

Diagenetic evolution of the DOP facies from the Atlantis II Deep (Red Sea) : evidence of early hydrothermal activity

Atlantis II Deep
Carbonate solid solution
Early diagenesis
Hydrothermalism

Fosse Atlantis II
Solution solide de carbonate
Diagenèse précoce
Hydrothermalisme

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ABSTRACT

The 23,000 year old sediments of the Atlantis II Deep rest on a basaltic substratum and are overlaid by a dense and hot brine pool. The facies of the lower sequence of the West basin consists essentially of bioclastic and detrital particles (DOP facies). The primary calcite and aragonite of planktonic tests of the DOP facies have been transformed into Ca-, Mg-, Mn-, and Fe-carbonate solid solutions. Pyrite amounts to about 1-2% (wt) at the bottom of the sedimentary series, and as much as 20% (wt) in the upper part of the sequence. These high iron – and manganese – bearing minerals are the product of early diagenetic processes in an environment favourable to bacterial activity, to which biogenic and detrital particles, organic matter, and iron and manganese oxides were supplied. The high proportion of pyrite and secondary carbonates indicates that the environment of the W basin was different from the Red Sea pelagic environment during the deposition of the DOP facies, which take place between 23,000 and 11,000 years B.P. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, approaching 0.708, and the conservation of siliceous tests indicate the occurrence of an initial brine pool in the Atlantis II Deep. The Deep was therefore hydrothermally active prior to 11,000 years B.P., *i.e.* before the deposition of the purely metalliferous facies that overlie the DOP facies.

RÉSUMÉ

Évolution diagenétique des premiers sédiments de la fosse Atlantis II (mer Rouge) : mise en évidence d'une activité hydrothermale précoce.

Les sédiments métallifères de la fosse Atlantis II reposent depuis 23 000 ans sur un substratum basaltique. Ils sont actuellement recouverts par une saumure dense et chaude (66°C). Le faciès inférieur des sédiments du bassin W, couramment appelé le faciès DOP (Bäcker et Richter, 1973), est essentiellement composé de particules biogènes et silicatées, de pyrite et passées à goethite. L'étude de dix-sept échantillons prélevés dans ce faciès montre des modifications de la composition minéralogique et chimique des tests planctoniques observés à la loupe binoculaire, par rapport à leur composition originelle. Des néoformations diagenétiques sont observées.

La calcite et l'aragonite primaires des tests de foraminifères et de ptéropodes ont été transformées en solutions solides de carbonates de Fe, Mn, Ca et Mg, et la silice amorphe issue de radiolaires et de diatomées, en quartz ou en calcédoine. Le fait qu'une grande partie du sédiment soit très riche en radiolaires et en diatomées est particulier à la fosse Atlantis II puisque les sédiments pélagiques contemporains de la mer Rouge contiennent une fraction biogénique presque exclusivement carbonatée. La pyrite apparaît dans les sédiments biodétritiques. Ce sulfure représente 1 à 2% (wt) de la roche totale à la base de la série et atteint une proportion de 20% (wt) dans la partie supérieure.

Les sédiments du faciès DOP ont été affectés par des réactions diagénétiques liées à l'oxydation bactérienne de la matière organique. Nos résultats permettent de préciser les conditions chimiques dans lesquelles ont siégé ces réactions. Les sédiments détritiques et biogènes qui se sont déposés dans la fosse Atlantis II durant cette période (de 23 000 à 11 000 ans), contenaient des métaux (Mn et Fe) sous la forme d'oxydes. Les oxydes ont été réduits et les métaux ont précipité en pyrite et en carbonates secondaires au cours de réactions biogéochimiques d'oxydo-réduction. La quantité des néoformations pyriteuses et carbonatées indique que les apports en oxydes ont été particulièrement importants, et l'activité bactérienne a été intense. Le milieu devait être fertile et abondamment alimenté en matière organique. L'environnement était également favorable à la conservation de la silice. Ces constatations suggèrent que les conditions physico-chimiques de la fosse étaient différentes de celles de l'environnement pélagique contemporain du reste de la mer Rouge.

La signature isotopique en Sr du faciès inférieur des sédiments du bassin W évolue du pôle eau de mer à la base (0,709) vers un pôle saumure (0,708). Ces valeurs de $^{87}\text{Sr}/^{86}\text{Sr}$ confirment l'existence d'une saumure initiale lors du dépôt et de l'évolution diagénétique des sédiments biodétritiques. La fosse Atlantis II a donc été alimentée par un fluide minéralisateur bien avant le dépôt des premiers sulfures hydrothermaux, daté à 11 000 ans. L'âge des premières minéralisations dans le faciès DOP est estimé à 19 000 ans B.P.

