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ELEMENTAL GEOCHEMISTRY OF SOME RECENT MARINE SEDIMENTS FROM NORTH RED SEA.

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ABSTRACT

Sediment samples from northern Red Sea were analysed for the elements: Ca, Co, Cu, Fe, Mg, Mn, Pb and Zn. The carbonate content was also determined. The concentration of different elements varied with location, however, on the average, the sediments had 32.3% Ca, 48 ppm Co, 16 ppm Cu, 0.132% Fe, 1.46% Mg, 55 ppm Mn, 75 ppm Pb and 70 ppm Zn. Carbonate constituted ca. 95% of total sample.

Carbonate are mostly magnesian calcite and aragonite. Samples from the Gulf of Aqaba contained relatively high Mg / Ca mole ratios. Dolomite was also detected in some samples. The Mg / Ca mole ratios in the sediments showed regular decrease in both the N - S direction and the E - W direction.

Carbonate phases seem to be the host of other elements. Iron and Mn are mainly associated with carbonate phases, probably substituting for Ca in the calcite crystal lattice. Lead and Zn are both present in relatively high concentrations. Sediments of the African side of the Red Sea have higher Pb content than sediments from the Arabian side. Zinc showed random distribution. The Cu content of the Red Sea sediments is well below the average content of sediments from other environments; Co content is higher. It is suggested that temperature may exert some effect on the process of concentrating these elements from sea water.

INTRODUCTION

During the Egyptian Expedition to the North Red Sea 1934-1935, sediment samples were collected from different parts of the area. Some of these samples were studied for their sedimentological and mineralogical characteristics (Shukry and Higazy, 1944 a, b). The samples preserved at the Museum of Marine Biological Station at Al-Ghardaqa, were later subjected to a detailed study of their recent foraminifera (El-Deep, 1978). The elemental composition of the samples, however, was not studied yet.

Samples collected as early as 1935 may yield good geochemical information about the sediments in the area which will shed some light

on the base line concentrations of the elements of environmental importance, and the mechanisms that may affect their distribution.

The present work deals with the elemental composition of some of these samples and the possible sources and association of the elements.

MATERIAL and METHODS

a- Materials

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The samples used for the present study were collected during the Egyptian preliminary Expedition to the Northern Red Sea on board the Egyptian R.V. Mabahiss 1934-1935. The samples were collected on seven profiles (Figure 1); these are



Fig. 1. Profiles of Mabahiss cruise in the N.R.S.

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- 1) Suez Ghardaqa profile (not included in the present study);
- 2) Agaba Sanafir Island profile;
- 3) Ghardaqa Sanafir Island profile;
- 4) Mersa Daba Island profile;
- 5) Safaga Mowila profile;
- 6) Qoseir No man's Island profile;
- 7) Deadelus Reef Mabahiss Deep profile (Crossland, 1939).

Samples collected were mostly dredge or grab samples. Figure 2 shows the location of sampling stations.



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Fig. 2. Location of sampling stations.

b- Methods of Analysis

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In order to study the distribution pattern of the elements among the various phases of the sediment, a separation technique was applied to the samples. Details of the separation techniques were discussed by different authors (see for ex. Chester and Hughes, 1967), however, in the present study, the method described by Hirst and Nichols(1958) using 25% acetic acid was applied.

Total samples were dissolved in HF and $HClO_4$ as described by Riley(1958).

The elemental composition was determined in both the sediment solution and the acetic acid extract, after suitable treatment and dilution were made; details of the procedure are described elsewhere (Beltagy, 1973). Pye Unicam Model 1900 AAS was used for the analysis.

Infra-Red technique was used to get a clue on the mineralogical characteristics of the sediments.

RESULTS

Tables 1 and 2 give information on the chemical composition of the total samples as well as the acetic acid extract of the same samples. A good area distribution of the elements, however, can not be given here, because of the limited number of samples and the large variability of the bottom topography.

