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Geochemistry of Some Carbonate Secreting Marine Living Organisms From North West Arabian Gulf

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ABSTRACT

A total, 15 chemical variables have been determined from 29 samples representing skeletons of some carbonate secreting organisms from the north west Arabian Gulf. The analysis are reported as percent SiO_2, Al_2O_3, FeO, CaO,MgO,CO_2, P_2O_5, Na_2O, K_2O, SO_3, TiO_2, MnO, NiO, PbO and SrO.

Mineralogical analysis revealed the presence of Aragonite, Low Magnesium Calcite (LMC) and High Magnesium Calcite HMC) as dominant minerals, and quartz. Dolomite and feld- spar as traces. Chemical analyses indicates that the main differences in the constituents of the studied skeletons are controlled by the water chemistry, mineralogy, growth rate, calcification processes and the nature of the constituents.

جيوكيميائية بعض الكائنات الحية الفارزة للكاربونيت من شمال غرب الخليج العربي

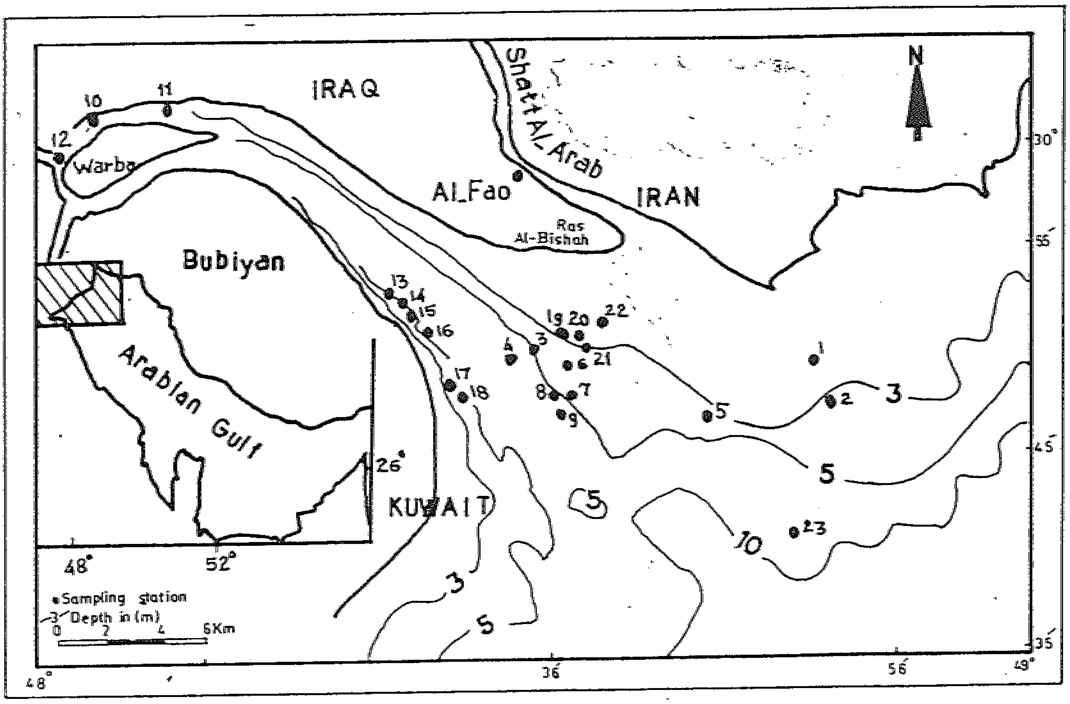
الملخص

ما مجموعة 15 متغير تم تعينهافي 29 نموذج تمثل هياكل بعض الكائنات الحية الفارزة للكاربونايت من شمال غرب الخليج العربي . ان هذه المتغيرات تم قياسها بالنسبة المئوية وهي SiO_2 ، Al_2O_3،FeO ، CaO ،MgO ، CO_2 ،P_2O_5 ، Na_2O ، K_2O ، SO_3 ، MnO TiO_2 ، NiO ،PbO ، SrO .

