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Origin of fluids and the evolution of the Atlantis II deep hydrothermal system, Red Sea: Strontium isotope study

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Abstract—Atlantis II is the largest and most mineralized of the deeps along the axis of the Red Sea spreading center. Its basaltic substratum is covered by recent layered metalliferous sediments, which precipitated from an overlying brine pool. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the strontium concentration of interstitial waters within these sediments range between 0.70708 and 0.70725 and between 43 and 53 ppm, respectively. They are close to what is found for the present-day deep brine pool (0.707105, 45.10 ppm). The strontium concentration and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Atlantis II Deep brines can be derived from those of the interstitial waters of the surrounding Miocene evaporite by hydrothermal interaction with oceanic basaltic rocks at a maximal water/rock ratio of 2–3. This water/rock ratio is similar to that calculated for oceanic hydrothermal systems on sediment-free ridges. Interstitial waters show a linear trend on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$. The highest strontium concentration and the most radiogenic interstitial waters correspond to sediment samples enriched in iron and manganese oxide minerals. These waters reflect the diagenetic release of strontium by oxide minerals that initially precipitated at the interface between the brine pool and more radiogenic seawater. The solid fraction of the sediment has $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions intermediate to those of the brines and seawater. The most radiogenic strontium values were observed in samples strongly enriched in marine microbiota. The gradual isotopic evolution in the lowest part of the western basin sediments testifies to the gradual influence of the hydrothermal activity in the deep in the beginning of the Atlantis II Deep sedimentary history. The strontium isotopic composition of solid samples from younger metalliferous facies is fairly uniform and close to that of the present-day brine. This isotopic homogeneity indicates that the isotopic composition of mineralizing fluids did not change during the time of deposition of the metalliferous sediment.

1. INTRODUCTION

Since the scientific community first became aware of the importance of oceanic hydrothermal activity in the global cycling of chemical species (Edmond et al., 1979, 1982), much attention has been focused on the processes that control hydrothermal fluid chemistry. One of the keys to defining the origin of the fluids at the spreading centers was the use of isotopic geochemistry, particularly strontium isotopes (Vidal and Clauer, 1981; Albarède et al., 1981; Elderfield and Grieves, 1981; Michard et al., 1984; Piepgras and Wasserburg, 1985; Hinkley and Tatsumoto, 1987). The strontium isotopic composition in the fluid depends strongly on exchange with various rock reservoirs and on mixing of fluids with different isotopic compositions (Faure and Powell, 1972; Faure, 1986; Allègre, 1987). Previous isotopic studies at sediment-free ridges clearly indicate that the chemistry of hydrothermal fluids results from seawater and basalt interactions. On sediment-covered ridges, the fluids also interact with the sediment (Von Damm et al., 1985; Campbell et al., 1994). At venting sites on sediment-free ridges, hydrothermal fluids are mixed and diluted with seawater and hydrothermal deposits are limited to the proximity of the vent.

Among the numerous hydrothermal fields (Rona and Scott, 1993), the Atlantis II Deep was discovered first (Miller et al., 1966). It is a large (60 km²) brine-filled basin located at the

axial zone of the young oceanic basin of the Red Sea (Fig. 1). The salt concentration of the lower part of the brine pool of about 27% TDS is close to saturation with halite (Anschutz and Blanc, 1993a) with temperatures between 60 and 66°C. The particular geological environment has allowed metalliferous sediments to be deposited over an area much larger than is typical for deposits forming close to the buoyant-plume systems at the mid-ocean ridges.

In spite of numerous investigations, the origin of the hydrothermal brine pool in the Atlantis II Deep is still a matter of debate. Based on salinity and on oxygen isotopes, the origin of the brine has generally been ascribed to the interaction of Red Sea water with the Miocene evaporites that underlie the Red Sea (Craig, 1969; Schoell and Faber, 1978). Previous isotopic studies of strontium, lead, oxygen, sulfur, and helium indicate that three major reservoirs strongly influenced the chemical and isotopic compositions of the brine: seawater, marine sedimentary rocks including evaporites, and oceanic basalts (Carwile and Faure, 1971; Schoell and Stahl, 1972; Delevaux and Doe, 1974; Lupton et al., 1977; Zierenberg and Shanks, 1986; Dupré et al., 1988; Blanc et al., 1995). The purpose of this paper is to estimate the contribution of the sedimentary and basaltic endmembers to the isotopic composition in strontium of the fluids and to define the parameters that influenced the isotopic composition of strontium through time. These results yield information about the dynamics of the system. The layered metalliferous sediments of the Atlantis II Deep, which precipitated from the overlying brine pool, record 25,000 years of hydrothermal history (Shanks and Bis-

