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GEOCHEMISTRY OF ZINC IN THE SEDIMENTS OF THE WESTERN CONTINENTAL SHELF AND SLOPE OF INDIA

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ABSTRACT

The bulk geochemistry of zinc in the sediments of the western continental shelf and slope of India and also the partition geochemistry of the sediments of the shelf and slope regions between Ratnagiri and Mangalore have been studied. The studies indicated that (1) the concentration of zinc varies very widely in these sediments from 2 to 159 ppm on the bulk sample basis and from 25 to 369 ppm on carbonate free basis; (2) the concentrations of zinc exhibit a decreasing trend away from the coast up to the shelf edge and then show an increasing trend in the slope region; (3) zinc co-varies with Al, Fe, Mn and organic carbon in these sediments and bears a strong inverse relationship with $CaCO_3$ content.

The partition studies of the sediments of the shelf and slope regions between Ratnagiri and Mangalore have indicated that (1) zinc has both a lithogenous and non-lithogenous components in these sediments; (2) the percentage contributions made by the lithogenous component to the concentrations of zinc in the bulk samples vary from 71 to 92% and in the case of non-lithogenous component, from 8 to 29%; (3) the inter-relationships of zinc worked out with other elements in the lithogenous component of the sediments separately for inner shelf, outer shelf and slope have indicated that in the inner shelf it co-varies with all the elements except $CaCO_3$, in the outer shelf and slope regions with iron and organic carbon only, and bears a strong negative correlation with manganese; (4) inter-relationships of zinc worked out with other elements in the non-lithogenous fraction of the sediments for the same three regions have shown that in the inner shelf it is associated with hydroxides of iron, manganese and also with organic carbon, while in the outer shelf and slope regions it is associated only with organic carbon. The partition studies have also indicated that part of zinc is present in the sediments in the adsorbed form on clays.

The type of association zinc has exhibited with other elements is confirmed by the R-mode factor analysis carried out for the sediments of the region between Ratnagiri and Cochin. Further, the association of zinc with organic carbon all over the shelf and slope regions is found to be similar to that reported from upwelling regions of other areas.

Key-words : Zinc, geochemistry, sediments, western continetal shelf of India.

INTRODUCTION

The bulk and partition geochemistry of zinc has been studied in the sediments of the western continental shelf and slope of India in relation to the distribution patterns of the sediments and environmental conditions and the results obtained are presented in this paper.

A few papers have appeared earlier reporting concentrations of zinc in these sediments from some parts of the shelf and slope regions (Gogate, Sastry, Krishnamurty, and Viswanathan, 1970; Marchig, 1972; Murty, Paropkari, Rao and Topgi, 1978; Paropkari, Topgi, Rao and Murty, 1980; Borole, Sarin and Somayajulu, 1982). However, all these studies were of a restricted nature only and did not cover the entire shelf and slope regions. Thus there is a wide gap in our knowledge of the geochemistry of zinc in these sediments (both bulk and partition) and its general distribution. Hence the detailed studies were undertaken.

It may not be out of place to mention here that Dr. Varadachari in whose honour this special issue of Mahasagar is being broughtout, had the distinction of planning, organising and leading the first systematic geological cruise along the western continental shelf during the International Indian Ocean Expedition period (Cruise no. 25 of INS Kistna in 1965).

MATERIALS AND METHODS

About 500 surficial sediment samples were collected from all over the shelf and slope regions along traverses roughly spaced at 20 Kms. apart between Indus canyon in the north and Cochin in the south, using La-Fond-Dietz snapper/Van Veen grab. In the region between Indus canyon in the north and Port Dabol, the sampling was carried out between 20 and 140 m; in the region between Ratnagiri and Mangalore between 20 and 200 m and in the region between Mangalore and Cochin between 17 and 1020 m water depths respectively.

Intially all the samples were digested with hydrofluoric and perchloric acids following the method of Chester and Hughes (1969) for the determination of zinc concentrations in the bulk samples. Estimations of zinc were carried out using Atomic Absorption Spectrophotometer Model H 1550 of Hihger and Watts make.

Partition studies were carried out on some of the samples to ascertain the percentage contributions made by the different chemical fractions of the sediments to concentrations associated with the bulk samples — (10% acetic acid leaches, hydoxylamine hydrochloride leaches, 50% hot HCl leaches and acid insolubles (Chester and Hughes, 1967; Murty, Cronan, Rao, Paropkari, Topgi, Gupta and Colley, 1983)

The precision of Atomic Absorption Analysis of both bulk samples and leached fractions is better than 10% on the basis of duplicate analysis. The accuracy was checked by analysis of U.S.G.S. rock standards.

