

Geochemical Trends in the Sediments and Manganese Nodules from a part of the Central Indian Basin

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Abstract: Geochemical analyses of eighteen surface sediment samples collected from an area between 1°-15° S latitudes and 73°-87° E longitudes exhibit significant variation in their chemical composition. Distribution patterns of the major and minor elements suggest a probable removal of a portion of Fe, Ti, Mg and Cr along with major portions of Mn, Ni, Cu and Zn as authigenic ferro-manganese colloids to the sediments.

The rare earth elements (REE) exhibit nearly an order of magnitude enrichment in the nodules compared to the surrounding sediments. The positive Ce anomaly in the Nodules (~0.25) is associated with negative Ce anomaly (0.04) in the host sediment indicating its oxidative scavenging preferentially by Fe-hydroxide colloidal flocs incorporating into the nodules. The shale (NASC) normalised patterns and end member ratios of REE indicate middle REE (MREE) enrichment over light REE (LREE) and heavy REE (HREE) in both nodules and sediments. The preferential uptake sequence of REE in the nodules could be given as MREE > LREE > HREE.

Keywords: Geochemistry; Manganese nodules; Marine geology; Central Indian Basin.

INTRODUCTION

Though the distribution of the major, minor and REE elements in manganese nodules and sediments from different areas of the oceans is extensively available, the knowledge of REE pattern in nodules and sediments from the Central Indian Basin (CIB) is rather obscure. Extensive studies in the basin in connection with identification of the Indian Mine-Site have been carried out (see Nair and Jauhari, 1993). However, there are limited publications describing REE behaviour pattern from the CIB area (Nath *et al.*, 1992 a&b, Pattan and Banakar, 1993). A number of publications in the past decade from this basin dealing with geochemistry are mainly restricted to 5 elements (Fe, Mn, Ni, Cu and Co) distribution in the nodules (Valsangkar and Khadge, 1991; Banakar, 1990; Pattan and Mudholkar, 1990; Sudhakar, 1989; Jauhari, 1987).

In view of the above, we have expanded our study to other major, minor and rare earth elements in a few selected nodules and

sediment samples from the CIB to understand their distribution trends and the relation of nodules with coexisting sediments.

MATERIAL AND METHODS

Figure 1 illustrates the locations of the eighteen surface sediments and four nodule samples selected for the present study. The samples form part of the repository of India's polymetallic nodules program. All these samples were analysed for major and trace elements while only six sediments and all the four nodules were analysed for REE.

In case of sediments, 0.5 gram of finely powdered, oven dried (at 105°C overnight) samples were taken in PTFE beakers. The aliquots were digested twice on a sand bath in a mixture of 10 ml HF + 2 ml HClO₄. The incipiently dried crystalline paste was diluted to 100 ml in 1N HCl. 75 ml each from six sediment solutions were loaded on columns filled with about 15 cm high settled DOWEX 50W-X8-200 mesh ion exchange resin for REE separation from the matrix elements.

Table I. Major and trace element composition of the CIB sediments.

