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# Ore transport and deposition in the Red Sea geothermal system: a geochemical model

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**Abstract**—Thermodynamic calculation of distribution of dissolved aqueous species in the Red Sea geothermal brine provides a model of ore transport and deposition in good agreement with observed accumulations of base metal sulfides, anhydrite, and barite.

The Red Sea brine is recirculated seawater that acquires high salinity by low-temperature interaction with Miocene evaporites and is subsequently heated to temperatures in excess of 200°C by interaction with recent rift zone intrusive rocks. At temperatures up to 250°C, $NaSO_4^-$ and $MgSO_4^0$ are the dominant sulfur-bearing species. $H_2S$ forms by inorganic sulfate reduction at the higher temperatures but is maintained at a uniform concentration of about 2 ppm by the strength of the sulfate complexes.

Chloride complexes solubilize metals at the higher temperatures, and thus sulfide and metals are carried together into the Atlantis II Deep. Below 150°C, the brine becomes supersaturated with respect to chalcopyrite, sphalerite, galena, and iron monosulfide due to chloride–complex dissociation. Sulfide precipitation rates, based on the rate of brine influx, are in good agreement with measured sedimentation rates. Anhydrite precipitates as crystalline fissure infillings from high-temperature inflowing brine. Barite forms from partial oxidation of sulfides at the interface between the lower hot brine and the transitional brine layer.

## INTRODUCTION

THE DISCOVERY and subsequent investigation of metal-bearing brines and actively accumulating metalliferous sediments in the axial rift zone of the Red Sea provide a modern analogy for many ancient hydrothermal ore deposits. The major questions concerning the genesis of the ancient deposits continue to focus on the nature and origin of the ore fluid, the mode by which the heavy metals are solubilized and kept in solution, and finally, the mechanism by which the metals become supersaturated and precipitate at the site of the deposit.

The purpose of this paper is to approach these questions as they apply to the Red Sea geothermal system, by attempting to reconstruct the chemistry of the brine at conditions likely encountered prior to discharge on the sea floor. We attempt to define these conditions based on, and constrained by, the large variety of field and laboratory observations previously made on the system.

## HYDROGRAPHY AND METALLIFEROUS SEDIMENTS

Geothermal brines and associated metalliferous sediments occur in several deeps within the axial rift of the Red Sea. The largest of these pools, the Atlantis II Deep (Fig. 1), measures 5 km by 14 km and contains approximately 5 km³ of supersaline brine (SCHOELL, 1976).

The Atlantis II Deep is divided into two major hydrographic units with several minor and transitional brine layers. The lower Atlantis II brine has a maximum temperature of 60°C (measured in 1972), a chlorinity of 156.5‰, and fills the deep to the 2040 m contour. The upper or transitional water mass has a temperature of 50°C, a chlorinity of 82.5‰, and occurs roughly below 1990 m. The temperature, salinity, and chemical composition of this upper brine indicate that it is a mixture of the lower brine and normal Red Sea deep water (CRAIG, 1969; TURNER, 1969).

Studies of the metalliferous sediments (BISCHOFF, 1969; HACKETT and BISCHOFF, 1973; BÄCKER and RICHTER, 1973) have established the nature of the Atlantis II deposits. The sediments are bedded metalliferous muds containing up to 95% interstitial brine and are composed of several different units or facies. Age dating indicates normal stratigraphic succession of metalliferous sediments going back to 25,000 yr and accumulating at an average rate of about 50 cm/1000 yr, a rate exceeding that of normal marine sediments outside the deeps by a factor of three (KU, 1969; KU et al., 1969; HACKETT and BISCHOFF, 1973). These observations lead to the conclusion that these sediments are chemically precipitated from the brine, and that the brine represents the fluid responsible for metal transport.

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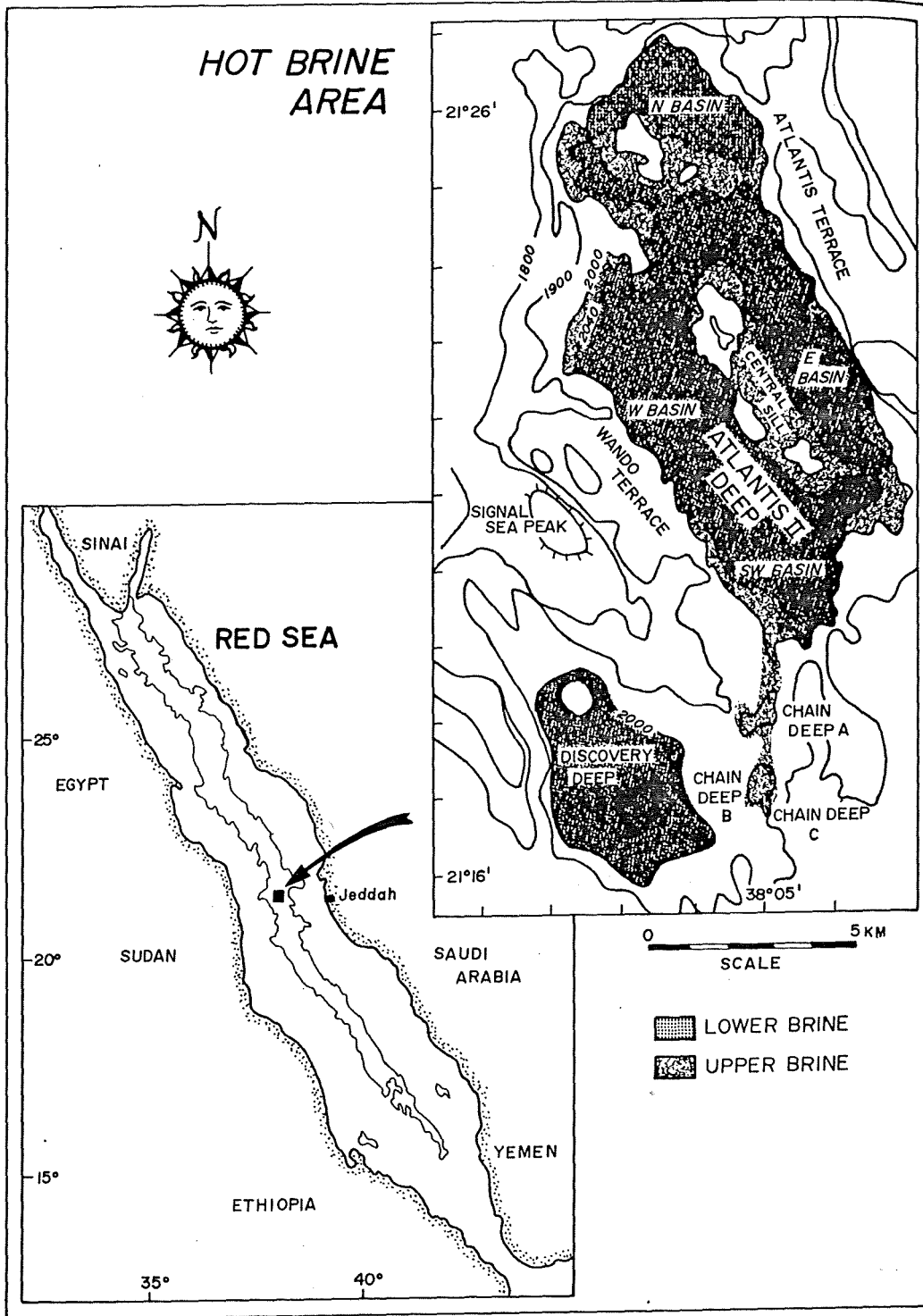
Fig. 1. Bathymetry of hot brine deeps and their location in Red Sea axial rift zone. In the Atlantis II Deep the upper brine has a temperature of 50°C, overlies and is transitional to lower brine at 60°C. Chlorinities are 80 and 156‰, respectively. Bathymetry and hydrography from Bäcker and Richter (1973).