التحاليل المعدنية أظهرت وجود الارغونايت والكالسايت قليل المغنيسيوم والكالسيات عالي المغنيسيوم كمعادن رئيسية والمرو والدولومايت والفلدسبار كمعادن اثرية . دلت التحاليل الكيميائية على ان الاختلافات في مكونات هياكل الكائنات الحية مسيطر عليها بكيمياء المياه ، المحتوى المعدني ، معدل النمو ، عمليةالكلسنة وطبيعة مكونات الهياكل

INTRODUCTION

The Arabian Gulf is a natural isolated arm of Indian Ocean (a marginal sea) with an average depth of 35 m and maximum of 100 near the straight of Hurmuz Figure (1). According to Hartman *et al.*, (1971), the regional currents attain velocities about 50 cm/sec influencing sediments, including skeletal particles, in all parts of the basin. The wind driven currents remain the most influenced mechanisms of sediments transported along the shallow Arabian Gulf part.



Fi g. 1: Location map

According to more and Morel - Laurens (1983), Organisms play an important and dominant role in controlling trace metal chemistry in the ocean . They may increase trace metal solubilities by releasing complexing agents in the medium or on the contrary they may enhance the incorporation of metals into particles and then faster metal sedimentation in aquatic systems.

It is well known that marine sediments undergo various diagenetic modification and parts of marine organisms usually show low degree of such modification. Therefore, the current study attempts to offer a review of the mineralogy and the abundance of major, minor and trace elements besides the factors controlling their enrichment in the skeletal elements of Arabian Gulf invertebrate organisms.

MATERIAL AND METHODS

The sample of the marine bottom sediments were collected from 29 localities distributed in the modern sediments of NW Arabian Gulf, Iraq. The collection was carried out using Van Veen grab on Al-Fao research ship. Various types of faunal biogenic components were separated from each sample. The mineral compositions of shell components were determined using the X- Ray diffraction technique (Phillips PW 1060 100 diffracto meter) under the following conditions:

Radiation: CuKα, voltage = 35 kv, current = 20 MA, filter = Ni, Scan speed = 1°/min, slit = 1-0.1-1, scanning range: from 2° to 34° 2θ degrees.

The SiO_2, TiO_2, Al_2O_3, FeO, MnO, MgO, CaO, K_2O, P_2O_5, CuO, PbO and SrO. Contents were determined for several skeletal fragments using Electron Microprobe analyses technique (Geol. Surv. Finland. Espoo), Standards used were:

Wollastonite: SiO_2, periclase : MgO, Celestite : SrO, SO_3, Oligoclase : Na_2O , Al_2O_3, Biotite; FeO, TiO_2, K_2O, Mn - Tentalite; MnO, Pentlandite; NiO, Chalcopyrite; CuO Galena: PbO, Apatite: P_2O_5.

The study area occupies the north western edge of the mesopotamian shallow shelf. The region has an arid , subtropical climate . The textural character of the sediments is mainly fine mud , followed by fine sands and Oolitic - pelletal carbonate bioclasts. Detailed studies are reported in separate paper by Darmoian and Lindquist (1988).

During 1976-1990 an intensive program concerning the Geology and Fisheries of the NW Arabian Gulf were carried out by Marine Science Centre, University of Basrah. This paper deals with the mineralogical and chemical properties of organic skeletal materials in the collected modern sediments. Samples provided for analysis were taken at the stations in Figure (1). The benthonic faunal individuals, found in the muddy and silty sediments as well as in the protected rocky and sandy environments, mostly composed of calcium carbonate secreting individuals . Darmoian and Lindquist (1988) reported the following skeletal materials; forams, ostracods, both micro and macro mollusk (including gastropods, bivalves (Scaphopoda), echinoderms spines and plates, sponge spicules, barnacles, crab fragments and polychaetae, (see also Karim and Salman 1988, Darmoian and Al-Rubaee 1988 and Al-Khuzaee 1988.

Skeleton chemistry has been used to solve many marine and oceanographic problems such as diagenesis of carbonate sediments, mechanism of dolomitization , age determination ..... etc.

Gunatlika (1975) found that the mineralogy of certain skeletons play an essential role in the distribution of Mg and Sr.

Al-Aasm and Veizer (1982) through the study of cretaceous Rudist trace elements, showed a similarity in chemical composition between cretaceous and Holocene sea as. Al-Khuzaee (1998), on the other hand, reported the possibility of using certain dominant species of foraminifera as indicator of industrial pollution's problems.