Sample code	Location °S Lat: °E Long	wt %										µg/g			
		Al	Fe	Mg	Ca	Ti	Mn	Sr	Zn	Ni	Cu	Cr	Ba		
R-2537	1.059	88.095	4.35	2.56	1.29	18.76	0.23	0.22	849	108	116	166	66	1708	
R-2520	1.125	87.020	3.41	2.30	1.10	21.16	0.20	0.19	859	72	105	126	49	1562	
R-2583	2.050	82.079	3.17	2.18	1.05	22.94	0.20	0.18	892	102	97	118	48	1443	
F-99	5.000	75.992	5.98	5.11	2.41	0.59	0.45	0.44	280	289	504	686	102	5996	
R-2533	5.075	88.180	5.72	2.61	0.93	1.09	0.22	0.31	154	134	111	149	34	1561	
F-157	6.468	77.439	6.77	3.27	1.25	0.84	0.28	0.39	173	102	131	165	53	2106	
F-155	7.004	78.495	4.72	3.65	1.51	0.64	0.32	0.43	213	155	302	359	65	3621	
F-101	7.027	76.002	5.60	3.54	1.55	0.78	0.31	0.19	181	177	139	191	70	2836	
F-156	7.067	79.500	6.67	2.79	0.99	0.79	0.23	0.32	148	75	109	135	38	1619	
F-153	8.024	76.967	4.70	3.64	1.42	0.69	0.29	0.51	181	190	291	289	62	3103	
S-139	11.514	81.490	4.42	2.78	1.01	0.81	0.21	0.53	188	174	231	277	32	3116	
S-128	11.969	75.465	3.73	2.72	1.13	0.63	0.20	0.24	162	163	104	167	35	3077	
S-129	12.006	76.452	3.44	2.73	1.14	0.49	0.21	0.43	164	132	203	264	39	3058	
S-121	12.007	73.003	1.88	1.23	0.63	27.09	0.09	0.46	1090	100	160	151	17	1822	
S-124	12.017	73.003	1.16	0.95	0.45	31.29	0.07	0.39	1219	47	125	128	8	1622	
S-183	13.510	78.979	8.35	5.63	2.08	1.03	0.43	0.67	126	240	124	280	91	470	
S-231	14.890	73.530	4.15	2.39	1.07	8.10	0.17	0.50	467	84	163	214	27	2402	
S-206	15.090	83.560	3.49	2.29	0.79	13.66	0.16	0.55	540	192	224	187	21	1920	
MAG-1	-----	8.12	4.96	1.92	0.88	0.49	0.07	0.07	163	138	53	31	108	516	

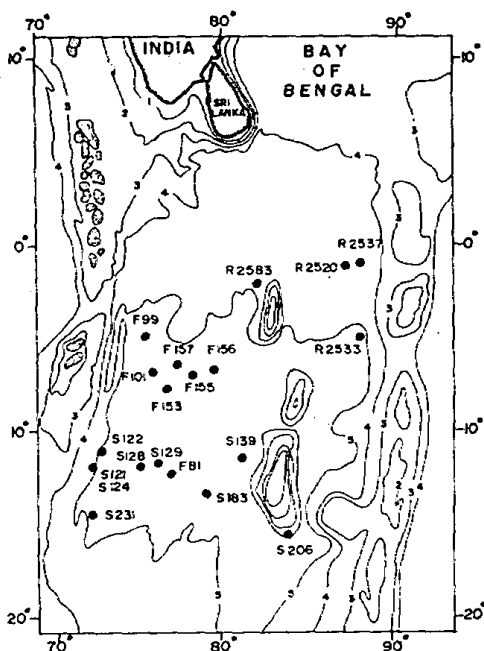


Fig.1. Locations of the samples studied.

The procedure adopted was according to Jarvis and Jarvis (1985).

In case of nodules, 0.2 gram of oven dried aliquots were leached in 6 M HCl at 40°C to extract only hydrolysate fraction of the nodules. The leachate was filtered through Watman-40 filter paper and washed thoroughly. The filtrates were made to 100 ml in 1N HCl and 75 ml from this was subjected to REE separation as described above.

For sediments as well as the nodules, a standard (USGS-A1 and MAG-1 respectively), a synthetic REE standard and a reagent blank were subjected to cation exchange process. The major, trace and REE elements were analysed on a Perkin-Elmer Plasma-400 ICP-AES. The accuracy of results were within $\pm 5\%$.

RESULTS AND DISCUSSION

The analytical results of major and trace elements for sediments and nodules are presented in Tables I and III respectively whereas REE results are presented in Tables

IV and V. Table II provides the correlation matrix of major and trace elements for the sediments, while Table VI presents various REE end member ratios in nodules and sediments.