Bischoff (1969) defined seven sedimentary facies that are roughly correlative throughout the deposit on the basis of mineralogical composition. Briefly, the youngest and presently depositing facies is iron-montmorillonite, composed primarily of ferroan nontronite. Next youngest is the goethite-amorphous facies, composed mainly of iron oxides ranging from amorphous ferric-hydroxide to well-crystallized hema-

tite and magnetite. The sulfide facies is the most important economically, is composed mainly of pyrite, chalcopyrite, and sphalerite, and immediately overlies a basal sequence of detrital biogenic carbonates.

Manganosiderite, manganite, and anhydrite are a relatively minor facies irregularly distributed throughout the Atlantis II Deep. Manganosiderite beds are often thin and intermittent and usually occur within the iron-montmorillonite or goethite-amorphous facies. Anhydrite is present as nodules or as discontinuous massive layers up to several centimeters thick.

## MODEL CONDITIONS

The hot brines of the Atlantis II Deep have provided a unique opportunity to study an active ore-depositing system. Much insight into submarine hydrothermal deposits has been gained by the careful studies of processes taking place in the brine deep. However, the important problems of ore metal solubilization, transport, and deposition have not been approached for this system, mainly because of the lack of observational data on the subsurface brine prior to its emergence on the seafloor.

The conclusion of CRAIG (1969) that the lower brine mass of the Atlantis II Deep closely corresponds to the chemistry of the brine at the point of seafloor discharge, plus the temperature estimates of SCHOELL

(1976) suggested that a model of the brine could be calculated by extrapolating the present bulk chemistry of the Atlantis II brine to higher temperatures. The following sections enumerate the constraints and parameters employed for such a calculation.

### Brine chemistry

Brine chemistry (Table 1) is characterized by relative enrichment with respect to normal seawater of Na, Ca, K and Cl, and depletion of Mg, I, $SO_4$, $NO_3$ and F. The heavy metals Fe, Mn, Pb, Zn and Cu are greatly concentrated over normal seawater and are obviously very important in the ore-forming processes.

The major element composition (Table 1) has been used to demonstrate that the (50°C) upper brine layer in the Atlantis II Deep is a transitional layer produced by mixing of Red Sea deep water and the 60°C brine (CRAIG, 1969; BREWER and SPENCER, 1969). An important question, however, is whether the lower brine has been modified by similar admixture of seawater or represents relatively uncontaminated ore fluid. CRAIG (1969) estimated the amount of seawater mixed into the lower brine mass using trace elements greatly depleted in the brine relative to seawater and concluded that the amount of admixed seawater cannot be greater than 5%.

An additional question concerns whether the heavy-metal concentrations have decreased significantly by active precipitation in the Atlantis II Deep. This is difficult to test, and, therefore, the analyzed concentrations represent, at the least, a lower limit.

Therefore, as a first approximation we take the analyzed composition of the 60°C brine as representative of the

Table 1. Composition of geothermal brines and seawater of the Red Sea (mg/kg)

| | Atlantis II Deep, lower brine mass | Atlantis II Deep, upper brine layer | Red Sea deep water |
|---|---|---|---|
| Na | 92,600 | 46,900 | 12,500 |
| K | 1,870 | 1,070 | 450 |
| Mg | 764 | 1,190 | 1,490 |
| Ca | 5,150 | 2,470 | 470 |
| Cl | 156,030 | 80,040 | 22,500 |
| $SO_4$ | 840 | 2,260 | 3,140 |
| Total $CO_2$ (as $HCO_3^-$) | 140 | 150–175 | 140 |
| Ba | 0.9 | – | .020 – .004 |
| Cu | 0.26 | .017 | .020 – .001 |
| F | ≤ .02 | – | 1.5 |
| Fe | 81.0 | 0.2 | .062 – .0001 |
| Li | 4.4 | – | 0.200 – .072 |
| Mn | 82.0 | 82.0 | .009 – .0001 |
| Pb | 0.63 | .009 | .00004 – .00002 |
| Si | 27.6 | – | 2.6 |
| Zn | 5.4 | 0.15 | .048 – .001 |

Data from BREWER et al. (1965), MILLER et al. (1966), and BREWER and SPENCER (1969). Trace element data listed under Red Sea deep water are ranges observed in normal oceanic waters (BREWER, 1975).
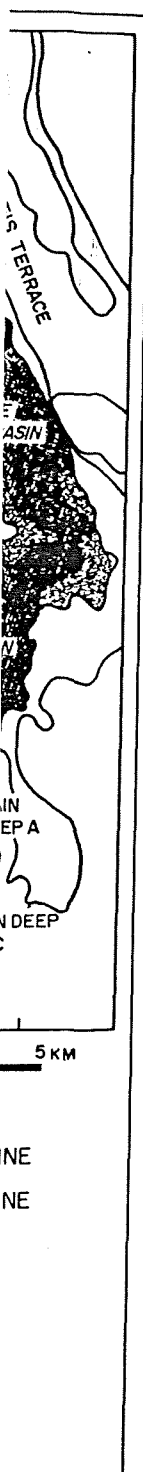
composition of the ore fluid at the point of seafloor discharge.

### Subsurface temperature

Estimation of the maximum temperature of the brine in the subsurface can be approached only indirectly. Temperature measurements of the lower brine from 1966 to 1975 (BREWER et al., 1971; ROSS, 1972; SCHOELL and HARTMANN, 1973; and SCHOELL, 1976) show a continuous increase of 0.75°C per year. The bathymetry of the Atlantis II Deep is well known and measured changes in the level of the brine can be translated into changes in brine volume. The temperature of the newly discharged brine can thus be estimated by combining the observed volume and temperature changes through time.

By using this technique, BREWER et al. (1971) and ROSS (1972) estimated the average input temperature of the brine to be about 110°C based on a 6 m rise of the brine level between 1966 and 1971. The brine level, however, was measured by hydrowire, which has an approximate uncertainty of ±5 m (BREWER et al., 1969), leaving very large uncertainty in the temperature estimate.

