

Geochemical dynamics of the Atlantis II Deep (Red Sea): silica behavior

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Abstract

Previous chemical analyses of Atlantis II Deep sediments and waters have shown that silica concentrations are abnormally high in comparison with those from other marine hydrothermal sites. New physical and chemical data have been obtained during recent cruises to the Atlantis II area. Seawater, free and interstitial brines have been analyzed for chloride and silica. The hydrographic measurements show that two additional brine layers have been created since 1977. These new observations allow us to re-evaluate the hydrodynamics and the consequences for mass transfer. Silica concentration in the lower brine pool is $913 \pm 18 \mu\text{mol/l}$. Within the upper brine layers, silica concentrations are higher than those expected from simple mixing between the lower brine and seawater. The chemical mass transfers through the brine interfaces are explained by double-diffusion phenomena. Silica concentrations in the interstitial waters ($< 200 \mu\text{mol/l}$) are much lower than those in the lower brine. The high silica concentration gradients observed at the brine–sediment interface suggest that silica precipitates at this boundary layer. Thermodynamic calculation indicates that the interstitial brines are undersaturated with respect to quartz and amorphous silica. These species act probably as major sources for silica, whereas authigenic clay minerals could be the major sink.

1. Introduction

In the submarine environment, the venting of hydrothermal solutions and the formation of mineral deposits occur mainly at spreading centres (see detailed reviews of Von Damm, 1990, and Rona and Scott, 1993). Hydrothermal fluids predominantly derive from interaction between seawater and basalt. Hydrothermal solutions are enriched in dissolved silica with respect to seawater by many orders of magnitude. At high pressures and high temperatures within the oceanic crust, the hydrothermal solutions are generally in equilib-

rium with quartz (Fournier, 1983; Von Damm et al., 1985, 1991). However, at the sites of venting the hydrothermal fluids are mixed with seawater and dilution prevents the precipitation of silica (Haymon and Kastner, 1981). Precipitation of hydrothermal minerals such as quartz, amorphous silica or clays occurs only by either trapping of fluids in the oceanic crust (Alt et al., 1987) or by fluids percolating through sediments (Kastner, 1982).

The Atlantis II Deep is located at the spreading center of the central area of the Red Sea. This axial rift zone is covered or surrounded by a thick evaporite sequence of Miocene age. The evaporites lead to the formation of dense NaCl-rich brines which accumulate in the depression. From 1965 to 1977, many studies have shown that the dense

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brines yield two layers with distinct temperatures and salinities (Brewer et al., 1971; Ross, 1972; Schoell and Hartmann, 1973, 1978; Hartmann, 1980), named the lower and upper brines. In 1977, the temperatures and the salinities of these brines were 61.5°C and 264‰ for the lower brine, and 49.9°C and 142‰ for the upper brine (Schoell and Hartmann, 1978). From 1965 to 1977, a temperature increase of 6°C has occurred in the lower brine, whereas the salinity remained almost uniform during this period of observation ($265 \pm 3\text{‰}$). The occurrence of this stratification has favored the deposition of metalliferous sediments over an area as large as some continental ore deposits such as the Kuroko formation in Japan (Ohmoto et al., 1983) or Troodos Massif in Cyprus (Elderfield et al., 1972; Robertson and Hudson, 1973).

The metalliferous sediments are fine grained, delicately banded silicates, sulfides, oxides and carbonates which have been accumulating for 28,000 years (Ku et al., 1969; Shanks and Bischoff, 1980). Basaltic glass collected at the bottom of some cores indicates that oceanic crust occurs below the sediments of the SW and W basins of the Atlantis II Deep (Fig. 1). The top of the sedimentary series has an interstitial fluid content of up to 95 wt% with a salinity similar to that of the overlying lower brine (Hendricks et al., 1969; Pushkina et al., 1981; Blanc, 1987).

Silica and iron are the predominant chemical components of the sediments. In the upper part of the sedimentary series, the Si and the Fe contents average about 9 wt% and 28 wt%, respectively (Blanc, 1987; Anschutz, 1993). Fe and Si form ferriferous silicates and Si-rich Fe-oxides, which reach up to 95 wt% of the solid fraction of the metalliferous sediments (Anschutz, 1993). The precise identification of silicate species along the sedimentary column allows three groups of clays to be distinguished (Bischoff, 1972; Goulart, 1976; Butuzova et al., 1977, 1979; Al Karguli, 1979; Singer and Stoffers, 1981; Cole and Shaw, 1983; Cole, 1988; Badaut, 1988; Badaut et al., 1985, 1990). They are: (1) detrital clays (kaolinite, illite and chlorite), (2) magnesian clay minerals, such as talc or serpentinite, (3) poorly crystallized and iron-rich compounds. In the most recent sediments, the latter group consists of ferrous smectite,