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INTRODUCTION

The sediments deposited in the Atlantis II Deep rest on the basaltic substratum of the Red Sea axial zone and are overlaid by a dense and hot (66°C) brine pool. The brine is maintained by the addition of a salty hydrothermal solution rich in dissolved metals. On the basis of extensive studies during the 1970s, the sediments are classified using the lithostratigraphic sequence of Bäcker and Richter (1973), whereby two kinds of deposits are distinguished (Fig. 1) : facies, occurring at the bottom of the sequence, which consist mainly of biogenic and detrital sediments and are described as detrital, oxide, and pyrite (DOP) facies (Bäcker and Richter, 1973); and facies occurring at the top, which are almost exclusively composed of hydrothermal minerals. Because previous work was stimulated by economic interests and by the exploration of the existing hydrothermal deposit, the sediments of the DOP facies have not as yet been the subject of a detailed description.

Radiocarbon analyses have shown that the DOP facies deposited between -25,000 and -11,000 B.P. (Ku *et al.*, 1969 ; Shanks and Bischoff, 1980). The sediments consist of biogenic carbonates and terrigenous silicates in equivalent proportions (Bäcker, 1976). They also contain diagenetic pyrite which results from the bacterial reduction of

sulphate (Kaplan *et al.*, 1969 ; Shanks and Bischoff, 1980). The DOP facies also contains some goethite and lepidocrocite layers.

Changes in the temperature of the lower brine pool support the assumption that the Atlantis II Deep is hydrothermally active (Ramboz and Danis, 1990 ; Blanc and Anschutz, 1995). The presence of metalliferous sediments in the upper layers indicate that hydrothermal activity has been occurring for 11,000 years, and the iron oxyhydroxide interlayers of the DOP facies argue for sporadic and brief hydrothermal events early in the history of the Atlantis II Deep (Blanc, 1987). The present paper deals with the following unsolved questions which concern the biogenic and detrital layers of the DOP facies : (1) Are there mineralogical and chemical anomalies in the biogenic and detrital sediments that can be linked to early hydrothermal activity ? (2) Was the depression filled by a brine pool during the deposition of the DOP facies ?

The early diagenesis of the marine sediments, or organic burial diagenesis, is well documented (Curtis, 1977 ; 1987 ; Froelich *et al.*, 1979 ; Berner, 1980 ; Stumm and Morgan, 1982 ; Coleman, 1985 ; Santschi *et al.*, 1990). A sequence of biogeochemical reactions corresponding to less and less free energy produced by the oxidation of organic matter in the microbial activity occurs in the uppermost few centimetres of sediment. A typical order of

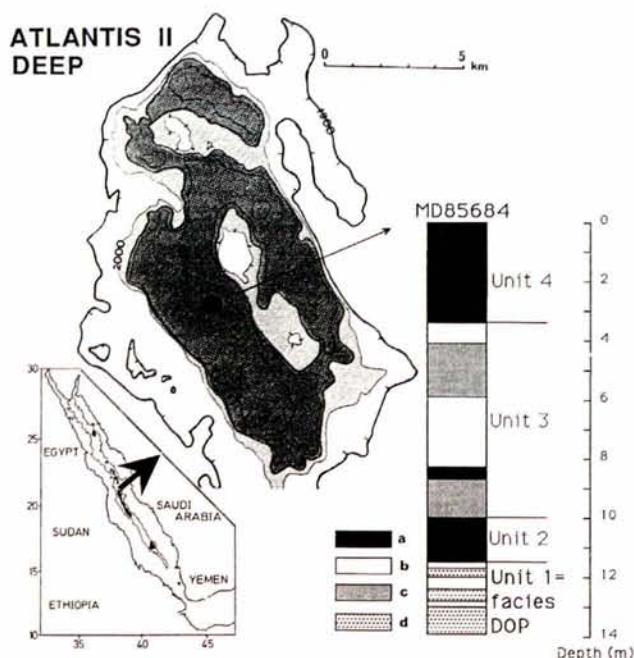


Figure 1

Bathymetric map of Atlantis II area showing the location of core MD85684 in the Atlantis II Deep. The contour lines were traced from seabeam investigations (Pautot, 1983), corrected after sound velocity calculations for Red Sea water. Corrections were also made for the higher sound velocity in the brines. The grey area marks the zone below 2000 m depth, which corresponds to upper limit of the brine-filled depression. The black area, limited by the 2050 m contour line, shows the extent of the Atlantis II lower brine. Lithostratigraphic columns of the core MD85684; a : sulphide and silico-ferric species facies ; b : iron oxides and oxyhydroxides facies; c : manganese oxides and oxyhydroxides facies ; d : biogenic and detrital facies.