SCHOELL (1976) provided a more accurate estimate of the temperature of brine input by comparing depth data from the 1964 Meteor cruise and the 1971–72 Valdivia cruises. Both vessels were equipped with the same high-precision ELAC narrow-beam (1.4°) echo sounding system. Direct comparison of echo sounder recordings indicated no measurable change in the level of the lower brine layer from 1964 to 1971. SCHOELL (1976) estimated the accuracy of the ELAC systems to be within 2 m, and assuming an undetected maximum rise of 2 m, he calculated a minimum input temperature of 210°C.

An independent method of estimating initial brine temperature is the empirical geothermometer developed by FOURNIER and TRUESDELL (1973) for hot springs and other natural waters. Using molar Na, K, and Ca data for the 60°C brine and their empirical relationship, an equilibration temperature of about 150°C is indicated. Consideration of silica solubility in the brine provides a somewhat lower estimate (MOREY et al., 1962).

Similar calculations by TRUESDELL (1976) yield 158°C by the Na–K–Ca geothermometer and 108°C for silica solubility. However, these temperatures estimated by chemical methods must be viewed as lower limits since the brine has resided in Atlantis II Deep at 60°C for a considerable period of time and re-equilibration is likely. This is particularly true for the silica method because iron silicates (nontronite) are known to be precipitating at present in the iron montmorillonite facies.

The isotopic geothermometer based on oxygen isotope exchange between sulfate ion and water in the geothermal fluid may be less susceptible to re-equilibration. In fact, Red Sea brine temperatures of 250° and 261°C have been calculated by this method by SAKAI et al. (1970) and TRUESDELL (1976), respectively. Truesdell also calculated a temperature of 211°C using the warm springs mixing model. In this respect, though, the oxygen–hydrogen isotope data and the trace element composition of the Red Sea brine as discussed by CRAIG (1969) suggest that very little admixture of sea water has occurred.

We infer, therefore, that the maximum subsurface brine temperature was in the range 150–250°C and use 250°C as an approximate upper limit for our calculations.

### Oxygen fugacity

A continuing enigma in the Red Sea system is the origin of base-metal sulfides in the Atlantis II Deep. Laboratory analysis of the brine has failed to detect dissolved $H_2S$, and yet metal sulfides are precipitating from the lower brine mass. However, the presence of some concentration of $H_2S$ is suggested by the blackening of a brass messenger reported by MILLER et al. (1966) after hydrocasts into the

Atlantis II Deep. In order to model the brine chemistry and heavy-metal solubility, it is necessary to estimate dissolved $H_2S$ concentration. First, we note that whereas dissolved sulfate is a major component (840 ppm), dissolved $H_2S$ in the present brine pool must be very low. Second, base-metal sulfides presently precipitating from the 60°C brine constitute a small fraction (1–5%) of the iron-montmorillonite facies.

Sulfur isotope composition of the dissolved sulfate (KAPLAN et al., 1969) indicates that it is identical to normal seawater sulfate ($\delta^{34}S = 20‰$). On the other hand precipitated metal sulfides have isotope ratios of +5 to +15‰ (HARTMANN and NIELSEN, 1966; KAPLAN et al., 1969; SHANKS and BISCHOFF, 1975). Thus, production of $H_2S$ by reduction of a significant proportion of sulfate cannot have occurred or the residual sulfate in the brine would necessarily be enriched in $^{34}S$ to balance the enrichment of $^{32}S$ in the precipitated sulfides.

These factors imply that the concentration ratio of total sulfate to sulfide in the brine has remained large throughout the evolution of the brine. With this condition in mind and given the analyzed brine chemistry, particularly total sulfate, the equilibrium distribution and concentration of sulfide species can be calculated from oxygen fugacity, which in turn is likely controlled by solid phases in the rocks and sediments through which the brine passes.

HACKETT and BISCHOFF (1973) observed that hematite is transformed to magnetite in the sediments of the southwest basin of the Atlantis II Deep. They calculated that the present 60°C brine is close to magnetite–hematite equilibria and suggested that magnetite forms in contact with inflowing fresh brine. Subsequently, SCHOELL and HARTMANN (1973) and SCHOELL (1976) have completed detailed hydrographic studies that confirm a present-day brine vent in the southwest basin.

The following reaction can be used to estimate oxygen fugacity ($f_{O_2}$) in the brine as controlled by magnetite–hematite equilibrium:

$$3Fe_2O_3 = 2Fe_3O_4 + 1/2 O_2. \quad (1)$$

hematite    magnetite
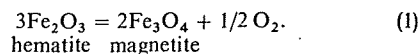
Temperature-dependent equilibrium constants for this reaction (HELGESON, 1969) can be used to calculate $f_{O_2}$ at higher temperatures (Fig. 2). The assumption of magnetite-hematite equilibrium in the incoming brine is probably reasonable, considering that the inferred heat source is recent basaltic intrusives in the rift zone. Such rocks con-
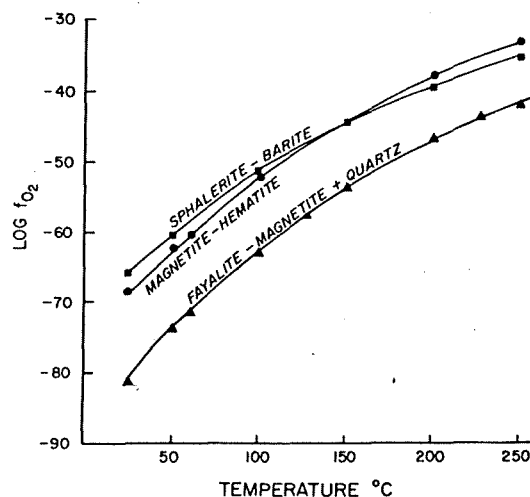


Fig. 2. Oxygen fugacity estimates for Red Sea geothermal brine. Calculated from thermochemical data of HELGESON (1969) for brine interaction with solid phases in rocks and sediments through which the brine migrates.

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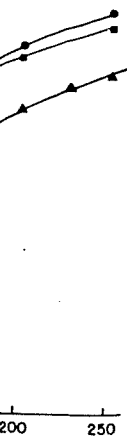
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tain ubiquitous minor magnetite, and any dissolved oxygen in the brine would be removed by production of minute quantities of hematite. In addition, DELEVAUX and DOE (1974) have shown a persistent mantle-lead component in the Atlantis II brine and sediments, which likely resulted from brine interaction with subsurface oceanic basalts.

