Marine Georesources & Geotechnology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/umgt20

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Published online: 31 Oct 2008.

To cite this article: J. N. Pattan, Ch. M. Rao, A. A. Migdisov, S. Colley, N. C. Higgs & L. Demidenko (2001) Ferromanganese Nodules and their Associated Sediments from the Central Indian Ocean Basin: Rare Earth Element Geochemistry, Marine Georesources & Geotechnology, 19:3, 155-165

To link to this article: http://dx.doi.org/10.1080/106411901109353810

Marine Georesources and Geotechnology, 19:155–165, 2001

1064-119X/01 $12.00 + .00

Ferromanganese Nodules and their Associated Sediments from the Central Indian Ocean Basin: Rare Earth Element Geochemistry

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The rare earth element (REE) distribution in nine deep-sea ferromanganese nodules and their associated siliceous sediments from the Central Indian Ocean Basin (CIOB) have been studied to elucidate the REE relationship among them. Total REE concentration varies from 398–928 ppm in the nodules and 137–235 ppm in the associated sediments, suggesting two- to four-fold enrichment in the nodules compared to associated sediments. REE of nodules and their associated sediments show a positive correlation, suggesting REE are supplied from a common source such as seawater. The positive correlation between REE of nodules and sediments from the CIOB is contrary to the competitive scavenging of REE between nodules and sediment in the equatorial Pacific Ocean. REEs in the nodules are carried by Fe, P, and

Received 16 July 1999; accepted 1 May 2001

The senior author is grateful to Dr. E. Desa, Director, N.I.O., Goa for permission to publish and to the British Council for the fellowship. Mr. G. Prabu is thanked for carrying out the X-ray diffraction. Financial support from the Department of Ocean Development, New Delhi (Govt. of India) is acknowledged. This is N.I.O. contribution No 3686.

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Ti, whereas in the sediment they are carried by P and Mn phases. A similar REE fractionation pattern with middle REE enrichment over heavy and light REE in both the nodules and their associated sediment suggest fractionation is independent of REE abundance and their carrier phases.

Keywords manganese nodules, deep-sea sediment, REE, Ce-anomalies, fractionation, Central Indian Ocean Basin.

The rare earth element (REE) concentration relationship in ferromanganese nodules and their associated sediments is complex and provides information on the factors controlling their uptake (Elderfield et al., 1981). There are different views regarding which phases control the abundance of REE in ferromanganese nodules such as multiple phases (Elderfield et al., 1981; Nath et al., 1992a) and single phase (Glasby et al., 1987; Pattan and Banakar, 1993). REE analysis of surface sediments in the Central Indian Ocean Basin (CIOB) showed that calcareous ooze has the lowest REE content with a strong negative Ce-anomaly, siliceous sediment has higher REE concentrations with a moderate positive Ce-anomaly, and red clay has the highest REE content although both positive and negative Ce-anomalies were observed (Banakar and Jauhari, 1994; Banakar et al., 1998; Nath et al., 1992b; Pattan et al. 1994). Upward diagenetic remobilization of REE in the sediment has been reported (Pattan and Banakar, 1997) and might be supplying REE to the lower buried portion of nodules. The coarse fraction of Indian Ocean sediment has a negative Ce-anomaly due to a biogenic component, whereas the finer fraction has a positive Ce-anomaly attributed to clays and oxyhydroxides (Tlig and Steinberg, 1982).

There has been no systematic study to understand the REE behavior in nodules and their associated sediments in the CIOB as has been attempted in the Pacific (Courtois and Clauer, 1980; Elderfield et al., 1981; Glasby et al., 1987; Rankin and Glasby, 1979) and Atlantic oceans (Addy, 1979). The present study on nine deep-sea ferromanganese nodules and their associated siliceous sediment from the CIOB is an attempt to understand the REE relationship, distribution patterns, carrier phases, and fractionation patterns.