Localisation et topographie de la fosse Atlantis II. Positionnement du site de carottage MD85684. Les courbes de niveau ont été tracées à partir de données Seabeam (Pautot, 1983) et du calcul des vitesses du son dans l'eau de la mer Rouge. Des corrections ont été apportées pour les vitesses du son supérieures des saumures. La zone grisée, limitée par la courbe de niveau -2000 m, est actuellement recouverte par des saumures hydrothermales. La zone la plus sombre, limitée par l'isobathe -2050 m, représente l'étendue de la saumure inférieure. Lithostratigraphie, a : faciès à sulfures ; b : faciès à oxyhydroxydes de fer ; c : faciès à oxyhydroxydes de manganèse ; d : sédiments biogéniques.

oxidant consumption is dissolved oxygen, dissolved nitrate, Mn (III, IV) and Fe (III) of oxide minerals, and dissolved sulphate. The respective location and importance of each reaction zone depend on the chemical composition of the system, and on the sedimentation rate. The main dissolved chemical species produced by the reactions are HCO_3^- , Fe^{++} , Mn^{++} and HS^- which can become saturated with respect to secondary minerals. Iron and manganese precipitate as secondary oxides when they diffuse upward from the anoxic medium into the oxidized zone. In the reduced zone of the sedimentary pile, availability of Mn^{++} and Fe^{++} determines sulphide/carbonate precipitation according to $\text{HS}^-/\text{HCO}_3^-$ availability. Reduced sulphur produced by bacterial sulphate-reducing activity can also react with particulate iron oxides and precipitated as pyrite (Berner, 1970 ; 1985 ; Canfield *et al.*, 1992). Thus, the secondary products of early diagenesis are relics from the depositional environments of marine sediments. The study

of the secondary phases provides information on the primary production of organic matter, on the input of primary iron and manganese oxides, on redox conditions, and on the intensity of bacteriological activity (Calvert and Pedersen, 1993). The objective of this work is to characterize the first hydrothermal events of the Deep through a detailed description of the mineralogy and chemistry of the DOP facies.

MATERIAL AND METHODS

Core MD85684, collected during the "Hydrotherm" cruise (May, 1985) on the RV *Marion Dufresne* (Blanc *et al.*, 1986), contained the entire sedimentary sequence of the W basin. The DOP facies constitutes the lower part of the core, from 13.85 to 11.55 m. A total of 13 samples from this facies were washed with deionized water to remove all salts, dried at 40°C, and powdered. The granulometric fraction above 63 μm was extracted for microscopic examinations. Results of the micropalaeontological study are reported elsewhere (Anschutz and Blanc, 1993).

Chemical composition

For the analysis of the major elements, a 100 mg sample of the powdered salt-free sediment was fused with 750 mg of lithium tetraborate at 1000°C in a glassy graphite melting pot and then dissolved in a glycerin-hydrochloric acid solvent (Samuel *et al.*, 1985). The alkaline fusion leads to complete dissolution of the major elements although the volatile Zn was partly lost. An open tri-acid attack ($\text{HCl}+\text{HF}+\text{HClO}_4$ at 120°C in Teflon crucibles) of 1g powdered sediment was therefore used for the determination of Zn, Fe, Mn, Si, Al, Ca, Mg, Zn, and Cu analyses were performed by means of Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The accuracy of the analyses was verified by analyzing rock standards. The precision of the analytical procedure was better than 2%, based on replicate analyses of samples and standards. Na and K were determined with flame emission spectroscopy, using Li as an internal standard. S and C were quantified by infrared absorption photometry using a Leco 125 instrument. The precision is 10% or better, for Na, K, C and S (see Tab. 1).

Mineralogy

The mineralogical composition was determined on powdered sediment with $\text{CuK}\alpha$ X-Radiation on a Philips PW 1710 diffractometer. The weight fraction of each mineral was calculated from the chemical data, using a normative procedure. The distribution of the cations in carbonate solid-solution was estimated both by the chemistry and by the position of the (104) diffraction peak. The peak was adjusted precisely using quartz as an internal standard. The semi-quantitative X-ray method of Hooton and Giorgetta (1977), which relies on empirically-derived intensity factors for the various minerals, was also used. The pro-

Table 1

Chemical composition in grams/kilograms of dry, salt-free sediments sampled in DOP facies of the W basin.

Composition chimique en g/kg des sédiments secs dessalés du faciès DOP dans le bassin W.