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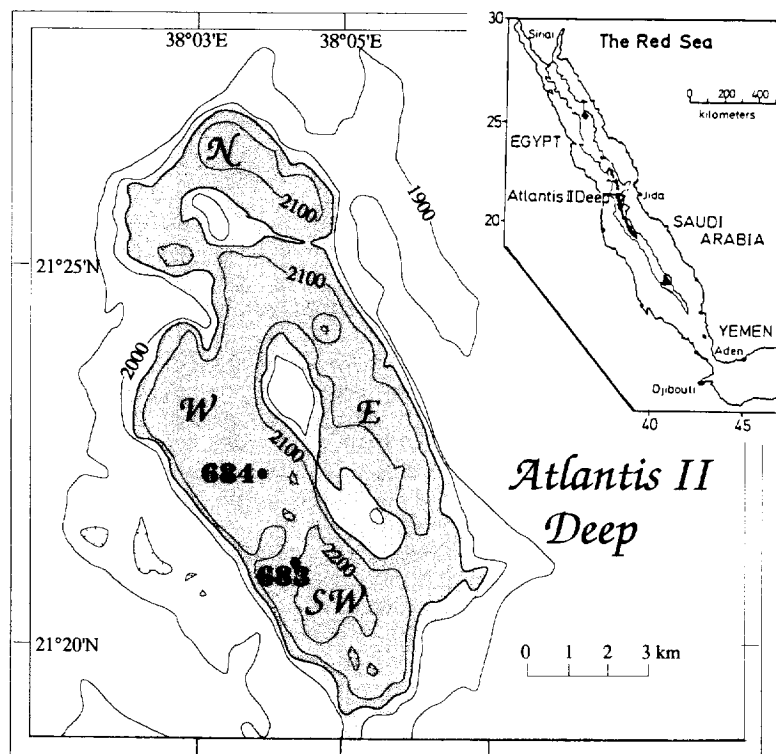


FIG. 1. Bathymetric map of Atlantis II area showing the location of cores 683 and 684 in the Atlantis II Deep. The contour lines are corrected for the higher sound velocity in the brines. The grey area corresponds to the brine-filled deeps. The 2000 m contour line corresponds approximately to the top of these areas. The dark area, limited by the 2050 m contour line, shows the extent of the Atlantis II Deep lower brine.

choff, 1980). Numerous studies (see Bischoff, 1969a; Bäcker and Richter, 1973; Bäcker, 1976; Pottorf and Barnes, 1983; Anschutz and Blanc, 1995a and references therein) showed that the nature of the sediment has changed through time; therefore, hydrothermal activity has also changed. However, one important question still remains unanswered: do the mineralogical variations correspond to the variations in hydrothermal fluid chemistry or do they reflect different stages of mixing of the fluids with seawater? Strontium isotopic data on sediment and interstitial water from two cores were obtained in order to define the origin and the evolution of the mineralizing fluid.

2. MATERIAL AND METHODS

2.1. Material

Two cores were collected during the Hydrotherm cruise (May, 1985) on the RV *Marion Dufresne* (Blanc et al., 1986). Core 683 was collected in the southwestern basin at 2174 m (21°20.75' N/38°04.85' E) and Core 684 in the western basin at 2110 m (21°22.30' N/38°03.55' E) (Fig. 1). Both cores reached the basaltic substratum and contain the entire sedimentary sequence. Disturbed layers such as breccias or slump deposits, which have been described in other Atlantis II Deep cores (Bäcker and Richter, 1973), were not observed in these cores. This suggests that the sedimentary sequence sampled reflects the undisturbed sequence of the deposits. The major mineral groups characterizing the sediment are sulfides, sulfates, carbonates, oxides, and silicates. Iron-rich clay compounds of both cores have been described in previous studies (Badaut, 1988; Badaut et al., 1990). A total of 120 samples were previously taken from these cores to define the mineralogical and chemical variability along the sedi-

mentary column. The analytical methods and the results of the mineralogy and the chemical composition of the sediments are described in detail elsewhere (Anschutz, 1993; Anschutz and Blanc, 1995a).

Core 684 from the western basin is divided into four main units (Fig. 2). Basalt was recovered at the base of this Core. Unit 1 (bottom to 1155 cm) consists mainly of detrital and biogenic material enriched in foraminifera, radiolaria, and pteropod fragments and most of this unit is not of hydrothermal origin. However, this sediment also contains mixed manganese, iron, magnesium, and calcium carbonates, including ankerite, kutnahorite, dolomite, and siderite, and three stratified intercalations of goethite or lepidocrocite mixed with siderite, which indicate the onset of hydrothermal activity. XRD analyses show that Unit 2 is characterized predominantly by sulfide minerals. Anhydrite is common at the bottom of Unit 2. Carbonates in this unit are siderites containing MnCO_3 in solid solution. Biogenic amorphous silica (diatoms and radiolaria) can comprise more than 20 wt% of some samples of Unit 2, estimated by microscopic examination. Few calcareous tests were found. Unit 3 is characterized by the predominance of iron and manganese oxides and oxyhydroxides. Goethite, hematite, manganite, groutite, and todorokite are the principal mineral species. They occur in variable proportions throughout the unit. Unit 4 (335 cm to top of the Core) is characterized by sulfides, clays, and poorly-crystallized material rich in Fe and Si.