Material and Methods

Nine surficial nodule-sediment pairs were collected with box core and Pettersson grab in the CIOB (Figure 1). All the nodule-sediment pairs are from siliceous ooze area where biogenic opal varied from 20–35% (Banakar et al., 1998; Pattan et al., 1992). Known amounts of finely powdered oxide layers of ferromanganese nodules and the bulk sediments were treated in a mixture of HF and $HClO_4$ in open PTFE beakers and evaporated to incipient dryness. Again HF and $HClO_4$ were added and evaporated until cake was formed, and to that 10 ml of 6 N HCl was added and final solutions were made to 100 ml with distilled water. Part of the solution was used for REE separation using Dowex AG 50W-X8 (200–400 mesh) ion exchange resin following the procedure of Jarvis and Jarvis (1985). REE and a few major elements were analyzed on a Phillips simultaneous Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). International sediment (MESS and BCSS) and nodule (A-1 and P-1) standards were used to assess the accuracy of the analyses. The accuracy of the analysis of sediments is +/−Fe (2.1), Mn (0.8), Ti (4.6), P (6.6),

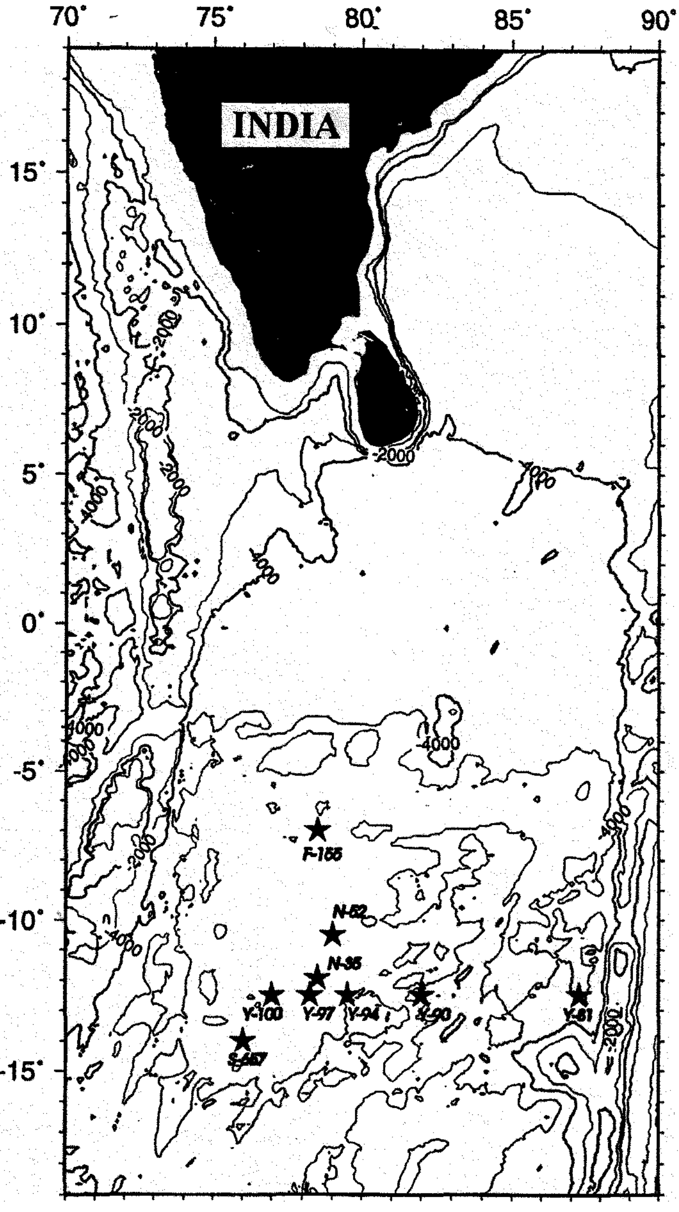

Figure 1. Schematic map showing ferromanganese nodule and their associated sediment location.

La (3.6), Ce (0.6), Nd (2.3), Sm (2.6), Eu (1.6), Gd (2.5), Dy (0.2) Er (6.8), Ho (7.2) Yb (1.5), and Lu (0.1), and that for nodules is Fe (5.0), Mn (5.0), Ti (1.3), P (5.0), La (0.9), Ce (5.8), Nd (0.1), Sm (7.8), Eu (5.6), Gd (0.1), Dy (3.3), Er (2.7), Yb (9.2), and Lu (10). Mineralogical study of ferromanganese nodules was determined on a Phillips X-ray diffractometer.

