Partition Patterns of Iron, Manganese, Nickel & Cobalt in the Shelf Sediments off West Coast of India

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The study has revealed that (i) concentrations of elements associated with total sediment samples of innershelf region as well as their lithogenous and non-lithogenous fractions are relatively higher than those associated with their counterparts in the outershelf and slope regions, and (ii) contributions made by the lithogenous fraction to the concentrations in total sediment sample in the innershelf region are higher than those in the outershelf and slope regions. Apart from showing this distribution along any given section, the concentrations of elements in different components of sediments also exhibit certain variations from north to south which appear to be due to (i) differences in the source rocks present along different parts of West coast, and (ii) differences in the stages of adjustment of the lithogenous material to the marine environment in different regions. While it is evident from the relatively higher concentrations of elements, associated with lithogenous fractions of sediments of innershelf region that there is a good supply of these elements from land through detrital minerals, the higher concentrations of elements associated with the non-lithogenous fractions of innershelf sediments appear to be due to (i) the floculation of colloids of iron and manganese along with their adsorbed trace elements, and (ii) adsorption of nickel and cobalt partly by organic matter. Relatively low concentrations of elements associated with non-lithogenous fractions of outershelf and slope regions are due to the bulk of this fraction being composed of calcium carbonate which does not contain these elements in appreciable amounts.

ARINE sediments fringing the West coast of India (between Bombay and Quilon) exhibit texturally, chemically and mineralogically certain well-defined distribution patterns. The innershelf (up to 20 fathoms depth) is carpeted by silty clays or clayey silts with low carbonate content and this is followed seaward by a zone of silty or clayey sands on the rest of the shelf and slope regions characterized by a high carbonate content1. This is particularly so, between Quilon and Karwar while off Bombay the shelf is covered for a greater part by fine-grained sediments characterized by a higher content of calcium carbonate than the finegrained sediments of other sections. The organic matter content of the sediments2 indicate that the sediments in the innershelf and the slope regions are characterized by a higher organic content than those in the region in between. Clay minerals also exhibit certain regional variations3 in that (i) the sediments off Bombay and Karwar are characterized by the presence of predominantly mixed layers of montmorillonite and illite with subordinate amounts of kaolinite group of minerals, (ii) the sediments off Mangalore by the presence of approximately equal proportions of mixed layers of montmorillonite and illite and kaolinite group of minerals, and (iii) the sediments off Kerala coast having predominantly kaoiinite group of minerals with subordinate amounts of montmorillonite and illite.

Present knowledge of the distribution patterns of iron, manganese, nickel and cobalt in the shelf sediments off the West coast of India (between Bombay and Quilon) is mainly from the studies of Murty et al.³⁻⁵. These studies do not give an overall

distribution pattern of the elements since the results reported were based on the analyses carried out on the silt-clay fraction of the sediments only. Further, except for the studies carried out by Gogate-et al.⁶ in a limited way on the sediment samples collected from the shelf and slope regions off Bombay and Ratnagiri, no information is available on the partition of the elements among the different components of the sediments which may throw somelight on the processes by which they have been incorporated in the sediments. Hence, further studies have been carried out in this direction and the results obtained are briefly discussed in this paper.

Materials and Methods

The locations of stations from where the bottom. sediment samples were collected are shown in Fig. 1. Representative samples, obtained from the collections made at each station, were washed chloride free. An amount of each representative sample was then leached with the acid-reducing agent as described by Chester and Hughes, and the residues were washed thoroughly with distilled water. Estimations of iron, manganese, nickel and cobalt were carried out (i) in the bulk sample with a view to understanding the concentrations of the elements. associated with the total sediment and their overall distribution patterns; (ii) in the leach of the acidreducing agent solution with a view to obtaining an idea of the contributions made by the non-detrital fraction (non-lithogenous fraction) of the sediments. to the concentrations in the total sediment; and (iii) in the acid insoluble fraction of the sediments toknow the concentrations of the elements held within.

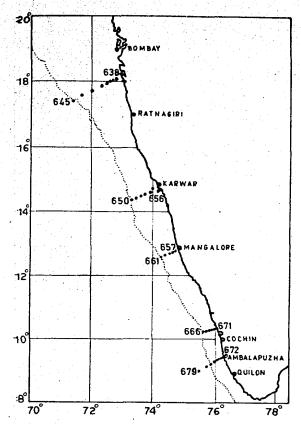


Fig. 1 - Map showing the station locations

the lattice structure of the detrital minerals supplied from land (lithogenous fraction or detrital fraction). For the estimation of manganese in the acid soluble fraction of the sediment, the leach used was 2N HCl and not the acid-reducing solution. All the elements were estimated spectrophotometrically using 'Unicam' SP 500 spectrophotometer. Iron and manganese in total sample and acid soluble and insoluble fractions were estimated by the method of Sandell⁸ and nickel and cobalt were estimated by the method of Chester and Hughes9.