Additional support for magnetite–hematite buffering of $f_{O_2}$ is the common association of sphalerite and barite in the sulfide facies (SHANKS, 1976). The following reaction can be written for equilibrium between these two minerals:

$$BaSO_4 + Zn^{2+} = ZnS + Ba^{2+} + 2O_2. \qquad (2)$$
$$\text{barite} \qquad\quad \text{sphalerite}$$
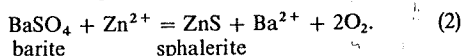
The equilibrium constant for this reaction, as a function of temperature, can be derived from data in HELGESON (1969). Zinc/barium ionic activity ratios can be calculated from concentrations in the present brine pool and the necessary activity coefficients.

Oxygen fugacity estimates from both sets of mineral pairs (Fig. 2) are surprisingly close, suggesting that the assumptions involved in these fugacity calculations are valid.

Moreover, calculations of the distribution of dissolved species at various temperatures and at $f_{O_2}$ set by magnetite–hematite indicate that total dissolved sulfate species greatly exceeds total dissolved sulfide species, as required by observations.

Buffering of $f_{O_2}$ by more reducing iron-bearing mineral reactions such as

$$3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2. \qquad (3)$$
$$\text{fayalite} \qquad\quad \text{magnetite quartz}$$
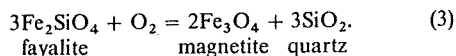
is unlikely, because the resulting $f_{O_2}$ (Fig. 2) is such that dissolved sulfide species should greatly exceed dissolved sulfate species. Therefore, magnetite–hematite buffering is assumed in our model as the control of $f_{O_2}$.

*Brine pH*

The final parameter needed for this model is an estimate of the pH of the brine at any given temperature. MILLER et al. (1966) and SHISHKINA and BOGOYAVLENSKIY (1970) have measured a pH of 5.5 on brine samples cooled to 25°C. pH at higher temperatures is calculated using the 25°C measurement and a mass balance relation for hydrogen-bearing species.

*The geochemical model*

The purpose of the model is to estimate the distribution of dissolved species in the brine and its vari-

ation with temperature. From these estimates we can then follow the degree of saturation of the brine with respect to the solids precipitated in the Atlantis II Deep to gain insight into the mode of solubilization, transport, and precipitation.

We make the following assumptions and approximations:

(1) The total composition of the brine has changed little during transport and cooling from its zone of maximum temperature. Inasmuch as mineral precipitation possibly takes place prior to discharge into the Atlantis II Deep, the error in this assumption (underestimation of total dissolved concentrations of certain components) will lead to a low estimate of the degree of saturation of certain minerals. However, the relative trend of the degree of saturation with temperature should remain unchanged, and it is this trend that we seek to understand.

(2) The maximum temperature of the brine is 250°C.

(3) $f_{O_2}$ is buffered by magnetite–hematite equilibria at the maximum temperature and during cooling. This results in a continuously decreasing $f_{O_2}$ with decreasing temperature (Fig. 2).

(4) Total dissolved sulfide is subordinate to total dissolved sulfate and is controlled by $f_{O_2}$.

(5) Other than for $f_{O_2}$, only homogeneous solution phase equilibria are considered. This means we disregard the effects of mineral dissolution or precipitation during the cooling process; this allows us to assess when components become available for precipitation or allow dissolution.

*Calculations*

Distribution of dissolved species is calculated using mass balance and mass action equations over the temperature range from 25 to 250°C. Computations were carried out by computer using an iterative process. In all, 72 aqueous species were evaluated (Table 2).

Equilibrium constants for aqueous species and

Table 2. Mass balance relations used to calculate distribution of dissolved species. Brackets represent concentration in molal

(1)  $\Sigma[SO_4] = [SO_4^=] + [HSO_4^-] + [NaSO_4^-] + [KSO_4^-] + [MgSO_4] + [CaSO_4] + [H_2S] + [HS^-] + [S^=]$

(2)  $\Sigma[CO_3] = [CO_3^=] + [HCO_3^-] + [H_2CO_3] + [NaCO_3^-] + [MgCO_3] + [CaCO_3] + [MgHCO_3^+] + [CaHCO_3^+]$

(3)  $\Sigma[Cl] = [Cl^-] + [HCl] + [NaCl] + [KCl]$

(4)  $\Sigma[Mg] = [Mg^{2+}] + [MgOH^+] + [MgSO_4] + [MgCO_3] + [MgHCO_3^+]$

(5)  $\Sigma[H] = [H^+] + [HSO_4^-] + [HCO_3^-] + 2[H_2CO_3] + 2[H_2S] + [HS^-] + [HCl] + [CaHCO_3^+] + [MgHCO_3^+] - [MgOH^+]$

(6)  $\Sigma[K] = [K^+] + [KSO_4^-] + [KCl]$

(7)  $\Sigma[Na] = [Na^+] + [NaSO_4^-] + [NaCO_3^-] + [NaCl]$

(8)  $\Sigma[Ca] = [Ca^{2+}] + [CaSO_4] + [CaCO_3] + [CaHCO_3^+]$

(9)  $\Sigma[Fe] = [Fe^{2+}] + [FeOH^+] + [Fe^{3+}] + [FeCl^{2+}] + [FeCl_2^+] + [FeCl_3] + [FeCl_4^-]$

(10)  $\Sigma[Cu] = [Cu^+] + [CuCl_2^-] + [CuCl_3^{2-}] + [Cu^{2+}] + [CuCl^+] + [CuCl_2] + [CuCl_3^-] + [CuCl_4^{2-}]$

(11)  $\Sigma[Zn] = [Zn^{2+}] + [ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}]$

(12)  $\Sigma[Pb] = [Pb^{2+}] + [PbCl^+] + [PbCl_2] + [PbCl_3^-] + [PbCl_4^{2-}]$
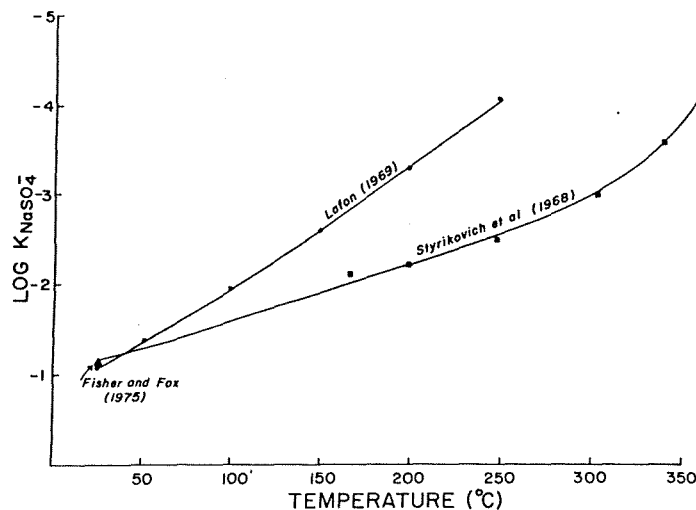
Fig. 3. Experimentally determined dissociation constants for the $NaSO_4^-$ complex. From the conductivity studies of FISHER and FOX (1975) and STYRIKOVICH et al. (1968). Thermodynamic estimate of LAFON (1969) included for comparison.

selected minerals are from HELGESON (1969) except for $NaCO_3^-$, $MgCO_3^0$, and $MgHCO_3^+$, which are from LAFON (1969), and were extrapolated to higher temperatures on the basis of constant enthalpy of a reaction. In the case of $NaSO_4^-$, which is of pivotal importance in sulfate–sulfide equilibria because it is a major sulfate species in the brine, the dissociation constant used is from the experimental work (Fig. 3) of FISHER and FOX (1975) and STYRIKOVICH et al. (1968).