Table 1
Rare earth elements (ppm) and Fe, Mn, Ti, and P (%) concentration in ferromanganese nodules and their associated sediments from CIOB

Sam. No	N-35	N-52	Y-81	Y-90	Y-94	Y-97	Y-100	F-155	S-657
La	Nod-73.6	121.5	137.5	94.3	59.2	84.1	97.8	134.1	125.5
	Sed-21.3	28.5	42.9	26.8	30.8	40.1	28.7	42.8	34.6
Ce	Nod-234.5	410.6	365.4	203.5	186.8	233.6	349.4	504.9	525.3
	Sed-69.2	86.5	79.9	77.6	83.3	83.9	88.6	95.5	94.1
Nd	Nod-99.4	149.7	155.8	112.0	83.7	104.2	121.2	158.5	146.7
	Sed-23.0	34.5	46.3	29.8	34.5	43.8	32.6	45.8	41.7
Sm	Nod-22.9	32.9	32.8	23.8	19.9	23.0	27.0	34.8	31.5
	Sed-6.1	8.9	11.6	7.3	8.9	10.9	8.5	11.4	11.3
Eu	Nod-5.4	7.8	8.0	5.6	5.6	5.5	6.5	8.2	7.6
	Sed-1.4	2.1	2.7	1.8	1.7	2.6	2.0	2.8	2.7
Gd	Nod-20.8	31.3	34.5	21.9	12.2	21.4	26.1	34.6	32.4
	Sed-5.3	7.8	10.7	7.4	8.0	9.9	7.7	10.8	10.3
Dy	Nod-17.1	26.3	29.6	18.1	14.0	18.0	21.8	27.7	26.9
	Sed-4.9	7.2	10.7	6.3	7.6	9.5	7.3	10.8	10.3
Ho	Nod-3.2	4.9	5.8	3.5	2.6	3.4	4.1	5.2	5.1
	Sed-0.9	1.4	2.2	1.3	1.5	1.9	1.4	2.2	1.8
Er	Nod-8.3	13.1	16.0	9.1	6.8	9.0	10.9	13.6	13.7
	Sed-2.7	3.9	6.3	3.5	4.4	5.5	4.1	6.3	5.2
Yb	Nod-7.7	11.0	13.2	8.1	6.2	8.1	9.8	12.1	12.0
	Sed-2.5	3.6	5.6	3.3	3.9	4.9	3.7	5.8	4.8
Lu	Nod-1.4	1.8	2.2	1.4	1.1	1.4	1.7	2.0	2.0
	Sed-0.4	0.6	0.9	0.7	0.6	0.8	0.6	0.9	0.8
Fe	Nod-4.8	8.0	8.4	5.5	3.3	5.3	7.1	10.6	9.2
	Sed-3.3	4.5	2.9	2.7	2.4	3.3	3.6	3.9	2.9
Mn	Nod-30.6	28.6	21.4	30.6	30.0	31.4	29.4	23.6	26.2
	Sed-0.37	0.78	0.59	0.56	0.41	0.95	0.92	0.75	0.60
Ti	Nod-0.18	0.27	0.32	0.19	0.16	0.19	0.23	0.50	0.31
	Sed-0.18	0.39	0.23	0.19	0.18	0.24	0.25	0.31	0.18
P	Nod-0.12	0.15	0.29	0.12	0.10	0.15	0.14	0.25	0.19
	Sed-0.06	0.14	0.11	0.08	0.05	0.10	0.08	0.13	0.13

Results and Discussion

REE Distributions and their Relation between Nodule-Sediment Pairs

REE concentration of ferromanganese nodules and their siliceous associated sediments are presented in Table 1, and some of the REE parameters and ratios are given

Table 2
Some REE parameters and ratios of ferromanganese nodules and their associated sediments

