Mineralogy of Metalliferous Sediments from Atlantis II Deep – Red Sea

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ABSTRACT. Mineralogical composition of 295 samples of Atlantis II, Deep metalliferous sediments was studied by X-ray diffraction analysis. Various types of silicates, iron and manganese oxides, carbonates, sulfates, sulfides are the common mineral phases. The minerals exhibit systematic distribution pattern in the sediments cores and facilitate a facies and subfacies classification. Typical mineralogical sequence from bottom to top is: sulfides, silicates, siderite, Ca-Fe-Mn carbonate, rhodochrosite, iron oxides, manganite and amorphous silica, iron or manganese oxides. Mineralogical variations in the Atlantis II, Deep sediments are considered to be due to the presence of repeated depositional cycles related to fluctuation in temperature, pH and perhaps oxygen fugacity, during the mixing of magmatic hydrothermal solution and sea-water.

Introduction

The Red Sea metalliferous sediments have received wide attention since the discovery of the rich copper-zinc mineralization in the Atlantis II Deep in 1965. The economic significance of these deposits has been investigated by Guennoc *et al.* (1984). Based on the data accumulated from hundreds of cores, the estimated reserves are two million tons of contained zinc and half a million tons of contained copper, in addition to significant amounts of silver and gold, for the top 20 m of the sediments (Guennoc *et al.* 1984). Zierenberg and Shanks (1983) indicated a vertical zonation of the sediments, basing on the mineralogy which is dominated by anhydrite, talc, smectite, pyrite, sphalarite and chalcopyrite.

The recent Meseda III Va 29 coring program, undertaken in the top 10-20 m of the Atlantis II Deep metalliferous sediments, provide an excellent opportunity to extend the studies on the nature and origin of the deposits.

A total of 295 samples from 32 cores spread over the NS and EW sections of the Atlantis II Deep were selected for mineralogical and geochemical studies (Fig. 1). This paper presents the result of the mineralogical investigation on these studied samples. Vertical as well as lateral variations, which could be identified in terms of specific mineral facies and subfacies that reflect episodic depositional cycles under different physico-chemical conditions, are discussed.

A brief discussion of the preliminary results of these studies was presented at Annual Meeting of the Geochemical Society of America (Gazzaz et al. 1983).

Methods of Investigations

Sample Collection and Preparation

The Atlantis II Deep metalliferous muds are laminated, and each lamina is characterized by a certain colour, and varies in thickness from few millimeters to several meters. Occasionally, the source coloured layers are characterized by different texture. Keeping in view these two variables, samples were collected from layers exhibiting different colours and textures.

From the samples, sodium chloride, which generally constitutes 0.25% to 0.75% of the bulk sediment by weight, was removed by washing with demineralized water. Since most of the mineral particles are less than 1 micron in diameter, as indicated by scanning electron microscope, the sediments were washed through 0.45 micron micromembrane filters to prevent the loss of fine particles during washing. After drying, samples were ground and well mixed before analysis.

X-Ray Analyses

X-ray diffraction was used for identification of the minerals in the sediments. For the identification of the clay minerals, each sample was first analysed untreated, then glycolated and X-rayed, both after heating at 350°C for one hour, and subsequently after heating at 550-600°C for one hour (Lin et al. 1987).

Results

XRD studies indicated that each lamina/layer is composed of a group of minerals, which appear to represent a certain range of temperature. Bischoff (1969a) divided the Red Sea geothermal brine deposits into seven bedded and laterally correlative facies as follows: detrital, iron-montmorillonite, geothite-amorphous, sulfide, manganosiderite, anhydrite and manganite. Zierenberg and Shanks (1983) indicated that the mineralogy of the Deep is dominated by anhydrite, talc, smectite, pyrite, sphalarite and chalcopyrite.