Two major units were defined in Core 683 of the southwestern basin (Fig. 2). The lower unit (Unit L) consists of anhydrite (10–70 wt%), talc, serpentine (up to 30 wt%), and Fe-oxides (20–60 wt%). The upper unit (Unit U) is essentially composed of anhydrite (80–90 wt%) in its lower part (1180–1100 cm). At 1090 cm, sulfides represent 55 wt% of the solids. Above, Unit U is characterized by the occurrence of sulfides and abundant clay and poorly crystallized Fe- and Si-bearing material.

The uppermost 10 m of Core 683 do not look like classical marine sediments since the solid fraction of the mud is only 5–12 wt% and the pore fluids represent up to 95%. However, this sediment does not

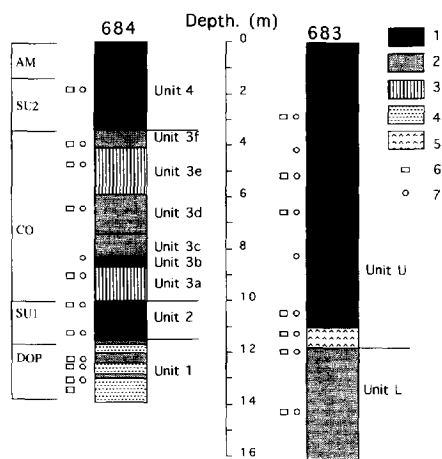


FIG. 2. Synthetic lithostratigraphy of the cores 683 and 684 and sampling positioning. 1: Sulfide-bearing facies; 2: iron-oxide and oxyhydroxide-rich facies; 3: manganese-oxide and oxyhydroxide-rich facies; 4: nonmetalliferous layers; 5: anhydrite facies; 6: solid fraction sampling for Sr analyses; 7: interstitial water sampling for Sr analyses. Corresponding facies proposed by Bäcker and Richter (1973) are shown for Core 684: detrital-oxide-pyrite (DOP), lower sulfide (SU1), Central oxide (CO), upper sulfide (SU2), and amorphous-silicate (AM).

behave like a liquid mud. It has the consistency of a coherent and very soft solid. At the bottom of Unit U, the porosity decreases and the solid fraction reaches 58 wt%. The solids content at the top of Core 684 (Units 4 and 3) is similar to that of Unit U in Core 683. The proportion of solids rapidly increases in Unit 2 becoming constant at 46 wt% in Unit 1. The interstitial water is, therefore, the most important fraction of the muds. The chemical analysis of the interstitial water has been reported by Blanc (1987). The concentrations of the major dissolved elements, such as the alkali metals, the alkaline earths, and chloride, show no variation within the cores. They are similar to those of the present-day lower brine that covers the sediment.

2.2. Sampling and Analytical Methods

The eighteen samples used for the study of the solid fraction were chosen as representative of each depositional unit (Fig. 2). Three aliquots were extracted from each sample. The first was sieved and used for microscopic examination to determine microbiota (Anschutz and Blanc, 1993b). The second was dried and powdered for X-ray diffraction and bulk chemical analysis (Anschutz and Blanc, 1995a). The third was used for the strontium isotope study. This aliquot was washed with distilled water in order to remove all salt and strontium contained in the interstitial water and then powdered. Approximately 150 mg aliquots of the powders were spiked and dissolved with a mixture of HF/HNO₃, HClO₄, and HCl in PTFE pressure vessels. After dissolution, the strontium was extracted using quartz ion exchange columns (Birck, 1979).

The samples used for the interstitial water studies (Fig. 2) were collected immediately after the recovery of the cores. Interstitial water was collected by squeezing under nitrogen pressure (Reeburgh, 1967). The brine pool was sampled at the coring site with 12 L Niskin bottles. The samples were filtered through 0.45 μm Millipore® filters, acidified, and stored in darkness at 4°C in pre-washed polypropylene bottles. The strontium spiked solutions were dried at 75°C in PTFE beaker. Sample were loaded in 2.5 N HCl solution onto quartz ion exchange columns.

Strontium concentrations and isotopic compositions were measured with a fully automated VG-sector mass spectrometer. A strontium standard (NBS987 Sr) was measured routinely each time samples were run. The 2σ errors listed in Table 1 for ⁸⁷Sr/⁸⁶Sr reflect in-run precision. However, these errors are often lower than those

associated with external reproducibility. More realistic minimum 2σ errors, based on the reproducibility of the standard, are probably ±0.000012.

3. RESULTS

3.1. Interstitial Water and Brine Pool

The concentration of strontium of the lower brine is 45.1 ± 0.4 ppm (two samples). This value was the same at different locations of the brine in 1966 (Brewer and Spencer, 1969), in 1976 (Danielsson et al., 1980), and in 1978 (Zierenberg and Shanks, 1986). This is four times higher than in the overlying seawater (10.74 ppm; Blanc, 1987). Strontium concentration in interstitial water from Core 683 is almost invariant throughout the sediment pile (Fig. 3), ranging between 45.0 and 48.1 ppm (Table 1). However, in Core 684, strontium concentrations are slightly higher and range between 45.5 and 52.7 ppm (Table 1). The highest concentrations occur in the manganese and iron oxide and oxyhydroxide-rich Unit 3, but they are not very different from the strontium concentration in the present-day lower brine.