The precision of chemical analysis were checked following the method of Rose *et al.* (1979), Maxwell (1968) and Stanton (1966) which are within the acceptable value, and the applied method were at high analytical accuracy (1-2%).

Mineralogy

The X-Ray diffractograms (Fig. 2 & 3) revealed that Low-Mg calcite (LMC), High - Mg calcite and Aragonite represent the dominant minerals whereas, quartz, feldspar and dolomite represent the trace mineral in the shells under study. Biogenic and terrigenous source were suggested for dominant and trace minerals, respectively.

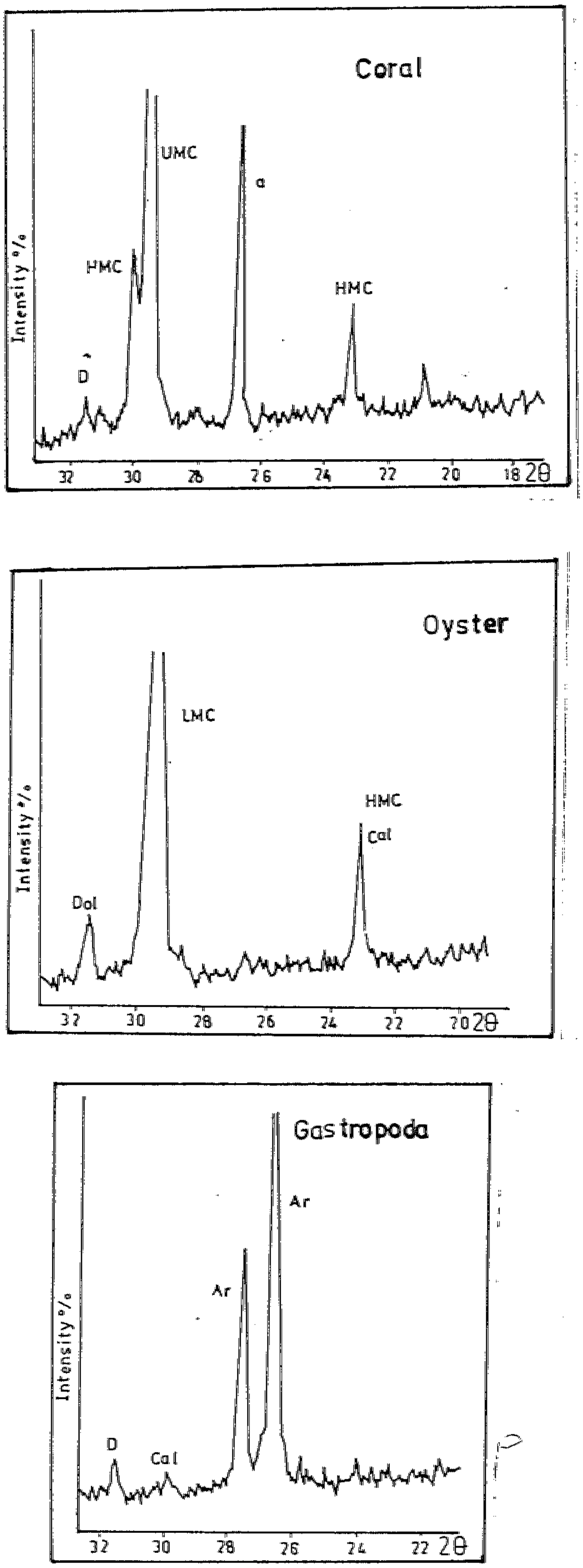


Fig. 2: X-ray diffractograms showing the main detected minerals in the shells of some organism of northwestern part of Arabian Gulf

