

SEDIMENT BORON AND ITS RELATION TO SEDIMENT PROPERTIES IN A TROPICAL ESTUARY

P.V. SHIRODKAR AND V.N. KAMAT DALAL*

National Institute of Oceanography

Dona Paula, Goa 403004

ABSTRACT

Boron in the sediments of Mandovi estuary varied from 8.0 to 258.0 ppm with an average of 118 ppm. It showed an inverse relation to the texture of sediments and was found to be concentrated in silt and clay fraction with generally decreasing concentrations from mouth towards upstream.

Seasonal variations of boron indicate all higher values during pre-monsoon (50.8 to 216.0 ppm; av. 128 ppm) while very low to very high concentrations during post-monsoon (8.0 to 258.0 ppm; av. 108 ppm). During monsoon itself narrow range was observed with moderate concentrations (87.0 to 148.0 ppm; av. 118 ppm).

Clay minerals by x-ray diffractometry of sediments showed the presence of Kaolinite + chlorite (av. 60%), Illite (av. 15%) and Montmorillonite (av. 6.5%) while the non-clay minerals like Feldspar (av. 4.84%) and Quartz (av. 8.67%) were found all along the estuary and the Gibbsite (av. 9.84%) was found only in the upstream.

Key-words: Boron, sediment, clay minerals, Mandovi estuary.

Boron in rocks and sediments is gaining an increasing attention in recent years as it is found to be an useful indicator of paleosalinity (Curtis, 1964; Adams, Haynes and Walker, 1965; Eager and Spears, 1966 and Porrenga, 1966) and measuring paleosalinity aids exploration (Frederickson and Reynolds, 1960; Walker and Price, 1963 and Walker, 1966).

In an aquatic system, sediments store boron by removing it from the overlying water through the physical processes of adsorption (Harder, 1970) and chemical complexation (Dyrssen and Hanssen, 1973; Byrne and Kester, 1974; Williams and Strack, 1966). Boron from the overlying water is removed by the differential adsorption onto suspended solids during the estuarine mixing of sea and river waters (Levinson and Ludwick, 1976; Liss and Pointon, 1973). Biological removal of boron by phytoplankton have also been observed which adds boron back to the sediments on the death and decay of phytoplankton (Subba Rao, 1981; Shirodkar, Singbal and Sen Gupta, 1982). However, information on boron in riverine/estuarine sediments in the Indian estuaries is scarce. This paper deals with the distribution,

* Department of Inorganic Chemistry, Goa University, Bambolim, Goa.

behaviour and relationship of boron with different sediment properties in the Mandovi river estuary.

Sediments were collected from nine different stations (M1 to M9) in the Mandovi river estuary (Fig.1) using a Petterson grab. The collections were made during monsoon (Sept. 1982), post-monsoon (Dec. 1982 and Jan. 1983) and pre-monsoon (Feb.1983). Water samples were collected simultaneously from the same stations from surface, mid-depth and bottom levels.

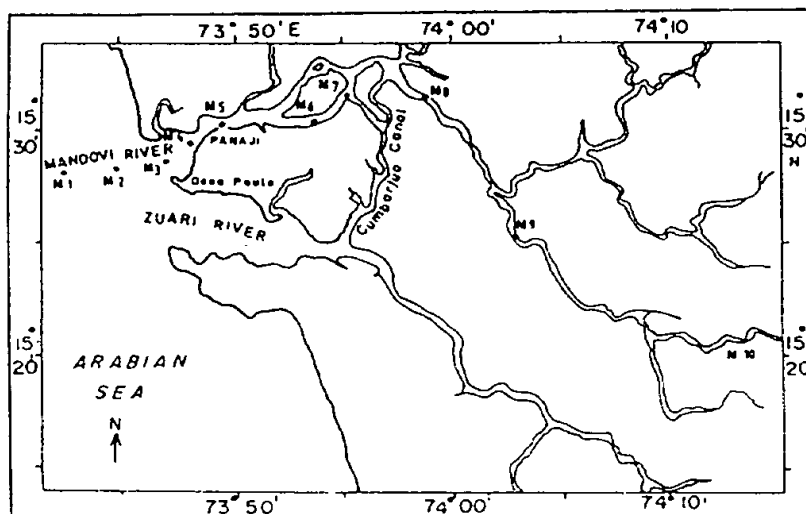


Fig. 1. Location of stations in the Mandovi-Zuari estuarine system.