Results

The results of analyses of total sediment samples, acid insoluble fraction of the sediments (concentrations in the lithogenous fraction), the acid soluble fraction of the sediments (contributions made by the non-lithogenous fraction of the sediments to the concentrations in the total sediment) and the contributions made by the lithogenous fraction to the concentrations in the total sediment are given in Table 1 along with the depth of sampling, texture of the sediments and the total carbonate content of the sediments. Since the quantity of the acid soluble fraction varies from sample to sample, for purposes of comparison, concentrations in the non-lithogenous fractions of the sediments have been computed and they are also given in Table 1. The concentrations of the elements in the total sediment samples and the non-lithogenous and lithogenous fractions of the sediments are given in Fig. 2. Percentage contributions made to the concentrations in

the total sediment by the lithogenous fraction of the sediments are given in Table 2.

An analysis of the data enables the following generalizations to be made in regard to the distribution patterns of the elements in different fractions of the sediments.

(i) Contributions made by the lithogenous fractions to the concentrations in the total sediment samples as well as the concentrations of the 4 elements in the lithogenous fractions of the sediments (Table 1 and Fig. 2) are, in general, relatively higher in the fine-grained sediments of the innershelf region than those in the outershelf and slope regions with the exception of manganese which does not show this trend clearly along the sections off Mangalore and Cochin. The percentage contributions made to concentrations in the total sediment samples by the lithogenous fractions of the sediments (Table 2) do not show any uniform pattern of distribution along all the sections and with a few exceptions here and there, the contributions made by the lithogenous fractions to the concentrations in the total sediment sample are very substantial. Average percentage contributions calculated from the values given in Table 2 indicate that contributions to the extent of 78.54, 69.60, 62.25 and 54.20% in respect of iron, manganese, nickel and cobalt respectively are made by the lithogenous fractions to the total sediment in the region under study.

(ii) While the contributions made by the nonlithogenous fractions to the concentrations in the total sediment samples (Table 1) do not show any uniform pattern of distribution along all the sections. the concentrations in the non-lithogenous fractions of the sediments exhibit in general a distinct distribution pattern, namely the non-lithogenous fractions of the fine-grained sediments in the innershelf region have higher concentrations of these elements than the non-lithogenous fractions of the sediments of the outershelf and slope regions (Table 1 and

Fig. 2).

(iii) Overall distribution patterns of the elements (based on the total sample analysis) parallels the distribution pattern of the elements in the lithogenous and non-lithogenous fractions of the sediments (Table 1 and Fig. 2) in that the fine-grained sediments in the innershelf region (below 20 fathoms depth) are characterized by higher concentrations of these elements than the sediments in the outershelf and slope regions. This is true in respect of all the four elements along all the sections except off Cochin where manganese does not show this distinct trend.

(iv) Apart from exhibiting the distribution patterns across the shelf as described above, the concentrations of the elements in the different fractions of the sediments also exhibit certain trends in regard to their distribution patterns from north to south.

(a) Lithogenous fractions of the sediments off Bombay and Karwar are characterized by higher concentrations of iron, manganese and nickel than the lithogenous fractions of the sediments off Mangalore, Cochin and Ambalapuzha. Lithogenous fractions of the sediments off Bombay, Karwar, Cochin and Ambalapuzha have relatively higher concentrations of cobalt than the lithogenous fractions of the sediments off Mangalore.

(b) Non-lithogenous fractions of the sediments off Karwar and Mangalore have higher concentrations of iron than the non-lithogenous fractions of

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A=Concentrations in the total sediment. B=Concentrations in the lithogenous fraction. C=Contributions made by the lithogenous fraction to the concentrations in the total sediment.

*Values for CaCO3 are taken from Nair et al.1.