Sample	Nod/ Sed	Tot. REE	3+ REE	Ce-anom	La_n/ Yb/n	La_n/ Sm/n	Yb_a/ Sm/n	Mn/ Fe
N-35	Nod	494	260	0.13	0.82	0.58	0.71	6.29
	Sed	138	68	0.18	0.73	0.62	0.86	0.11
N-52	Nod	811	400	0.17	0.94	0.67	0.71	3.58
	Sed	185	98	0.13	0.70	0.58	0.85	0.17
Y-81	Nod	811	435	0.08	0.89	0.76	0.85	2.54
	Sed	220	140	−0.05	0.66	0.67	1.02	0.16
Y-90	Nod	501	298	0.008	1.00	0.72	0.72	5.54
	Sed	166	88	0.13	0.65	0.63	0.95	0.21
Y-94	Nod	398	211	0.12	0.82	0.54	0.66	9.92
	Sed	185	102	0.09	0.60	0.66	0.93	0.05
Y-97	Nod	512	278	0.09	0.89	0.66	0.74	5.87
	Sed	214	130	−0.007	0.62	0.66	0.95	0.27
Y-100	Nod	676	327	0.20	0.85	0.74	0.76	4.09
	Sed	185	97	0.15	0.61	0.61	0.92	0.26
F-155	Nod	936	431	0.23	0.95	0.70	0.73	2.23
	Sed	235	140	0.02	0.58	0.68	1.07	0.16
S-657	Nod	929	403	0.28	0.90	0.72	0.80	2.86
	Sed	218	124	0.08	0.57	0.56	0.90	0.20

Ce-anomaly calculated according to Elderfield et al., (1981). n is the North American Shale Composite concentration.

in Table 2. Total REE concentration of nodules and sediments varies from 398–928 ppm and 137–235 ppm respectively, suggesting a two- to four-fold REE enrichment in nodules compared to sediments (Table 1). REE concentration of CIOB nodules are more or less similar, whereas sediments are nearly two- to three-fold depleted compared to nodules and siliceous sediments from the equatorial Pacific ocean (Table 3) (Elderfield et al., 1981). A plot of total REE of nodules and their associated sediments from CIOB showed a reasonably good positive correlation ($r = +0.6$) suggesting seawater as the probable source (Figure 2). Diagenetic remobilization of REE in a sediment core (Pattan and Banakar, 1997) from the siliceous sediment suggests supply of REE to the lower portion of buried nodule. The moderate positive correlation observed between REE of nodules and sediments in CIOB is quite different from that of the equatorial Pacific ocean where Elderfield et al. (1981) found that the highest REE in the nodules is associated with the lowest REE concentration in the associated siliceous sediment and vice versa, suggesting competitive scavenging of REE between them. On the contrary, Courtois and Clauer (1980) and Glasby et al. (1987) did not find any such relationship between nodules and their associated sediments from the southeast and southwest Pacific ocean

Table 3
Comparison of average REE concentrations (ppm) in ferromanganese nodules and their associated sediments from CIOB and Equatorial Pacific Ocean

	Central Indian Ocean Basin #		Equat. Pacific Ocean $	
REE	Nodule	Sediment	Nodule	Sediment
La	103	33	101	65
Ce	335	84	421	91
Nd	125	37	143	93
Sm	28	9	34	23
Eu	7	2	8	5
Gd	26	9	33	25
Dy	22	8	30	23
Ho	4	1.6	–	–
Er	11	4.6	16	13
Yb	10	4.2	15	12
Lu	1.6	0.7	–	–

= Mean of nine ferromanganese nodules and their associated sediment.
$ = Mean of seven ferromanganese nodules and their associated sediment (Elderfield et al, 1981).
– = data not available.

respectively. Todorokite and δ-MnO_2 are the only minerals identified in these nodules. The nodules with high REE content (e.g., samples 155 and 657) are associated with comparatively more δ-MnO_2 than todorokite, whereas nodules with low REE content (sample 94, 90, 97) are associated with comparatively more todorokite than δ-MnO_2. Nodules with δ-MnO_2 are associated with low Mn/Fe, suggesting a seawater or hydrogenetic source, while nodules with todorokite phase have high Mn/Fe ratio, suggesting a diagenetic source (Halbach et al., 1981).