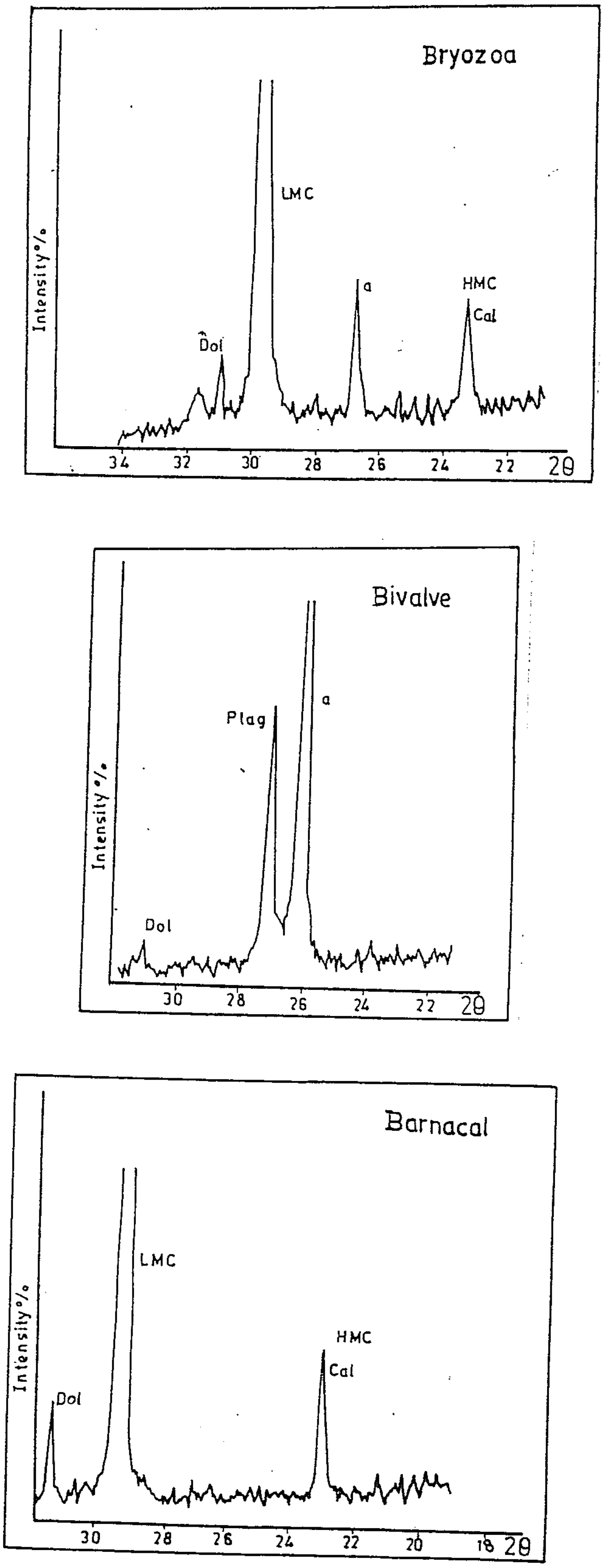


Fig. 3: X-ray diffractograms showing the main detected minerals in the shells of some organism of northwestern part of Arabian Gulf

Geochemistry

The result of chemical analysis shows that the studied skeletal materials are of high $CaCO_3$ contents. CaO and CO_2 make up more than 90 % of the chemical constituents.

The average concentration of Ca and Si in sea water are 4.1 x 10^5 and 3 X 10^3 ppb, respectively (Faure, 1998). These two elements involved in biological cycle, therefore, their concentrations fluctuated from place to place and with depth of ocean basin (Mason and Moore, 1982). Large part of dissolved Ca and Si were abstracted from seawater to build shell tests. This is suggested by Al-Imarah and Jawad. (1994), who reported low concentration of Ca and Si in Arabian Gulf water relative to normal sea water. Most of silica occurred in the form of quartz as detected by XRD. While Ca is distributed in more than one phase; Low-Mg calcite, High-Mg calcite and Aragonite.

The analysed skeletal material showed minor amounts of TiO_2, FeO and Al_2O_3 (Table 1). TiO_2 and FeO could be related to the presence of anatase disseminated as lithogenous materials. These materials make the fillings of the pore space scavenged by marine organism (Collier and Edmond, 1983).

Most Mg is associated with carbonate minerals; Low-Mg calcite and High - Mg calcite rather than aragonite. Minor part of Mg possibly occurs as $Mg(OH)_2$ (brucite) minerals (Schmitz, 1965 in Dodd, 1967).

Phosphorus represent members of nutrient elements, and it's distribution is affected by organism. The P concentration in sea water increases with depth; most of P abstracted from seawater and incorporated in non-skeletal part (soft tissuse), then recycled, after death and decomposition of these organism. The present P possibly occurs in the form of biogenic apatite.

