showing that chloride and bisulfide complexes are of equal stability only when Cl\textsuperscript{−} is about 10\textsuperscript{3} times the HS\textsuperscript{−} concentration. For chloride transport to be significant, the ore solution would have to be essentially free of any sulfide. In the natural reducing environment required by equilibration with many silicate rocks in depth, this low a bisulfide concentration is virtually impossible. It appears that the ore solution is probably a brine solution but that the presence of Cl\textsuperscript{−} contributes to no significant extent to sulfide solubilities. In fact, the presence of brine reduces the solubility of sphalerite.

(B) Certainly, thiosulfate solutions are commonly found at low temperatures. In fact thiosulfate complexes are used in analytical chemistry not only for silver but also for many other metals. However, complexes formed by S\textsubscript{2}O\textsubscript{3}\textsuperscript{−}, S\textsuperscript{−} and polythionates although common at low temperatures are definitely metastable as shown by Barnes and Kullerud, as well as Garrels and Naeser. Heating, ultra-violet light, and so forth cause the breakdown of these species to H\textsubscript{2}S (or HS\textsuperscript{−} or S\textsuperscript{−} depending on pH) plus SO\textsubscript{4}\textsuperscript{2−} (or HSO\textsubscript{4}\textsuperscript{−}) by reactions such as:

\[
S\textsubscript{2}O\textsubscript{3}\textsuperscript{−} + H\textsubscript{2}O \rightarrow H\textsubscript{2}S + SO\textsubscript{4}\textsuperscript{2−}
\]

INGERSON E. (AUSTIN, U.S.A.)

Experimental studies of metal transport are very useful, but in applying these results to actual deposits it is necessary to make certain assumptions. Most of the recent studies appear to have assumed the following:

1. That the original water-content of the magma can be estimated fairly accurately.

2. That the difference between this amount and that now in the igneous rock was all available for transport, i.e., it all travelled through the veins of the deposit. This also involves an estimate of the total amount of igneous rock.

3. That all of this water was saturated with the postulated metal compound or complex.

4. That essentially all of the metal was deposited in the veins or other structures.

I should like to suggest that some of these assumptions may not be justified and that the differences between assumption and actual conditions may amount to several, or possibly many, orders of magnitude. These differences are likely to be in the direction of too much water. That is, the postulated solutions will be much more dilute than the actual ones.

Many of the theoretical and experimental studies lead to a result of only a few hundred p. p. m. of the metal(s) concerned. Such direct geological evidence as there is, however, indicates much higher concentrations. For example, liquid inclusions commonly contain some 10—15% solute and some (with solid chlorides at ordinary
temperatures) contained more than 50 weight per cent solutes, after most of the ore-forming components have been deposited.

In the Cedar City district, in southern Utah, there are quartz-monzonite intrusions with associated iron deposits. Detailed mapping and numerous chemical and mineralogical analyses have indicated that the iron, and the water that transported it, have been derived by deuteric alteration of selvages along joints in the intrusive rock. The quantities of iron and water are roughly equal. That is, the indicated concentration of iron in the ore-forming solution is of the order of 50%. Calculations show that the amount of iron derived from the selvages is about the same as that contained in the ore deposits.

We should look for more examples where quantitative data of this kind can be obtained in Nature. This could help to guide experimental work and its application to natural environments.

HOLLAND H. D. (PRINCETON, U.S.A.)

Professor Barnes criticized my hypothesis on three grounds and I would like to reply to them.

1. Zoning — We do not yet have sufficient information on the solubility of ore minerals at high temperatures to make meaningful statements on the origin of zoning. They may well serve as a useful criterion in choosing between the several methods of ore transport.

2. Oxidation — It should be pointed out that if Barnes’ concept is correct, it is not only necessary to oxidize the HS⁻ to SO₄²⁻ but also to remove 99% of the sulfur initially present in the fluid inclusion. This seems most unlikely.

3. Hydrogen supply — It is, of course, true that 4 moles of H₂ are needed to reduce one mole of SO₄²⁻ to HS⁻, but it looks as if there is enough H₂, CO and CH₄ present in hydrothermal solutions to reduce a sufficient quantity of SO₄²⁻ to account for the observed deposition of sulfides.