Depth (cm)	Fe	Mn	Si	Al	Ca	Mg	Zn	Cu	S	C	Na	K
1159	405	38.3	32	3.7	17.2	4.8	7.0	1.15	11.2	31.5	12.6	1.3
1162	469	53.3	50	3.2	7.2	3.3	5.2	0.18	2.1	13.2	1.6	2.1
1176	100	108.1	48	13.2	125.8	21.4	5.4	0.54	39.1	85.5	2.6	4.0
1194	115	8.8	189	49.7	32.2	17.3	16.8	1.36	113.0	21.9	10.8	12.5
1209	494	8.9	52	8.5	15.0	12.4	4.6	0.23	4.8	23.0	3.6	2.9
1229	490	4.0	19	2.4	4.5	4.5	0.9	0.07	2.7	11.9	3.1	0.8
1244	88	5.3	166	50.2	59.3	17.1	6.1	0.42	66.8	35.4	10.5	11.6
1266	98	1.9	186	33.6	54.0	14.0	8.0	0.45	107.4	29.4	3.9	4.2
1293	416	5.0	37	6.9	36.5	13.5	3.8	0.46	2.4	44.0	3.4	1.8
1295	313	11.2	14	4.2	71.5	31.2	4.5	0.20	2.5	96.2	3.9	1.3
1300	90	4.6	106	27.6	126.3	16.3	1.0	1.00	53.0	54.9	3.8	3.7
1326	32	4.4	96	27.6	208.6	22.5	0.3	0.07	3.5	70.2	3.2	4.0
1368	52	7.8	89	25.4	211.6	23.9	0.1	0.06	2.8	78.1	5.0	8.4

portion of each mineral was deduced by comparing with an internal standard. Simultaneous use of the semi-quantitative X-ray method and chemical analyses allow normative mineralogy with a relative error < 20%, except for clay minerals. These were taken as a whole, because it was not possible to quantify each specific clay. The measured concentrations of carbon in the DOP facies were about 1 or 2% (wt) higher than accounted for by carbonates. This excess corresponds to the fraction of remaining organic matter determined previously (Blanc *et al.*, 1990).

The strontium isotopic composition of the bulk sediment was determined on four samples from the tri-acid attack using a VG Sector mass spectrometer. A $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710266 ± 0.000011 (2σ , $n = 18$) was measured for the NBS987 standard.

RESULTS

The core MD85684 from the W basin can be divided into four main units (Fig. 1). Biogenic and detrital sediments (Unit 1) at the bottom are overlaid by layers composed of two sulphide facies (Units 2 and 4) that are separated by a Mn- and Fe-oxide-rich facies (Unit 3). The DOP facies corresponds to Unit 1 and consists of 2.3 m of multicoloured sediments that overlie directly the basaltic substratum (Blanc, 1987 ; Anschutz, 1993). A synoptic log of the relative abundance of minerals contained in the DOP facies is presented in Figure 2. The chemical data are given in Table 1.

The DOP facies is composed of mixed carbonate and silicate layers separated by three iron oxyhydroxide interlayers. The position of the X-ray diffraction peaks (Fig. 3) and the chemical composition of the sediment (Tab. 1) show that primary calcite and aragonite, which normally compose the observed foraminifera and pteropod tests, are rare or absent. The recognizable major carbonate species consist of various solid solutions (see Fig. 2). The concen-

DOP Facies, Core MD85684 Normative mineralogy (wt%)

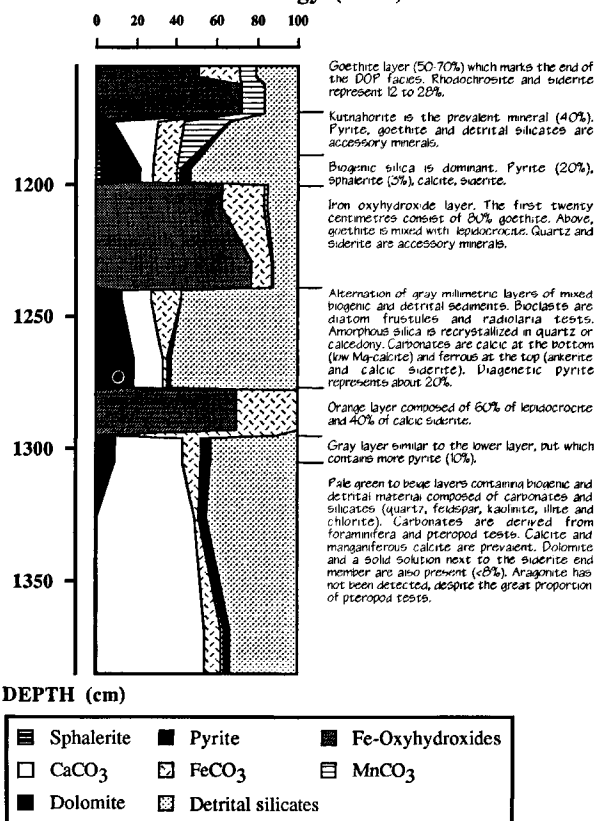


Figure 2

Mineralogical variation along the DOP facies of core MD85684 in weight percent age of dry, salt free sediments.