The average ⁸⁷Sr/⁸⁶Sr ratio of the interstitial water from Core 683 is 0.707112 ± 0.000010 (Fig. 3). This value is close to that of the lower brine, i.e., 0.707104 (Blanc et al., 1995). Carwile and Faure (1971) made the same observation based on ⁸⁷Sr/⁸⁶Sr ratios of connate waters removed by washing from sediment in R/V *Chain* Core 128P from the Atlantis II Deep. The scatter of the ⁸⁷Sr/⁸⁶Sr values in the interstitial water from Core 684 is more significant (Fig. 3). The ratio ranges between 0.70715 and 0.70747 (Table 1). The highest ratios correspond to samples with highest strontium concentrations. The strontium in Atlantis II Deep interstitial solutions is significantly less radiogenic than strontium in Red Sea normal seawater (0.70916; Blanc et al., 1995).

3.2. The Solid Fraction

Most of the bulk sediment contains Sr-rich minerals such as anhydrite, calcite, and manganese oxide, and strontium concentrations are as high as 1860 ppm (Table 1). The sediments that are most depleted in strontium (<100 ppm) are those that are essentially composed of iron oxide or oxyhydroxide. In contrast to the interstitial waters, the isotopic composition of the solid fractions is highly variable, ranging between those of the brine and more radiogenic values up to 0.70895 (Fig. 3). The most radiogenic values correspond to the sample collected in the nonmetalliferous sediment of Unit 1 at the bottom of Core 684. This sediment contains mainly biogenic particles. Sample 84-15 has a ⁸⁷Sr/⁸⁶Sr ratio of 0.70895, which is close to, but slightly below, the measured value for seawater (0.70916). With decreasing depth, the ⁸⁷Sr/⁸⁶Sr ratio of the sediments gradually decreases to 0.707564 (sample 84-11, collected in sulfide bearing Unit 2). Despite the great mineralogical variability of the metalliferous sediment of Units 2, 3, and 4, the ⁸⁷Sr/⁸⁶Sr ratios do not change significantly further towards the top of the core. Sample 84-12 corresponds to one of the goethite layer in Unit 1. Its isotopic ratio is 0.70803, which is intermediate between the metalliferous and the biogenic sediments. This sample contains no biogenic components.

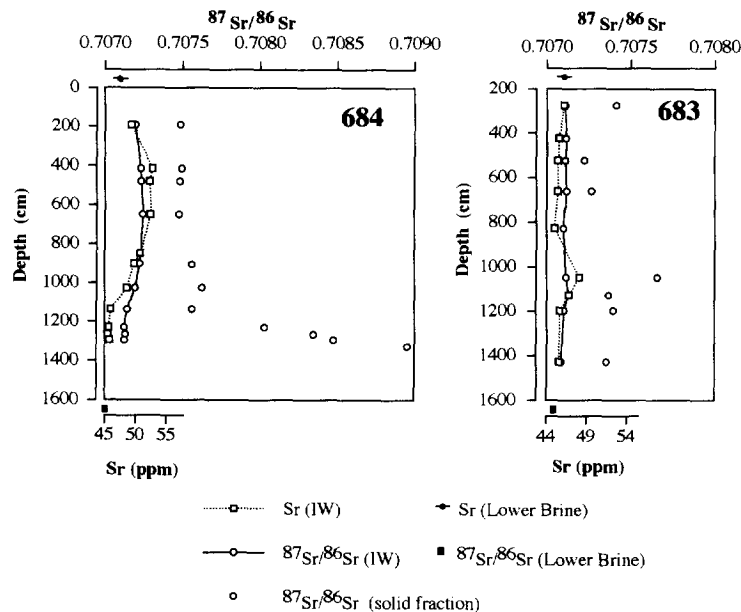


FIG. 3. Strontium isotopic ratio and Sr concentration of interstitial waters and strontium isotopic ratio of solid fraction vs. depth for the Atlantis II Deep cores 683 and 684.

Three anhydrite-rich samples from bottom of Core 683 show similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, ranging between 0.707357 and 0.707398. The strontium concentration of these sample is highly variable, ranging from 47.56–1860 ppm. The strontium content in the bulk samples is most likely related to the anhydrite abundance. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the four sulfide-rich samples from Unit U, which range between 0.707228 and 0.707659, are similar to those of Unit L and the metalliferous sediments from Core 684. Our results agree with those of Carwile and Faure (1971) and Cocherie et al. (1994) who obtained average ratios of 0.7073 ± 0.0005 and 0.70755 ± 0.00015 , respectively, for sediment samples from the Atlantis II Deep. These values are significantly lower than the value for mixed biogenic and detrital sediments of the Red Sea Holocene, i.e., 0.7092 ± 0.0002 (Cocherie et al., 1994).