Sodium and potassium represent the main alkaline elements incorporated in skeletal material under study. These two elements constituent the major cation in many surface and subsurface waters. Hence, their concentrations in shells of NW Arabian Gulf organisms related mainly to their aqueous concentrations. In general, the value of K is very low in comparison with Na. This is believed to be due to firstly original low K concentration in sea water (Faure, 1998), and secondly , the low coprecipitation of K as the aqueous Na increases (White, 1977).

The average concentration of Sr in most of the skeletons under study is higher than that reported in sea water (8 ppm), Table (1). This result could be attributed to the mineralogical composition of the studied skeletons which consist mainly of calcite and subordinate aragonite.

These two minerals are suitable to accommodate Sr and Mg in solid solution as Sr CO_3 and Mg CO_3, beside many trace elements such as Na, Mn and Fe. In general aragonite contains more Sr than calcite. Sr occurs mainly in the form of $SrSO_4$ (Celcetite) in aragonite and $SrCO_3$ (Strontinite) in calcite (Al-Aasm and Veizer, 1986). This fact possibly eluciclate the occurrence of low amount of SO_3 in the studied skeletons. Owing to Nelson, 1963 in Dodd (1967), the variation in Mg and Sr contents in the skeleton of the organisms of the Arabian Gulf may be related to their growth rates, the faster the growth rate, the lower the Sr contents. Mg varies with the growth rate in a somewhat different pattern than does Sr.

Table 1: NW Arabian Gulf Faunal shells analysis in weight %

Sample	Pellet No.	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	CO_2	P_2O_5	NiO	PbO	SrO	SO_3	Sr/Ca X10^3
Ammonia	1	0.02	0.0	0.07	0.04	0.00	0.33	53.93	0.22	0.0	44.34	0.84	0.05	0.0	0.12	0.04	2.63
	2	0.02	0.07	0.0	0.04	0.04	0.21	53.05	0.19	0.0	45.41	0.76	0.0	0.0	0.14	0.06	3.123
	3	0.0	0.0	0.0	0.04	0.0	0.31	54.43	0.21	0.0	44.09	0.79	0.03	0.10	0.18	0.00	3.912
	4	0.0	0.0	0.0	0.02	0.03	0.11	54.25	0.55	0.05	43.18	0.18	0.0	0.83	0.12	0.03	2.618
Triloculina	5	0.02	0.00	0.0	0.43	0.04	5.69	44.52	0.10	0.00	47.29	0.83	0.00	1.94	0.09	0.13	3.382
	6	0.03	0.01	0.02	0.29	0.00	6.16	45.22	0.21	0.02	46.94	0.86	0.05	0.05	0.10	0.04	2.161
Spirolocutina	7	0.03	0.0	0.0	0.20	0.0	5.21	44.53	0.23	0.02	47.59	0.74	0.02	1.03	0.08	0.33	2.124
	8	0.03	0.0	0.04	0.32	0.06	5.09	44.81	0.18	0.03	47.18	0.80	0.01	1.04	0.20	0.18	5.28
Elrlidium	1	0.02	0	0.0	0.37	0.0	0.08	53.25	0.11	0.0	44.44	0.83	0.0	0.90	0.0	0.0	--
	2	0.28	0.01	0.05	0.12	0.0	3.57	50.45	0.19	0.01	44.39	0.82	0.0	0.0	0.10	0.0	--
	3	2.5	0.0	0.60	0.59	0.06	6.96	44.22	0.25	0.14	43.33	0.81	0.02	0.27	0.17	0.08	4.55
	4	1.24	0.0	0.45	0.43	0.01	6.94	44.04	0.24	0.07	44.70	0.90	0.0	0.45	0.20	0.08	5.37
Oyster (1)	1	0.0	0.03	0.01	0.0	0.04	0.81	53.49	0.39	0.00	43.38	0.99	0.00	0.72	0.08	0.06	1.768
	2	0.02	0.0	0.02	0.0	0.0	0.83	50.49	0.71	0.01	45.19	0.98	0.02	0.50	0.07	0.12	1.64
Bryozoa	3	0.83	0.06	0.27	0.49	0.03	2.68	49.62	0.11	0.05	44.57	0.96	0.00	0.00	0.19	0.09	4.531
	4	0.06	0.02	0.01	0.08	0.01	1.24	51.73	0.20	0.01	44.91	0.99	0/01	0.00	0.73	0.00	16.697
Oyster (2)	5	0.03	0.00	0.00	0.03	0.01	1.06	45.8	0.66	0	45.06	0.99	0.03	0	0.13	0.13	3.357
	6	0.02	0.08	0.00	0.01	0.03	1.029	52.35	0.92	0.04	43.68	0.96	0.66	0.14	0.08	0	1.807
Bivalve	7	0.02	0	0	0	0.02	0.02	54.02	0.54	0	44.23	0.89	0.02	0	0.014	0.10	0.306
	8	0.04	0.06	0.02	0.02	0.03	0.03	53.07	0.92	0	44.0	0.86	0	0	0.24	0	--
Gastropod	1	0.04	0.03	0	0	0	0.03	54.2	0.88	0.01	43.49	0.94	0	0	0.33	0.05	7.202
	2	0.04	0.02	0	0.01	0	0.02	54.39	0.93	0.00	43.04	1.05	0.03	0.06	0.30	0.07	6.526
Bivalve	3	0	0	0.01	0.01	0	0.07	52.32	0.54	0.02	44.97	1.86	0	0	0.14	0.07	3.166
Coral	1	0.02	0.01	0.03	0	0.04	0.18	52.76	0.97	0	43.65	0.35	0.04	0.36	1.04	0.55	23.322
	2	0.05	0	0.01	0.01	0	0.20	52.23	0.73	0.01	43.91	0.39	0.02	1.14	0.96	0.94	21.747
Barnacl	3	0	0.06	0.03	0.01	0.03	1.62	51.22	0.59	0.05	42.98	0.38	0.03	0.42	0.46	2.1	10.626
	4	0.01	0	0.01	0.03	0.02	0.80	52.88	0.68	0.03	42.88	0.43	0	0	0.52	1.7	11.634
Gastropoda	5	0.03	0	0	0	0	0.04	54.03	0.60	0	44.08	0.37	0.01	0	0.24	0.08	5.254
	6	0.04	0.03	0	0.01	0.10	0.02	54.46	0.64	0.01	43.94	0.38	0.00	0.01	0.26	0.10	5.647