ROEDDER E. (WASHINGTON, U.S.A.)

I would like to raise some objections to three points made by my friend Dr. Ingerson.

1. He spoke of the need for high concentrations of ore elements in the ore fluid, because “unreasonable” quantities of water are needed if the ore elements are in low concentrations. I take exception to this statement. If one examines the quantities of water and ore elements available in geologically reasonable volumes of rocks, it becomes readily apparent that the ore-forming process must be a very inefficient one, or we would have far more ore deposits than we do have, even with the assumption of very dilute ore fluids.
2. Dr. Ingerson speaks of fluid inclusions as the "last residua" of the ore fluid, remaining after deposition of the ore and gangue minerals. I maintain that primary fluid inclusions, in various zones of zoned crystals of ore minerals or coprecipitated gangue minerals, are not residua from the ore-forming process, but are actual samples of the ore fluids from which these particular zones were crystallizing at the time of trapping, minus any constituents that might have leaked out later through the crystal.

3. Dr. Ingerson has proposed a mechanism of formation for an iron ore deposit in Utah that indicates the existence of ore fluids with more than 50% iron in solution. If such ore fluids existed, at least some small amounts should have been trapped as fluid inclusions in ore and gangue minerals in the deposit. I would like to see such inclusions. Thank you.

RIEDER M. (PRAGUE, CZECHOSLOVAKIA)

I would like to say only a few words on the question of metal transport. In Professor Krauskopf's lecture concerning the transport of metals by gases there was a section dealing with stabilities of various compounds of arsenic and antimony. The author noted that the stability field of $\text{Sb}_2\text{O}_3$ is much larger than that of $\text{As}_2\text{O}_3$, which could probably be (in view of no known occurrences of hypogene $\text{Sb}_2\text{O}_3$) due to some mistake in the chemical data on the basis of which the stabilities were computed. I should like to draw attention to the fact that in the deposit Dúbrava (The Low Tatras) there is known hypogene senarmontite in the form of considerably thick veins belonging to the last mineralization stage (Jakeš 1963). The hypogene origin of senarmontite in Dúbrava is beyond all doubt and therefore it seems that there need not be any mistake in the chemical data from which the stabilities were derived, but this rather indicates that Professor Krauskopf's theoretical assumptions are well confirmed by this.

BOYLE R. W. (OTTAWA, CANADA)

We have heard much about high temperature processes of ore deposition, but I would like to remind you that low temperature processes are also capable of moving the metals.

About half of Canada is underlain by permafrost, and in the permafrost zone we have a number of mines. In one at Yellowknife some years ago I found native gold in an ice lens in a fault (Boyle 1951).\footnote{Příspěvek k poznání antimonitových žil na SZ svahu Nízkých Tater v oblasti lokality Dúbrava. — Acta Univ. Carol. (Geologica) No. 3, 159—178. (Studies in the stibnite veins on the north-western slope of Nízké Tatry Mts. in the area of the Dúbrava deposit.)}

\footnote{An Occurrence of Native Gold in an Ice Lens, Giant Yellowknife Gold Mines, Yellowknife, Northwest Territories. — Econ. Geol. 46, 223—227.}
Later while working at Keno Hill, Yukon, I found a number of occurrences of native silver in ice lenses (Boyle 1960)\(^2\).

The zones in which these ice lenses occur are at a temperature of \(-5\) to \(-1^\circ\text{C}\), and there is no movement of liquid ground waters but rather a migration of water vapour at low temperature. Perhaps the gold and silver were also transported in the water vapour at a low temperature. I really do not know the answer. I leave the problem with you to think about.

KULLERUD G. (WASHINGTON, U.S.A.)

In the preceding discussions on metal transport the correlation between dry and wet systems has not been pointed out. Whenever hydrates are not involved, it is quite clear that equilibrium relations obtained in dry systems must form the basis for solubility experiments. The results of studies of dry systems provide indications of the temperatures, and partial pressures (\(P_{S_2}, P_{O_2}\) etc.) which existed when ores formed and therefore indicate the physico-chemical conditions under which solubility experimentation must be undertaken.