The sediments were transferred to polyethylene bags and kept in deep freeze. They were then filtered through 0.45 μm membrane filter by suction under a pressure of 12 mm Hg, to remove pore water.

The filtered sediments were washed with distilled water till they were salt free; then dried at a constant temperature of 70°C and then powdered and sieved through a 100 mesh sieve.

Suspended solids were determined using standard methods (Anon, 1976) and boron in sediments was estimated by the Carminic acid method of Hatcher and Wilcox (1950), with a standard deviation of $\pm 4.9\%$ and standard error of 0.0041. Potassium and Aluminium in sediments were analysed by the flame photometry and atomic absorption spectrophotometry respectively after digesting the sample in a teflon bomb using the method of Loring and Rantala (1977). The standard deviations for the methods were $\pm 0.31\%$ for aluminium and $\pm 0.25\%$ for potassium. Organic carbon in sediments was determined by the method of El Wakeel and Riley (1957). Grain sizes were determined by sieving and pipette analyses using Folk's (1961) method and classification nomenclature is based on sand-silt-clay ratio from the model given by Shepard (1954). Clay minerals of the 2 μ size fraction were analysed by x-ray diffraction (Carroll, 1958) and the

percentages of clay minerals were estimated by the weighted peak area method of Biscaye (1965).

Sediments were a variable mixture of different textural types, the sand content of which varied from 1.67 to 89.0% while the clay and the silt varied within narrow limits along the length of the estuary. Spatial variation in the grain sizes is shown in Fig.2. Clayey sediments were found near the mouth of the estuary while the sandy sediments in the upstream. Silt was the major fraction relative to clay and its abundance decreased considerably in the upstream (clay/silt ratio > 4.0).

Among the important clay minerals, kaolinite + chlorite was found in greater abundance forming the major fraction (av. 60%) followed by Illite (av. 15%). The montmorillonite was the least (av. 6.5%) in these sediments. The kaolinite + chlorite showed a decreasing trend from mouth towards upstream with variation in the range from 51.2 to 76.5%. At station M2 its concentration was highest (76.5%) and lowest (51.2%) at station M5. Illite also varied in abundance from 6.6 to 26.5% and showed an alternate increase and a decrease from station M1 to M6. It was highest (26.5%) at station M3 and lowest (6.6%) at station M5 (Table I).