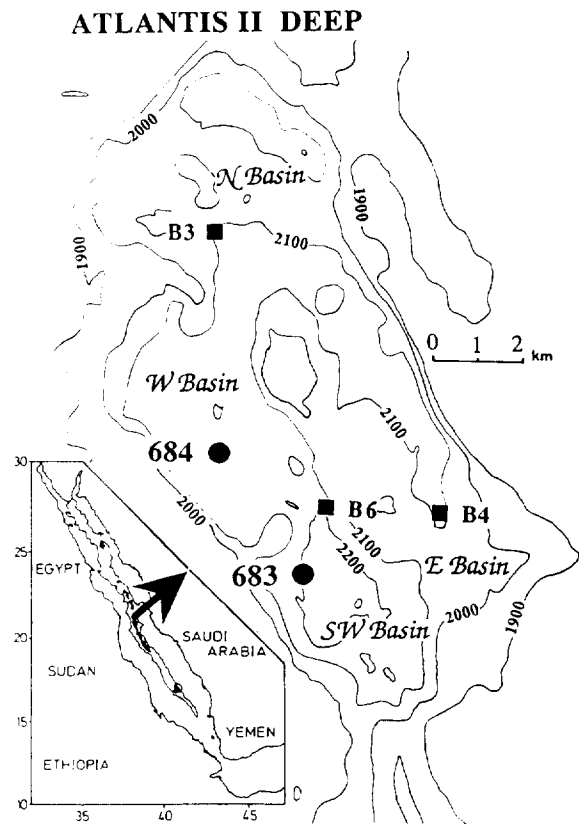


Fig. 1. Map of the Atlantis II Deep area with the position of cores 684 and 683 collected during the HYDROTHERM cruise, in May 1985. B3, B4 and B6 are the locations of seawater and brine collection, sampled in September 1992 during the REDSED cruise.

hisingerite, ferric nontronite, and iron oxides which contain a few percent Si, such as ferrihydrite and ferroxihyte. In the oldest sediments, iron-rich compounds consist of well crystallized ferripyrophyllite (Badaut, 1988; Badaut et al., 1985, 1990).

The enrichment in silica within the Atlantis II Deep metalliferous sediments characterizes this oceanic hydrothermal site. This paper focus on mass transfers and diagenetic processes involving Si-bearing minerals and silica dissolved in free and interstitial brines. We attempt to determine the internal reactivity in the brine system, using hydrodynamic and thermodynamic considerations. Diffusion is considered as a major process affecting the mass transfers at the brine interfaces. A

thermodynamic model for the behavior of silica in the interstitial and lower brine is described.

2. Sampling and analyses

The material used in this study was collected during the RV *Marion Dufresne* cruises HYDROTHERM 1985 and REDSED 1992. During the HYDROTHERM cruise, two cores were collected into the west part of the Atlantis II Deep (Blanc et al., 1986). Core 683 was collected in the southwest (SW) basin ($21^{\circ}20,75'N$; $38^{\circ}04,85'E$) at 2174 m and core 684 in the west (W) basin ($21^{\circ}22,30'N$; $38^{\circ}03,55'E$) at 2110 m (Fig. 1). Both cores reached the basaltic substratum and contained the whole

sedimentary sequence (Blanc, 1987). Textural types and mineralogic distribution versus depth are shown in Fig. 2. Sediments from the W basin of the deep (core 684) contain a biodetrital series at the bottom (unit 1) with some iron oxyhydroxide layers. The planktonic tests of unit 1 have been transformed by diagenetic reactions. Calcite and aragonite have been transformed in solid solutions of orthorhombic Ca–Mg–Fe–Mn–carbonate, and amorphous silica has been recrystallized into chalcedony or quartz. Iron, zinc and copper sulfides and ferric silicates compose units 2 and 4. Poorly-crystallized iron and silica compounds are the major species of unit 4. Unit 3 contains essentially iron and manganese oxides and oxyhydroxides. The sediments from the SW basin (core 683) are