Individual ionic activity coefficients were calculated from the extended Debye–Hückel limiting law, using the $B^0$ factor to correct for swamping concentrations of NaCl (HELGESON, 1964, 1969).

Equilibrium constants of aqueous complexes change with temperature and many complexes contain $H^+$, therefore, in situ pH may be quite different from pH in a cooled solution. It is thus necessary to evaluate pH at temperature by a hydrogen mass-balance calculation similar to that of BISCHOFF and DICKSON (1975). Total hydrogen concentration was first evaluated at 25°C according to equation (5) of Table 2. After solving for $\Sigma[H]$ at 25°C and assuming that this total does not change with temperature, molality of free hydrogen ion at any temperature ($[H^+]_T$) is calculated by

$$[H^+]_T = \Sigma[H] - \Sigma[H_i]_T \qquad (4)$$

where $\Sigma[H_i]_T$ refers to the sum of the concentrations of hydrogen-bearing species (except free hydrogen ion) at temperature.

## Results

Distribution of dissolved species was calculated for 250, 200, 150, 100, 50 and 25°C. Results for the lower brine layer of the Atlantis II Deep (Fig. 4) indicate that the dominant hydrogen-bearing species is $H_2CO_3$. Hydrogen ion activity rises with temperature mainly due to the increased stability to the $MgHCO_3^+$

complex and hydrogen ion is released in the process:

$$H_2CO_3 + Mg^{2+} = MgHCO_3^+ + H^+. \qquad (5)$$

The distribution of dissolved sulfur-bearing species (Fig. 5) shows that the $NaSO_4^-$ is of overwhelming importance except at higher temperatures and that free sulfate ion activity is quite low.

Total sulfide species remain subordinate to total sulfate at all temperatures owing to the strength of the $NaSO_4^-$ and $MgSO_4$ complexes and to $f_{O_2}$ control by hematite–magnetite. This result is in excellent agreement with inferences from field observation and sulfur isotope studies. $H_2S$ and $HS^-$ actually increase as temperature falls from 100 to 60°C, with total sulfide concentration reaching a maximum of 2 ppm at 60°C. Much of this sulfide is likely removed by base metal precipitation, a process the model ignores.

Calculated activities of sulfide species abruptly decrease from 60 to 25°C, while $f_{O_2}$ is maintained at the 60°C value of the magnetite–hematite buffer to simulate removal from the solid phases during hydrographic sampling. Thus, there is little hope of observing dissolved sulfide in a water sample that has undergone the pressure and temperature changes inherent in raising it through 2000 m of water, even if atmospheric $O_2$ contamination is precluded. However, the present model does suggest an explanation for the blackening due to sulfidation of the brass messenger reported by MILLER et al. (1966). $H_2S$ may be present but in very low quantities and could not be detected except by careful on site sampling and analysis.

More importantly, consideration of free metal ions and metal–chloride complexes (Fig. 6) indicates that ionic activities of $Zn^{2+}$, $Pb^{2+}$, $Cu^+$ (not shown) and $Fe^{2+}$ decrease with temperature, as do activities of Cu, Zn and Pb chloride complexes. This is due to activity coefficient effects and, in fact, molalities of chloride complexes increase with temperature.

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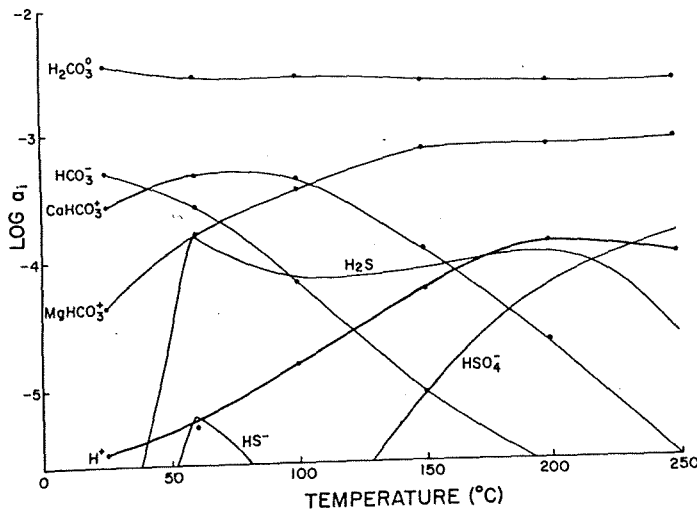for those sul
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Fig. 4. Variations in activity ($a_i$) of hydrogen-bearing species with temperature, used to calculate *in situ* brine pH at high temperatures. Calculated from an ion association model using the bulk chemical composition of the lower brine mass of the Atlantis II Deep.

Because chloride complexes make up the greater portion of total dissolved copper, lead, and zinc, this small change in molality of complexes is reflected by a large change in free-metal ion activity (Fig. 6). Ferrous ion dominates the iron species under the conditions of this model. However, activity of $Fe^{2+}$ decreases with temperature, because of the increasing stability of $FeOH^+$.

In order to evaluate possible transport and precipitation processes in the geothermal system, it is necessary to determine trends of degree of saturation of various solid phases. Solubility relations of some important solid phases are plotted (Fig. 7) as a function of temperature and degree of saturation. The plots for those sulfide minerals observed in the Atlantis II Deep sediments (Fig. 7) show that above 150°C, the brine is undersaturated for each and thus could act

as an active transport system, solubilizing metals during subsurface interaction with rocks or sediments. Upon cooling the brine becomes supersaturated successively with chalcopyrite, galena, sphalerite, and finally iron monosulfide.