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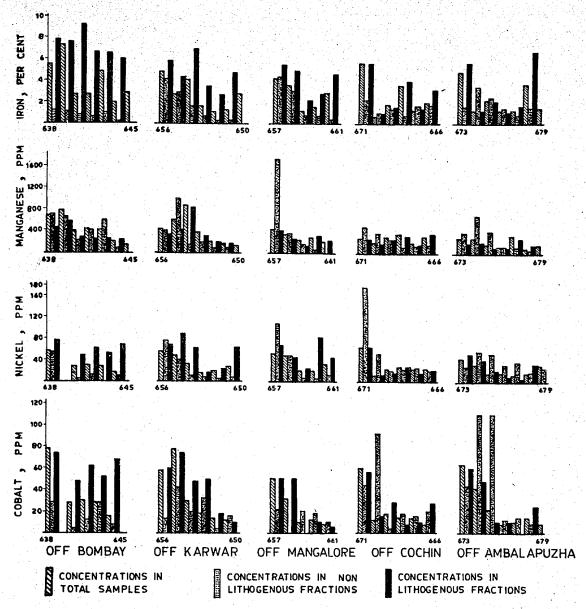


Fig. 2 — Concentrations of iron, manganese, nickel and cobalt in different components of sediments, along different sections

the sediments off Bombay, Cochin and Ambalapuzha. Even among the latter 3 sections, the sediments off Bombay have the lowest concentrations. The concentrations of manganese in the non-lithogenous fractions of the sediments off Bombay, Karwar and Mangalore are higher than the concentrations in the non-lithogenous fractions of the sediments off Cochin and Ambalapuzha. The concentrations of nickel in the non-lithogenous fractions of the sediments off Karwar, Mangalore, Cochin and Ambalapuzha are relatively higher than the concentrations in the sediments off Bombay. The nonlithogenous fractions of the sediments off Cochin and Ambalapuzha contain relatively higher concentrations of cobalt than the corresponding fractions of the sediments off Bombay, Karwar and Mangalore.

(c) On the total sample basis, the sediments off Bombay have relatively higher concentrations of iron than the sediments along the other sections. The manganese concentrations in the sediments off Bombay and Karwar are much higher than the concentrations in the sediments off Mangalore, Cochin and Ambalapuzha. The concentrations of nickel in the sediments off Ambalapuzha are relatively less when compared with the concentrations in the sediments of 4 northerly sections. The cobalt concentrations in the sediments off Bombay, Karwar, Cochin and Ambalapuzha are relatively higher than the concentrations in the sediments off Mangalore. Even on a carbonate free basis, the same trend is exhibited by the 4 elements indicating thereby that the carbonate content of the sediments is not the factor

TABLE 2 — PERCENTAGE CONTRIBUTIONS TO THE CONCENTRATIONS IN TOTAL SEDIMENT BY LITHOGENOUS FRACTION OF SEDIMENTS

Station No.	Iron	Manganese	Nickel	Cobalt
638	93.8	64.5	66.6	88.3
639	92.5	57.3		70.7
640	75.7	60-0	89-3	72.7
641	87.7	45.1	80.0	71.4
642	91.6	27.5		21.7
643	93-0	70-5	66-6	78.9
645	·			93.0
656	76.5	73.9	63-1	89.7
655	74.6	61.1	69.4	66.3
654	80.7	90.6	84.4	
653	85.0	72.9	80.0	16.0
652	74.1	70.5	83-3	71·4 7·7
651	79:1	63.5	73-1	7-7
650				~ ~
657	87.6	49.8	73.1	94.0
658	70.6	66.5	67.4	100.0
659	65.0	58.4	84.2	
660	69.3	87.0	84.2	8.3
661	51.7		70.6	11.0
671	93.2	69.3	52.4	86.5
670	83.6	79.5	57.1	9.1
669	76.4	75.8	73.9	88.8
668	87.9	82.8	53.6	33.3
667	59.0	77.5	63.6	64.3
666	68.7	82-6	70.8	22.2
673	92.7	65.6	86.3	84.4
672	54.5	70.0	81.8	69.0
674	77.2	68.5	60.0	40.9
675	73.1	76.9	46.3	62:5
676	84.3	90.7	33.0	60.0
677	66.5	90.0	20.0	42.9
679	91-4		58-9	

giving rise to the differences observed in the regional values.