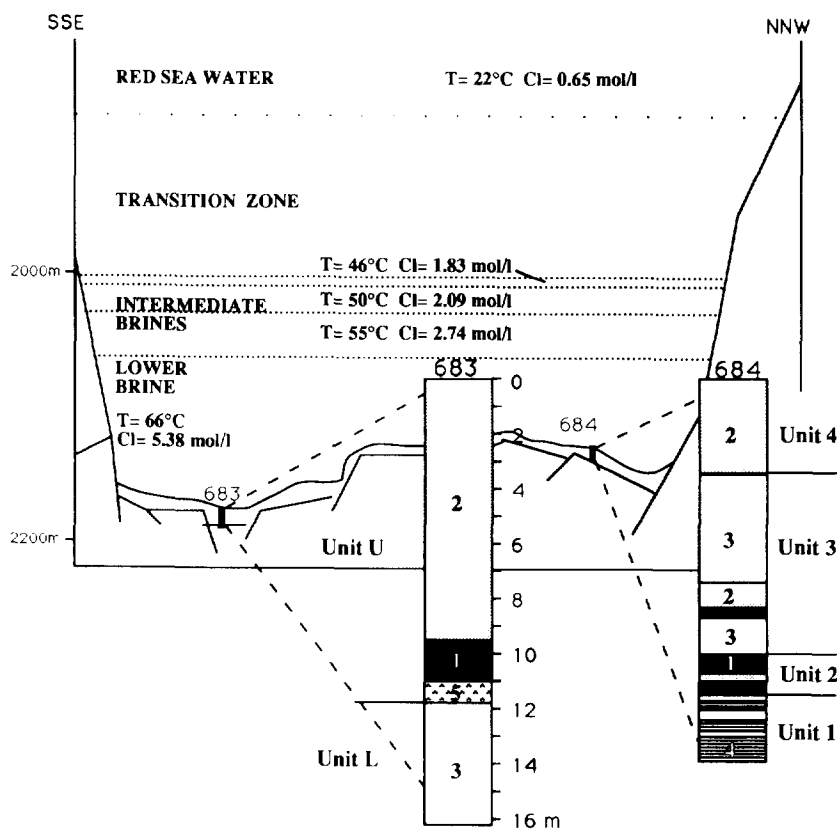


Fig. 2. Schematic NNW SSE transect in the Atlantis II Deep showing the thermal and chlorinity stratification of the brines. The position of the brine interfaces was deduced from bathyprobe data. The vertical scale for Core 684 is the same as Core 683. Lithostratigraphy: 1 = hydrothermal sulfides dominant (pyrite, sphalerite, chalcopyrite); 2 = iron-rich clays dominant; 3 = iron and manganese oxide or oxyhydroxide facies (goethite, lepidocrocite, hematite, magnetite, manganite, todorokite, groutite); 4 = biodetrital sediments facies (foraminifera, pteropods, radiolaria, ..., quartz, feldspar, clays); 5 = anhydrite facies.

divided into two main facies. At the bottom, unit L consists of hematite, magnetite, anhydrite, and magnesian silicate clays. The mineralogy of unit U is similar to that of unit 4 of core 684. The interstitial water samples were collected just after core recovery. Interstitial water collection was performed by squeezing under nitrogen pressure. During the REDSED cruise the seawater and brine column were sampled at three sites (Fig. 1) located in the E basin (site B4), in the W-SW passage (site B6), and in the N passage (site B3). A modified Bissett-Berman CTD bathyprobe system was used with a rosette equipped with twelve 12 L capacity Niskin bottles. The rosette was lowered to the seafloor and samples were collected as the rosette returned to the surface. Brines and interstitial waters were filtered through 0.45 µm Millipore filters, acidified and stored in darkness at 4°C in polypropylene bottles until analysis in the laboratory. Silica concentration was measured by a Technicon autoanalyser using the silicomolybdate method. Precision of the measurements, as determined from duplicate analyses, is 1%. Chloride determinations were carried out by means of potentiometric titration with silver nitrate. The potential was measured with the electrode couple Ag/Ag₂S. The Gran method was used to evaluate the equivalence volume (Jagner and Aren, 1970). Accurate results to within about 0.5% of the

IAPSO seawater standard were obtained with this method. Precision of the analyses, as determined from duplicates, is better than 2% for brines. The chloride and silica concentration are expressed in moles per liter (mol/l), and micromoles per liter (µmol/l), respectively, and given in Table 1.

3. Results

The chloride concentration of the seawater and the free brines is plotted versus depth in Fig. 3. The depth location of the samples was determined using the acoustic record of a pinger and the records of pressure determined by the bathyprobe during REDSED cruise. The major result of the cruise was the discovery of two additional brine layers overlying the preexisting upper brine (Blanc and Anschutz, 1995). The lower brine yields similar chlorinity to that previously determined (Hartmann, 1980). The high chloride concentration (5.38 mol/l) remains its main feature, which is close to saturation with respect to halite (Anschutz and Blanc, 1993a). From the bottom to the Red Sea deep water, the chloride concentrations of the upper brine layers are 2.74 mol/l, 2.09 mol/l and 1.83 mol/l, respectively. Between the upper boundary of the brine pool and the Red Sea deep water, a chloride concentration gradient

Table 1
Concentrations of chloride and silica of seawater and brines sampled at three locations in the Atlantis II Deep