The brine is calculated to be greatly supersaturated with respect to pyrite, even at the highest temperatures of this model. However, experimental studies have shown that reaction kinetics for precipitation of pyrite from aqueous solution at temperatures <100°C are unfavorable except in the presence of elemental sulfur (BERNER, 1970). Instead, iron monosulfides such as mackinawite form by direct reaction of ferrous ion with $H_2S$, and pyrite may form later by the following reaction:
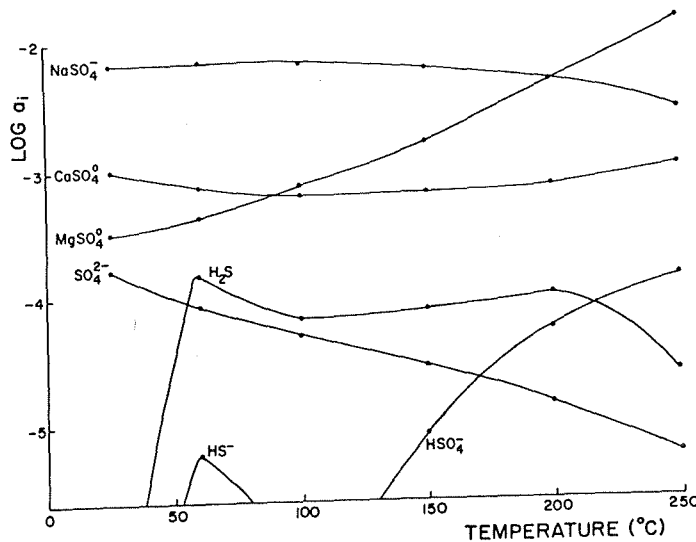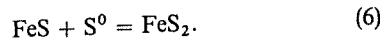
$$FeS + S^0 = FeS_2. \tag{6}$$



Fig. 5. Variations in activity ($a_i$) of sulfur-bearing species with temperature. Calculated using the bulk chemistry of the lower brine mass of the Atlantis II Deep, the calculated *in situ* pH at each temperature, and oxygen fugacity fixed by magnetite–hematite equilibria.

Fig. 6. Variations in activity ($a_i$) of heavy metal ions and complexes with temperature. Calculated using the bulk chemistry of the lower brine mass of the Atlantis II Deep, the calculated *in situ* pH at each temperature, and oxygen fugacity fixed by magnetite–hematite equilibria.
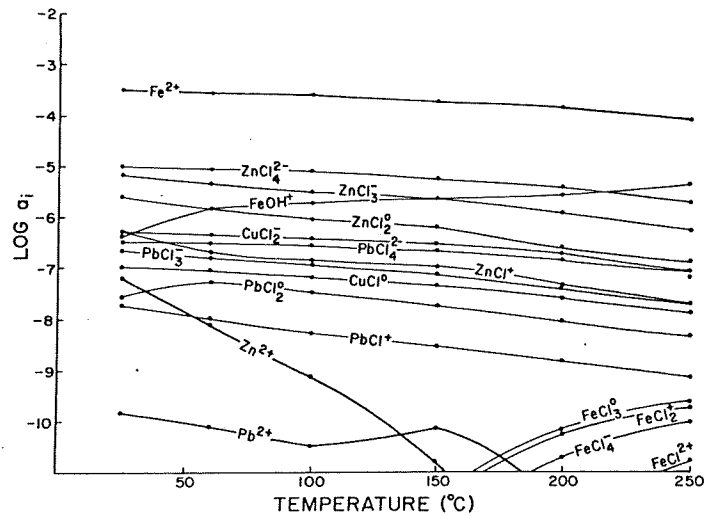
Elemental sulfur is provided by the oxidation of $H_2S$ by dissolved oxygen or $Fe^{3+}$ in iron oxides.

In the Atlantis II Deep, direct pyrite precipitation is probably similarly inhibited, especially at the high degree of saturation (FARRAND, 1970) calculated in this model. Initial iron sulfide precipitation is probably as the monosulfide which is later converted to pyrite or marcasite (STEPHENS and WITTKOPP, 1969). KAPLAN *et al.* (1969) have observed elemental sulfur in the metalliferous sediment and textural observations (SHANKS, 1976) indicate that pyrite grain size is large compared to other sulfides. These observations strongly suggest that the pyrite forms after sediment deposition either in the Atlantis II Deep or, possibly, during core storage if atmospheric oxygen is excluded.

Other important hydrothermal phases (Fig. 7) are barite, anhydrite and siderite. Barite and siderite are fairly close to saturation at lower temperatures but remain slightly undersaturated. The hydrothermal carbonate actually found in the Atlantis II sediments is a manganosiderite solid solution for which thermodynamic data are not available. Anhydrite is close to saturation at all temperatures, becoming slightly supersaturated at higher temperature.

## DISCUSSION

### Brine source

The strongest evidence concerning the source of the hot brines is provided by the oxygen and deuterium isotope studies of CRAIG (1966, 1969). He has shown
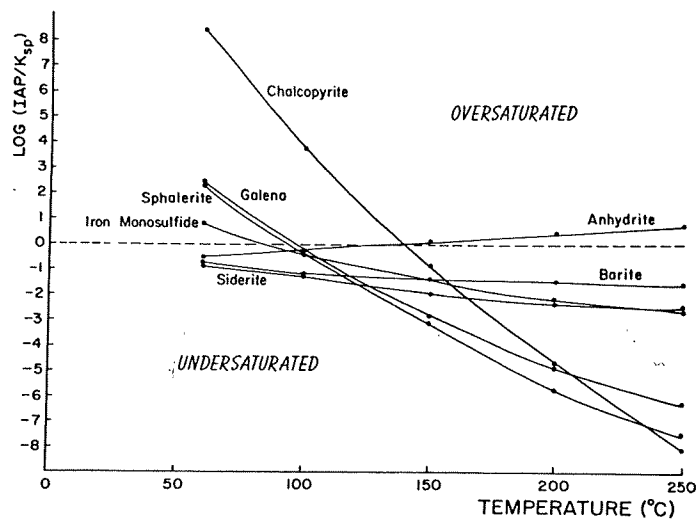


Fig. 7. Degree of saturation of the Red Sea geothermal brine with respect to various important hydrothermal minerals, expressed as a ratio of ion activity product to solubility product constant (IAP/$K$sp) for each mineral. Calculated based on an ion association model for the heated lower brine of the Atlantis II Deep (see text).

that the Atlantis II brine is derived from and is isotopically identical to normal Red Sea waters and has not undergone the oxygen isotope shift typical of many continental geothermal waters (CRAIG, 1963; WHITE, 1974). CRAIG (1969) attributes this to a lack of isotopic exchange with the rocks, owing to relatively low brine temperatures (<100°C) during subsurface circulation. This suggestion, however, is at variance with the temperature estimates utilized in this model and, in fact, isotopic shifts have been observed in pore waters in Red Sea sediments at temperatures as low as 30°C (MANHEIM, 1974).

Much field and laboratory data suggest that oxygen isotope exchange is relatively rapid for silicates and carbonates at temperatures above 100°C (CLAYTON, 1959; CLAYTON et al., 1968; ESLINGER and SAVIN, 1973; CLAYTON and STEINER, 1975; CRAIG, 1969). Thus, it seems certain that the brine underwent high-temperature isotopic exchange with the rocks, but the amount of isotope shift in the waters was very small. In this case, the most important constraint on isotope shift in the geothermal brine is the integrated water–rock ratio for the system (the total amount of water that exchanges with the rock over the life of the system). Approximate calculations using methods similar to those in SHEPPARD et al. (1969) indicate that brine–rock ratios could have been about 10–30 at temperatures up to 250°C without appreciably changing the isotopic composition of the brine.