Discussion

A consideration of the sedimentary geochemistry of iron and manganese shows that both iron and manganese in minerals of igneous rocks are partly oxidized during weathering and partly dissolved as ferrous and manganous ions Fe²⁺ and Mn²⁺. These ions can be transported long distances if the solution stays reducing and slightly acidic and if it is not admixed with other ions that form insoluble compounds. A great variety of ions may cause precipitation, the most common being carbonate, sulphide and silicate. They may be precipitated by oxidation in streams, lakes or swamps when the water is aerated in sea water as oxide if the water is aerated, as carbonate or silicate if the water is mildly reducing, as sulphide if the redox potential is low and sulphur is abundant. When the conditions are favourable for the oxides to precipitate, they often remain in suspension as stable sols and may be carried long distances in aerated surface waters. These colloids are floculated where streams enter the sea10. Krauskopf11 made an extensive study of the factors controlling the concentrations of several trace elements in sea water. He investigated in detail 4 processes, viz. (i) precipitation of insoluble compounds with ions normally present in sea water, (ii) precipitation 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.

His studies have shown that adsorption is the most important process for the removal of minor and trace elements from the sea water and their incorporation in the marine sediments. Chester 12 has discussed the mechanisms by which the trace elements are adsorbed on to the clay mineral surfaces and has shown that the clay mineral illite is capable of adsorbing > 50% of the cobalt and > 90% of zinc from sea water containing metals at their normal concentrations. Kharkar et al.13 who have studied the distribution of a number of trace elements in river waters and detritus and carried out laboratory studies on the adsorption and desorption of trace elements on and from minerals commonly occurring in the river detritus have concluded that trace elements which have been adsorbed from solution by the clay mineral species in the river environment are released to a greater or lesser extent on contact with sea water. They have also observed that there was considerably less desorption of trace elements from iron and manganese oxides than from the clay minerals on contact with sea water. Nicholls and Loring¹⁴ and Hirst¹⁵ suggested that there is a correlation between nickel and organic carbon and between cobalt and organic carbon contents of the sediments and they considered that organic carbon content of the sediments acts as an adsorbant.

The relatively higher concentrations of the elements associated with the fine-grained sediments of the innershelf region by way of contribution made by the lithogenous fraction to the concentrations in the total sediment sample as well as the higher concentrations associated with the lithogenous fractions of these sediments than with their counterparts in the outershelf and slope regions clearly establish the fact that there is a substantial supply of these elements from land to the innershelf region through While the percentage contridetrital minerals. butions made to the concentrations in the total sediment sample by the lithogenous fractions of the sediments also support this conclusion, the absence of any uniform distribution in regard to the percentage contributions may be attributed to the individual sample differences. The higher concentrations of the elements associated with (in general) the nonlithogenous fractions of the fine-grained sediments of the innershelf region than with their counterparts in the outershelf and slope regions is suggestive of the fact that the elements are removed more effectively from the overlying waters in the innershelf region. Similar overall distribution of the elements observed along the different sections appear to be nothing but a reflection of the contributions made by the lithogenous and non-lithogenous fractions of the sediments to the total sediment sample and the concentrations of the elements in the fractions themselves.

From the point of view of regional variations, the differences observed in the concentrations of the elements in the lithogenous fractions of the sediments along the different sections can be attributed to the differences in the source rocks present along the different parts of the west coast of India and to the corresponding differences in the mineralogical composition of the sediments in the different regions. While this is so, the differences observed between the regional variations in the distribution patterns of the elements on the total sample basis and in the lithogenous fractions of the sediments may perhaps

be attributed to differences in the stages of adjustment of the lithogenous material to the marine

environment in the different regions.

While the elemental concentrations associated with the lithogenous fractions represent concentrations held within the lattice structure of the detrital minerals introduced into the marine environment in the solid state, the concentrations associated with the non-lithogenous fractions of the sediments may have been fixed in a number of ways and the possible factors governing their distribution and fixations in the sediments are discussed below briefly.