Since open vessel HF digestion eliminates the Si, Al was used here as the indicator of lithogenous detritus in the sediments. Two distinct trends in the Al variation could be seen from Table I wherein, $>4.5\%$ Al invariably is associated with low Ca ($<1.5\%$) and Sr (<250 ppm) while $<4.5\%$ Al is associated with high Ca ($>8.0\%$) and Sr (>400 ppm). Ca and Sr in these sediments are in the carbonate fraction. Significant negative correlation is noticed (>0.7 ; Table II) between Al and Ca and Sr. Fe varies between 0.95% to 5.11% and Ti ranges from 0.07 to 0.45% (Table I) and these two elements exhibit a strong positive association with Al (>0.8 , Table II), indicating their incorporation into the sediments as detrital elements. This interpretation could be substantiated by antithetic association of Ca and Sr (carbonate fraction) with Fe and Ti (Table II). On the other hand, Mn, Ni, Cu and Zn do not associate with detrital indicator (Al) and show moderately positive association with Fe, Ti, Mg and Cr (Table II). This behaviour suggests an independent phase carrying most of the Mn, Ni, Cu and Zn along with small amounts of Fe, Ti, Mg and Cr as ferro-manganese oxihydroxide colloidal precipitate to the sediments. Though Ba variation is quite large (470 ppm to 5996 ppm, Table I), it is insignificantly associated with all other elements (Table II) probably due to its association with siliceous biogenic detritus (Dymond *et al.*, 1992).

Thus two major fractions, lithogenous detritus and calcium carbonate and two minor fractions, authigenic Fe-Mn hydroxide colloids and biogenic detritus constitute the sediment in the studied area with varying degree of influence in space (Fig.2).

Area 3 (Fig.2) which is dominated by siliceous sediment is the prime area for manganese nodule occurrence. The abundance

Table II. Interelemental correlation matrix for sediments of the CIB

	Al	Fe	Mg	Ca	Ti	Mn	Sr	Zn	Ni	Cu	Cr	Ba
Al	1.00											
Fe	0.83*	1.00										
Mg	0.69	0.95*	1.00									
Ca	-0.74*	-0.71*	1.00									
Ti	0.82*	0.98*	0.97*	-0.67	1.00							
Mn	0.21	0.35	0.19	-0.25	0.20	1.00						
Sr	-0.75*	-0.69	-0.52	0.99*	-0.64	-0.26	1.00					
Zn	0.49	0.81*	0.78*	-0.56	0.76*	0.44	-0.55	1.00				
Ni	0.11	0.48	0.56	-0.33	0.50	0.42	-0.26	0.68	1.00			
Cu	0.32	0.69	0.77*	-0.44	0.70*	0.40	-0.37	0.77*	0.93*	1.00		
Cr	0.69	0.90*	0.96*	-0.46	0.95*	0.03	-0.42	0.67	0.45	0.65	1.00	
Ba	-0.13	0.12	0.17	-0.47	0.13	0.02	-0.41	0.29	0.59	0.48	0.08	1.00

n = 18

significance level (*) = > 99.5%

Table III. Major and trace element concentration in the ferromanganese nodules of the CIB.

Sample code	Location	wt. % <										> μg/g <	
		Mn	Fe	Mg	Ca	Ti	Ni	Cu	Co	Ba	Sr	Ba	Sr
S-139	11.511	81.493	33.12	12.01	1.94	2.02	0.75	1.51	0.96	0.21	1885	919	
S-122	11.603	72.948	31.63	12.92	2.00	2.10	0.76	1.52	0.92	0.19	1555	965	
F-81	12.490	77.000	31.64	10.81	2.81	1.80	0.36	1.54	1.25	0.18	1758	670	
S-183	13.511	78.980	33.00	10.52	2.58	2.08	0.66	1.49	1.08	0.24	1834	799	
USGS-AI	-----	-----	19.23	11.46	2.77	10.30	0.38	0.62	0.10	0.30	1776	1685	

