

Geochemical Studies on the Shelf Sediments Off Bombay*

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Distribution patterns of calcium and magnesium carbonates, organic matter, phosphate, sulphide-sulphur and sulphate-sulphur have been studied in the sediment samples, surficial as well as cores, collected from the region between Bombay Floating Light Point and Bombay High. An integrated study of these distribution patterns with the chemistry of interstitial waters and the bacterial populations present in the sediments has revealed the presence of reducing micro environments (within the sediment column) in a milieu which is largely oxidizing. It is tentatively suggested that these reducing micro environments are induced by bacterial activity.

DURING the 6th cruise of *RV Gaveshani* in May 1976, a number of sea floor sediment samples, surficial as well as cores, were collected from the region between the Bombay Floating Light Point and Bombay High. Among the various studies that were carried out on these samples, geochemistry of sediments was one. These studies which were carried out in a limited manner were aimed at understanding the environmental conditions obtaining within the sediment column in the region of study. For this purpose, the parameters chosen were calcium and magnesium carbonates, organic matter, phosphates, sulphide-sulphur and sulphate-sulphur, and the results obtained are reported in this communication. It may be mentioned here that the earlier reports¹⁻⁹ on the distribution patterns of some of the parameters such as calcium carbonate, organic matter and phosphates in the sediments of the study region were based on samples, collected from a few stations which were far apart and further in most of the cases the studies were confined to surficial sediments only with the consequence they do not throw any light on the environmental conditions obtained within the sediment column.

Methods

Locations of stations from where the samples were collected are shown in Fig. 1. In all 22 stations were occupied and 22 surficial samples and 18 core samples were obtained. All the parameters listed above were determined in the surficial samples as well as in the bottom portions of the core samples. Calcium and magnesium carbonates were estimated by the method of Muller¹⁰. Organic carbon was estimated by the method of El Wakeel and Riley¹¹ and the organic carbon values were multiplied by a factor of 1.723 to obtain organic matter content. Phosphate was estimated by the method of Rochford¹². Sulphide-sulphur was determined by digesting the samples with aqua-regia and concentrated hydrochloric acid

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in the manner described by Groves¹³ and precipitating sulphide as barium sulphate. Total sulphur and sulphite-sulphur were estimated in the sediments following the methods of Robinson¹⁴ and Groves¹³ respectively and the difference between the total sulphur value and the combined value of sulphide-sulphur and sulphite-sulphur is taken as sulphate-sulphur in the absence of free sulphur present in the sediments.

Results

The following generalizations can be made in regard to the distribution patterns of various parameters from the data obtained (Table 1).

(1) In the region between stations 1 and 11 (0-60 m), clays and silty clays of surficial sediments as well as bottom portions of the core samples are characterized by a very low calcium carbonate content. In the region between stations 12 and 22 (60-77 m), clays and silty-clays of sediments are characterized by low calcium carbonate content. Sands and clayey sands, on the other hand, whether they are from the surface or from the bottom portions of the core samples, are characterized by a high

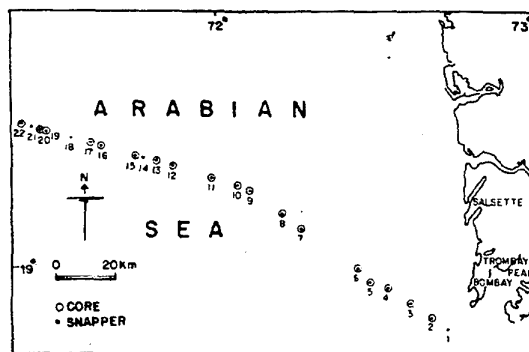


Fig. 1— Location of the stations from where sediment samples were collected

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TABLE 1 — CHEMICAL ANALYSIS OF SEDIMENTS