B3			B4			B6		
Depth (m)	Si (µmol/l)	Cl (mol/l)	Depth (m)	Si (µmol/l)	Cl (mol/l)	Depth (m)	Si (µmol/l)	Cl (mol/l)
1088	9.3	0.66	1481	7.9	0.67	1587	7.2	0.69
1884	8.9	0.68	1897	9.3	0.65	1916	24.1	0.70
1912	27.9	0.71	1942	33.2	0.73	1957	37.2	0.73
1944	36.1	0.72	1970	42.2	0.74	1992	63.9	0.74
1955	39.7	0.73	1990	57.6	0.78	2006	424.6	1.83
1973	44.8	0.74	2015	496.2	2.09	2020	635.5	2.74
1995	245.8	1.28	2035	619.8	2.74	2041	643.4	2.73
2015	496.2	2.09	2050	916.8	5.38	2056	931.9	5.38
2034	619.8	2.82	2086	901.8	5.38	2086	931.9	5.38
2054	916.8	5.38	2101	909.3	5.38	2126	931.9	5.38
2070	916.8	5.38	2119	894.2	5.38	2158	931.9	5.38
2087	500.0	5.38	2135	871.8	5.38	2176	901.8	5.38
bottom: 2091			bottom: 2140			bottom: 2180		

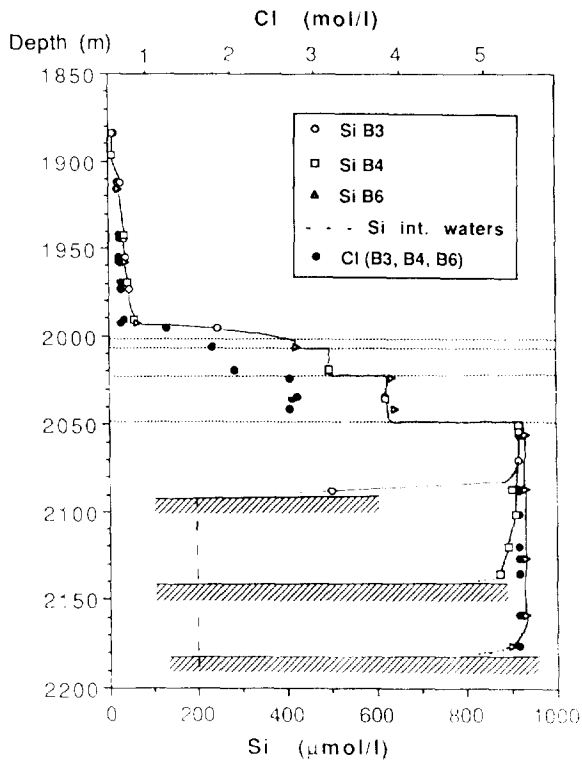


Fig. 3. Concentration versus depth profiles of silica ($\mu\text{mol/l}$) and chloride (mol/l) in seawater and in the different brines at B3, B4 and B6. The position of the brine interfaces was determined from hydrographic measurements. Maximum value of the interstitial waters ($200 \mu\text{mol/l}$) is indicated by a dashed line. The concentration scales have been chosen in such a way that the concentrations of chloride and silica are superimposed in Red Sea deep water and in lower brine. Therefore, chloride profile of the intermediate brine layers corresponds to the theoretical profile of mixing of silica based on chloride concentration.

defines a transition zone, with chlorosity values of 1.83 mol/l and 0.65 mol/l at its lower and upper limits. Silica concentration-depth profiles show a general pattern comparable to that of chloride, however, some differences occur. Silica concentration shows quite uniform values (e.g. $913 \pm 18 \mu\text{mol/l}$) for twelve of the samples collected in the lower brine. However, the sample collected just above the sediment–brine interface at the site B3 has a Si-concentration of $500 \mu\text{mol/l}$. The Si content of the upper brine layers decreases upwards at each brine interface. The values are successively $630 \pm 11 \mu\text{mol/l}$, $496 \pm 5 \mu\text{mol/l}$ and

Table 2
Silica concentrations of interstitial waters of cores 683 and 684

683		684	
Depth (cm)	Si ($\mu\text{mol/l}$)	Depth (cm)	Si ($\mu\text{mol/l}$)
5	48.4	40	110.0
110	84.4	195	126.0
275	46.6	420	59.4
315	72.3	485	69.8
420	86.2	555	90.0
525	82.9	655	83.0
662	81.2	853	145.0
728	66.6	906	74.4
828	138.0	1031	150.0
918	169.0	1141	90.7
1048	127.0	1234	74.7
1128	80.4	1271	118.0
1198	49.2	1300	61.8
1273	87.6	1331	7.5
1428	200.0		
1508	138.0		
		Lower brine	913.0

$425 \pm 4 \mu\text{mol/l}$. The Si-concentration decreases in the transition zone down to the Red Sea deep water value ($9.1 \pm 0.2 \mu\text{mol/l}$).

Alkali, alkaline earth and Cl concentrations of the interstitial waters of the metalliferous sediments have relatively constant values from one core to another (Blanc, 1987). These values are similar to that of the lower brine. Thus, the mineralogical variability that we observe in the cores is not reflected in the chemistry of dissolved major species in the interstitial waters. Dissolved silica concentrations, which range from 7.5 to $200 \mu\text{mol/l}$ (Table 2), are many times lower than that of the overlying brine pool. The changes of silica concentrations in the interstitial water column (Fig. 4) cannot be directly linked to the lithological variations.