RESULTS AND DISCUSSION

From the concentrations of zinc obtained in the bulk samples, an areal distribution map has been prepared (Fig. 1). The relationship zinc has with some of the important elements such as aluminium, iron, manganese, and

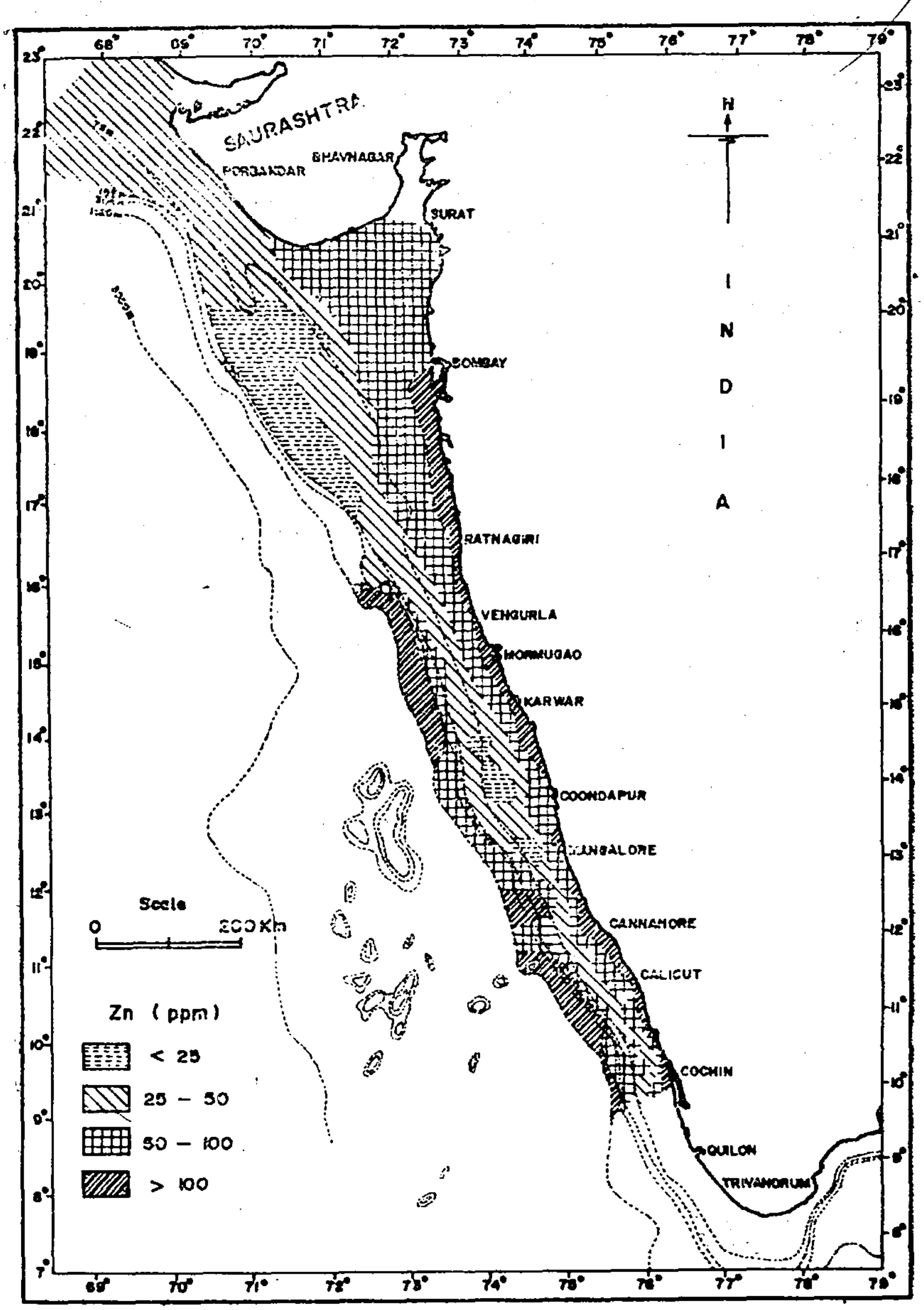

Fig. 1. Map showing the distribution of Zinc.

organic carbon and also with $CaCO_3$ is shown in the form of correlation matrix prepared separately for the regions (i) Indus canyon to Ratnagiri; (ii) Ratnagiri to Mangalore and (iii) Mangalore to Cochin (Table I).

Table I. Correlation Matrix on the bulk sample basis.