DISCUSSION

The Red Sea is a narrow inland sea that lies in a very arid zone between the African Plateau and the Arabian Plateau.In its northern part it recieves very little sediments of terrestrial origin. Because of the scarcety of rain, land drainage and streams or rivers, evaporation largely exceeds precipitation and runoff, hence a compensating current flows over the sill into the Red Sea through Bab Al-Mandab. Also, the source of sediments to the Basin is largely autocthonus, mainly biogenic or chemical precipitation of different mud facies. Minor amounts of terriginous material are added by wind, and on a local basis small amounts are added through the small wadi systems on both sides of the Basin. Near the deeps, in the central part of the Basin, hydrothermal flux through certain paths has its clear effect on the sediment composition in the nearby areas (Degens and Ross, 1969).

In the samples examined, Mg-calcite and aragonite were identified. Dolomite was detected only in samples from the Gulf of Aqaba. Calcium carbonate constituted over 90% of the bulk mineral phases; except in the two deep stations in the Gulf of Aqaba, and near Mabahiss deep. The Mg/Ca mole ratios (Table 3) show that most of the carbonates in the samples studied are Mg-calcite that contain between 3% and 10% Mg carbonate

Sample No.		ELEMENT (ppm)							
	% Carbonate	Ca "	Mg	Fe	Mn	РЬ	Zn	Cu	Co
1	90	26.8	1.57	2150	140	- 90	200	3	60
2	62	13.1	1.75	4990	155	50	230	8	32
3	95	39.0	1.30	301	13	110	10	27	51
4	98	28.0	0.93	625	21	80	-	23	45
5	98	35.8	1.30	301	8	90	160	6	49
6 ·	82	26.0	1.90	2090	418	60	330	7	40
7	94	32.6	N.d.	148	35	80	-	7	33
B	98	36.8	1.13	270	2	65	-	7	39
)	96	27.5	1.47	1241	27	60	-	39	29
10	98	39.0	1.70	1.296	33	10	-	20	54
11	100	34.9	1.75	2050	65	100	-	60	60
12	98	38.3	0.75	115	11	90	175	-	55
13	98	32.1	2.02	457	30	90	-	8	40
14	96	35.0	1.85	3850	47	80	40	7	60
15	98	38.7	1.90	635	44	80	150	4	50
16	98	34.4	1.71	420	28	70	180	-	61
17	97	35.0	1.55	1075	33	60	80	3	44
18	97	33.2	1.17	2500	37	90	100	37	44
19	98	32.7	1.90	1504	18	65	15	5	[·] 51
20	98	28.4	1.36	1595	17	65	-	5	43
21	98	33.7	1.99	2040	43	60	-	6	55
22	98	29.1	0.64	95	15	90	170	2	65
23	94	36.0	1.35	1520	55	97	-	79	50
24	97	28.0	1.98	465	25	70	-	22	46
25	73	21.0	1.26	1791	65	60	45	11	40
26	98	31.0	0.85	190	7	60	-	8	52
	95.17	32.21	1.457	1322	55	75.0	70.7	16	48

 TABLE 1

 CARBONATE AND TRACE: ELEMENTS CONCENTRATION IN THE TOTAL SAMPLES.

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N.B.

Ca and Mg are given in percentage.

ELEMENT (ppm)							
Sample <u>No.</u>	Fe	Mn	РЬ	Źn	Cu	Co	
1	1680	50	78	27	2	54	
2	4150	51	39	22	5	27	
3	230	5	81	-	19	45	
4	520	7	62	-	16	40	
5	260	3	62	-	4	43	
6	1590	149	47	31	4	35	
7	120	12	58	-	5	30	
8	200	0.0	55	-	5	30	
9	970	10	52	-	25	21	
10	1005	11	9	-	18	46	
11	1670	22	70	-	39	52	
12	92	4	68	26	-	50	
13	350	10	82	-	7	35	
14	3120	16	58	3	6	51	
15	499	15	66	12	2	47	
16	325	10	59	22	-	53	
17	840	12	41	7	-	40	
18	1985	13	65	15	30	42	
19	1263	6	53	-	2	37	
20	1216	6	59	-	3	35	
21	1712	15	45	-	4	61	
22	79	5	71	18	-	61	
23	1290	19	73	-	53	· 39	
24	378	9	50	-	18	42	
	1064	19.16	58.45	7.7	11.13	41.9	

 TABLE
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 TRACE METAL CONTENT OF THE ACID SOLUBLE FRATION

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Sample No.	Mg/Ca Mole ratio % 100
1	9.7
2	21.9
3	5.0
4	5.5
5	6.0
6	12.0
7	
8	5.1
9	8.8
10	7.0
11	8.3
12	3.2
13	10.4
14	8.7
15	8.1
16	8.2
17	7.3
18	5.8
19	9.6
20	7.9
21	9.7
22	3.6
23	6.2
24	11.3

TABLE 3										
Mg	1	Ca	MOLE	RAŤ	10	IN	Ν.	RED	SEA	
-			SEDEM	ENT	SA	MPL	ES.			