The cerium occurs as Ce^{3+} under reducing conditions and is oxidized to insoluble Ce^{4+} under oxidizing conditions (Elderfield, 1988). Therefore, its concentration can be used to understand the redox conditions of a depositional environment. Cerium concentration in sediments and nodules varies from 70–95 ppm and 203–504 ppm respectively suggesting a two- to five-fold enrichment in the nodules compared to associated sediments. The Ce-anomaly is calculated as log = [Ce/2/3/La + 1/3 Nd] based on shale normalized values (Elderfield et al., 1981). Ferromanganese nodules have positive Ce-anomalies while associated siliceous sediment shows negligible to moderately positive Ce-anomalies, suggesting a fairly oxidizing environment (Table 2). As expected the Ce-anomaly in the nodules is more positive compared to the sediment. Two sediments (N-35) and Y-90) had more positive Ce-anomaly than their corresponding nodules (Table 2). This could be due to a low concentration of Ce and a larger diagenetic signature (high Mn/Fe ratio) of nodules suggesting nodule burial within the sediment, or the associated sediment might have a large quantity of Fe-Mn oxyhydroxide materials which have generally large positive Ce-anomalies. The positive Ce-anomalies in the siliceous sediment could be due to clays or authigenic components of Fe-Mn oxyhydroxides because

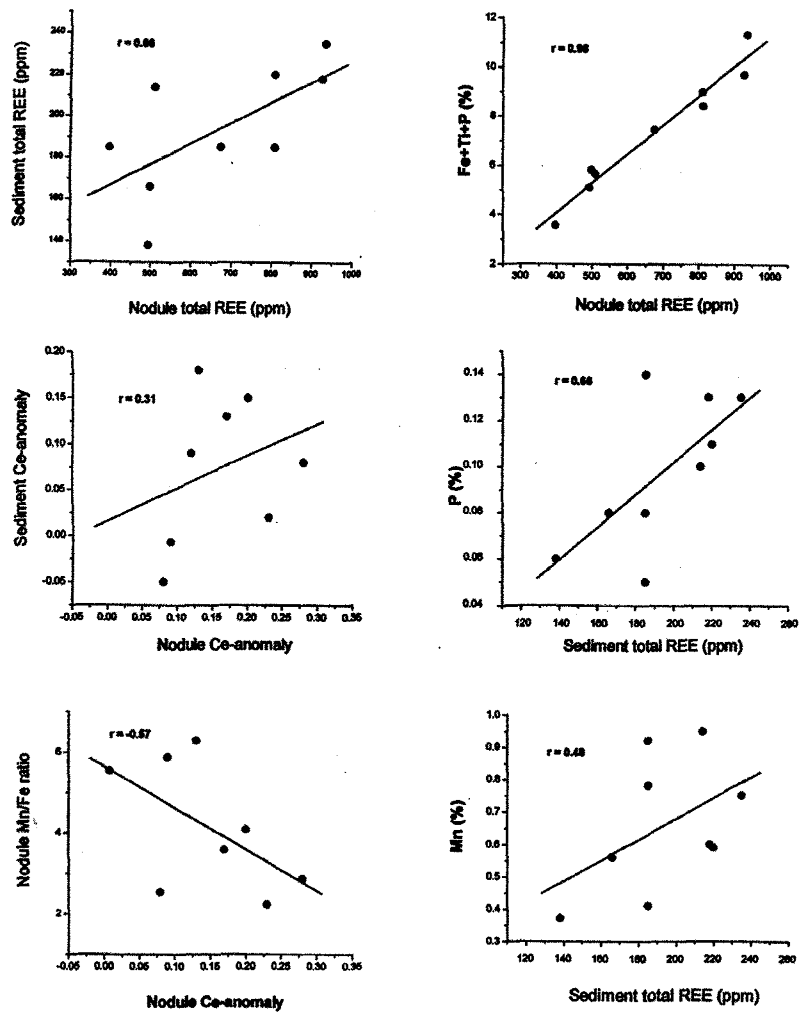

Figure 2. REE relation between ferromanganese nodules and associated sediments and REE carrier phases in nodules and sediments.

siliceous oozes generally have negative Ce-anomalies (Elderfield et al., 1981; Piper, 1974; Toyoda et al. 1990). A comparison of Ce-anomalies of nodules and their associated sediments does not show any significant correlation (Figure 2) and is contrary to equatorial Pacific Ocean nodule-sediment pairs where nodules with large Ce-anomalies are associated with small negative Ce-anomalies in the sediment (Elderfield et al., 1981). The negative Ce-anomaly could be due to the fact that siliceous sediment in the equatorial Pacific contains comparatively more phosphorus (P-0.23%, Elderfield et al., 1981) which normally displays negative Ce-anomalies (Toyoda et al., 1990) while siliceous sediment from CIOB has positive Ce-anomaly due to Fe-Mn oxhydroxides which have generally positive Ce-anomaly. Therefore, different components present in the associated sediment affect the REE relationship between nodule-sediment pairs. Nodules with strong diagenetic signature (high Mn/

Fe ratio) are generally associated with low Ce-anomalies and vice versa (Figure 2), suggesting seawater as the source for cerium.