4. Discussion

The silica and chloride concentrations profiles in free and interstitial brine are compared and discussed in term of mode of silica transfers from the lower brine to overlying seawater and to the underlying sediment. Different sources of silica are

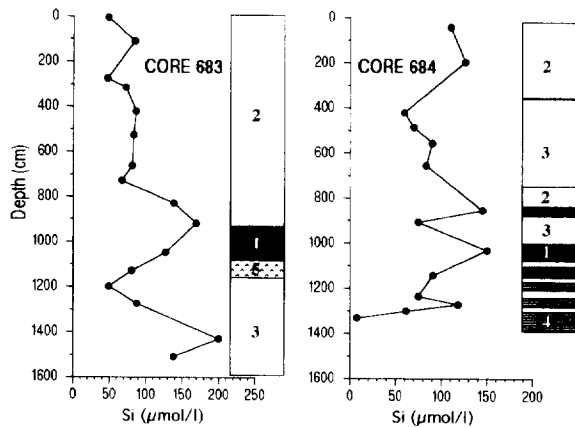


Fig. 4. Concentration versus depth profiles of dissolved silica ($\mu\text{mol/l}$) in the interstitial waters of cores 683 and 684. Lithological facies as in Fig. 2.

tested in order to explain the high content of silica within the sediment.

4.1. Brine stratification

Initial stratification of the brine pool in two layers, as observed from 1965 to 1977, showed that the bottom of the deep was filled by a hot brine called the "lower brine". The lower brine was separated from seawater by the "upper brine", a second brine pool with an intermediate salinity and temperature. This configuration led to an explanation of the mass transfers between the lower brine and seawater in term of mixing. Our present observations, which show that the upper brine is stratified in three layers, calls into question the simple model of mixing between the lower brine and seawater. If these three intermediate brine pools and the transition zone showed a decrease in silica concentration parallel to that of chlorosity (Fig. 3), the chlorosity of the deepest upper brine layer ($\text{Cl}=2.74 \text{ mol/l}$) would correspond to a mixture of 44% lower brine and 56% seawater, whereas the concentration of silica ($630 \pm 11 \mu\text{mol/l}$) corresponds to a different mixing ratio of 69% lower brine and 31% seawater. For the other intermediate brine bodies, the lower brine end-member is also more important for silica than for chloride. Therefore, the simple mixing model does not fit with the silica concentrations.

For different reasons, the enrichment in dissolved silica relative to mixing of the intermediate brines cannot be explained by favourable conditions for the dissolution of detrital or biogenic silica deposition in the Atlantis II Deep. First, the brines are more concentrated in Si than seawater. This decreases the dissolution rate of silicates in brines relative to seawater. Second, at the neutral and acid pH of the brines (Danielsson et al., 1980; Blanc et al., 1986), the dissolution rate of silica mineral species is lower than that in seawater, where the pH is slightly alkaline (Dove and Elston, 1992). Third, the present-day productivity of biogenic silica in the Red Sea surface water is low (Rosenberg-Hermann, 1965). For explaining the silica profile, we propose alternatively that the flux from the lower brine to the upper brines is relatively more important for silica than for chloride. Experimental studies of fluid mechanics (Huppert, 1971; Turner, 1974; Huppert and Linden, 1979) show that mass and heat transfers in a stratified system similar to the Atlantis II Deep system, where a hot brine body is overlain by a cooler, less salty, and less dense solution, consist only of molecular diffusion through the interface which separates the water bodies. In such an experimental system, the stratification is maintained by the different molecular diffusivities of heat and salt, which make opposing contributions to the vertical density gradient. When a hot, dense brine pool is covered by cooler seawater, successive layers of brine are formed which are separated by thin interlayers (Huppert, 1971; Turner, 1974). Heat is the driving force for convection, which homogenizes the brine layers and restricts the thickening of the interlayers, whereas the jump in density is maintained by the excess of salinity in the lower layer. This phenomenon called thermo-haline (or double-diffusive) convection, was invoked for the Atlantis II system on the basis of the physical parameters (temperature, salinity, density) of the brines (Turner, 1969, 1974; McDougall, 1984). If molecular diffusion is the main mechanism of dissolved species transport through the interfaces, the flux of each species should be dependent on its own diffusivity (Griffiths, 1979). However, the Atlantis II Deep brines are characterized by high ionic strengths dominated by Na and Cl, where