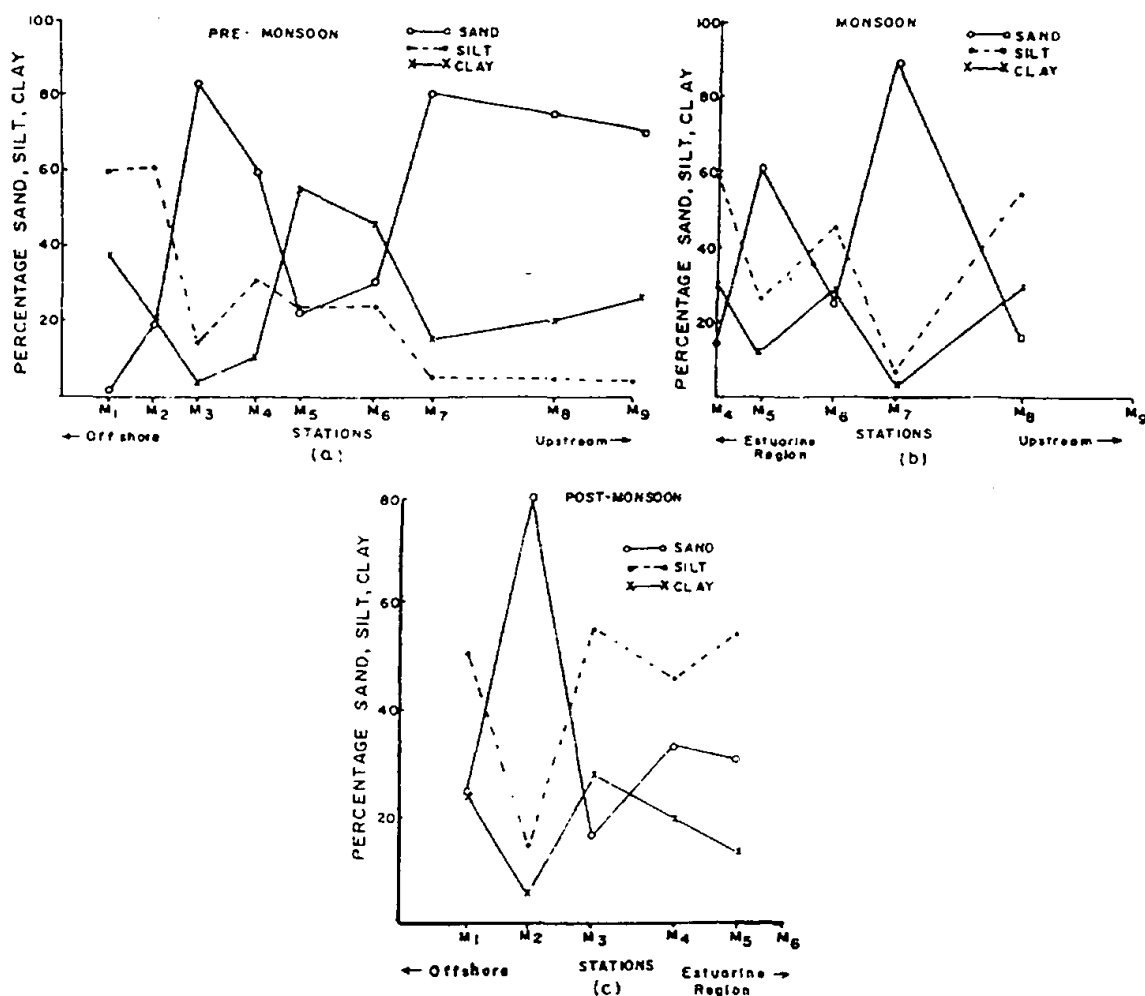


Fig.2. Major sediment fractions along the estuary.

Table I – Clay mineral abundance in the estuarine sediments

Stations	Clay Minerals			Non-Clay Minerals		
	Weighted peak area percentages			Feldspar	Quartz	Gibbsite
	Kaolinite + Chlorite	Illite	Montmorillonite			
M1	63.7	19.5	2.1	10.5	4.2	-
M2	76.5	16.9	0.8	2.3	3.4	-
M3	56.7	26.5	3.6	6.8	6.4	-
M4	54.0	7.6	8.0	3.0	11.2	16.2
M5	51.3	6.6	14.7	3.9	14.3	9.1
M6	58.6	11.8	10.1	2.6	12.6	4.2

Unlike the dominant ones the mineral montmorillonite showed an increase in its abundance from mouth towards upstream. Its abundance decreased at station M2 and then increased from 0.8% to 14.7% at station M5. Such a distribution of this mineral is partly antipathetic to that of the dominant ones. Other non-clay minerals found were feldspar and quartz at all the stations while gibbsite was found only in the upstream from station M4 to M6. The average feldspar content was 4.8%, quartz 8.6% and gibbsite 4.9%.

Organic carbon showed increase paralleling the increase in clay fraction of the sediments and varied from 0.07 to 2.9% (av. 1.6%) throughout the period of investigation. High organic carbon was observed during monsoon (1.25 to 2.9%) and pre-monsoon (0.18 to 2.87%) while it was low during the post-monsoon (0.07 to 1.93%). During the latter period however a reverse trend was observed in its distribution whereby the higher concentrations were found in the upstream and the lower ones near the mouth (Fig.3).

Boron in the estuarine sediments showed a wide variation ranging from 8.0 to 258 ppm (av. 118 ppm) and remained high during post-monsoon (8.0 to 198 ppm with a peak value of 258 ppm) and pre-monsoon (50.8 to 216 ppm) and becomes low during the monsoon (87 to 148 ppm), (Table II). Organic carbon showed an insignificant relation with boron ($r = 0.23$), (Fig.3).

Relationship of boron with grain sizes revealed its association in less sandy sediments with decreasing concentrations from mouth towards upstream. Linear regressions of boron versus the percentages of sand, silt and clay yielded the correlation coefficients of -0.93, +0.74 and +0.69 respectively, significant at 95% confidence limit. This indicates the association of boron with silt and clay, Fig.4 (a,b,c).