REE Carrier Phase

REEs in the ferromanganese nodules are carried by a single authigenic phase comprised of Fe, P, and Ti ($r = +0.98$, Figure 2). Phosphorous is enriched in the nodules (av 0.17%) nearly two-fold relative to the associated sediments (av 0.09%). The strong positive correlations between Fe and P ($r = 0.8$) and Fe and Ti ($r = 0.8$) in the nodules are consistant with ferriphosphate and colloidal Ti-hydrate containing an Fe-rich phase, respectively (Halbach et al., 1981; Pattan and Banakar, 1993; Pattan et al., 1994). A similar observation was made previously for the buried nodules from the same basin (Pattan and Banakar, 1993). Though Fe, P, and REE in nodules showed strong positive correlations, Nath et al. (1992a) suggested that the REE are carried by two independent phases containing P and Fe. In the present study our data clearly show that REE are carried by a single phase consisting of Fe, Ti, and P in a manner similar to buried nodules from the same basin (Pattan and Banakar, 1993). Associations of REE in the sediments appear to be more complex and show moderate positive correlation with P ($r = +0.6$) and Mn ($r = +0.5$) (Figure 2). Phosphorus in the sediments is mostly in the form of biogenic apatite (fish teeth). Biogenic apatite is an important REE scavenger from seawater and displays high REE concentrations (Elderfield and Pagett, 1986; Toyoda and Tokinama, 1990). Apatite has large crystal defects and impurities that permit REE to be adsorbed on teeth enamel and incorporated into the lattice of the dentine (Toyoda and Tokonami, 1990). High biogenic opal concentration was noticed in the CIOB surface sediments (Banakar et al., 1998; Pattan et al., 1992), and the formation of Fe-rich smectite in the CIOB sediment was reported by Rao and Nath (1988). Iron-rich smectite is formed by the diagenetic reaction between opal and Fe-oxyhydroxides (Lyle et al. 1977). During Fe-rich smectite formation, the REEs associated with the Fe phase are released to pore waters and associated with Mn in the sediment.

REE Fractionation Pattern

The North American Shale Composite (NASC) normalized REE pattern of nodules and sediments exhibit a convex pattern (Figure 3). The ratios of light REE to heavy REE $(La/Yb)_n$, light REE to middle REE$(La/Sm)_n$ and heavy REE to middle REE $(Yb/Sm)_n$, and shale-normalized pattern suggest enrichment of middle REE (MREE) over heavy REE (HREE) and light REE (LREE) (Table 2). The REE concentrations of nodules, when normalized to the REE content of associated sediments (Figure 3), show higher Ce values, and a gradual decrease from La to Lu suggesting seawater as the REE source. Similar patterns were noticed through the partition coefficient by De Carlo and McMurtry (1992) suggesting a seawater REE source. The seawater REE pattern is generally enriched in HREE over LREE with a strong negative Ce-anomaly (Elderfield and Greaves, 1982; Piepgras and Jacobsen, 1992; Sholkovitz et al. 1994). The HREE enrichment over LREE in seawater has been explained as resulting from the greater tendency of HREE to form complexes with seawater ligands compared to LREE (Turner et al. 1981). As a result, LREEs are removed more effectively from seawater by adsorption or scavenging, leaving