Stn No.	Depth m	Nature of the sample	Texture	Composition, %					
				CaCO ₂	MgCO ₂	Organic matter	P ₂ O ₅	Sulphide-sulphur	Sulphate-sulphur
1	12	S	Clay	7	5.9	3.33	0.22	0.24	0.09
		C 25* (-)†	—	—	—	—	—	—	—
2	18	S	Clay	7	6.75	2.65	0.21	0.22	0.03
		C 130 (36-46)	Clayey sand	80	3.37	0.65	0.1	0.21	0.02
		S	Clay	6	8.43	2.6	0.2	0.35	0.03
3	24	C 225 (205-215)	Silty clay	38	3.37	2.08	0.17	0.43	0.02
4	30	S	do	13	8.43	2.76	0.22	0.64	0.01
		C 283 (273-283)	do	39	5.06	2.56	0.16	0.69	0.01
5	31	S	do	9	7.59	2.52	0.19	0.53	0.01
		C 216 (191-201)	do	12	5.9	2.89	0.19	0.72	0.01
6	33	S	Clay	8	7.59	2.41	0.2	0.38	0.01
		C 219 (193-203)	do	10	5.06	3.14	0.32	0.39	0.01
7	45	S	do	7	9.28	1.96	0.18	0.28	0.06
		C 309 (284-294)	do	8	5.06	2.76	0.19	0.45	0.04
8	46	S	Silty clay	6	6.75	2.27	0.17	0.2	0.06
		C 345 (320-330)	Clay	8	6.75	2.71	0.19	0.39	0.03
9	50	S	do	7.5	6.32	2.03	0.18	0.27	0.07
		C 305 (280-290)	Silty clay	9	5.48	2.6	0.19	0.48	0.05
10	51	S	Clay	6	6.75	2.38	0.24	0.23	0.06
		C 322 (298-308)	do	9	5.48	2.65	0.19	0.46	0.04
11	57	S	do	7	7.59	2.6	0.19	0.28	0.04
		C 282 (256-266)	Silty clay	10	8.43	3.27	0.19	0.46	0.03
12	61	S	do	20	8.43	2.22	0.21	0.32	0.09
		C 230 (66-76)	Clayey sand	52	5.05	0.7	0.09	0.21	0.06
13	64	S	Silty clay	13	3.37	2.65	0.19	0.29	0.06
		C 299 (273-283)	Clay	10	2.53	3.08	0.18	0.61	0.03
14	60	S	Clayey sand	76	4.2	0.84	0.23	0.22	0.05
		C 66 (-)	—	—	—	—	—	—	—
15	66	S	Clay	10	5.9	2.89	0.19	0.44	0.03
		C 175 (50-60)	Sand	8.7	2.52	0.6	0.11	0.46	0.02
16	64	S	Clayey sand	50	4.22	1.18	0.25	0.22	0.06
		C 196 (186-196)	do	66	4.22	1.95	0.12	0.29	0.05
17	70	S	Silty sand	12	3.48	2.86	0.19	0.33	0.05
		C 230 (205-215)	Clayey sand	7	4.22	1.28	0.1	0.47	0.02
18	72	S	Silty clay	20	6.75	2.7	0.2	0.32	0.07
		C 23 (-)	—	—	—	—	—	—	—
19	74	S	Sand silt clay	44	4.22	1.95	0.23	0.43	0.06
		C 73 (20-30)	do	86	4.22	1.96	0.21	0.59	0.05
20	72	S	Clayey sand	55	5.06	1.46	0.31	0.23	0.08
		C (-)	—	—	—	—	—	—	—
21	77	S	Silty clay	21.5	6.75	2.98	0.02	0.44	0.06
		C 46 (-)	—	—	—	—	—	—	—
22	78	S	Silty clay	26.5	6.32	2.89	0.19	0.49	0.07
		C 212 (202-212)	Sand	84	5.06	1.29	0.1	0.28	0.04

*Figure indicates total length of core in cm.

†Figure in the brackets indicate levels at which samples were analysed (in cm).

S = snapper; C = core.

calcium carbonate content.) Invariably a higher amount of calcium carbonate is associated with the bottom portions of the core samples than with the surficial sediments. Calcium carbonate in clays and silty clays from the region 0-60 m mainly comes from the shell fragments associated with them. In the sediments of the region 60 and 77 m depth, calcium carbonate is contributed by shell fragments, colites and rock fragments consisting of colitic and coralline algal limestones. Higher content of calcium carbonate is due to oolites and the sediments in this region are relict.

(2) In general a higher amount of magnesium carbonate is associated with clays and silty clays of the region 0-60 m water depth as compared to sediments in the region 60-77 m. Invariably the surficial sediments contain a higher percentage of magnesium

carbonate than the bottom portions of the core samples. As in the case of calcium carbonate, while the bulk of magnesium carbonate in the sediments may have been contributed by the skeletal and/or skeletal carbonate components of the sediments, relatively high magnesium carbonate contents associated with the sediments of the region 0-60 m water depth may be due to the association of magnesium with the clays.