Potassium in sediments closer to the river mouth showed higher percentages (3.08 to 5.97%) compared to those in the estuary (1.27 to 3.14%) with decreasing concentrations in the upstream. This indirectly indicates the dominance of a mineral other than the potassium containing one (Illite). A linear relation was found between sediment boron and potassium with

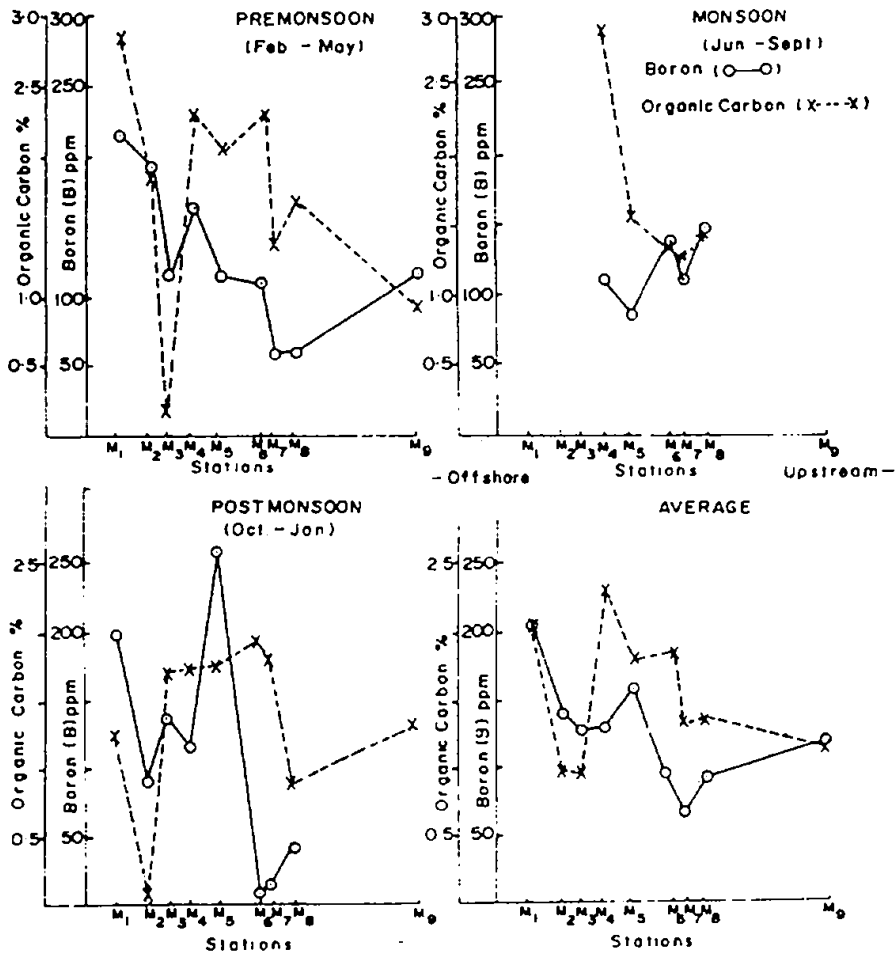


Fig.3. Spatial variation of boron and organic carbon in sediments.

a positive correlation coefficient, $r=0.45$, significant at 95% confidence limit, (Fig.4d; Table II). Variation in aluminium was similar to potassium and its relationship with boron was significant ($r=0.75$) with a linear variation.

Sediments in the Mandovi river estuary fall into different categories and the textural changes are brought about by the variable relief of the estuary floor as well as the variation in the velocity of tidal currents which bring the sediments from the coastal region as well as from the upstream and redistribute them.