In the present study, the identified minerals are classified into facies; some of these facies are subdivided into subfacies according to the dominant mineral of the group (Table 1).
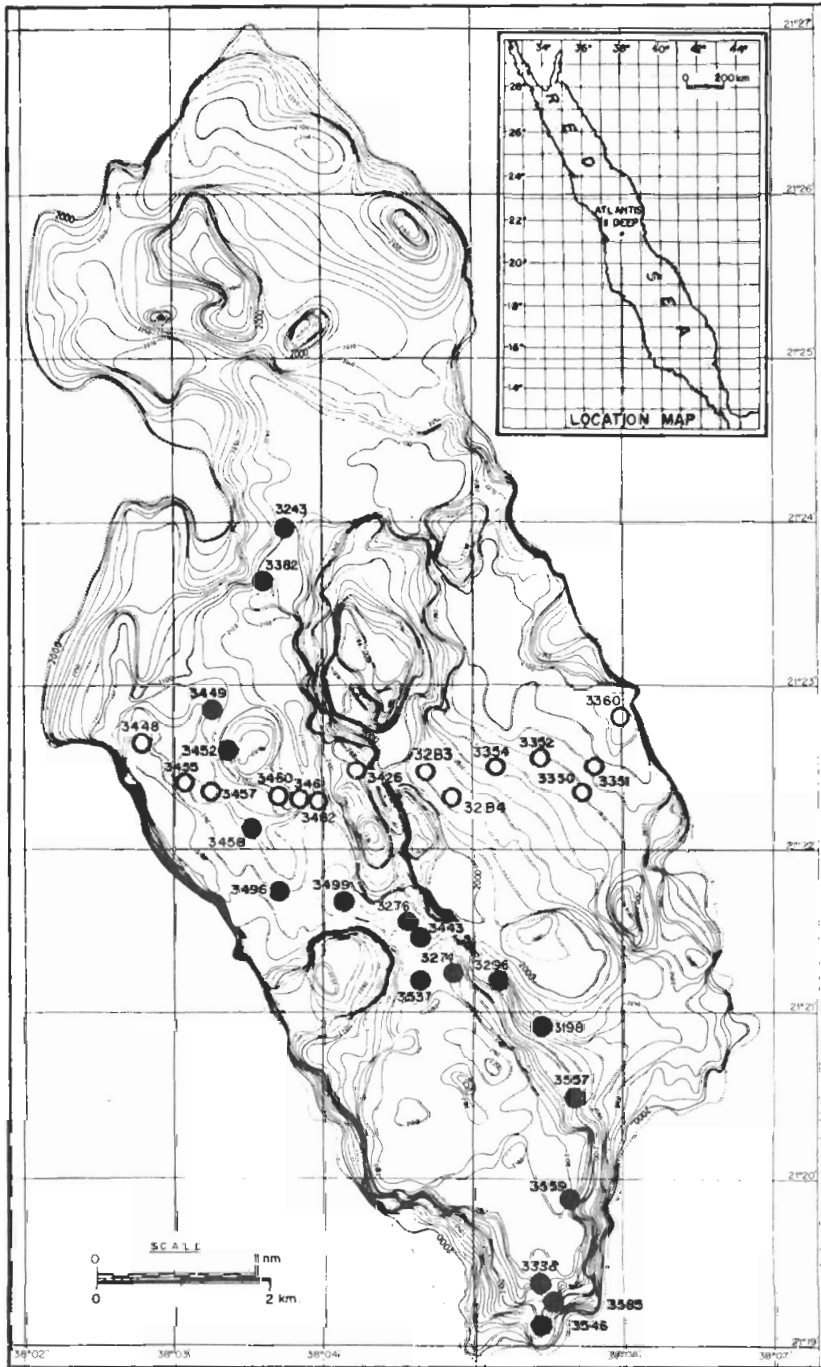
FIG. 1. Location map of the sediment cores in the Atlantis II Deep, Red Sea.

TABLE 1. Grouping of the studied 295 samples of the Red Sea muds into facies according to their mineral composition.