The concentrations in the non-lithogenous fractions of the sediments include all concentrations associated with (i) all adsorbed cations, (ii) iron, manganese, nickel and cobalt of defined authigenic iron, manganese or ferromanganese compounds and the colloidal fraction of the sediments, and (iii) the carbonate phase of sediments. In order to understand the concentrations associated with the carbonate phase of the sediments, the bulk of which is contributed by the shell fragments and oolites in the sediments of the outershelf and slope regions, shell fragments and oolites separated from a few samples from the different regions were spectrographically analysed for their iron, manganese, nickel and cobalt contents. This analysis has revealed that they contain only 0.5% iron, 50 ppm manganese and less than 10 ppm of nickel and cobalt indicating that the carbonate phase does not contain appreciable amounts of these elements. Precipitation of the elements by sulphide ion is also unlikely in the area under study, in view of the fact that considerable mixing takes place in the shelf waters. pH measurements carried out by Rao and Madhavan16 have shown that the environment is not the reducing type. of heavy mortality of bottom animals¹⁷ during certain seasons and consequent anoxic conditions are perhaps a transient or passing phase and not long enough to maintain low redox potentials and hence, reducing conditions. It may also be relevant to mention here that no sulphide odour is noticed in any of the samples collected. In the present case it is possible that direct precipitation of nickel and cobalt as insoluble compounds does not take place as the sea water is greatly under saturated with regard to these elements. With a view to understanding the concentrations of nickel and cobalt associated with the clay fractions and the sort of distribution they exhibit, clay fractions separated from a few samples taken from the different sections have been analysed for their nickel and cobalt contents. This analysis has revealed that the nickel content varies from 14 to 27 ppm and the cobalt content from 6 to 26 ppm. If the nickel and cobalt contents of the clay fractions were due to adsorption only by the clay minerals, they should show a decreasing trend from north to south in view of the regional variations observed in their distribution since montmorillonite and illite have greater adsorption capacities than the kaolinite group of minerals. But since no such trend has been observed in the present case, it is regarded that adsorption by clay minerals may not be an important factor in the fixation of nickel and cobalt in these sediments. The clay minerals in the shelf region being mainly of detrital nature, perhaps the desorption taking place on contact with sea water may be responsible for the absence of any particular

Table 3 — Correlation Coefficient Values between Various Elements in Different Components of Sediments

Correlation between	r value in bulk samples	r value in acid soluble fraction	r value in the litho- genous fraction
Iron and organic matter.	+0.16	11 114	
Iron and CaCO ₃	-0.06		
Iron and manganese	+0.58	+0.59	+0.46
Iron and nickel	+0.76	+0.61	+0.24
Iron and cobalt	+0.69	÷0.56	+0.55
Manganese and organic	-0.25	ga di Maria	
matier		100	100
Manganese and CaCOa	+0.01		
Manganese and nickel	+0.48	+0.57	+0.33
Manganese and cobalt	+0.55	+0.25	+0.33
Nickel and organic matter.	+0.59		
Nickel and CaCOa	-0.43		
Nickel and cobalt	+0.92	+0.34	+0.67
Cobalt and organic matter	+0.58		-
Cobalt and CaCO	-0.54		
0			

^{*}Values of organic matter from Murty et al.2

trend in the trace elements associated with the clay fraction of the sediments.

It is evident from the foregoing that neither the carbonate phase nor the sulphide ion nor the clay fractions are responsible for the concentrations associated with the non-lithogenous fractions of the sediments to any great extent. The west coast of India being a zone of intense weathering, it is quite likely that the iron and manganese leached from the rocks and carried by the rivers in the colloidal state to the sea may be getting flocculated in the nearshore regions giving rise to high concentrations of iron and manganese observed in the non-lithogenous fractions of the sediments in the innershelf region. The presence of silts and clays in the innershelf region and quite close to the shore also supports this contention. It is also likely, that adsorption by hydrated ferric oxide and manganese oxides may be responsible for the higher concentrations of nickel and cobalt noticed in the non-lithogenous fractions of the innershelf region. Further, part of nickel and cobalt may also be associated with the organic matter of the sediments. Correlation coefficients calculated between various elements in the different components of the sediments (Table 3), especially in the total sample and the non-lithogenous fractions, support the observations made above and also exhibit a certain measure of covariation of the 4 elements among the different components of the sediments. Thus the presence of the favourable conditions in the innershelf region, viz. the presence of fine-grained sediments with high organic matter content and the flocculation of the colloidal matter brought by the rivers and the associated trace element content, may be responsible for higher concentrations of the elements associated with the nonlithogenous fractions of the sediments of the fine-grained sediments. While this is so, the low concentrations of the elements in the non-lithogenous fractions of the seidments of the outershelf and slope regions may be due to the bulk of the non-lithogenous fraction being composed of the carbonate phase of the sediments which has very low concentrations of the elements. This may also be the reason why

the non-lithogenous fractions of the fine-grained sediments of the Bombay region have relatively low concentrations of certain of these elements when compared with the corresponding fraction of the finegrained sediments of the other regions. Apart from this, the regional variations exhibited by the concentrations of the elements in the non-lithogenous fractions of the sediments may be due to the differences in the intensities of the processes operating in the different regions.

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