Seasonal variation of boron which showed higher range of concentrations during post-monsoon (8.0 to 198 ppm) with the exception of one or two low values compared to other seasons seems to be due to the prior contribution of suspended solids by adsorption as well as from the tidal input. This has been confirmed in the earlier investigations by Shirodkar and Anand (1985), who observed the removal of dissolved boron upto 31.30% by suspended solids during monsoon. Subsequent to monsoon, the incursion of coastal sea water to a considerable distance upstream develops strong concentration gradients depending on which the labile boron from the

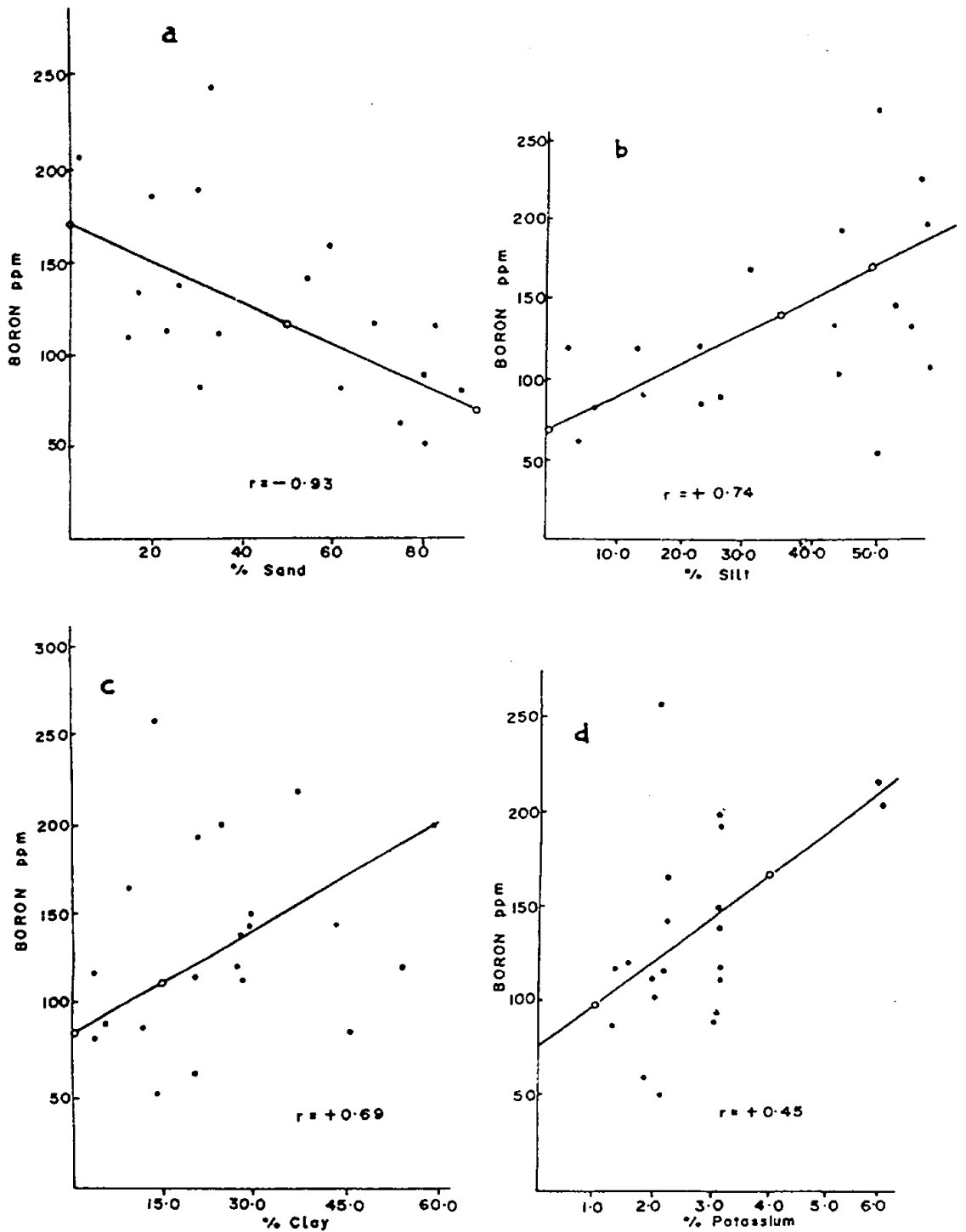


Fig.4. Relationship of boron with sand (a), silt (b), clay (c) and potassium (d) in the sediments.

tidal water diffuses into the interstitial water of the sediments from where it is adsorbed differentially onto the respectively available sediment particles giving rise to low values in water.