the diffusivity of other ionic species is not known because of ion pairing effect and electroneutrality constraint. Furthermore, the ratio of density steps due to salt and temperature of the Atlantis II Deep interfaces is above the maximal value which has been investigated in laboratory experiments. Therefore, the mode of species transfer in the Atlantis II Deep system is not well known. Some dissolved species of the brines, such as Na, Ca, and K, show concentration versus depth profiles which are equal or close to a conservative behavior in comparison with Cl (Danielsson et al., 1980; Hartmann, 1985; Blanc, 1987). This argues more favorably for a transfer of dissolved species from a brine layer to another by mixing rather than by diffusion. But other species such as SO_4 or Mg show non-conservative behavior (Hartmann, 1985), indicating that diffusion must also be important. At pH of the brines, dissolved silica occurs as the species H_4SiO_4 (Iler, 1955). This uncharged species does not enter in the electroneutrality budget of the brine. Therefore, molecular diffusion mode must be shown by silica profile better than by charged species profiles since H_4SiO_4 can be independently transferred from one brine to another according to its own diffusion coefficient, whereas charged species have to diffuse mutually because of the electroneutrality constraint. The value of the tracer diffusion coefficient of H_4SiO_4 at 25°C is $D_{\text{Si}} = 2.2 \times 10^{-9} \text{ m}^2/\text{s}$ (Applin, 1987). The mutual tracer coefficient of the dominant species Na and Cl is $D_{\text{NaCl}} = 1.61 \times 10^{-9} \text{ m}^2/\text{s}$ (Li and Gregory, 1974), i.e. a lower value than that of silica. This fact could explain the shift of the silica profile relative to the chlorosity profile. Therefore, the inconsistency registered between the silica profile and the chlorosity profile suggests that molecular diffusion intervene in mass transfers between the brines. This hypothesis is valid since the Atlantis II Deep system is not in steady state as shown by successive measurements in the Deep in the last thirty years.

Hartmann (1985) noted the same deviation of silica concentrations relative to the theoretical mixing profile, but he explained the silica enrichment of the upper brine by a complex succession of reactions of precipitation or adsorption of silica in the transition zone, followed by re-dissolution

of silica in the water column of the upper brine. However, Hartmann (1985) used a mixing model which did not take into account the diffusivities of the dissolved species. But the double-diffusive behavior of the Atlantis II Deep brines suggests that molecular diffusion cannot be ruled out. Thus, we propose that the dissolved silica profile mainly reflects the upwards output of silica from the Atlantis II Deep to the seawater by diffusion.

4.2. Silica precipitation

We observe that the concentration of dissolved silica in the interstitial waters is depleted with respect to that of the lower brine, and that the silica concentration of the lower brine shows a large decrease near the seafloor (Fig. 3). These results suggest that the silica precipitation does not occur in the water column, but at the sediment–water interface or in the sedimentary column. This hypothesis is emphasized by the following points.

Silica precipitation from a hydrothermal fluid corresponds to a dehydration of H_4SiO_4 :



This reaction is kinetically slow (Ohmoto et al., 1983), and silica may not precipitate during cooling of hydrothermal fluids in contact of cold seawater, even though the saturation index becomes much greater than 1. The absence of silica precipitation is observed in many oceanic hydrothermal settings (Von Damm et al., 1985; Campbell et al., 1988). According to experimental studies by Rimstidt and Barnes (1980) the rate of silica precipitation decreases linearly with decreasing A/M value of the system, where A/M is defined as the ratio of the surface area (*A*) available for nucleation of silica to the mass (*M*) of water. During the venting of a Si-rich hydrothermal fluid that mixes with cold seawater, the A/M ratio of the plume is low, because the only surface area available for nucleation is disseminated sulfides, sulfates or oxides that may precipitate from the same solution. The low A/M ratio makes silica precipitation unlikely in such systems, whereas in the Atlantis II Deep, the hydrothermal solution enriched in silica accumulates in contact with the sediments, instead of being diluted into seawater.

The A/M ratio of the brine at the sediment–water interface is probably higher than that of the ridge hydrothermal sites, and the authigenic silicates occurring at the top of the sedimentary column presumably precipitate at this level.

For the youngest sediments of the Atlantis II Deep, ferrihydrite is the most abundant solid species. Ferrihydrite is a hydrated iron oxide ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), which is poorly crystallized. In Atlantis II Deep, ferrihydrite can contain up to 10% of silica (Badaut, 1988). This mineral could act as the main sink for Si. Experimental results on the formation of ferrihydrite from Fe^{2+} -containing solution (Towe and Bradley, 1967; Atkinson et al., 1968; Chuckrov et al., 1973; Schwertmann and Fischer, 1973; Karim, 1984; Taylor, 1984), suggest that $\text{Fe}(\text{OH})_2$ forms first, before $\text{Fe}(\text{OH})_3$. Ferric hydroxide monomers coalesce ($n\text{Fe}(\text{OH})_3$) and build the framework that constitutes ferrihydrite. Schwertmann and Thalmann (1976) and Karim (1984) showed that the transformation of $\text{Fe}(\text{OH})_3$ into ferrihydrite is enhanced in a silica-rich solution. During this stage, silica is incorporated into the structure of the iron oxide. Depending on the silica content, ferrihydrite can be transformed into a ferric clay mineral (Harder, 1976) or into well crystallized iron oxide or oxyhydroxide (Feitknecht and Michaelis, 1962; Langmuir, 1971; Fischer and Schwertmann, 1975; Schwertmann and Murad, 1983; Cornell and Giovanoli, 1987; Cornell et al., 1987; Cornell, 1988). All these stages are present in the Atlantis II Deep: $\text{Fe}(\text{OH})_3$ occurs as suspended matter in the lower brine (Danielsson et al., 1980; Hartmann, 1985), silica-bearing ferrihydrite occurs in the upper sediments, and iron-rich clays and iron oxides compose the major fraction of the youngest metalliferous sediments (Badaut, 1988).