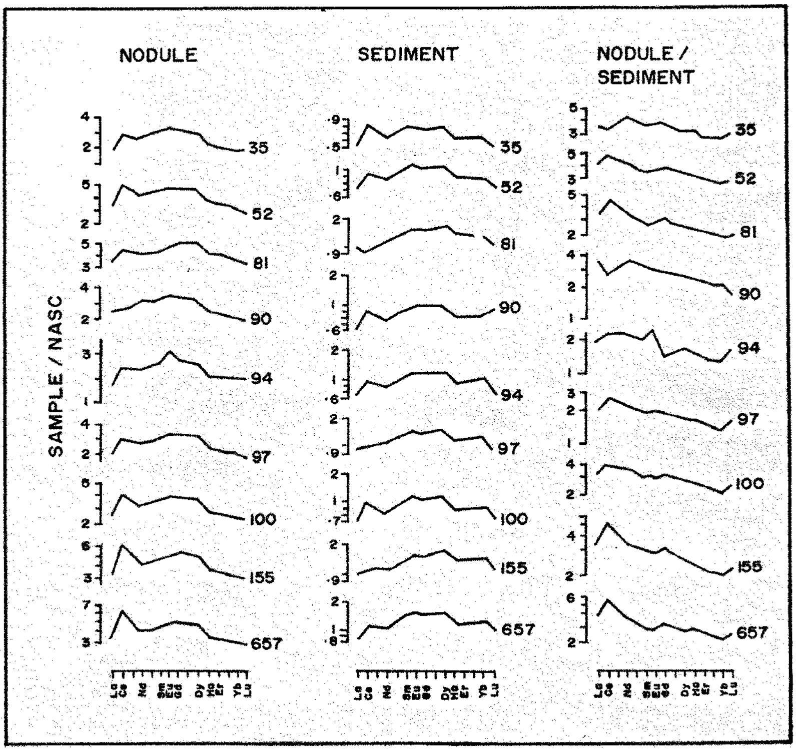

Figure 3. Shale-normalized REE pattern of nodules and sediment and associated sediment normalized nodule REE concentration

behind a HREE-enriched pattern. P is one of the REE carrier elements in both nodules and sediment which generally retains the seawater enrichment pattern, while Fe-Mn oxyhydroxides develop a positive Ce-anomaly and enrichment of middle REE. Therefore the fractionation patterns noticed in the present study are the result of a combination of P and Fe-Mn oxyhydroxides.

Conclusions

The REE studies of ferromanganese nodules and their associated sediment from CIOB suggest:

1. REE concentration in the nodules are enriched two- to four-fold compared to the underlying sediment. Relation of REE between nodule and sediment depends upon the components present within the sediment.
2. REE in the nodules are carried by Fe, Ti, and P, while that in the sediments are carried by P and Mn.
3. The fractionation pattern is independent of REE concentration and their carrier phases.

The fractionation pattern is controlled by the combination of P and Fe-Mn oxyhydroxides.

References

Addy, S. K. 1979, Rare earth element patterns in manganese nodules and micronodules from northwest Atlantic. *Geochimica et Cosmochimica Acta* 43:1105–1115.

Banakar, V. K., and P. Jauhari. 1994. Geochemical trends in the sediments and manganese nodules from a part of the Central Indian Basin. *Journal Geological. Society India* 43:591–598.

Banakar, V. K., G. Parthiban, J. N. Pattan, and P. Jauhari. 1998. Chemistry of surface sediment along a north-south across the Equator in the Central Indian basin: An assessment of biogenic and detrital influences on elemental burial on the seafloor. *Chemical Geology* 147:217–232.

Courtois, C., and N. Clauer. 1980. Rare earth elements and strontium isotopes of polymetallic nodules from the Southeastern Pacific ocean. *Sedimentology* 27:687–695.

De Carlo, E. H., and G. M. McMurtry. 1992. Rare earth geochemistry of ferromanganese crusts from the Hawaiian Archipelago, Central Pacific. *Chemical Geology* 95:235–250.

Elderfield, H. 1998. The oceanic chemistry of the rare earth elements. *Phils. Trans. R/Soc. London* A325:105–126.

Elderfield, H., and M. J. Greaves. 1982. The rare earth elements in sea water. *Nature* (London) 296:214–219.

Elderfield, H., C. J. Hawkesworth, M. J. Greaves, and S. E. Calvert. 1981. Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments. *Geochimica et Cosmochimica Acta* 45:1231–1234.

Elderfield, H., and R. Pageét 1986. Rare earth elements in icthyoliths: Variations with redox conditions and depositional environments. *Science of Total Environment* 49:175–197.