In summary, interstitial waters of Atlantis II Deep sediments have strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are close to those of the present-day lower brine. Because the variable abundance of Sr-rich mineral species, the strontium concentration varies a great deal throughout the metalliferous sediment series. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios do not vary drastically from one sample to another. These ratios are close to, but slightly above the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the interstitial water. In the nonmetalliferous sediment at the bottom of Core 684, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases downward.

4. DISCUSSION

4.1. Origin of the Lower Brine

The Atlantis II Deep lower brine has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.707104, which is lower than that in seawater, but higher than in open oceanic hydrothermal solutions. Hydrothermal endmembers of East Pacific Rise at 21°N (Albarède et al., 1981; Piepgras and Wasserburg, 1985), and at 13°N (Grimaud et al., 1984; Michard et al., 1984), on the Juan de Fuca

ridge (Butterfield et al., 1990), and on the mid-Atlantic ridge, at TAG and MARK (Edmond et al., 1990) have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging between 0.70281 and 0.70465. The strontium isotopic composition of hydrothermal solutions produced at sediment-free ridges reflects the exchange of seawater strontium with basaltic strontium during the alteration and metamorphism of the oceanic crust (Albarède et al., 1981; Piepgras and Wasserburg, 1985). Seismic records and borehole 227 of the DSDP Leg 23, located a couple of miles from the Atlantis II Deep, show that beyond the Atlantis II Deep area the oceanic crust is covered by a thick sequence (several hundred meters) of Neogene sediment consisting of Miocene evaporite and Plio-Pleistocene carbonate and black shale (Whitmarsh et al., 1974). Uncovered basaltic crust occurs in the southern part of the Red Sea axial valley far from the Atlantis II Deep. Therefore, direct infiltration of seawater into the basaltic substratum is unlikely. Instead, seawater recharge to the hydrothermal system must be predominantly through the sediment cover. The salinity of the present-day brine in the Atlantis II Deep points to the important role that Miocene evaporites have in producing the mineralizing fluids in the system and is a major difference between the Atlantis II Deep and open-ocean systems (Zierenberg and Shanks, 1986; Blanc et al., 1995).

Knowing the strontium parameters for the different reservoirs (Fig. 4), the strontium isotopes may clarify the fluid evolution. The strontium isotopic composition and strontium concentration of the present-day Red Sea water are 0.709167 and 10.74, respectively (Blanc, 1987). The strontium isotope ratio of upper Miocene evaporite collected in borehole DSDP 227 is close to that of seawater and averages 0.70894 ± 0.00002 (Zierenberg and Shanks, 1986). The interstitial brine from this sediment contains 100–150 ppm of dissolved strontium (Manheim et al., 1974). The $^{87}\text{Sr}/^{86}\text{Sr}$ of these interstitial brines has not been measured, but it can be expected

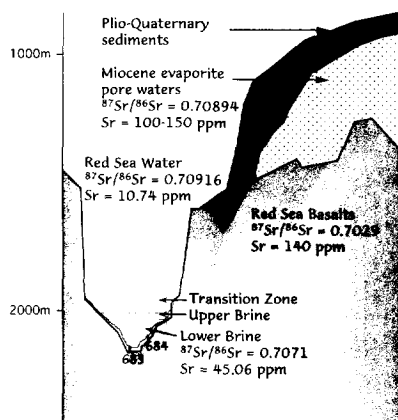


FIG. 4. Schematic cross section of present-day environment of the Atlantis II Deep, showing the isotopic composition and concentration of Sr: Red Sea water (Blanc, 1987); Atlantis II Deep lower brine (this study); upper Miocene evaporite (Manheim et al., 1974; Zierenberg and Shanks, 1986). Crustal basalt of the Red Sea (Barbieri et al., 1980; Eissen et al., 1989; Bosch, 1991; Volker et al., 1993).

to equal 0.70896 if in isotopic equilibrium with the soluble salts. Thus, we assume that the hydrothermal recharge solution had an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70896 and an initial strontium content of 100–150 ppm prior to interaction with the basaltic crust. Basalt collected at the axial rift of the Red Sea yields $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70269 to 0.70315 (Barbieri et al., 1980; Eissen et al., 1989; Bosch, 1991; Volker et al., 1993). The average Sr content of Red Sea fresh basalt is 140 ppm (Eissen et al., 1989). The strontium isotopic composition of the Atlantis II lower brine is between that of the Miocene evaporite (or present-day seawater) and that of Red Sea basalt. Therefore, the strontium isotopic composition of lower brine must reflect the water/rock ratio between the recharging fluid and the basaltic crust. Since direct interaction of seawater with the basaltic substratum is unlikely, we can assume that most of the strontium in the hydrothermal brine results from the interaction of an interstitial brine, which exchanged with the Miocene evaporites and underlying basalts, as previously suggested by Zierenberg and Shanks (1986).