	Area	Al	Fe	Mn	$CaCO_3$	C_{org}
Zn	Between Indus Canyon and Ratnagiri (n = 75)	0.46	0.49	0.18	−0.36	0.56
	Between Ratnagiri and Mangalore (n = 220)	0.75	0.72	0.63	−0.76	0.87
	Between Mangalore and Cochin (n = 136)	0.68	0.73	0.33	−0.10	0.56

From the concentrations of zinc obtained in the different leaches, the percentage contributions made by each fraction to the concentrations of zinc in the bulk sample have been computed. The inter-relationships obtained between zinc and other elements in the lithogenous and non-lithogenous fractions are shown in Tables II and III respectively.

Before the results are presented, in order to enable the readers to follow them in the proper perspective, it is considered appropriate to briefly

Table II. Correlation Matrix in the lithogenous fraction of the sediments between Ratnagiri and Mangalore.

	Area	Al	Fe	Mn	$CaCO_3$	C_{org}
Zn	Inner shelf (n = 119)	0.89	0.84	0.81	—	0.88
	Outer shelf (n = 62)	—	0.45	—	−0.57	0.79
	Slope (n = 39)	—	0.56	−0.40	—	0.89

Table III. Correlation Matrix in the non-lithogenous fraction of the sediments between Ratnagiri and Mangalore.

	Area	Fe	Mn	$CaCO_3$	C_{org}
Zn	Entire region between Ratnagiri and Mangalore (n = 220)	0.61	0.67	−0.79	0.79
	Inner shelf (n = 119)	0.46	0.72	—	0.85
	Outer shelf (n = 62)	—	—	—	0.63
	Slope (n = 39)	—	—	—	0.63

describe the distribution pattern of sediments in the study area which exhibits a clear cut zonation. Fine grained sediments (clays, silty clays, clayey silts) are confined to the innershelf region (less than 50 m) upto Cochin. These are followed seaward by sands, silty sands and clayey sands in the outer shelf region (50–120 m). While this is the distribution of sediments in the region between Gulf of Kutch and Cochin, the entire shelf region north of Gulf of Kutch is completely covered by fine grained sediments. The continental slope region (120–2000 m) is carpeted by laminated muds, olive grey muds and dark brown muds-the last category of sediments occurring at the foot of the slope and beyond. Chemically also, these sediments show distinct differences. The finegrained sediments in the innershelf region are characterised by very low calcium carbonate content while coarser sediments in the outer shelf region are associated with high calcium carbonate content, mostly contributed by skeletal and non-skeletal components. This distribution pattern of calcium carbonate is found to be characteristic of the region between Gulf of Kutch and Mangalore. In the southern region, though, sands occur in the outer shelf region as in the north, they differ chemically in that they are mostly quartz sands. In the slope region, the carbonate content of the sediments is relatively low compared to the carbonate content of the sediments of the outer shelf region, in the region between Gulf of Kutch and Mangalore while in the south the reverse is the case. (Nair and Pylee, 1968; Schott, 1968; Stackelberg, 1972; Rao, 1978; Nair and Hashimi, 1980; Rao, 1983; Paropkari, 1983).

With the background given in the preceding paragraph, the results pertaining to the bulk and partition geochemistry of zinc are described in the following paragraphs.

Bulk Geochemistry

(1) From the basic data (not presented in the paper) it is observed that zinc concentrations closely follow the texture of the sediments — higher concentrations associated with the fine grained sediments and lower concentrations with coarser sediments.

(2) On the bulk sample basis (from the basic data) the concentration of zinc varies very widely 2 to 159 ppm with an average of 67 ppm for the entire study area. On the carbonate free basis, the concentration varies between 25 and 366 ppm, the average concentration being 104 ppm.

(3) Fig. 1 shows the following distribution pattern of zinc in these sediments:

(a) The fine grained sediments of the innershelf region (less than 50 m) are characterised by two ranges of concentrations, greater than 100 and 50 to 100 ppm. The former range is confined to the nearshore regions between Bombay and Cochin while the latter range is present in the sediments seaward of this zone in this region and in the entire innershelf region between Gulf of Cambay and Bombay. While this is the distribution pattern between Gulf of Cambay and Cochin, the shelf region north of Gulf of Cambay (between Gulf of Kutch and the southern end of Saurashtra coast) is characterised by concentrations of zinc in the range of 25 to 50 ppm.