Diagramme synoptique de la composition lithologique du faciès DOP dans la carotte MD85684 en pourcentage massique.

tration of the iron and manganese carbonate end members of the solid solutions increases gradually from the bottom to the top of the DOP facies (Fig. 3). The secondary calcium carbonate end member remains prevalent. Siderite is present in low amounts (< 8% (wt)) at the bottom of the

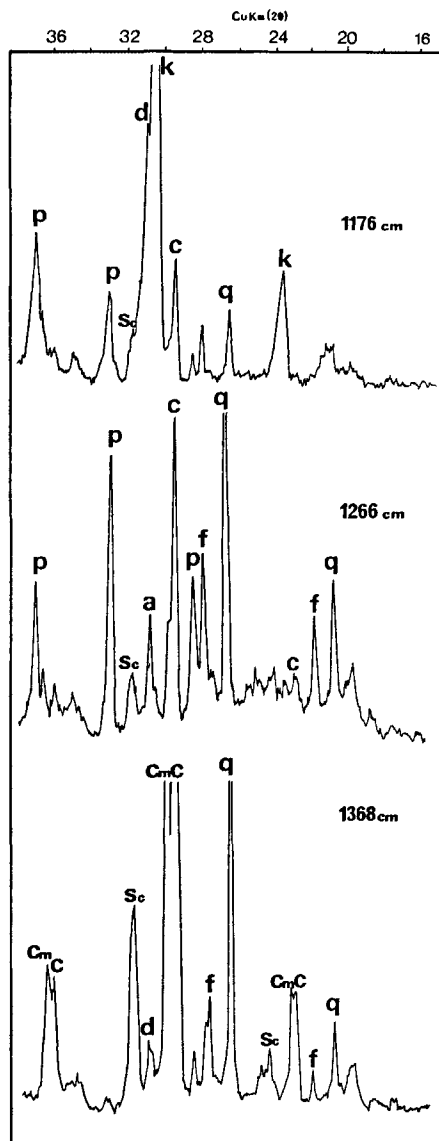


Figure 3

X-ray diffractograms showing the shapes and positions of the primary and secondary peaks of quartz (q), feldspar (f), pyrite (p), calcite (c), dolomite (d), ankerite (a), kutnahorite (k), calcic-siderite (Sc) and manganiferous-calcite (Cm). The three samples show the evolution of the pyrite content and the solid-solution carbonates from the bottom to the top of the DOP facies.

Diagrammes de diffraction des rayons-X représentant la taille et la position des pics principaux et secondaires du quartz (q), du feldspath (f), de la pyrite (p), de la calcite (c), de la dolomite (d), de l'ankérite (a), de la kutnahorite (k), de la sidérite calcique (Sc) et de la calcite manganésifère (Cm). Les trois exemples choisis montrent l'évolution de la teneur en pyrite et de la distribution des solutions solides de carbonates de bas en haut dans le faciès DOP.

facies, but increases to about 20% (wt) at the top. Manganese constitutes a minor end member of carbonate solid solution at the bottom of the sedimentary series where the calcium carbonate end member is predominant. But from 1200 cm to the top of the series (1155 cm) Mn occurs as rhodocrosite and kutnahorite. The sediments also contain a magnesian carbonate end member which is mostly incorporated into dolomite and, to a lesser degree, into ankerite.

Biogenic amorphous silica originating from radiolaria and diatoms is associated with calcedony and quartz. Recent