According to Faure (1986), the water/rock ratio can be calculated as follows:

$$\frac{W}{R} = \frac{C_{\text{rock}}^i (\epsilon_{\text{rock}}^i - \epsilon_{\text{rock}}^f)}{C_{\text{solution}}^i (\epsilon_{\text{rock}}^f - \epsilon_{\text{solution}}^i)}, \quad (1)$$

where W and R are the mass of water and rock, respectively. C and ϵ are, respectively, the Sr concentrations and the stron-

tium isotopic compositions of the solution and the rock. Superscripts i and f refer to the initial and the final state. The ϵ parameter is defined relative to a standard (CHUR) (DePaolo and Wasserburg, 1976):

$$\epsilon = 10^4 \left[\left(\frac{^{87}\text{Sr}/^{86}\text{Sr}}{(^{87}\text{Sr}/^{86}\text{Sr})_{\text{CHUR}}} \right) - 1 \right] \quad ({}^{87}\text{Sr}/^{86}\text{Sr})_{\text{CHUR}} = 0.7045. \quad (2)$$

Assuming that complete isotopic exchange has been reached, i.e., $\epsilon_{\text{rock}}^f = \epsilon_{\text{solution}}^f$, a W/R ratio for the Atlantis II brine pool of about 2–3 is calculated from the values compiled in Table 2. However, the use of Eqn. 1 implies total reaction and a simple mixing relationship in the reaction zone of water and basalt. In fact, experimental studies (Seyfried and Janecky, 1985; Berndt et al., 1988, 1989) showed that strontium data of oceanic hydrothermal systems provide an estimate of the amount of Sr-bearing primary phase of oceanic crust which have been converted to secondary phases. Use of strontium data to calculate the actual W/R ratio requires knowledge of the reaction paths (Berndt et al., 1988), a fact which has not been recognized here. Thus, the value of W/R ratio of 2–3 calculated with Eqn. 1 is a maximum value. However, this number agrees with the value of 1.5–2.5 determined using the same equation for the hydrothermal system of the East Pacific Rise at 21°N (Albarède et al., 1981; Piepgras and Wasserburg, 1985), and suggests that the chemical and physical mechanisms governing composition of the hydrothermal mineralizing fluids are similar for these two systems. The main difference between them is that the chemical composition of the initial solution that leached the basaltic substratum is a salt-enriched solution for the former and seawater for the latter.

4.2. Brine Pool History

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the solid fraction of metalliferous sediments (i.e., units 2, 3, 4, L, and U) show little variation, ranging between 0.707228 and 0.707659 (Table 1), although mineralogy changes considerably from one sample to another. For comparison, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of solids in hydrothermal chimneys of the East Pacific Rise show larger variations with values ranging between 0.70554 and 0.70795 (Albarède et al., 1981; Vidal and Clauer, 1981). These variations have been attributed to seawater and hydrothermal fluid mixing in different proportions during precipitation, and to post-depositional adsorption of Sr from seawater. The homogeneity of the strontium isotopic signature in the Atlantis II Deep sediments suggests that the deep has been isolated from seawater

Table 2: Sr concentration and isotopic composition of environments surrounding the Atlantis II Deep and of the lower brine.

ENVIRONMENT	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	ϵ	REFERENCES
Seawater	10.74	0.709167	+66.25	1
Lower Brine	45.10	0.707104 0.70702	+36.96 +35.77	1 and this study 2
Interstitial waters of Miocene evaporites	100-150 (3)	0.70894 (2)	+63.02	3-2
Red Sea Basalts	140 (4)	0.70269-0.70315	-25.69- -19.16	4, 5, 6, 7

1: Blanc (1987), Blanc et al. (1995); 2: Zierenberg and Shanks (1986); 3: Manheim et al. (1974); 4: Eissen et al. (1989); 5: Barbieri et al. (1980); 6: Bosch (1991); 7: Volker et al. (1993).

by a brine pool, the isotopic composition of which remained constant and close to 0.707 since the deposition of Unit 2, i.e., for at least 11,000 years (Shanks and Bischoff, 1980).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the solid fraction of the metalliferous facies are always slightly higher than in the interstitial brines. A detailed microscopic observation indicates that the excess radiogenic strontium relative to brines in the sulfide-rich Units 2, 4, and U can be linked to the content of biogenic particle that precipitated from the photic zone of seawater (i.e., foraminifera, pteropods, and radiolaria). We suggest that strontium isotopic composition of the sulfide minerals, the iron-rich clays, and the anhydrite is similar to that of the interstitial water. These minerals were probably precipitated from a solution with a constant isotopic signature similar to the present-day lower brine, i.e., a solution which has percolated through the Miocene evaporite and reacted with basaltic substratum with a maximum water/rock ratio of 2–3.

The sediment of Unit 3 contains no or very few (<0.1 wt%) biogenic particles. The strontium isotope ratio in Unit 3 solids higher than that of the lower brine indicates that the iron and manganese oxides and oxyhydroxides in this unit were formed from a more radiogenic solution than the present-day lower brine or interstitial water. This solution could be derived from a mixture of seawater and hydrothermal brine endmembers.