High fluctuations in Pb content were recorded in the skeletons, Triloculina and coral exhibit high concentration of this element (Table, 1) i.e hypoaccumulator organism. Therefore, it could be used as marine environmental pollution indicator for Pb Side-by-Side with the sediments, it is apparent here, that most of pb is derived from urban area surrounding Arabian Gulf.

The sea water contents of Mn is completely dependent on atmospheric and river fluxes (Mason and Moore, 1982). Moreover, Ni is mainly associated with hydrocarbons (accident oil - spill), organic matter from industrial effluent, and from decomposition of marine organisms debris (Al-Khalaf *et al.,* 1982). In general, Mn and Ni, discharged as river budget, usually associated with Fe - Oxide and nickelferrous silicate (Faure, 1998). Most of the present Mn and Ni possibly associated with biogenic carbonate mineral. According to Al-Aasm and Veizer (1986) Mn is largely enriched in diagenetic Low Mg Calcite (LMC) during transition of aragonite to LMC.

Foraminifera

Four groups are represented in the present study comprising main known genera; Triloculina, Spiroloculina, Ammonia and Elphidium, plate (1). The mineralogical analysis of skeletal material revealed that. Triloculina and Spiroloculina composed of High-Mg calcite, while Ammonia and Elphidium are of Low - Mg calcite. The high Sr contents in Triloculina shells reflect the high aragonite portion of shell because the larger Sr ion (1.12 A) would fit into the more open aragonite structure very readily. The high value of SO_3 and CO_2 together with Sr (Table), in Triloculina shells possibly reflects the presences of celestite and strontianite . According to Travis (1970) these two components are readily incorporated into calcite structure. On the other hand, spiroloculina shows high concentration of PbO (Table, 1), possibly as $PbCO_3$ (Cerussite) due to high CO_2 contents, Therefore, such shells could be used as indecation for the level of environmental pollution. Relatively low Ca values were reported in Triloculina and Spiroloculina skeletal material, this is related to the high Mg content possibly as high $MgCO_3$ Substitution in calcite.