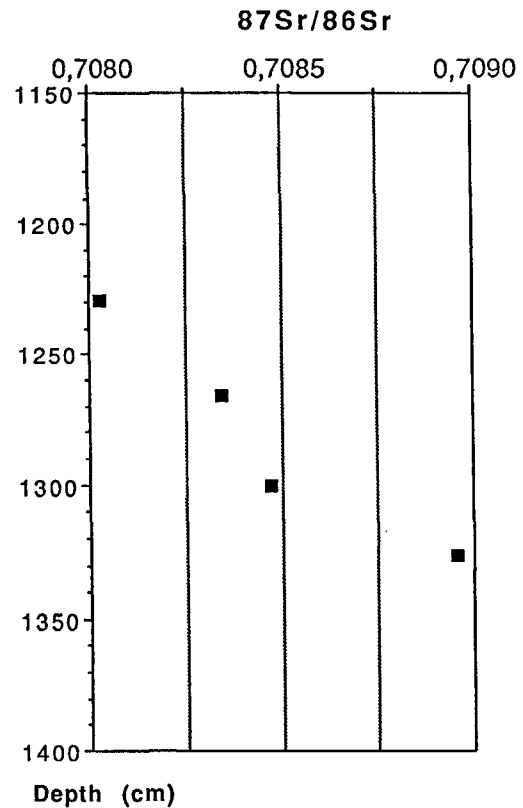


Figure 4

Evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios along DOP facies, core MD85684.

Évolution des valeurs de la composition isotopique du strontium dans le faciès DOP.

sediments of the Red Sea do not contain layers of siliceous ooze (Risch, 1976). Moreover, Red Sea sediments of the 18,000-11,000 B.P. interval, which is contemporaneous to the siliceous ooze of the Atlantis II Deep, contain the highest content of calcium carbonate, and the lowest content of silica of the past 18,000 years (Locke and Thunell, 1988). Hence, radiolaria and diatoms have been preserved in the DOP facies of the Atlantis II Deep, whereas they have been dissolved after settling in the other area of the Red Sea. The first silica-rich layer of the DOP facies appears just above the first oxyhydroxide layer. It records specific physico-chemical conditions allowing the preservation of silica and suggests the input of a first brine pool in the deep, enriched in dissolved Si.

Clay minerals are abundant in the DOP facies. They can account for more than 25% (wt) of the sediment. Kaolinite, illite, and chlorite have been determined. We could not detect an evolution of the relative abundance of these different mineral species. Clay minerals of the DOP facies are considered generally as detrital clays inherited from Tertiary sedimentary series (Badaut, 1988).

Diagenetic pyrite represents less than 2% (wt) of the solid fraction from the bottom to 1305 cm (Fig. 2). Near the top, pyrite amount reaches 20% (wt) of the DOP facies, and is accompanied by minor amounts of sphalerite (< 2% (wt)).

The most radiogenic Sr value ($^{87}\text{Sr}/^{86}\text{Sr} = 0.709$), corresponding to the sea water value; has been observed in the deepest sample (Fig. 4) which is strongly enriched in marine microbiota and relatively depleted in secondary pro-

ducts. Strontium isotopic composition gradually shifts upwards to a value of 0.708. This value approaches that of the present-day hot brine ($^{87}\text{Sr}/^{86}\text{Sr} = 0.707$; Zierenberg and Shanks, 1986; Anschutz *et al.*, 1993). No basaltic fragments have been detected in these particular samples. Thus, the less radiogenic strontium must be present in authigenic mineral species.

DISCUSSION

The DOP facies differ from the sediments of the Red Sea deposited during the same time, outside the Atlantis II Deep described by Bäcker (1976). The DOP facies contains high concentrations of metallic elements (Fe, Mn and Zn) (Fig. 5) and consequently elevated proportion of pyrite and carbonate solid solutions.

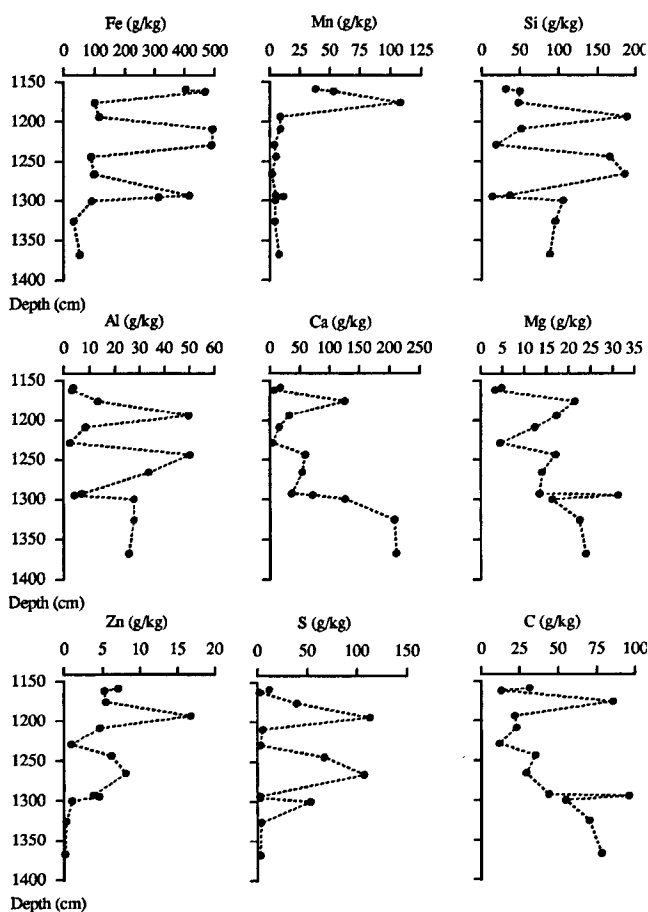


Figure 5

Profiles of concentrations (g/kg) versus depth (cm) for some major elements contained in the solid fraction of the DOP facies.