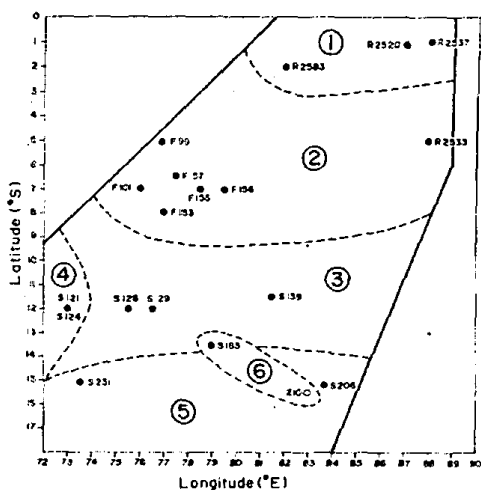


Fig.2. Tentative geochemical zones demarcated in the studied area. (Zone-1: carbonate dominant sediment with low Mn(0.2%) and Fe(2.3%). Zone 2: Carbonate free siliceous sediment with high Al (5.7%) and Ba(3000 ug/g). Zone 3: Carbonate free siliceous sediments with high abundance of manganese nodules and low Al (3.8%) and Fe (2.7%). Zone 4: Carbonate ooze with very low Al (1.5%), Fe (1.1%) and Ti (0.08%). Zone 5: Carbonate dominant red clays (transition zone) with high Mn (0.5%). Zone 6: Terrigenous dominant sediment with very high Al(8.4%), Ti (0.4%) and Fe (5.6%). Station No. 210 is from Nath *et al.* (1989).

and grade of nodules diminish northwards and southwards of this zone (PMN survey data). High Ba content (av. ~ 3000 ppm) is recorded in Areas 2 and 3. More than 20% biogenic silica has been reported from these areas and attributed to high productivity surface waters (Pattan *et al.*, 1992). The carbonate dominant areas (1 and 4) are limited to the less than 4600 m water depth in the vicinity of seamount zones (Fig.1).

Above geochemical zonation provides a

Table IV. Rare Earth Element composition of the CIB sediments (all values in $\mu\text{g/g}$).

Sample code	La	Ce	Nd	Sm	Eu	Dy	Lu	Ce*
R-2537	27.2	60.4	26.6	5.98	1.65	5.50	0.40	0.04
F-101	33.4	81.5	33.2	7.76	2.18	7.53	0.56	0.07
F-157	31.7	80.2	30.4	6.46	1.53	6.55	0.56	0.10
F-155	45.1	87.3	48.4	11.1	3.12	10.9	0.85	-0.04
F-156	31.5	90.9	30.5	6.83	1.73	6.76	0.57	0.15
S-124	16.0	31.2	17.6	4.02	1.13	4.00	0.31	-0.04
MAG-1	43.0	88.0	34.7	5.90	1.42	5.03	0.35	-

Ce* = Cerium anomaly = $\log(\text{Ce}/2/3\text{La} + 1/3\text{Nd})$; sample/shale normalised values are used (Elderfield *et al.*, 1981).

preliminary idea of the element distribution trends in this basin. The occurrence of one isolated patch (Area 6 in Fig.2) dominated by aluminosilicate detritus (Al=8.35%; Fe = 5.63% and Ti = 0.43%, Table I) could be due to submarine alteration of the seamount basalts in this region.

Though there is no systematic variation between major elements and REE, lowest REE and 3+ REE concentrations are associated with highest Ca and vice versa (Table I, III and VI) suggesting biogenic carbonate as inefficient carrier of REEs to the sediments in conformity with the findings of Elderfield *et al.* (1981). All the six analysed sediments exhibit very low positive or negligible negative Ce anomaly (Fig. 3) indicating

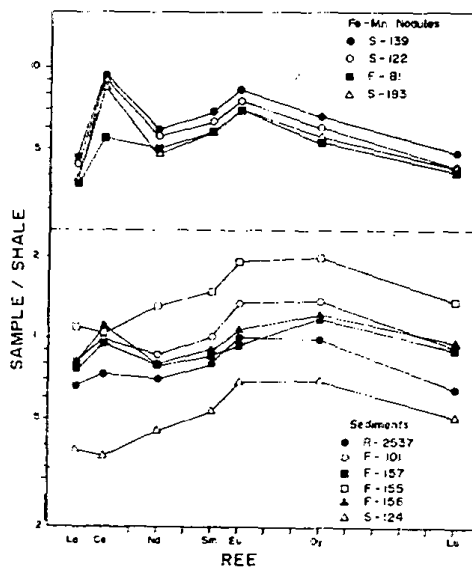


Fig.3. Shale normalised patterns of the rare earth elements in manganese nodules and the sediments of the Central Indian Basin.

fairly oxidising bottom environments in the study area which may be due to Antarctic Bottom Water (AABW) movement (Banakar *et al.*, 1991; Glasby *et al.*, 1987; Johnson and Nigrini, 1982; Warren, 1982).