Table II – Distribution of boron, potassium, organic carbon and suspended solids in sediments along the estuary.

Seasons	Stations	Boron (ppm)	Potassium (%)	Organic Carbon (%)	Suspended Solids mg l ⁻¹
Pre-monsoon	M1	216.11	5.97	2.87	13.60
	M2	193.23	3.13	1.90	50.80
	M3	116.96	3.15	0.18	70.90
	M4	165.26	2.23	2.32	23.70
	M5	116.96	1.27	2.04	14.03
	M6	112.0	3.14	2.32	17.63
	M7	50.85	2.13	1.35	16.70
	M8	61.02	1.87	1.69	15.30
	M9	119.50	1.52	0.93	18.23
Monsoon	M4	112.38	1.97	2.90	11.90
	M5	86.95	1.27	1.55	62.24
	M6	142.38	2.22	1.32	54.33
	M7	102.50	2.02	1.25	43.33
	M8	147.97	3.13	1.45	44.67
Post-monsoon	M1	198.32	3.13	1.24	17.27
	M2	89.50	3.08	0.07	105.60
	M3	137.80	3.13	1.72	23.60
	M4	114.92	2.10	1.75	40.24
	M5	257.80	2.05	1.73	20.50
	M6	8.0	N.A	1.93	18.73
	M7	15.24	N.A	1.66	12.75
	M8	43.00	2.15	0.89	11.70
	M9	N.A	N.A	1.31	9.00

N.A : Not analysed.

The observed boron content and the grain sizes are antipathetic to each other and showed significant correlation of boron with silt and clay. The abundance of aluminium in sediments is a measure of clay minerals (Harder, 1970). Since the aluminium content of the sediments and the grain sizes are antipathetic the boron and aluminium content should be sympathetic.

The correlation of sediment boron with silt and clay was significant ($r = +0.74$ and $+0.69$ respectively), due to their greater abundance and finer size. Although it is understood that boron resides in finer fractions of the sediments, the relatively greater affinity of boron towards a particular mineral decides its fate.

Clay mineralogy of the estuarine sediments upto station M6 though indicated greater abundance of Kaolinite + Chlorite and Illite, a clear picture of the relationship of boron with these minerals is not possible as the data on mineral percentages were inadequate. Therefore an indirect approach was adopted to understand to a certain extent the relationship of boron to the clay mineral content.

The significant relationship of boron with clays and silt indicates its presence in these fractions. However the mineral Illite contains potassium whereas montmorillonite are calcium and magnesium bearing while the kaolinite contains aluminium and silica (Calliore and Herin, 1949; Grim, 1953; Marshall, 1954; Rex, 1967 and Carroll, 1970). So the observed significant relationship of boron with potassium ($r=+0.45$) as well as the relationship of potassium with clay ($r=+0.95$) being significant than that of potassium with silt ($r=+0.35$) leads one to infer that boron apart from its residence in aluminosilicates has an affinity towards potassium and/or potassium bearing clay minerals of the sediments in Mandovi river. To understand the relationship of boron with montmorillonite and kaolinite + chlorite to a greater extent, the study has to be continued further with analyses on Ca, Mg, Si and the clay minerals of the sediments.

ACKNOWLEDGEMENT

The authors are grateful to Dr. B.N. Desai, Director, NIO; Dr. R. Sen Gupta, Head, Chemical Oceanography Division for their encouragement. The authors are also thankful to Mr. Purnachandra Rao, Scientist, Geological Oceanography Division for the assistance in x-ray diffraction analyses.