Unit 1 of Core 684 is rich in biogenic material and has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.709 at the bottom and 0.708 at the top. These values are more radiogenic than those of the interstitial waters, suggesting that the strontium in the interstitial fluids is not representative of that originally trapped during sedimentation and indicating that the Sr in the solid fraction is not re-equilibrated with the strontium in the present-day porewater. Previous studies (Anschutz and Blanc, 1995b) have shown that calcite and aragonite in the planktonic tests in Unit 1 were transformed to calcium, magnesium, manganese, and iron carbonate solid solutions through bacterially mediated reactions. These high iron and high manganese-bearing minerals developed in an environment favourable to bacterial activity, containing biogenic carbonate, organic matter, and iron and manganese oxides. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio suggests that this environment was distinct from the Red Sea pelagic environment during the time of Unit 1 deposition. The Atlantis II Deep was, therefore, under the influence of hydrothermal activity before the deposition of the metalliferous facies that succeed the Unit 1 facies (i.e., more than 11,000 years ago).

4.3. Diagenetic Environment

The strontium isotopic composition and the strontium concentration in the interstitial water of Cores 684 and 683 are similar to those of the lower brine. The salinity of these solutions is also similar (Blanc, 1987). The interstitial water seems to have re-equilibrated with the lower brine through advection and is, therefore, younger than host sediment. Slight variations in the strontium isotopic composition of porewater result probably from reaction with the host sediment. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are in the interstitial waters of Core 683 and of the bottom of Core 684 (i.e., 0.70712 ± 0.00003), where calcite and anhydrite are the major Sr-bearing minerals. It indicates that little or no exchange of Sr has taken place

recently between the more radiogenic solid fraction (0.707228–0.708955) and the interstitial water. Indeed, calculation showed that both calcite and anhydrite are in thermodynamic equilibrium with the porewaters of the Cores 683 and 684 (Anschutz, 1993). Therefore, these minerals do not release strontium by dissolution.

The diagram of the strontium isotopic composition vs. the reciprocal of concentration shows that the interstitial waters lie on a line with negative slope which intercept with the $^{87}\text{Sr}/^{86}\text{Sr}$ ordinate at $1/\text{Sr} = 0$ is at 0.7080–0.7084 (Fig. 5). The interstitial waters collected in the Mn- and Fe-oxide-rich sediment from Unit 3 are the most radiogenic ($^{87}\text{Sr}/^{86}\text{Sr} > 0.70722$). The linear trend suggests that additional strontium with a ratio of 0.7080–0.7084 was released by solid particles in the interstitial environment of the Unit 3. The ratio of 0.7084 is too low to assign the input of strontium to the dissolution of microbiota or Miocene salts, therefore, the manganese and iron oxide of the Unit 3 themselves must have furnished the additional radiogenic Sr.

The mode of manganese and iron oxide precipitation in the Atlantis II Deep is well documented (Bischoff, 1969b; Danielsson et al., 1980; Hartmann, 1985; Anschutz, 1993). Diffusive and advective transport of dissolved iron and manganese from the lower brine to the overlying oxic upper brine or to the transition zone with seawater induces oxidation and precipitation of amorphous manganese and iron hydroxides. The salt and the strontium content of these environments, where initial precipitation of hydroxides occurs, is intermediate between seawater and lower brine composition (Blanc et al., 1995). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of strontium adsorbed during precipitation on the hydroxide must be, therefore, between 0.707 and 0.709. The initial hydroxide precipitates of the Unit 3 were diagenetically recrystallized in more stable forms, such as goethite, hematite, manganite, or todorokite (Anschutz, 1993). Thus, the trend with more radiogenic composition defined by the interstitial waters could be explained by partial isotopic re-equilibration of the hydroxides with the interstitial

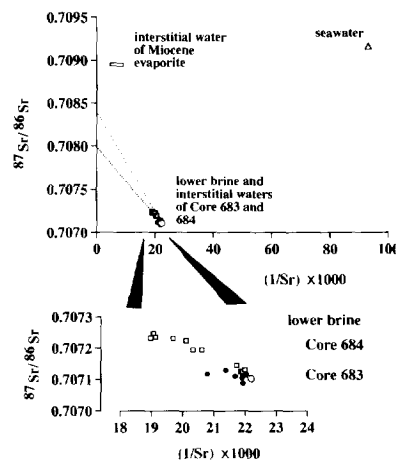


FIG. 5. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ for aqueous solutions of the Atlantis II Deep hydrothermal system. Interstitial waters of cores 683 and 684 described approximately a linear trend. Note the extension of the trend, which excludes a binary mixing of seawater or porewater of Miocene evaporite with lower brine for explaining the origin of the linear trend.

waters due to recrystallization of the initial phases, leading to a release of strontium with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close to 0.708.