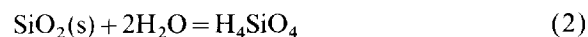
4.3. Water–rock equilibria

Among the silicate minerals present in Atlantis II Deep metalliferous sediments, quartz is ubiquitous, but in low quantity (1 to 20 wt%; Anschutz, 1993). Quartz is mainly of detrital origin (Bäcker, 1976). We have recently shown that diagenetic quartz and chalcedony occur, resulting from the recrystallization of biogenic amorphous silica

(Anschutz et Blanc, 1993b). However, the diagenetic quartz particles and the remaining amorphous silica occur only in the oldest sediments of the deep, in units 1 and 2 of core 684. No quartz neof ormation has been recognized in the most recent sediments, and only a small amount of detrital quartz occurs. In fact, silica occurs in the solid fraction mainly as Si-bearing iron oxides and ferri ferous clays. It is therefore possible that the dissolution of detrital quartz and biogenic amorphous silica occurs in the youngest sediments. Silica contained in authigenic ferrihydrite or clay minerals probably originated from the Si-bearing hydrothermal brine, but an additional source of silica can be supplied by the dissolution of the detrital input if the interstitial waters are undersaturated with respect to quartz. Thus, calculation of the state of saturation of silica in the interstitial brines allows the possibility of an additional source of silica to be tested.

The solubility of the different forms of silica (quartz, chalcedony and amorphous silica) is given by the activity of H_4SiO_4 . An increase in dissolved salt (NaCl) concentration lowers the SiO_2 solubility (Marshall, 1980a,b; Dandurand et al., 1982). On the other hand, the solubility of SiO_2 is enhanced by temperature and pressure increases (Chen and Marshall, 1982).

For the equation of dissolution of SiO_2 :



the activity product is defined as follows:

$$Q = [\gamma_{\text{H}_4\text{SiO}_4} \cdot m_{\text{H}_4\text{SiO}_4}] / [a_{\text{SiO}_2}(\text{s}) \cdot a_{\text{H}_2\text{O}}^2] \quad (3)$$

where $\gamma_{\text{H}_4\text{SiO}_4}$ and $m_{\text{H}_4\text{SiO}_4}$ are the activity coefficient and the molality of H_4SiO_4 , respectively, $a_{\text{H}_2\text{O}}$ is the activity of water and $a_{\text{SiO}_2}(\text{s}) = 1$.

In order to determine the saturation state of the interstitial water and the lower brine with respect to the different forms of silica, the activity of H_4SiO_4 has been calculated using the equation of Marshall (Marshall, 1980a,b; Marshall and Warakowski, 1980; Marshall and Chen, 1982; Chen and Marshall, 1982). The activity coefficient for dissolved silica is calculated as follows:

$$\log(\gamma_{\text{H}_4\text{SiO}_4} / a_{\text{H}_2\text{O}}^2) = E_m + Fm^2 \quad (4)$$

where m is the molality of dissolved salt, E and F are experimentally determined polynomials which depend on the temperature (T , in K):

$$E = a + bT + cT^2$$

$$F = d + eT + fT^2$$

For an aqueous solution of sodium chloride, $a = 0.031949$; $b = 4.6982 \times 10^{-4}$; $c = -8.7442 \times 10^{-7}$; $d = 0.031961$; $e = -1.8951 \times 10^{-4}$; and $f = 2.4453 \times 10^{-7}$ (Chen and Marshall, 1982).

Values of the ionic activity products Q , which have been calculated for Atlantis II Deep solutions, have been compared to the solubility products of quartz, chalcedony and amorphous silica, calculated for the in situ conditions of pressure and temperature from the thermodynamic data of Helgeson et al. (1978) (Fig. 5). The pressure at the bottom of the deep is 220 bars. The temperature of the lower brine was 66°C in 1992 (Blanc and Anschutz, 1995). The temperature of the bottom of the deep was not measured in 1985 during the core collection from which the interstitial waters were sampled. The temperature of the bottom of the deep was 61°C in 1977