Although it seems well established that the Red Sea brine is derived from normal Red Sea waters, controversy continues over the geographic location of the recharge area, and the processes that convert these waters into heated supersaline brine (MANHEIM, 1974). Much of the uncertainty stems from the lack of observational data on the subsurface waters. Nonetheless, certain speculations can be put forth, based on brine chemistry, geologic observations, and inference from basalt–seawater interaction experiments (BISCHOFF and DICKSON, 1975).

CRAIG (1966, 1969) has suggested that source waters are near the southern terminus of the Red Sea, on the basis of isotope–salinity systematics in Red Sea waters. Ross (1972) and MANHEIM (1974) have criticized this proposal because it requires subsurface flow of 400–900 km at a geologically rapid rate across several crosscutting transform faults. MANHEIM (1974) provides an alternative mechanism whereby waters penetrate the flanks of the Red Sea adjacent to the hot brine area. He suggests artesian flow in sedimentary sequences beneath impermeable Miocene evaporites, taking many thousands of years to reach the brine area.

Regardless of the exact pathway of subsurface circulation, water chemistry is altered substantially prior to discharge in the Atlantis II Deep and the processes can be visualized as follows: descending Red Sea waters attain high salinity by leaching of Miocene evaporites that are composed mainly of halite and anhydrite. Concomitantly, these brines are heated along the geothermal gradient, and the high chloride content provides potential for metal solubilization.

As the brines come into contact with recent intrusive rocks in the axial rift zone, they are heated, perhaps to 250°C, and further altered by interaction with the hot basalts. Anhydrite becomes insoluble at higher temperatures and is precipitated while calcium is leached out of the rocks. Magnesium is removed from the brine into basalt alteration products such as clay minerals, and pH falls to about 5. Dissolved oxygen is depleted to levels controlled by the magnetite–hematite buffer. At this point the heated brine, which has achieved maximum capability for metal solubilization, is convected upward and begins cooling as it approaches the Atlantis II Deep.

### Sulfate reduction and sulfide precipitation

The mechanism of sulfide production implied by this model is inorganic reduction of a small amount of dissolved sulfate at high temperatures by ferrous iron in the rocks. Although thermodynamically possible, it is uncertain whether the kinetics of such reduction are favorable within the time framework of brine evolution.

It is possible that inorganic sulfate reduction takes place only at the higher temperatures (>200°C) and that strong activation energy barriers prevent such reduction at lower temperatures. These considerations suggest that a small amount of sulfide may be produced in the subsurface at high temperature but that there is some threshold temperature below which sulfide production is insignificant. Probably the bulk of the sulfide is carried into the Atlantis II Deep by the inflowing brine and is precipitated because of increased concentration of free metal ions caused by dissociation of chloride complexes. Such precipitation may also occur prior to discharge at temperatures as high as 150°C (Fig. 7), with the sequence of appearance dictated by the temperature at which a given sulfide mineral first becomes supersaturated. For example, we might predict that chalcopyrite is the only sulfide precipitating in the region where the brine temperature is between 150 and 100°C. Alternatively, if the brine is above 150°C at the point of discharge, no sulfides will have precipitated prior to discharge. In either case, however, lateral sulfide mineral zonation in the Atlantis II Deep would likely be governed more by hydrographic and sedimentologic considerations than by solubility relations.

BARNES and CZAMANSKE (1967) have suggested that metal transport by chloride complexing in sulfide-bearing brines is geochemically unfeasible. It should be pointed out, however, that they assume an excess of total sulfur over total metals in ore deposits. In the Red Sea brine it is clear that ore metals greatly exceed the concentration of $H_2S$ in the ore fluid, as evidenced by the high metal concentrations in the 60°C brine and the abundant metal-oxides and silicates in the deposit. In a sulfide-deficient system such as the Red Sea, metal–chloride complexing is a viable

transport mechanism, as suggested by WHITE (1968) and the results of our model, and the need for metal solubilization by bisulfide complexing is eliminated.

An important consequence of this model is that sulfide–sulfate equilibria in hydrothermal solutions cannot be calculated without considering the entire aqueous system, including all dissolved species. For example, $NaSO_4^-$ and $MgSO_4^0$ are the major sulfur-bearing species in the brine, thus maintaining uniformly low $H_2S$ concentrations and allowing metal transport at higher temperatures. If simple $SO_4^{2-}$–$H_2S$ equilibria were calculated assuming free sulfate equal to total dissolved sulfate and ignoring the sulfate complexes, as from the equation:

$$H_2S + 2O_2 = 2H^+ + SO_4^{2-}, \tag{7}$$
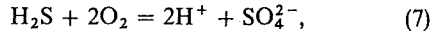
$H_2S$ would appear to be the dominant sulfur species and the predicted high concentrations would preclude base metal solubilization by the brine regardless of chloride complexing. Aqueous sulfate complexes obviously play an extremely important, although indirect, role in ore transport by hydrothermal brines.

*Brine flux and metal sulfide accumulation rates*

The geochemical model suggests that conditions very similar to those in the brine pool may be adequate to account for sulfide transport and deposition. An estimate of how much sulfide is being delivered to the Atlantis II Deep by the present brine can be calculated from brine flux and sulfide concentration. SCHOELL (1976) calculates an approximate rate of brine influx of $2.4 \times 10^4$ l/min ($1.6 \times 10^{13}$ kg/$10^3$ yr). This estimate is based on the observed temperature increase since 1964 and the maximum allowable increase in brine level (2 m, which coincides with a brine input temperature of 210°C).

The rate of sulfide precipitation can be estimated assuming that the incoming brine is 150–200°C and that all dissolved sulfide is precipitated. This seems a reasonable assumption since the 60°C brine is apparently supersaturated with respect to the sulfide minerals. The estimated concentration of $H_2S$, about $10^{-4.2}$ M, and flux of brine $1.6 \times 10^{13}$ Kg/$10^3$ yr, would precipitate $9.6 \times 10^{11}$ g sphalerite/$10^3$ yr. This amount of sphalerite would constitute about 0.5% by weight of the total sediment being deposited, assuming a sedimentation rate of 50 cm/$10^3$ yr, 1.5 g/cm³ bulk density, and a depositional area of 42 km² (present brine pool).

This calculated percentage of sphalerite is lower than the actual amount (3%) in the iron-montmorillonite facies indicated by averaged chemical analysis (BISCHOFF, 1969), but higher than in the other facies excepting the sulfide facies itself. If cooling is the cause of deposition, however, then it is likely that sulfide precipitation is localized near the brine vent. In fact, sulfides may be precipitated prior to discharge and be carried into the deep as particulate matter. It may be that while sulfides are precipitated rapidly near the vent, more oxidized material, which settles

out uniformly from the transitional brine layer, predominates in other areas. Recalculation of sphalerite content, assuming only a 10 km² depositional area near the vent, gives 6% by weight in the sediment. Thus it appears that this model can successfully account for precipitation of sulfides in the iron-montmorillonite facies, if reasonable sedimentary processes are considered.