The curve-shaped profile of strontium concentration and the discussion in the former paragraphs suggest that the timing of the strontium release within the pore media of the Unit 3 can be calculated by using a diffusion model. Calculations on diffusion can be made, assuming an original strontium concentration in the porewater as the concentration in the present-day lower brine and a release of supplementary strontium from host sediment of Unit 3 (Fig. 6). After some simplification, the solution of Fick's second law becomes (Crank, 1975)

$$C(x, t) = C_i + (C_0 - C_i) \operatorname{erfc}(x/2(Dt)^{1/2}),$$

where $C(x, t)$ is the concentration of strontium at a distance x of Unit 3 boundary at time t ; C_i is the initial concentration of strontium (45 ppm); C_0 is the concentration of strontium in Unit 3 (50–53 ppm); erfc is the complementary error function; and D is the effective diffusion coefficient of strontium in interstitial water. Value of diffusion coefficient in free water at standard condition is given by Li and Gregory (1974). True value of D was calculated by applying a correction of salinity, temperature, and porosity (Anschutz, 1993). D is $7.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in Units 3 and 4. In Units 1 and 2, the porosity is lower and the mean value for D is $5.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

The value of t which fits in with the concentration profile of strontium is within an interval of 100 and 300 years (Fig. 6). Aside from the upper decimeters of the sediment column, this age is many times lower than the age of sediment indicating that the porewaters are younger than the host sediment. Recent intrusion of water in the interstitial environment also agrees with data of dissolved hydrocarbons (Blanc et al., 1990).

5. CONCLUSION

The difference between the hydrothermal solution in the Red Sea and the hydrothermal solutions in sediment-free oceanic ridges can be attributed to the different initial composition of the fluid that interacts with the hot oceanic crust. Recharging fluid is seawater in the case of sediment-free ridges and connate or evolved seawater that has dissolved evaporites in the case of the Red Sea. Using the strontium isotopic compositions of the brine and the interstitial water from the Atlantis II Deep, a maximum water/rock ratio similar to that of the hydrothermal solutions in the sediment-free East Pacific Rise is calculated (i.e., 2–3).

The decrease from the bottom to the top of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Unit 1 sediment indicates progressively increasing influence of a hydrothermal brine with a basaltic signature component during deposition of Unit 1 and is interpreted to indicate the initiation of the brine pool. Since deposition of Unit 1, the bottom of the Atlantis II Deep has remained isolated from seawater by a brine pool with a constant strontium isotopic composition. The observed changes in mineralogical compositions along the sedimentary columns cannot be ascribed to the succession of mineralizing fluid supplies of various origin nor by episodic mixing of brine with seawater. The mineralogical changes must reflect variation in the past of temperature and flow rate of the hydrothermal solution into

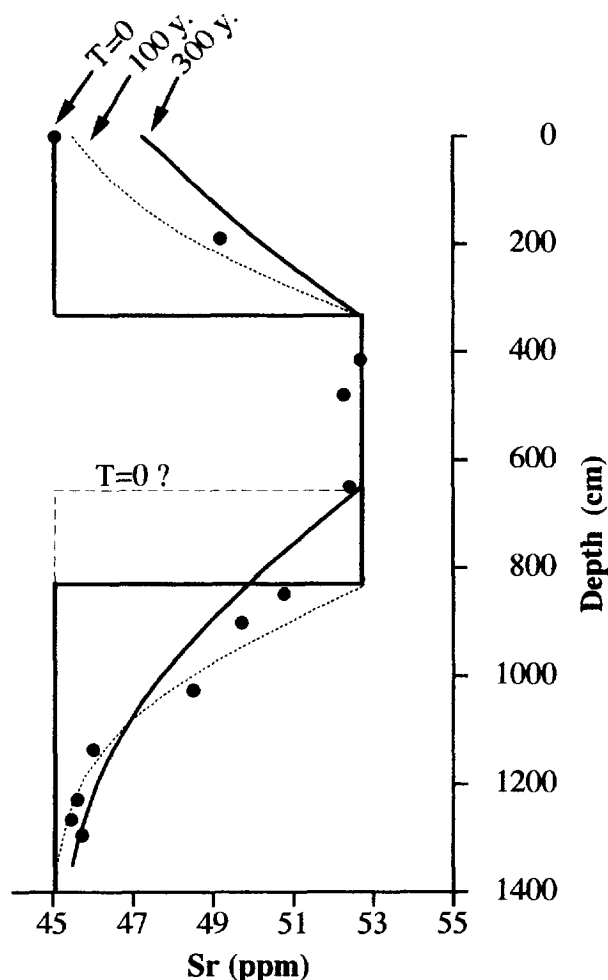


FIG. 6. The calculated (lines) and observed (plots) Sr vs. depth profiles for core 684. At the beginning ($T = 0$), the Sr concentration of interstitial waters is 45 ppm. The concentration is higher (52.7 ppm; the highest measured value) in the layers enriched in amorphous Mn and Fe-oxides of Unit 3 because of the release of adsorbed or coprecipitated Sr to the porewater. For calculation convenience, this value of 52.7 ppm is considered to remain constant, which insinuates that Sr-concentration is buffered by adsorption-desorption equilibria with the sediment. Depending on where the bottom of the layer which releases Sr is fixed (between samples 84-6 and 84-7), the molecular diffusion time which fits in with data is within an interval of 100 and 300 years. This interval can be interpreted as the age of porewater in the core 684.

the Deep responsible for variations in the metal and sulfur input and the physicochemical properties of the brine pool.

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