REFERENCES

- Adams, T.D., J.R. Haynes and C.T. Walker, 1965. Boron in Holocene illites of the Dovey estuary, Wales and its relationship to Paleosalinity in cyclotherms. *Sedimentology*, 4: 189-195.
- Anon, 1976. Standard methods for the examination of water and waste water. American Public Health Association (APHA), (1960-67-75), Broadway, New York 19, N.Y.
- Byrne, R.H. and D.R. Kester, 1974. Inorganic speciation of boron in seawater. *Journal of Marine Research*, 32: 119.
- Biscaye, P.E., 1965. Mineralogy and sedimentation of recent deep sea clays in Atlantic Ocean and adjacent seas and oceans. *Geological Society of America Bulletin*, 76: 803-832.
- Curtis, C.D., 1964. Studies on the use of boron as a paleoenvironmental indicator. *Geochemica Cosmochemica Acta*, 28: 1125-1137.
- Carroll, D., 1958. Role of clay minerals in the transport of iron. *Geochemica Cosmochemica Acta*, 14: 1-27.
- Carroll, D., 1970. Clay minerals: A guide to their X-ray identification. The Geological Society of America, Colorado 80302.
- Calliore, S. and S. Herin, 1949. *Mineral Magazine*, 28: 612.
- Dyrssen, D. and I. Hansson, 1973. Ionic medium effects in sea water - a comparison of acidity constants of carbonic acid and boric acid in sodium and synthetic sea water. *Marine Chemistry*, 1: 137-149.

- Eager, R.M.C. and D.A. Spears, 1966. Boron content in relation to organic carbon and to paleosalinity in certain British carboniferous sediments. *Nature*, **209**: 177-181.
- El Wakeel and J.P. Riley, 1957. The determination of organic carbon in marine muds. *Journal du Conseil International Exploration du mer*, **22**: 180-183.
- Frederickson, A.F. and R.C. Reynolds, 1960. How measuring paleosalinity aids exploration. *Oil and Gas Journal*, **1**: 154-158.
- Folk, R.L., 1961. Petrology of sedimentary rocks. Hemphills, Austin, Texas, 1970.
- Grim, R.E., 1953. Clay mineralogy. McGraw Hill, New York, 384.
- Harder, H., 1970. Boron content of sediments as a tool in facies analyses *Sedimentary Geology*, **4**: 153-175.
- Hatcher, J.T. and L.V. Wilcox, 1950. Colorimetric determination of boron using carmine. *Analytical Chemistry*, **22**: 567-569.
- Levinson, A.A. and J.C. Ludwick, 1976. Speculation on the incorporation of boron into argillaceous sediments. *Geochimica Cosmochimica Acta*, **30**: 855-861.
- Liss, P.L. and M.J. Pointon, 1973. Removal of dissolved boron and silicon during estuarine mixing of sea water and river water. (*Geochimica Cosmochimica Acta*, **37**: 1493-1498.
- Loring, D.H. and R.T.T. Rantala, 1977. Geochemical analyses of marine sediments and suspended particulate matter. Fisheries and Marine Services, Canada, *Technical Report No.700*.
- Marshall, C.E., 1954. Clays and Clay Minerals. *Proceedings of the 2nd National Conference*, National Academy of Sciences, Publications 327, Washington, D.C. 364-385.
- Porrenga, D.H., 1966. Boron content of core samples from Alliance 28, Surinam as an indicator of paleosalinity. *Proceedings of the VIIth Guiana Geological Conference*.
- Rex, R.W., 1967. Authogenic kaolinite and micas evidence for phase equilibrium at low temperatures in clays and clay minerals. Thirteenth National Conference on clays and clay minerals, New York, Pergamon Press, 95-104.
- Subba Rao, D.V., 1981. Utilization of boron during primary productivity of phytoplankton. *Canadian Journal of Fisheries and Aquatic Sciences*, **38**: 52.
- Shepard, F.P., 1954. Nomenclature based on Sand-Silt-Clay ratio. *Journal of Sedimentary Petrology*, **24**: 157-158.
- Shirodkar, P.V., S.Y.S. Singbal and R. Sen Gupta, 1982. Studies on boron along the Central west coast of India. *Indian Journal of Marine Sciences*, **11**: 251-252.
- Shirodkar, P.V. and S.P. Anand, 1985. Behaviour of boron in Mandovi estuary. *Mahasagar – Bulletin of the National Institute of Oceanography*, **18**: 439-448.

- Walker, C.T. and N.B. Price, 1963. Departure curves for computing paleosalinity from boron in illites and shales. *Bulletin of American Association of Petrological Geology*, 47: 833-841.
- Walker, C.T., 1966. Boron as a paleosalinity indicator not affected by carbon in clay fractions. *Bulletin of American Association of Geology*, 50: 652 (Abstract).
- Williams, P.M. and P.M. Strack, 1966. Complexes of boric acid with organic cis-diols in water. *Limnology and Oceanography*, 11: 401-404.