Facies	Subfacies	No. of samples	%	Color
Amorphous		9	3	
	Iron oxides, Manganese-oxides Silicate			Light brown
	Manganite			Dusky yellowish brown, olive black, dark grey
Iron oxide		71	24	
	Goethite Hematite Lepidocrocite			Light brown, Moderate reddish brown light brown; grayish-orange
Carbonate		39	13	
	Siderite Ankerite-rhodochrosite Calcite Aragonite			Dark yellowish brown dusky yellow, Moderate brown, light brown to moderate, reddish brown, olive gray, yellowish gray
Silicate		131	44	
	Smectite Chamosite Quartz			Moderate brown, pale olive, dark to light yellowish
Sulfate		25	8	
	Anhydrite Gypsum			Moderate yellowish brown, olive gray, medium gray, white
Sulfide		12	4	
	Sphalerite Pyrite Chalcopyrite Galena			Light olive gray to medium gray dark yellowish brown
Total number of samples		295	100%	

Sulfide Facies

Sulfide facies constitute the most important group in these sediments, since they contain the most valuable mineral deposits from economic point of view. They mark the bottom horizon of each depositional cycle (Fig. 2 and 3), and are characterized by dominantly grey colour of microlaminated appearance.

The sulfide minerals identified are mainly sphalerite and pyrite with minor chalcopyrite (Table 1). According to the dominant sulfide mineral present, this facies is further subdivided into a sphalerite-rich subfacies which represent the high temperature form of the sulfide facies and the lower temperature pyrite-rich subfacies with minor chalcopyrite.
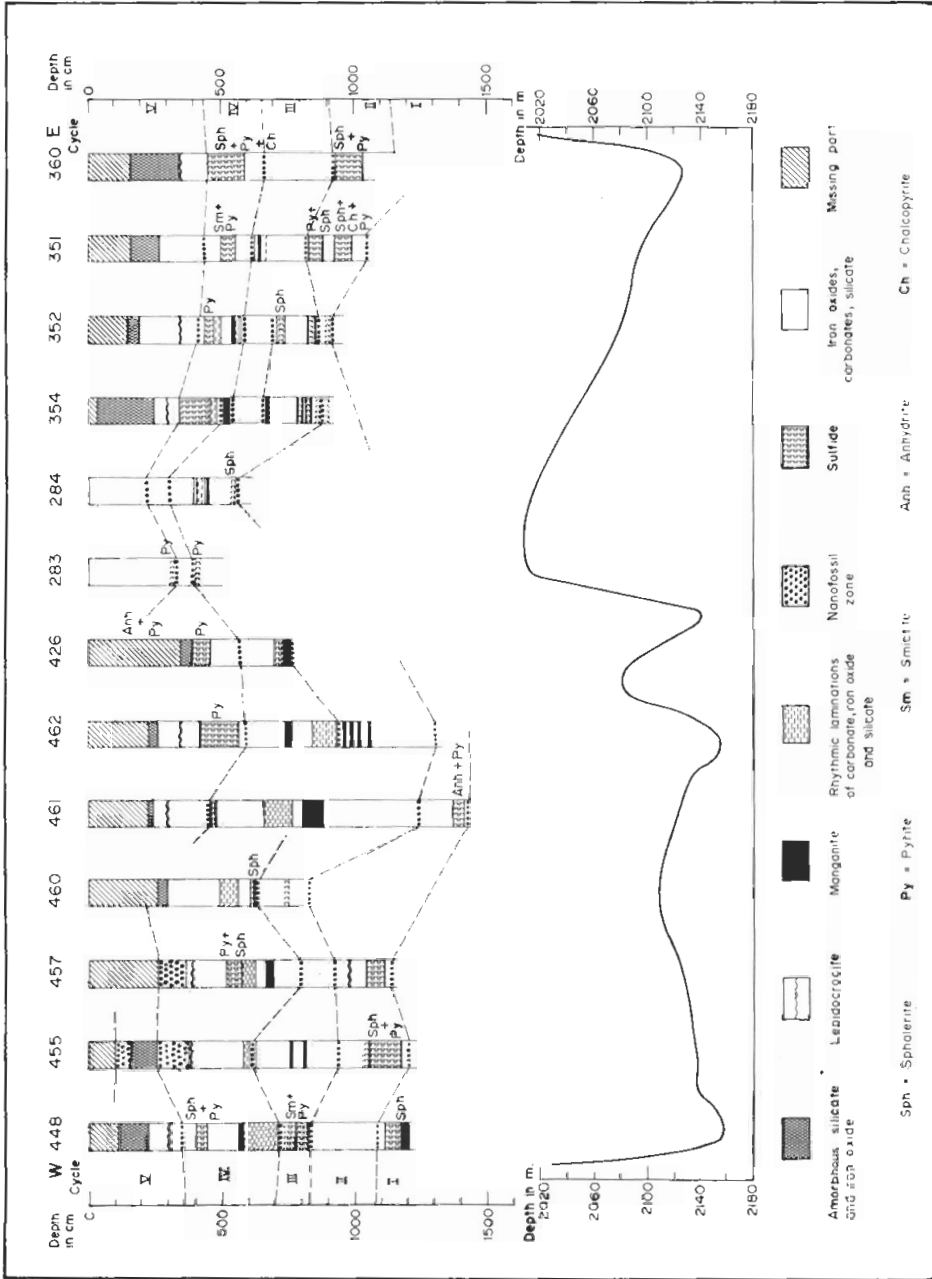
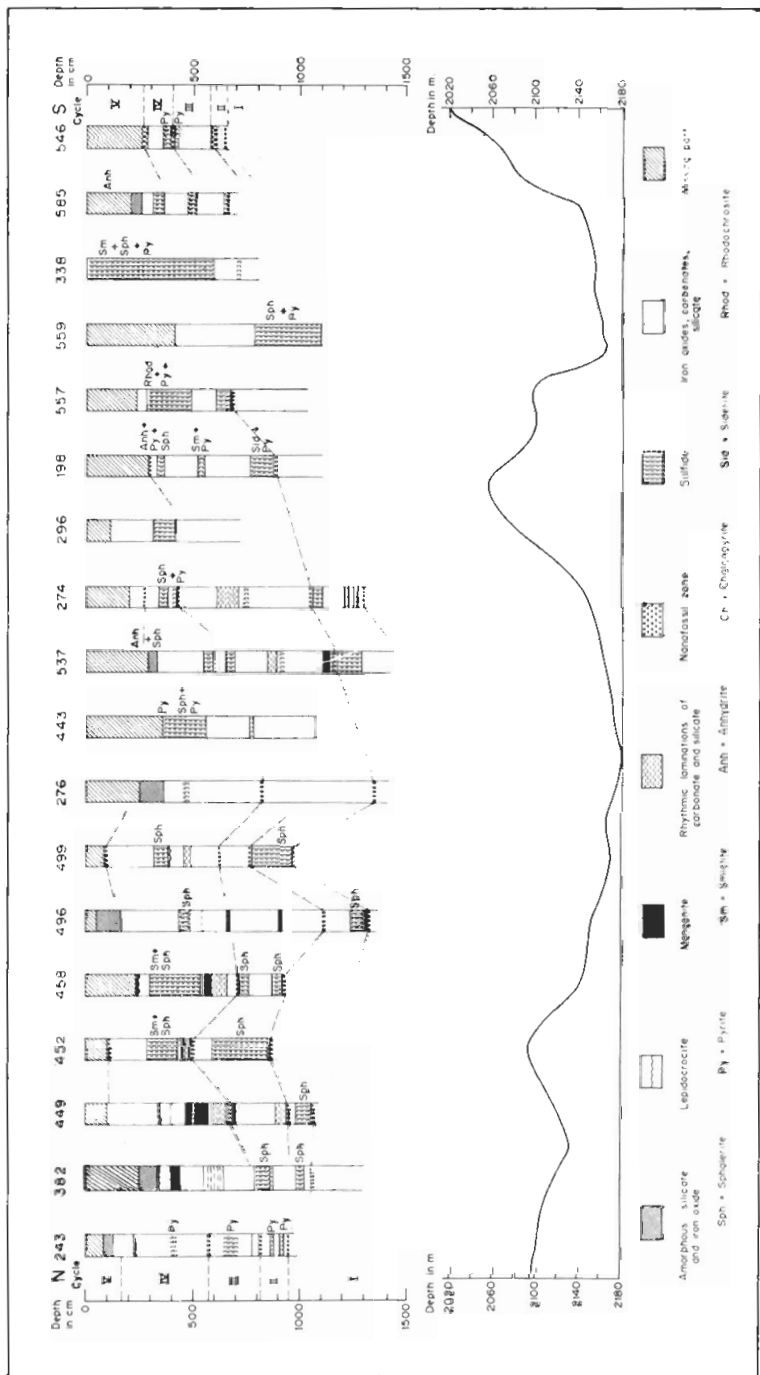Fig. 2. The vertical zonation in the E-W profile.