(mole ratio). In a sample from the Gulf of Aqaba, the ratio was slightly over 21%, which may indicate some degree of dolomitization. This is in agreement with Mohamed(1980), Friedman (1980) and El-Sayed(1984). These authors reported the presence of the three mineral phases in different parts of the northern Red Sea, however, the samples they examined were of localized nature,(i.e. from the Gulf of Suez, Gulf of Aqaba and Al-Ghardaqa regions respectively).

In the northern Red Sea, Mg/Ca mole ratio in carbonate sediments tends to decrease in the direction NE - SW (Figure 3). This tendency may be due to: i) increase of the contribution made by recent coral and other reef building organisms with carbonate skeletons of low Mg content, to the bottom sediments in the direction NE - SW; ii) difference in the rate of diagenitic processes, probably due to differences in the rate of



Fig. 3. Change of Mg / Ca Mole ratio with Longitude and Latitude.

sedimentation in the NE and the SW parts of the area; iii) general change in the Mg/Ca ratio in sea water due to selective and intensive consumption of the two elements by marine organisms as it travels north-ward along the eastern side; iv) the effect of changes in water temperature in different parts of the Red Sea.

In the eastern side of the Red Sea water has higher temperature and lower salinity compared to waters of the western side (Morcos, 1970). Waters of the western side show increase in temperature from north to south, and decrease in salinity in the same direction (Beltagy, 1983; El-Sabh and Beltagy, 1983). Thus, the Mg/Ca ratio may be increasing with temperature and decreasing with salinity. This is evidenced by the notable change in the Mg/Ca mole ratios at Al-Ghardaqa at the foot of the Gulf of Suez, and near Qoseir ca. 50 miles to the south. The change of Mg/Ca ratio with temperature was also reported in the literature(see for ex. Bathrust, 1971).

Iron and Manganese

The average Mn content of the total samples is 55 ppm and the average Fe content is 1322 ppm. Both elements are geochemically associated, and in many sediments they are trace element scavengers, particularly in the form of Fe-Mn oxides.

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In the Red Sea samples, most of Fe and Mn are present in association with the carbonate fraction, probably sorbed on the surfaces of the particles, or more likely, they substitute for Ca in the calcite crystals, where Fe^{+2} and Mn^{+2} can form solid solutions with Ca in the crystal lattices. Fe and Mn oxides seem to be present in very small amounts. This is indicated by the small difference between the Fe and Mn concentrations in the total samples and the separated samples, since the separation technique used in the present study does not affect the Fe-Mn oxides.

According to Schmalz (1972), calcite may has between 0.0% and 0.29% FeO. The Red Sea samples examined had on average, 0.132% Fe, which fits well in the range reported above. The correlation between Fe and Ca, however, is not very high. This could result if Fe ions in the water were available at highly variable concentrations in different parts of the area. It may also result if there was an active leaching process of the element. As for the high variability in the concentration of both Fe and Mn, Beltagy (1982) had shown that the concentration of both elements vary significantly, even over a very short distance in the area of Al-Ghardaqa. On the other hand, the low concentration of the two elements reveals the poverty of the source material and/or the high rate of sedimentation with an early diagenisis that may lead to leaching and migration of these elements, particularly in view of the disappearance of organic matter despite the high biological activity in the area.

Lead and Zinc

The average Pb concentration in the total sediment samples is 75 ppm. About 80% of the Pb content is acid leachable, i.e mainly associated with carbonate phases. Pb can form solid solution in calcium carbonate aragonite crystals; but with calcite the atomic size would not allow such substitution. Nevertheless, calcite from different localities contain high concentrations of Pb. Beltagy (1973) has shown that Pb in the sediments, is mainly present in association with carbonate phase and organic matter, with much higher correlation between Pb and carbonate. It could be thus, that Pb in the present samples was originally associated with organic matter and carbonate phases, upon decay of organic matter Pb may have been fixed in a position within the aragonite cement of the carbonate.