Four nodule samples around 12° S latitude (Table III) exhibit Mn/Fe ratios around 2.5 suggesting their hydrogenous accretion (De Carlo *et al.*, 1987; Halbach *et al.*, 1981). The element concentration data (Table III) is in good agreement with earlier reported values for the nodules of this basin (Valsangkar and Khadge, 1991; Banakar, 1990; Pattan and Mudholkar, 1990; Jauhari, 1987).

The REE concentration in the nodules are presented in Table V. They exhibit nearly an

order of magnitude enrichment in the nodules compared to the surrounding sediments. The REE concentration in both sediment and nodules (Table IV and V) are well within the range reported for various ocean basins (Pattan and Banakar, 1993; Nath *et al.*, 1992a & b; Elderfield *et al.*, 1981; Piper, 1974a & b). The Ce anomaly in all the nodules is moderately positive (~0.25), suggesting accretion of the nodules under oxidising bottom environment (Elderfield, 1988) developed as a result of AABW movement. The positive Ce anomaly in these nodules is associated with the negative Ce anomaly in the sediment sample of the same location (S-124, ~12° S latitude) indicating preferen-

Table V. Rare Earth Element composition of the Fe-Mn nodules (all values in $\mu\text{g/g}$).

Sample code	La	Ce	Nd	Sm	Eu	Dy	Lu	Ce*
S-139	193	784	224	51.4	13.3	36.5	2.9	0.27
S-122	181	745	213	47.0	12.1	33.0	2.6	0.27
F-81	152	460	191	43.3	11.2	29.4	2.5	0.12
S-183	156	713	188	43.9	11.2	30.4	2.6	0.32
USGS AI	120	701	99	23.3	5.2	24.0	2.1	-

Ce* = cerium anomaly (see Table 4)

Table VI. REE ratios in the nodules and sediments of the CIB

Sample code	$\frac{\text{LREE}}{\text{MREE}}$	$\frac{\text{LREE}}{\text{HREE}}$	$\frac{\text{MREE}}{\text{HREE}}$	$\Sigma \text{ REE}$	$\Sigma 3 + \text{ REE}$
Sediments:					
R-2537	4.5	68.0	15.0	132.7	72.3
F-101	4.3	59.6	13.8	174.5	93.0
F-157	4.9	56.6	11.5	164.3	84.1
F-155	4.1	53.1	13.1	217.5	130.2
F-156	4.6	55.3	12.0	176.2	85.3
S-124	4.0	51.6	13.0	78.1	46.9
Average	4.4	57.4	13.1	-	-
Nodules:					
S-139	3.8	66.6	17.7	1305	521
S-122	3.9	69.6	18.1	1234	489
F-81	3.5	60.8	17.3	889	429
S-183	3.6	60.0	16.9	1145	432
Average	3.7	64.3	17.5	-	-
Nod/Sed	0.8	1.1	1.3	-	-
NASC	5.5	67.2	12.3	177.2	94.2

LREE = La; MREE = Sm; HREE = Lu

NASC data is given to compare the various REE ratios in nodules and sediments with the reference sample (NASC).

For Nodule/Sediment (Nod/Sed), the average ratios in nodules and sediments are used.

tial removal of oxidised Ce to the nodules via Fe-hydroxide colloidal flocs from the water column (Elderfield *et al.*, 1981; Glasby *et al.*, 1987; Nath *et al.*, 1992a).

Considering NASC (North American Shale Composite-reference material) REE values as the background we have calculated REE end member ratios (LREE-La, MREE-Sm and HREE-Lu) and presented in Table VI. These ratios clearly reflect the MREE enrichment over LREE and HREE both in sediments and nodules. The MREE enrichment is ~ 20% in sediments while more pronounced (~ 35%) in nodules. This observation is suggestive of preferential uptake of Sm in sediments and nodules. HREE enrichment trend over LREE (Lu over La) in sea water (Elderfield, 1988) has been

retained in the sediments of CIB while nodules exhibit marginal LREE enrichment over HREE (Table VI, Fig. 3).

When nodule to sediment ratio of averaged end member REE ratios are considered, MREE is most preferred followed by LREE and HREE in ferromanganese nodules as compared to sediments (Table VI). Based on this observation the preferential uptake sequence of REE in these nodules could be given as MREE > LREE > HREE.

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