Mollusca (Bivalves)

Shell chemistry of bivalve showed that calcite is low in Mg as compared to most other groups. The Sr. concentration in bivalve calcite is the lowest of all invertebrates under study (Table, 1). Similar result were also documented by Dodd (1967). The latter author related the above results to the evolutionary trend in biochemistry of the calcification process through which foreign ions (Mg and Sr) were excluded from skeleton. Mineralogcally, the shells of bivalves consist mainly of LMC, while other shells (such as Gastropoda) consist predominatly of aragonite, Fig (1).

Coral

The mineralogical composition of coral in the study area exhibit that (LMC) is the dominant mineral in comparison whit that reported by Veizer *et al.* (1978) which is mainly consist of aragonite Fig (1). The available coral calcite shows very high Sr as compared to other invertebrates (Table 1). Consequently, the Sr/Ca ratio is higher than in most other groups. Three factors appear to control Sr content in coral skeleton: water chemistry , mineralogical composition and physiology .

Bryozoa

Detailed analyses of Bryozoa chemistry are lacking in the literature, because of their small size which makes separation procedures tedious. The Sr contents are very near to that present in Barnacles and greater than that of other in vertebrates organisms except Triloculina (Table, 2). The available bryzoan skeletons consist mainly of LMC Fig (3). The reported low Ca value may reflect a high content of organic matrix within the skeleton .

Table 2: Mineralogy & Ca, Mg and Sr. contents in some type of fossils after flugel and Flugel - Kahler cited in Veizer *et al.*, 1971 (A), and present work, (B).

Type of fossils	Mineralogy	Ca %	Mg %	Sr %	Sr/Ca x 10^3
			A		
Algae	Mg-Calcite	32	4.27	0.27	3.86
		32.6	4.03	0.31	4.35
Coral	Aragonite	37.6	-	0.88	10.7
Echinoids	Mg-Calcite	--	2.7	0.15	--
Miliolids	Mg CO_3	13.6	--	--	--
Foraminifera					
Benthonic	Mg-Calcite	35.3	1.35	0.16	2.07
Planktonic	Mg-Calcite	--	--	--	--
Clobigerina	Calcite	--	0.18	0.13	--
			B		
Foraminifera					
Ammonia	Low Mg-Calcite	38.529	0.25	0.118	3.073
Triloculina	High Mg-Calcite	31.575	5.93	0.803	25.441
Spiroloculina	High Mg-Calcite	31.926	5.30	0.084	2.65
Mollusca					
Bivalve, 1	Low Mg-Calcite	37.157	0.82	0.063	1.706
Bivalve, 2	Low Mg-Calcite	35.077	1.045	0.093	2.651
Castropoda, 1	Aragonite	38.808	0.03	0.211	5.441
Castropoda, 2	Aragonite	38.772	0.07	0.118	3.043
Coral	Low Mg-Calcite	37.52	0.19	0.846	22.537
Barnacl	Low Mg-Calcite	37.2	1.21	0.414	11.137
Bryozoa	--	36.22	1.97	0.389	10.74

Barnacles

The barnacle skeletons were once thought to be entirely calcite. But the XRD study of the present barnacle skeletons (Plate, 2) indicates a LMC with trace of aragonite Fig (3). The calcitic portion of barnacles is rather low in Mg while the same samples have the Sr content is higher than that of the other studied foram except coral (Table, 2).

CONCLUSIONS

The calcareous skeletons of the selected invertebrate fauna from the northwest Arabian Gulf consist mainly of Low-Mg calcite (Foraminifera, pelecypoela, Barnacles and coral), aragonite (Gastropoda), with traces of quartz, feldspar and dolomite.

The variation in the obtained chemical constituents among the studied skeletons are attributed to many factors such as the chemistry of sea water, skeleton mineralogy i.e aragonite contain higher concentration of Sr compared to low - Mg calcite, nature of chemical constituents, nutrient elements exhibit high concentration (Cu, Si, K, P) in comparison with the rest of elements, orgamisms physiology, the faster the growth rate the lower Sr contents and biochemistry of the calcification process, through which Mg and Sr ions are excluded from some skeletons.

Triloculina and coral show high tendency to accumulate Pb. Therefore they could be used to measure the level of pollution in the Arabian Gulf aquatic ecosystem.