(3) Organic matter in the sediments closely follows the texture of the sediments. Clays and silty clays have relatively high organic matter content than sands and clayey sands. In cases where the texture of the surficial sediments and the bottom portions of the cores is similar, the bottom portions of the cores have relatively high content of organic matter.

(4) Phosphate content of the sediments does not show any marked pattern of distribution. Despite the fact that the sediments in the relic zone contain high calcium carbonate content and low organic matter, phosphate content in them is similar to those of clays and silty clays of the region 0-60 m which have a low carbonate content and high organic matter content. Phosphate appears to be associated with the sediments of the 2 regions somewhat differently. In the region 0-60 m water depth, in the absence of any discrete phosphate minerals, it is quite possible that it is mostly associated with the organic matter and iron of the sediments. In the region 60-77 m water depth, it is possible that it is mostly associated with the carbonate phase of the sediments — oolites, shells, etc. The analyses of the oolitic rocks, collected earlier from the nearby areas, show their phosphate content to range from 0.5 to 1%. Surficial sediments have a relatively high phosphate content than the bottom portions of the cores.

(5) Distribution of sulphide-sulphur does not conform to any regular pattern in the region. However, higher sulphide-sulphur content is invariably associated with the bottom portions of the core samples. Coarse fraction studies have revealed the presence of pyrite occurring as infillings in the foraminiferal tests in most of the sediment samples¹⁵.

(6) Like sulphide-sulphur, no regular pattern is found in the case of sulphate-sulphur also across the shelf. Sulphate-sulphur content of the sediments is far less than sulphide-sulphur content. Invariably, surficial sediments have a higher content of sulphate-sulphur than the bottom portions of the core samples.

Discussion

General hydrographic features of the shelf waters off Bombay do not indicate the presence of any anaerobic conditions. Occasional heavy mortality of fish and other animals during certain seasons and the resultant anoxic conditions created are perhaps transient and do not give rise to any sustained reducing conditions at the sea bottom. Hydrographic surveys conducted over tidal cycles at 4 different stations in the area of study during March 76 have revealed the presence of oxygenated waters in the water column throughout and even near the sea bottom. Investigations carried out for the detection of hydrogen sulphide in the waters yield negative results¹⁶. Studies on the pH, Eh and dissolved oxygen content of the bottom waters at the

22 stations, where the sediment samples were collected, have also revealed the environment to be an oxidizing one near the sea bottom. Thus the environment in the shelf waters is largely an oxidizing one, in order to have an integrated approach for understanding the environmental conditions obtaining within the sediment column, the chemistry of the interstitial waters of the surficial sediments as well as the bottom portions of the core samples and the bacterial populations of the surficial sediments have been also simultaneously studied. The range of values obtained for some of the parameters such as pH, Eh, Ca, Mg and PO₄-P in the interstitial waters of the surficial sediments and bottom portions of the cores are given in Table 2. As to the bacterial population, 3 types of bacteria, viz. iron bacteria, sulphur oxidizing bacteria and hydrogen sulphide producers, have been identified in the sediments, and the range of values obtained for each type of bacteria are given in Table 3 along with their mean count percentage in the 22 samples.

pH and Eh values of the interstitial waters of the surficial sediments and the bottom portions of the core samples do not indicate the presence of any reducing environment in the sediment column. Detailed examination of the stationwise data has revealed the following distribution patterns for the parameters listed in Table 2. In the majority of the cases, pH showed an increasing trend towards the bottom portions of the cores while Eh showed a decreasing trend. Calcium showed a decreasing trend from surface to bottom while PO₄-P showed an increasing trend from surface to bottom. Magnesium did not show any specific trend.