Profil de concentration (g/kg) en fonction de la profondeur (cm) de Fe, Mn, Ca, C, S, Zn et Si dans le faciès DOP de la carotte MD85684.

Pyrite

From 1385 to 1305 cm, pyrite represents less than 2% (wt) of the solid fraction, whereas its relative abundance ranges between 7 and 20% (wt) between 1305 cm and the top of

the sequence (Fig. 2). To explain the abundance of pyrite in the DOP facies, diagenesis involving the microbial reduction of dissolved sulphate and the reaction with particulate iron oxides and an increase of the iron oxide supplies in the sediment through hydrothermal activity are required. These assumptions are argued below.

In anoxic marine sediments, pyrite forms through several steps after the initial precipitation of iron sulphides (Berner, 1971; 1980; Morse *et al.*, 1987). Ferrous iron is produced by the reduction of reactive iron oxides either by bacterial respiration or by autocatalytic interaction with reduced sulphur (Berner, 1970; 1985; Canfield *et al.*, 1992). The pyrite of the DOP facies in many cores from Atlantis II Deep has strong negative values of $\delta^{34}\text{S}$ (-35% to -20%) (Kaplan *et al.*, 1969; Shanks and Bischoff, 1980). Such isotopically light values are characteristic of reduced sulphur produced by bacterial reduction of sea water sulphate (Kaplan *et al.*, 1969). The present-day lower brine pool contains dissolved sulphate of isotopic composition comparable to that of the sea water *i.e.* $\delta^{34}\text{S} = +20\%$ (Shanks and Bischoff, 1980). Thus, the reduced sulphur produced during the formation of the DOP facies can originate from bacterial reduction of the sulphate contained in sea water as well as in an initial brine pool. It is noteworthy that positive values of $\delta^{34}\text{S}$ ($+5\%$) characterize the sulphide minerals of the upper metalliferous sediments, which originate in hydrothermal activity. Thus, the pyrite in the DOP facies cannot originate directly from a hydrothermal solution.

Because the abundance of pyrite formed is mostly limited by the amount of available iron oxides, it never exceeds a few per cent, even in the most anoxic and organic matter-enriched marine sediments (Jorgensen, 1982; Berner, 1980; Elsgaard and Jorgensen, 1992). The low pyrite content at the bottom of the DOP facies, *i.e.* $< 2\%$ (wt), is similar to that of pelagic sediments of the Red Sea, outside the Atlantis II Deep (unpublished data). Thus, this low pyrite content reflects the supply of detrital iron oxide through normal sedimentation in the Red Sea. Conversely, the pyrite content of 20% (wt) in the DOP facies above 1305 cm, is extremely high compared to present-day marine environments, and must be related to additional supply of reactive iron oxide, over the detrital input. This additional supply can originate only from hydrothermal inputs. The Atlantis II Deep was, therefore, under the influence of hydrothermal activity during the deposition of the upper DOP facies.

Carbonate solid solutions

The three oxyhydroxide layers in the DOP facies separate three biogenic and detrital interlayers with different carbonate composition (Fig. 2). At the bottom, calcite and manganese calcite are dominant; calcic siderite and dolomite also occur. In the second interlayer, biogenic silica is prevalent; the carbonate fraction is enriched in iron, with calcic siderite and ankerite. The upper biotrital interlayer contains, in addition, rhodocrosite and kutnahorite. Low-Mg-calcium carbonate dominates the initial mineralogical composition of the biogenic remains. Carbonate solid solu-

tions are secondary species associated with the biogenic fraction.

The main reactions which could lead to the precipitation of secondary carbonates in the DOP facies sediments are the following. Bacterial sulphate reduction in Atlantis II Deep layers of mixed biogenic and detrital material produces CO_2 and HS^- (or H_2S). Mn^{++} , Fe^{++} , and CO_2 can be produced through organic matter oxidation by bacteria using iron and manganese oxides as electron acceptors. CO_2 enrichment of the interstitial environment destabilizes the original biogenic calcite and aragonite. Intense bacterial activity linked to an important organic matter input therefore induces the release of cations which then can then precipitate as secondary carbonates. This pattern of chemical reactions has been described in many recent sediments of marine environments (Froelich *et al.*, 1979 ; Berner, 1980 ; Emerson and Archer, 1990).