(b) The coarse grained sediments of the outer shelf region (50 to 120 m) are also characterised by the presence of two ranges of concentrations, however, less than those encountered in the innershelf region. These two ranges are 25 to 50 ppm and less than 25 ppm. While the former range occurs all along the outer shelf region, the lower range occupies a wider area between Gulf of Cambay and Ratnagiri (seaward of the higher range) and in a few patches amidst higher range in the southern region.

(c) In the upper and middle continental slope regions, the concentrations of zinc show an increasing trend again higher than 100 ppm.

(d) In the transition zones between the innershelf and outer shelf and outer shelf and slope regions, concentrations higher than those encountered in the outershelf region are present. Perhaps these higher concentrations may be the result of mixing of the sediments of higher concentrations with lower concentrations.

(e) In general, the distribution pattern of zinc shows a decreasing trend away from the coast upto the shelf edge and again shows an increasing trend in the slope region.

(4) On the bulk sample basis (Table I), zinc shows a strong correlation with Al, Fe and organic carbon in these sediments. With respect to Mn, it shows strong correlation in the regions between Ratnagiri and Cochin while it does not in the region north of it. In so far as $CaCO_3$ is concerned, it shows a strong negative correlation in the region between Gulf of Kutch and Mangalore while in the region between Mangalore and Cochin, it does not show any relation. Perhaps it is due to the fact that the outer shelf region is characterised by the presence of quartz sands unlike in the northern region where it is dominated by carbonate sands.

Partition Geochemistry: Partition geochemistry has been studied in great detail in the sediments of the region between Ratnagiri and Mangalore on the lines outlined in the section 'Materials and Methods'. An examination of the basic data leads to the following generalisations.

(1) The partition studies have indicated that zinc has both a lithogenous and non-lithogenous component in these sediments.

(2) The ranges of percentage contributions made by the different leaches to concentrations of zinc in the bulk samples are given below:

Leach	Range of % contributions made to concentration of zinc in bulk sample.
1. Acetic Acid	7.14 to 16.93
2. Hydroxylamine hydrochloride	0.0 to 19.54
3. 50% Hot HCl	44.32 to 69.64
4. Insolubles	20.00 to 37.04

It can be seen from the ranges given above that the percentage contributions made by the lithogenous component (HCl leaches + Insolubles) dominate over the percentage contributions made by the non-lithogenous component in these sediments. To be more precise, 8–29% of total zinc is held in the non-lithogenous fraction and the remainder (71–92%) in the lithogenous fraction.

(3) The contributions made by all the four chemical fractions to concentration of zinc in the bulk samples are more in the inner shelf region and increase with decreasing grain size. The percentage contributions made by the insolubles and acid reducing fractions exhibit a trend similar to that of total zinc distribution. However, the percentage contributions made by HCl soluble fraction do not show a decreasing trend away from the coast. Contrastingly it shows an increase. The percentage contributions made by acetic acid soluble fraction does not show any trend.

(4) Conspicuously zinc concentrations in the acid reducible fraction are not detected in some of the slope sediments.

(5) Correlation matrix prepared for Zinc with other elements i.e. Al, Fe, Mn, $CaCO_3$ and organic carbon separately for innershelf, outer shelf and slope (Table II) indicated that in the innershelf zinc co-varies with all the elements excepting $CaCO_3$ with which it does not show any relationship, in the outershelf with only Fe and organic carbon and negative correlation with $CaCO_3$ and in the slope with organic carbon only and negative correlation with Mn. This is in the lithogenous fraction of the sediments.

(6) Correlation matrix prepared for the non-lithogenous fraction separately for the innershelf, outer shelf and slope (Table III) shows that in the inner shelf region zinc covaries with Fe, Mn and organic carbon and shows a strong negative correlation with $CaCO_3$; in the outershelf and slope it exhibits a strong correlation with organic carbon only and no other element.

Zinc is introduced into the marine environment principally in two ways — (i) in the solid state in association with the detrital minerals (clays and the most resistant minerals) and (ii) in solution. In the former state, it can be in the form of discrete minerals of zinc or in association with the various minerals held in their crystal lattices. In regard to zinc introduced in solution, it can be removed from sea water and introduced into the sediments in several ways — (i) through precipitation of insoluble compounds with ions normally present in sea water, (ii) preciptation by sulphide ion in local regions of low oxidation potentials, (iii) adsorption by materials such as ferrous sulphide, hydrated ferric oxide and hydrated manganese dioxide and clay and (iv) removal by metabolic action of organisms (Krauskopf, 1956). Further in regions of upwelling and high biological productivity, zinc is reported to be associated in high concentrations in muds rich in organic carbon (Calvert and Price, 1971).