Fig. 3. The vertical zonation in the N-S profile.

Sphalerite-rich subfacies generally occur as purplish to medium grey layer, varying in thickness from a few millimeters to several meters and extending along the two traverses for several kilometers as this indicated in cores 460, 284, and the lower sulfide layer of core 352 (Fig. 2) and cores 382, 449, 452, 458, 496 and 499 (Fig. 3). Sphalerite is a major constituent of about 88% of the samples of the sulfide facies and about 5% of the total number of the collected samples. It is mostly associated with nontronite, siderite and chalcopyrite and to lesser extent with anhydrite, Ca-Fe-Mn carbonate and barite.

Pyrite-rich subfacies occur as light olive gray to medium dark grey layers; a few centimeters thick. This layer occurs throughout the Deep as indicated in cores, 462, 426, 283 and the upper sulfide layer in core 352 (Fig. 2) and core 243 (Fig. 3).

In some cases, sphalerite and pyrite occur as mixed layers as in the upper sulfide layers of cores 448, 455, 457 and 360 (Fig. 2) and cores 443, 274, 198, 557, 559 and 338 (Fig. 3).

Chalcopyrite could be observed only as a minor constituent associated with sphalerite and pyrite in cores 351 and 360 (Fig. 2).

Sulfate Facies

The sulfate minerals in the Atlantis II Deep metalliferous sediments are mainly anhydrite with minor gypsum and barite. The latter represents the higher temperature form of the sulfate facies. The appearance of gypsum in many anhydrite samples is suggested to be due to recrystallization of anhydrite during core storage. In general, the anhydrite and gypsum subfacies occur as discontinuous beds or lenses of variable thickness or as concordant and discordant vein in the margin of the sulfide facies, associated with nontronite and pyrite, on the other hand the barite occurs as accessory mineral disseminated in the sphalerite subfacies.

Silicate Facies

In the Red Sea metalliferous sediments, the silicate mineral constitute the major mineral facies. In the 295 investigated samples, 131 are silicate minerals. Nontronite, Mg smectite, and chamosite are the common silicate minerals according to Baker and Richer (1973), Bischoff (1969a) and Zierenberg and Shanks (1983). However, the present detailed X-ray diffraction studies and chemical analyses indicate that nontronite, glauconite and mixed-layer glauconite/nontronite, are the most common silicate minerals with minor amounts of Fe-rich chlorite, possibly chamosite and glass shards (Lin *et al.* 1987).

Carbonate Facies

The carbonate minerals noticed in the carbonate facies are siderite, rhodochrosite, calcite, and minor aragonite. The presence of aragonite is indicated by the characteristic 3.4 Å, 1.98 Å and 3.2 Å peaks. Transitional X-ray diffraction patterns between siderite and rhodochrosite are also common in the analyzed samples. These transitional forms have been loosely called Ca-Fe-Mn carbonates.

In the carbonates' facies, siderite represents the high temperature hydrothermal carbonate and calcite, the lowest temperature variety. The presence of nanofossils, including *Gephyrocapsa oceanica* and *Helicosphaera carteri* may suggest the low temperature of formation of these subfacies (21°C to 23°C) (Tan *et al.* 1987).

According to the dominant carbonate mineral in the samples, this facies is further subdivided into siderite subfacies about 5-140cm thick layers, Ca-Fe-Mn carbonate-rhodochrosite subfacies, calcite subfacies ranging from 2cm-4m thick layers and aragonite subfacies as thin layers about 2-10cm thick. Siderite subfacies is mostly associated with nontronite and goethite, Ca-Fe-Mn carbonate subfacies with nontronite goethite, calcite subfacies mostly with nontronite and quartz, and to lesser extent with pyrite, hematite, and aragonite subfacies with calcite and quartz.

Iron Oxide Facies

The iron oxide facies consist of goethite subfacies, hematite subfacies and lepidocrocite subfacies. Magnetite has not been detected in the investigated cores, but was reported in some recrystallized cores (Hackett and Bischoff 1973, Zierenberg and Shanks 1983). Goethite is the most abundant iron oxide. Hematite and goethite occur in alternating laminae or layers of variable thickness, which extend for several kilometers across the Atlantis II Deep. Hematite is generally deposited at the bottom, whereas goethite on the top of the depositional sequence. Lepidocrocite generally occurs as thin laminations, which are apparently continuous for several kilometers.