The variability of solid solution carbonate in the DOP facies suggests that the original proportion of reductible iron and manganese oxide particles changed during the deposition of the DOP facies. The supply of manganese was not sufficient to form a typical manganiferous mineral except for the last biotrital interlayer between 1187 and 1173 cm, where kutnahorite and rhodocrosite occur. Iron-rich carbonate *i.e.* calcic-siderite, is present from the bottom to the top of the DOP facies. However, the FeCO_3 end member only begins to be important above 1305 cm, where large amounts of pyrite occur. Therefore, 1305 cm seems to represent the level that corresponds to the beginning of strong input of metalliferous elements to the deep. The averaged sedimentation rate of the DOP facies of the Core MD85684 is 19 cm/ky. Assuming that the 230 cm of sediment of the DOP facies were deposited at a constant rate, the 1305 cm level corresponds approximately to 19,000 y B.P.

The chemical environment of the Atlantis II Deep during the deposition of the DOP facies

The strontium isotopic composition of sediments collected below 1305 cm is not anomalous when compared to carbonates precipitated from sea water ($^{87}\text{Sr}/^{86}\text{Sr} = 0.709$). But the sediment at 1305 cm and above, where iron- and manganese-rich secondary minerals occur, corresponds to decreasing values of the strontium isotopic ratio, from 0.7085 to 0.7080 (Fig. 4). These $^{87}\text{Sr}/^{86}\text{Sr}$ ratios move toward the values of the present-day lower brine (0.7071; Zierenberg and Shanks, 1986 ; Blanc, 1987) and the overlying metalliferous sediments (0.7073; Anschutz *et al.*, 1993). This suggests that diagenesis took place in an interstitial environment influenced by hydrothermal fluids. Above 1305 cm, the presence of biogenic silica and iron oxyhydroxide layers (Fig. 2) indicates the time during which the W basin of the Atlantis II Deep was filled by a silicate-rich solution. Thus, the iron and manganese enrichments responsible for the formation of the observed secondary mineral have to be related to the first occurrence of a brine pool in W basin.

The association of pyrite and siderite in the same samples is surprising and needs some explanation. Because the

solubility of pyrite is very low, its formation implies that the iron concentration of the interstitial waters was below the saturation level of the more soluble siderite. Siderite has been considered to represent a later stage of carbonate precipitation in marine sediments (Curtis, 1977). However, the formation of authigenic siderite in the zone of sulphate reduction may result from a deficiency of bacterially produced H_2S relative to Fe^{++} production. This has been invoked by Pye *et al.* (1990) for the formation of recent intertidal carbonate concretions that contained pyrite and siderite. Thus, the siderite-pyrite association confirms that the Atlantis II Deep environment was supplied with large amounts of iron while nevertheless being favourable to biological activity.

CONCLUSIONS

The biogenic and detrital sediments from the W basin of the Atlantis II Deep have the same mineralogy and chemistry as the recent sediments of the Red Sea at the bottom of the sequence. However, the content of iron and manganese becomes abnormally high in the upper part of the sequence (*i.e.* from 1305 cm to the top of the DOP facies). These elements are incorporated into secondary pyrite and solid-solution carbonates. The occurrence of large amounts of these minerals is explained by early diagenetic processes that took place in an environment favourable to bacterial activity, where biogenic and detrital particles, organic matter, and hydrothermal iron and manganese oxides accumulated.

The strontium isotopic composition which reaches a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.708, the conservation of siliceous biota, and the high content of secondary Fe and Mn-minerals in the upper part of the DOP facies strongly suggest that the W basin has been filled by a brine pool since 19,000 y B.P. The Atlantis II Deep was therefore under the influence of hydrothermal activity long before the deposition of the metalliferous facies that succeeded the formation of the DOP facies.

The environment that prevailed during the formation of the DOP facies was unable to generate an ore deposit, not because the supply of metals was low, but because the ore-forming minerals were transformed by bacterial activity, and because the background accumulation of biogenic and detrital particles remained prevalent. Thus, the inhibition of biological activity, and the dissolution of most of the background particles, are necessary for an ore deposit to form. The transition from the DOP facies to the upper facies probably corresponded to increased hydrothermal activity which severely inhibited bacterial activity in the deep, and which made the environment corrosive for biogenic and detrital minerals.

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