The distribution pattern of zinc on the bulk sample basis, the decreasing trend which the concentrations exhibit away from the coast in the shelf region, the significant inter-relationships obtained between zinc and Al, Fe, Mn on the bulk sample basis and the high percentage contributions made by the lithogenous fraction to the concentrations in the bulk samples suggest that major portion of zinc in these sediments is incorporated in association with detrital minerals derived from land and physically deposited in the shelf region. In view of the fact that no discrete zinc minerals are reported from the study region, it is regarded that the zinc is held mostly in the crystal lattice of the various minerals only. The negative correlation which Zinc exhibits with $CaCO_3$ clearly indicates that carbonate phase is not a contributing factor for zinc concentrations in these sediments.

Apart from the above mode of incorporation of zinc in these sediments, the partition patterns indicate that it is associated with lhe non-lithogenous fractions of the sediments to a certain extent (8 to 29%). In the present case it is possible that precipitation of zinc as insoluble compound does not take place as the sea water is greatly under-saturated with regard to this element. Also precipitation of zinc by sulphide is unlikely in the shelf region in view of the considerable mixing that takes place in the shelf waters and the oxic conditions prevailing at the bottom. However, Mallik (1972) has reported the occurrence of pyrite in the innershelf sediments off Mangalore. The significant correlation that zinc exhibits with Fe and Mn of non-lithogenous fraction in the innershelf region as well as for the entire region between Ratnagiri and Mangalore shows that it is incorporated into the sediments in association with the hydroxides of these two minerals. Murty, Rao and Reddy (1973) established the presence of these hydroxide phases in the sediments and the association of several trace elements with them in the shelf region. Incorporation of zinc into sediments in the adsorbed form in association with clay minerals is also evident from the fact that acetic acid leaches contribute 7.14 to 16.93% of zinc in the bulk samples and that $CaCO_3$ is not a contributing factor at all in these sediments. The clay mineral assemblage dominated by montmorillonite aslo supports this surmise.

As regards the relationship between zinc and organic carbon, it can be seen that it covaries strongly with organic carbon all over the shelf region and in the different chemical fractions. Association of zinc with organic carbon has been reported from several areas which are under the influence of strong upwelling (Calvert and Price, 1971; Seibold, 1970; Bostrom, Joensu and Brohm 1974). Western continental shelf of India, being a region of seasonal upwelling, Banse, 1959; 1967; Carruthers, Gogate, Naidu and Laevastu, 1959; Varadachari and Sharma, 1964; Sharma, 1968) and high biological productivity (Qasim, 1977) and the underlying sediments, are characterised by a good amount of organic carbon, (Paropkari, Rao and Murty, in press) the strong correlation observed forms a natural corollary and not an exception. It further shows that the element is not lost by remineralisation and is still held in the organic matter.

As against the distribution pattern of zinc described in the earlier paragraphs for the shelf region the distribution pattern of zinc in the slope region exhibits certain marked differences. Firstly, the sediments are characterised by higher concentrations of zinc than those encountered in the inner shelf region on the bulk sample basis and secondly, the strong positive correlation it exhibits with organic carbon and Fe and the negative correlation it shows with Mn of lithogenous component (Table II and III). The continental slope region is under the influence of oxygen minimum layer and organic carbon as high as 8 to 12% is recorded in these sediments. A consideration of the C/N ratios computed for the region indicates that most of the organic matter present in these sediments is derived from Planktonic organisms and therefore it is reasonable to expect most of the zinc being bound with it and hence the strong correlation with organic carbon. The high metal/Al ratios present in this region support this surmise. The significant correlation of lithogenous zinc with lithogenous Fe could be due to the presence of zinc in the crystal lattice of clay minerals of which Fe is also an essential constituent. Secondly, this relationship could be due to the presence of zinc in the form of sulphides in association with Fe under the reducing conditions obtaining in the slope sediments. The negative correlation observed between zinc and Mn in the lithogenous fraction of the sediments could be due to (i) under reducing conditions prevailing in the region, more and more zinc being bound to organic matter and not released for being fixed with any other element, and (ii) more and more manganese going into solution under the reducing conditions. The very low values of Mn encountered in the slope sediments and the absence of zinc in some of the acid reducible fractions of the sediments in the slope region confirms to some extent this surmise.

The R-mode factor analysis carried out on the sediments of the region between Ratnagiri and Cochin has indicated the following factors — fine grained aluminosilicate factor, carbonate factor, organic carbon factor and quartz sand factor — control the distribution pattern of zinc observed in these sediments confirming the processes of incorporation of elements into the sediments inferred from the bulk and partition analysis.

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