According to Purdy (1965) needles of aragonite cement can precipitate from sea water under certain conditions, and the process is active in some parts of the ocean, like the Bahamas. It could be precipitated chemically or biologically as skeletal material. In view of the low production of the Red Sea, it is likely that chemical precipitation is the active process in the area, due to rapid thermal changes, particularly in shallow water areas.

The close association of Pb with carbonates in the Red Sea samples masks the effect of terrestrial input in the total samples. However, sediments of the western north Red Sea have higher Pb concentrations than sediments of the eastern Red Sea and the Gulf of Aqaba. Zinc showed a random distribution, with a very little association with non-detrital phases, although Zn ions can fit well within the calcite lattice. This may indicate that Zn in the Red Sea sediments was not derived from sea water directly through biological or chemical precipitation of carbonte phases, it is rather introduced to the environment in association with detrital particles. Analysis of some sediment samples collected recently from Al-Ghardaqa region, have shown much high concentration of Zn (ca 540 ppm) Anon (1981). The distribution of Zn between different mineral phases however, was not given.

The association of Pb with carbonate provides the Red Sea waters with a natural cleanup agent for this element. On the other hand, if we take the concentration of Zn in the samples analyzed during the present study as the back ground concentration of that element, and the average figure given by Anon (1981) as the present day concentration, it is evident that the rate of supply of Zn ions or metal to the sediments is very high. In view of the lack of any rich source for Zn in the area, it is difficult to explain such increase in a simple manner, and further studies on the behaviour of Zn in the Red Sea area are solicited.

Cobalt and Copper

The average Co content of the total samples is 48 ppm and the average Cu content is 16 ppm. About 89% of Co is associated with carbonate phases, while 71% of the Cu is present in carbonate minerals.

Samples of the Northern Red sea had more Co than sediments from other shallow marine environments, particularly recent marine deposits. There is evidence however, that sediments of older age in deep sea sediments, do contain higher Co content (Beltagy, 1973; and Beltagy, 1981). Deep sea deposits contain between 70 and 75 ppm (Curtis, 1972). Co may enter the lattice of calcite and become concentrated in this phase of the sediment. It is also known that Co is an active element in the biological system; it is possible therefore that Co concentrated in the living parts of organisms may become included later on, into the hard parts. Also, Co may be concentrated in the hard parts directly, as it partially replaces calcium in the crystal lattice of calcite which constitutes the hard shells of several mollusc species.

Cu has a concentration similar to that concentrations found in the polar Atlantic regions. Cu is usually included in the soft parts of several marine organisms. It seems however, that unlike Co, Cu is not stabilized in the latice structure of calcite, it rather escapes and move through the sediments, and possibly returns back to the water column upon the death of organisms.

According to Curtis (1972) Cu during weathering and sedimentation may be compared with Zn. This view seems to be unvalid for these sediments, since the major source of both elements seem to be the water column or possibly leaching and migration from older sdiments. Older sub-bottom sediments in the Northern Red Sea are mainly evaporites depleted in Cu.

CONCLUSION

Carbonate phases of the sediments in the northern Red Sea seem to be the host of most of the trace elements. Carbonates in the sediments studies are mostly magnesian calcite and aragonite, except for the samples from the Gulf of Aqaba which contained high magnesian calcite, with advanced stage towards dolomitization. The Mg/Ca mole ratios in the sediments showed regular decrease in both the E-W direction and S-N direction which reflects the effect of temperature, and may be the effect of salinity also.

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Iron and manganese are mainly concentrated in calcite replacing Ca in the lattice structure. Lead and zinc are both present in relatively high concentrations. Sediments of the African side have higher Pb content than the sediments of the Arabian side. Pb ions are concentrated in the aragonite phase of the carbonate. The source of Zn added to the basin seem to be unknown and further work on the geochemistry of this element in the Red Sea is needed. The high content of Co in the sediments may be linked with the high content of molusc shell fragments that may host the element within the calcitelattice, while low Cu concentrations may be related to rapid diagenesis and loss of organic matter, which also affect Mn in the sediments.

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