According to Bischoff (1969b), the hematite in the Red Sea brine is formed at a temperature near 115-120°C or higher, whereas goethite is formed at a lower temperature. Lepidocrocite is believed to form at a temperature lower than that for goethite in the Red Sea environment, because lepidocrocite-rich laminae generally overlie goethite-rich laminae.

The hematite is commonly associated with goethite and nontronite and to lesser extent Ca-Fe-Mn carbonate, whereas the goethite with hematite, nontronite and to lesser extent with Ca-Fe-Mn carbonate and manganite.

Manganite Facies

Manganite occurs as black laminae varying in thickness from few millimeters to several centimeters overlying goethite layers and extending for several kilometers. Fe- and Mn-oxides overlying iron-rich sulfide deposits have been widely used as one of the most reliable guides to ores in areas of deep weathering. Bischoff (1969a) attributed the Atlantis II Deep manganese oxides to possible local "weathering" products of preexisting manganosiderite beds. Manganite layers have also been found on top of Zn-Cu-Pb mineralization in Kuroko deposits, where they are associated with chert (Ishihara 1974).

Amorphous Facies

Amorphous material in the Atlantis II Deep metalliferous sediments constitute

the upper-most part of the succession. It is characterized by a reddish colour without obvious textures and with no X-ray diffraction pattern.

However, this facies has not been previously described in detail. The authors have found, according to chemical data (in preparation) that the amorphous material, which forms about 70% of this facies, is mostly amorphous iron oxide, amorphous silica and amorphous manganese oxide. They are mostly associated with nontronite, geothite, and manganite, and to lesser extent with Ca-Fe-Mn carbonate and anhydrite.

Discussion

The present investigation on the Atlantis II Deep metalliferous sediments indicates a complicated mineral composition, deposited in laminae or layers of variable colours and thicknesses. Each lamina/layer is composed of an assemblage of minerals, and they are grouped as different mineral facies. Most of these facies can again be subdivided into subfacies. The sulfide facies is characterized by sphalerite-rich subfacies and pyrite-rich subfacies with minor amounts of chalcopyrite. The sphalerite subfacies represent the high temperature hydrothermal sulfide, whereas pyrite the lower temperature. It is deposited over the sphalerite in the depositional sequence. The sulfate facies is characterized by anhydrite subfacies minor barite subfacies. The silicate facies consists mainly of nontronite and glauconite with mixed layer of glauconite and nontronite. The carbonate facies consist mainly of siderite subfacies, the high temperature form of the carbonate facies, rhodochrosite, Ca-Fe-Mn carbonate, calcite and aragonite subfacies. The iron oxide facies are characterized by hematite subfacies, goethite subfacies and lepidocrocite subfacies. The manganite facies is composed mainly of manganite. The presence of manganite over goethite and lepidocrocite indicates temperature of formation lower than of goethite but still higher than the temperature to form aragonite. The amorphous facies, which only exist in the upper most part of the sediments consists of amorphous iron oxide, amorphous silica and amorphous manganese oxide.

Vertical mineral zonation indicates that the precipitation of muds took place in different cycles. Five major cycles could be identified. Each complete cycle begins with a high temperature sulfide facies followed by sulfate, silicate, carbonate, iron oxide, manganite and ends with amorphous facies or fossils composed of aragonite and calcite which indicates the lowest temperature. It is not necessary, however, that a cycle shows all the mineral sequence (Fig. 2 and 3). Shanks and Bischoff (1980) indicated that facies variations are related to rate of brine influx and size of the brine pool rather than to changes in temperature or bulk composition of the incoming brine. However, in the present study the investigators believe that the geochemical zonation of the Red Sea metalliferous sediments may be governed by many factors, including temperature, and mixing of hydrothermal solution with sea water.