Deposition of the sulfide facies, which contains up to 40% metal sulfide by weight and is confined to an early period in the history of the system, could have resulted from a number of different processes. The simplest and most attractive explanation is that sulfide minerals greatly predominate in areas close to the vent. Thus, localized deposition of massive sulfide beds is due to differential precipitation and sedimentation of sulfide minerals.

A second possible explanation might be increased sulfide production in the past in the brine owing to lower $f_{O_2}$ conditions than at present. This could occur as a result of brine interaction with shales rich in organic material as suggested by KAPLAN et al. (1969). This is unlikely, however, because reduction of a large percentage of the sulfate would result in the residual sulfate being enriched in $^{34}S$, and observed $\delta^{34}S$ ratios of sulfide minerals in the sulfide facies closely approximate those in the iron-montmorillonite facies (SHANKS, 1976).

Another process for precipitating massive sulfide beds is simply an increased brine flux. This would require an increase of about an order of magnitude over present influx, and it is difficult to determine if this has ever occurred. However, BÄCKER and RICHTER (1973) suggest that there is stratigraphic evidence that most of the important sulfide deposition occurred when the brine pool was at its maximum extent. Considering the uncertainties involved in the flux estimate, greatly increased brine flux is certainly a possibility.

At present it is impossible to evaluate the relative importance of these mechanisms for the formation of the relatively rich sulfide zones, and in fact, all three factors may operate.

*Sulfate deposition*

Anhydrite is a common mineral in the Atlantis II Deep, where it occurs either as crystalline infillings of voids and fractures in the southwest basin or as discontinuous massive beds. Solubility considerations (Fig. 7) indicate that anhydrite becomes slightly undersaturated with decreasing temperature, so transport and precipitation by simple cooling of the brine are precluded. Precipitation of anhydrite by mixing of the brine with Red Sea deep water, as suggested by BISCHOFF (1969), is also unlikely, because calculations on the distribution of species for the 50°C brine indicate undersaturation with respect to anhydrite. These results suggest that anhydrite precipitation is related to thermal events in the Deep, which coincides

with the observed fissure anhydrite in the southwest basin where brine is now actively venting.

A similar origin can be proposed for the massive anhydrite beds and the discontinuous nature of these sediments may be explained by tectonic disruption in the vent area (BÄCKER and RICHTER, 1973). Alternatively, some massive anhydrite may be mechanically emplaced from Miocene evaporites which are believed to outcrop in the southwest basin of the Deep (ROSS et al., 1973). Sulfur isotope analysis of Miocene anhydrite indicates $\delta^{34}S$ ratios of +22 to 24‰ (SHANKS et al., 1974), similar to some sulfur isotope ratios measured on Atlantis II Deep anhydrites (KAPLAN et al., 1969; SHANKS, 1976).

Barite is a persistent minor component of the sulfide-facies samples (SHANKS, 1976). Since barite is undersaturated in the 60°C brine pool, and does not occur as massive beds or layers, but occurs intimately associated with metal sulfides, it is suggested that barite forms only when sulfate concentration is greater than usual in the lower brine mass or when oxygen fugacity is above the sphalerite–barite boundary (Fig. 2). Both of these conditions may be fulfilled at the interface between the lower and upper brine masses in the Atlantis II Deep. The upper brine layer is relatively oxidizing, as evidenced by iron precipitation, and contains abundant sulfate (Table 1). Unfortunately, barium concentration has not been measured in the 50°C brine layers, and the degree of barite saturation there cannot be evaluated. However, Schoell (1976) has shown that the hot brine injected into the southwest basin (Fig. 1) convects upward to the 50°C brine interface and then spreads laterally into the other basins. Thus precipitated sulfides carried by the convecting brine may be brought into immediate contact with sulfate-rich, oxidizing upper brine layer. Barite may form by alteration of sphalerite and additional sulfate may be supplied from the upper brine.

Sulfur-isotope ratios of coexisting sulfide minerals and barite (Fig. 8) are consistent with this proposed mechanism of barite formation. Sulfur isotope ratios of barites are always heavier than coexisting sulfides by variable amounts but are never heavier than seawater (or brine sulfate). Thus, barite forms from a mixed sulfur source consisting of dissolved sulfate and oxidized sulfide sulfur.

### Genesis of the ore fluid

The geochemical calculations presented in this paper provide a workable model for transport of base metals and sulfide by a single ore solution. Red Sea brine evolution based on the results of this model and on earlier observations may be visualized as taking place in the following steps:

(1) Normal Red Sea waters percolate into the subsurface and achieve high salinity by dissolution of Miocene evaporites.

(2) The supersaline brines circulate downward and are heated to 200–250°C in contact with recent basaltic intrusive rocks in the axial rift zone.
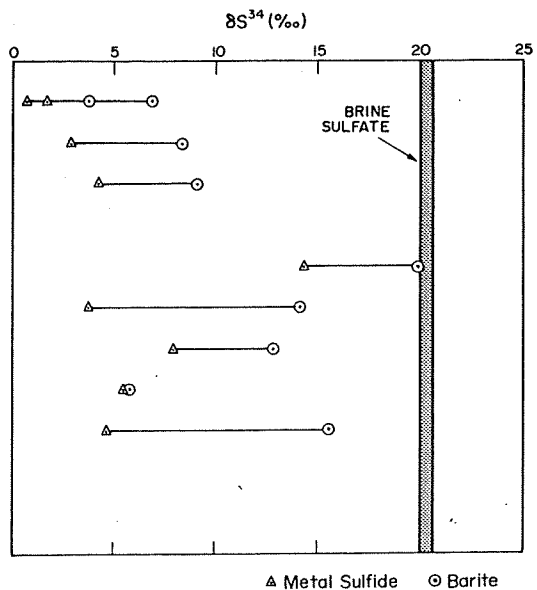


$\delta S^{34}$ (‰)

Fig. 8. Sulfur isotope fractionation between coexisting barite and sulfide minerals in the Atlantis II Deep sediments. $\delta^{34}S$ (‰) expressed in the conventional manner relative to the Cañon Diablo troilite sulfur standard. Sulfur isotope ratio of brine sulfate (KAPLAN et al., 1969) is identical to present-day seawater.

(3) As the brine is heated, sulfate is depleted by anhydrite precipitation, magnesium is removed into basalt alteration products such as clays, pH falls concomitantly to about 5, a small amount of sulfate is reduced owing to low oxygen fugacities (controlled by the magnetite–hematite buffer) and metals are solubilized as chloride complexes.

(4) Base-metal sulfides are deposited from the ascending, cooling brine owing to dissociation of metal-chloride complexes. Metal precipitation rates based on brine flux estimates and the assumption that sulfide is quantitatively precipitated (excess of metals) are in good agreement with measured sedimentation rates and metal contents in the iron-montmorillonite facies.

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