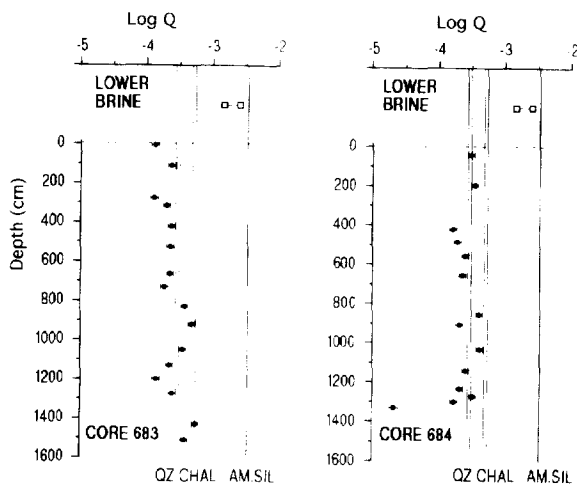


Fig. 5. Activity product ($\log Q$) of silica in interstitial waters (dots) and in the lower brine. Values are compared to the solubility products ($\log K$) of quartz (-3.56 and -3.51), chalcedony (-3.31 and -3.26), and amorphous silica (-2.48 and -2.47), for 220 bars pressure and 61° and 66°C (pressure correction calculated from Helgeson et al., 1978). Error bars correspond to the standard deviation of silica activity coefficient given by Chen and Marschall (1982).

(Hartmann, 1980). Therefore, the in situ temperature of the interstitial environment was certainly between 61° and 66°C. Thus, both temperatures have been used for the thermodynamic calculations. The values of the activity coefficient of Marshall at 61° and 66°C are approximately the same (2.53 and 2.49, respectively) and are within the standard deviation of 6.4% of $\log(\gamma_{\text{H}_4\text{SiO}_4}/a_{\text{H}_2\text{O}^2})$ given by Chen and Marschall (1982). The equilibrium constants of silica phases slightly differ from 61° to 66°C. Values for each mineral are shown in Fig. 5. These calculations show that the lower brine is between saturation with respect to chalcedony and saturation with respect to amorphous silica. This thermodynamic diagnostic indicates that radiolaria tests and diatom frustules which are composed of amorphous silica, are unstable and should dissolve or be transformed into chalcedony or quartz. Interstitial waters are either in equilibrium with quartz, or undersaturated. The samples from units 1 and 2 of core 684, from 1000 to 1200 cm, are near equilibrium with quartz. Therefore, detrital quartz cannot be dissolved, but biogenic silica can be transformed into quartz. In fact, recrystallization of radiolaria into quartz has been observed in these samples (Anschutz and Blanc, 1993b). In a significant part of both cores, interstitial waters are undersaturated with respect to quartz. Therefore, diagenetic quartz cannot precipitate, and detrital quartz and biogenic silica may dissolve and supply an additional amount of Si for the metalliferous sediment. Furthermore, iron oxides, which represent the major fraction of the sediment, have been found to accelerate the dissolution of both amorphous silica and quartz (Beckwith and Reeve, 1964). The silica concentration of the interstitial waters must be controlled by the suite of authigenic clay minerals, which must have a solubility lower than quartz. The saturation state of the interstitial water with respect to the authigenic iron-rich silicates cannot be calculated, because of the lack of thermodynamic parameters for iron in concentrated solutions and because of the difficulty of estimating the equilibrium constants of the poorly crystallized mineral species that compose Atlantis II Deep sediments. Finally, the main result of the thermodynamic calculations is that the silica

present in the authigenic phases is not exclusively of hydrothermal origin, but may also result from the dissolution of detrital quartz or biogenic silica present in the sediments. This conclusion agrees with mass balance calculations for the chemical components of Atlantis II Deep sediment, which are presented elsewhere (Anschutz and Blanc, 1995).

5. Conclusions

The distribution of chloride and silica versus depth in the Atlantis II Deep shows that the brine pool which fills the depression was stratified in four layers in 1992. The study of silica behavior in the Atlantis II Deep gives some indication of the geochemical dynamics of this natural laboratory of mineralization. The mass transfer directions between the different reservoirs (brines, seawater, and sediments) have been defined. Silica concentrations follow the chemical stratification of the brines. Dissolved silica is brought to the lower brine pool by an inflowing mineralizing fluid. Silica escapes upwards mainly by molecular diffusion. Since the diffusion coefficient of silica is high, the distribution of silica and chloride indicates that the elemental flux of silica from the lower brine to seawater is proportionally greater than that of the major dissolved components. Therefore, concentrations of silica in the intermediate brine bodies argue for a general pattern of chemical dynamics of the Atlantis II Deep governed by the double-diffusive phenomenon. The abundance of silicate minerals contained in the metalliferous sediments of the deep also indicates that silica escapes downwards by precipitation. Silica concentration in the interstitial waters are many times lower than that of the lower brine. The high silica concentration gradients observed at the brine–sediment interface suggests that silica precipitates at this boundary layer. The dissolution of biogenic amorphous silica and detrital quartz, which are mostly undersaturated in the interstitial environment of Atlantis II sediments, probably acts as a significant source for silica contained in authigenic minerals.

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