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Plate – I

1.Quinqeloculina sp. x 180
2.Triloculina sp. x 180
3.Eliphidium sp. x 180
4.Spiroloculina sp. x 100
5.Gastropoda (cerlthium) x 60
6.Gastropoda (epitonium) x 60
7.Gastropoda (tupbo) x 60
8.Pelecypoda (cyclymeris) x 30
9.Pelecypoda (corbula) x 30
10.Bryozoa (three pieces) x 100

Plate - II

Selected photographs; A-Solitary corals from shallow subtidal rock bottom. B-small barnacles, Balanus sp., found attached to intertidal rocks.

Plate – I

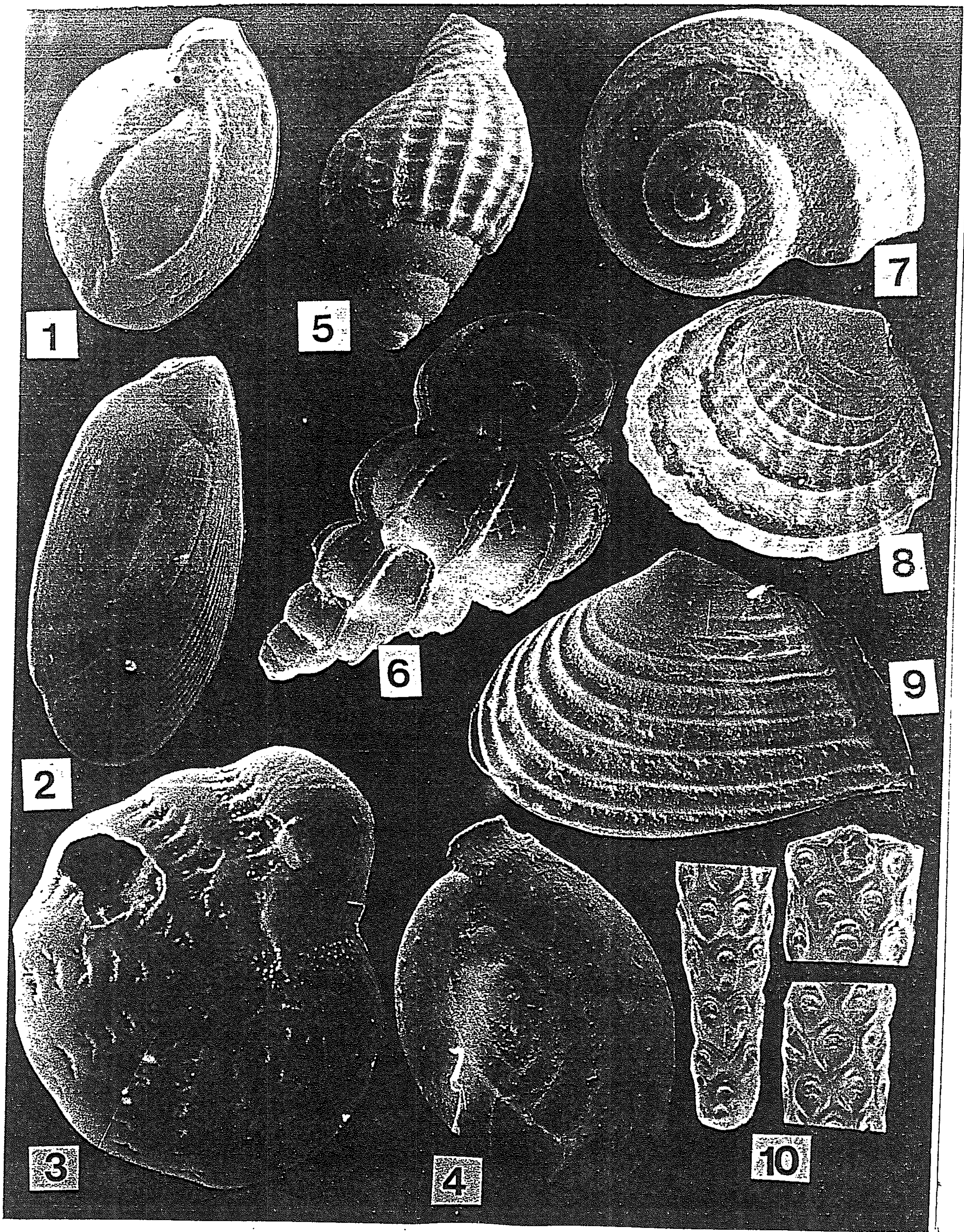

Plate - II