Glasby, G. P., R. Gwozdz, H. Kunzendorf, G. Friedrich, and T. Thijssen. 1987. The distribution of rare earth and minor elements in manganese nodules and sediments from the equatorial and SW Pacific. *Lithos* 20:97–113.

Halbach, P., C. Scherhag, U. Hebisch, and V. Marchig. 1981. Geochemical and mineralogical control of different genetic types of deep sea nodules from the Pacific Ocean. *Mineralium Deposita* 16:59–84.

Jarvis, I., and K. E. Jarvis. 1985. Rare earth element geochemistry of standard sediments: A study using Inductively Coupled Plasma-Spectrometry. *Chemical Geology* 53:335–344.

Lyle, M., J. Dymond, and G. R. Heath. 1977. Copper-nickel enriched ferromanganese nodules and associated crusts from the Bauer Deep, NW Nazca Plate. *Earth Planetary Science Letters* 35:55–64.

Nath, B. N., V. Balaram, M. Sudhakar, and W. L. Pluger. 1992a. Rare earth element geochemistry of ferromanganese deposits from the Indian Ocean. *Marine Chemistry* 38:185–205.

Nath, B. N., I. Roelandta, M. Sudhakar, and W. L. Pluger. 1992b. REE patterns of the Central Indian Basin sediments related to their lithology. *Geophysical Research Letters* 19:1197–2000.

Pattan, J. N., V. K. Banakar. 1993. Rare earth element distribution and behavior in buried manganese nodules from the Central Indian Basin. *Marine Geology* 112:303–312.

Pattan, J. N., and V. K. Banakar. 1997. Diagenetic remobilization of rare earth elements in sediment core from the Central Indian Basin. *Indian Journal Marine Sciences* 26:341–344.

Pattan, J. N., S. Colley, and N. C. Higgs. 1994. Behavior of rare earth elements in coexisting manganese macronodules, micronodules and sediments from the Central Indian Basin. *Marine Georesources & Geotechnology* 12:283–295.

Pattan, J. N., S. M. Gupta, A. V. Mudholkar, and G. Partiban. 1992. Biogenic silica in space and time in sediments of central Indian basin. *Indian Journal Marine Sciences* 21:116–120.

Piepgras, J, and Jacobsen, S. B. 1992. The behaviour of rare earth elements in seawater: Precise determination of variation in the North Pacific water column. *Geochimica et Cosmochimica Acta* 56:1851–1862.

Piper, D. Z. 1974. Rare earth elements in the sedimentary cycle: A summary. *Chemical Geology* 14:285–297.

Rankin, P. C, and G. P. Glasby. 1979. Regional distribution of rare earth and minor elements in manganese nodules and associated sediments in the southwest Pacific and other localities. In J. Bischoff and D. Z. Piper (Eds.) *Marine geology and oceanography of the Pacific manganese nodule Provinence*. (pp. 681–697), NY, Plenum.

Rao, V. P., and B. N. Nath. 1988. Nature, distribution and origin of clay minerals in grain size fraction of sediment samples from Central Indian Ocean basin. *Indian Journal Marine Sciences* 17:202–207.

Sholkovitz, E. R., W. M. Landing, and B. C. Lewis. 1994. Ocean-particle chemistry: The fractionation of rare earth elements between suspended particles and sea water. *Geochimica et Cosmochimica Acta* 58:1567–1579.

Tlig, S., and M. Steinberg. 1982. Distribution of rare earth elements in size fraction of recent sediments of the Indian Ocean. *Chemical Geology* 37:317–333.

Toyada, K., Y. Nakumura, and A. Masuda. 1990. Rare earth elements in Pacific pelagic sediments. *Geochemica et Cosmochimica Acta* 54:1093–1103.

Toyada, K. and M. Tokinama. 1990. Diffusion of REEs in fish teeth from deep-sea sediments. *Nature* (London) 345:607–609.

Turner, D. R., M. Whitfield, and A. G. Dickson. 1981. The equilibrium speciation of dissolved components in fresh water and sea water at 25 degree centigrade and 1 atom pressure. *Geochimica et Cosmochemica Acta* 51:597–605.