Comparative study of the distribution patterns of calcium carbonate magnesium carbonate and phosphates in the surficial sediments and bottom portions of the core samples with the distribution patterns of

TABLE 3 — BACTERIAL POPULATION (0.1 mm) FOR SNAPPER SAMPLES¹⁹

(10%g dry weight mud)

	Range	Mean count percentage
Iron bacteria	0.09-10.54	1.27
Sulphur oxidizing bacteria	0.02-11.99	2.29
H ₂ S producers	5.26-41.66	8.99

TABLE 2 — CHEMICAL ANALYSIS OF INTERSTITIAL WATERS¹⁷

Parameter	Surface sample*		Bottom sample*	
	Min.	Max.	Min.	Max.
pH	7.4	8.22	7.3	8.68
Eh (mV)	+208	+392	+216	+3.84
Calcium (mg/litre)	204	733	204	8.02
Magnesium (mg/litre)	995	2473	1060	19.46
PO ₄ -P (µg-at/litre)	2.28	73.31	4.56	59.84

*These terms refer to the samples collected, as shown in Table 1.

calcium, magnesium and $\text{PO}_4\text{-P}$ in the interstitial waters of the surficial sediments and bottom portions of the core samples indicates that the distribution patterns observed in the sediments are just opposite to the distribution patterns revealed in the interstitial waters of the sediments. As already indicated, the bulk of the calcium and magnesium carbonates associated with the sediments are contributed by the shell fragments, oolites, etc. Distribution patterns of calcium and magnesium in the interstitial waters of the sediments suggest the removal of calcium from the waters and addition of magnesium to the waters in the bottom portions of the cores. Perhaps these changes are taking place through adsorption on the clays in the case of calcium and desorption in the case of magnesium and thus to a certain extent account for the differences found in the distribution patterns of calcium and magnesium in the sediments. In the case of phosphate, its distribution in the interstitial waters of the sediments suggests leaching from the sediments in the bottom portions of the core samples. Distribution patterns of organic matter, phosphates, sulphide-sulphur and sulphate-sulphur coupled with the occurrence of pyrite as infillings in the foraminiferal tests suggest the presence of reducing microenvironments¹⁹ in a milieu which is largely oxidizing as evidenced by the interstitial water chemistry and the general hydrographic features of the shelf waters. It is quite possible that reducing microenvironments are induced by bacterial populations present in the sediments.

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References

- MURTHY, P. S. N., REDDY, C. V. G. & VARADACHARY, V. V. R., *Proc. natn. Inst. Sci. India*, **34** (1968), 34.
- MURTHY, P. S. N., REDDY, C. V. G. & VARADACHARY, V. V. R., *Proc. natn. Inst. Sci. India*, **35** (1969), 377.
- GOGATE, S. S., SASTRY, V. N., KRISHNAMURTY, T. M. & VISWANATHAN, R., *Curr. Sci.*, **39** (1970), 171.
- KIDWAI, R. M. & NAIR, R. R., *Indian J. mar. Sci.*, **1** (1972), 116.
- SETTY, M. G. A. P. & RAO, CH. M., *Proc. int. Geol. Congr.*, (1972), 182.
- SIDDIQUE, H. N. & CHOWDHURY, A. N., *Bull. natn. Inst. Sci. India*, **38** (1968), 483.
- VON MARCHIG, V., *Meteor* (Forsch-Ergeb, Reiche, C., No. 11, Berlin, Stuttgart), 1972, 1.
- STEWART, R. A., FILKEY, O. H. & NELSON, W. B., *Mar. Geol.*, **6** (1965), 411.
- VON STACKELBERG, U., *Meteor* (Forsch-Ergeb, Reiche, C., No. 9, Berlin, Stuttgart), 1972, 1.
- MULLER, G., in *Methods in sedimentary petrology* (Schweizerbart Verlag, Stuttgart), 1967, 283.
- EL WAKEEL, S. K. & RILEY, J. P., *J. Cons. Perm. int. Explor. Mar.*, **22** (1957), 180.
- ROCHFORD, D. J., *Aust. J. mar. Freshwat. Res.*, **2** (1951), 1.
- GROVES, in *Silicate analysis* (George Allen & Unwin Ltd, London), 1951.
- ROBINSON, *Soil Sci.*, **59** (1945).
- HASHIMI, N. H., GUPTHA, M. V. S., KIDWAI, R. M. & NAIR, R. R., *Mahasagan—Bull. Nat. Inst. Oceanogr.*, (in press).
- ZINGADE, personal communication
- ANAND, S. P. & FONDEKAR, P., personal communication.
- LOKABHARATI & SHANTA NAIR, personal communication.
- KAPLAN, I. R. & RITTENBERG, S. C., *The sea 3, The earth beneath the sea history* (John Wiley & Sons, New York), 1963.