The temperature of the Red Sea metalliferous sediments was approximately 150-230°C, indicated by the oxygen isotopes of the associated nontronites studied by the

investigators (in preparation) following the Yeh and Savin's methods (1977). This temperature range is apparently lower than the formation temperatures 200-350°C, of the cubanite-chalcopyrite-pyrrhotite assemblage of the Red Sea sediments identified by Pottorf and Barnes (1983). The cubanite and pyrrhotite associations is believed to be a rare high-temperature assemblage in the Red Sea metalliferous sediments, which has not been found in the investigated samples. The isotopic study also indicates that the silicate facies was deposited at temperature between 70 and 170°C. This temperature is, in general, lower than the temperature of the formation of sulfide facies, which is as high as 230°C and encompass the range of the temperature of the formation of hematite, which is 115-120°C (Bischoff 1969b). Cole *et al.* (1983) distinguished between 3 ranges for the temperature of formation of smectites in recent marine sediments: (90-140°C) for smectites associated with sulfide and Fe-rich material, (80°C) for smectite associated with carbonate and Fe-oxide, and (160-200°C) for smectite associated with anhydrite and sulfides. The range determined by the investigators includes apparently the three ranges of Cole. The temperature of the boundary between hematite and goethite was calculated as 115°C by Bischoff (1969b), who postulated that the temperature of the Atlantis II brine of 56°C was favorable for the deposition of goethite and too low for hematite. The deposition of goethite is possibly completed at temperature near 50°C because most iron in the hot brine has been deposited, but manganese remained in the water at 44°C (Brewer and Spencer 1969). The iron content decreases more than 80% from 52 to 25°C (Bubnov *et al.* 1977). The manganese is believed to be deposited as manganite at a temperature between 44 and 23°C, and close to 35°C. The final fossil zone indicates a temperature near 21-23°C according to the fauna found by this study (Tan *et al.* 1987). The amorphous facies is believed to be deposited in a relatively short period, resulting in an amorphous form.

The pH of normal Deep Red Sea water is generally near 6.5, but it is 7.9 at a depth of 2000 m in the Atlantis II Deep. The pH decreases to 6.6 abruptly below a depth of 2,050m accompanied by an increase in temperatures from 25°C at 2000m to 52°C at 2,100m (Bubnov *et al.* 1977; Danielsson *et al.* 1980). The original outflow of the hydrothermal solution of the Atlantis II brine pool is estimated at 140-280°C by Hartmann (1980) and the pH of the outflow should be much lower than 6.6. Pottorf and Barens (1983) estimated a pH of 4.6 $\pm$ 0.5 for the deposition of a rare cubanite -chalcopyrite-pyrrhotite assemblage. However, the frequent association of siderite and sulfide facies should not be much lower than 6.0 according to the Eh-ph diagram of Garrel and Christ (1965).

Acknowledgement

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معدنيــة الرواسب الفلزيــة من منخفض الأتــلانتِس ٢ – البحــر الأحمــر

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مستخلص . أُجريت دراسـة على التركيب المعدني لـ ٢٩٥ عينة من الطين المتمعدن المستخرج من منخفض الأتلانتس II باستخدام حيود الأشعة السينية . ولقد تم التعرف على أطوار متعددة للمعادن السائدة ، وهي المعادن السليكاتية وأكاسيد الحديد والمنجنيز ، والمعادن الكربوناتية ، ومعادن الكبريتات والمعادن الكبريتية . وقد كان توزيع هذه المعادن منتظماً في اللب الرسوبي ، مما ساعد على تصنيفها إلى سحنات رئيسة وفرعية . وقد تبين أن التتابع المعدني المميز من أعلى إلى أسفل هو كبريتيتات – سيليكات – سيدريت – كربونات الكـالسيوم والحـديد والمنجنيز – رودوكروسيت – أكاسيد الحـديد – منجانيت ومواد غير متبلورة من السيليكا وأكاسيد الحديد أو المنجنيز . ولقد تم إرجاع هذا التنوع المعدني في رسوبيات حوض الأتلانتس II إلى دورات ترسيبية متكررة ذات علاقة بتغيرات في درجات الحرارة ، والأس الهيدروجيني (pH) ، وربما كذلك بالنشاط الكيميائي للأكسجين أثناء اختلاط المياه الصهارية الساخنة بمياه البحر .