

Diagenetic remobilization of rare earth elements in a sediment core from the central Indian basin

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Received 12 May 1997, revised 30 June 1997

Rare earth elements (REE) distribution in a 36 cm long sediment box core from the Central Indian Basin is studied. REE concentration is generally higher in the upper oxic zone than in intermediate suboxic zone suggesting REE diffusion upwards the sediment column and subsequent incorporation in the oxyhydroxide phase. The similarity in depth distribution of bulk REE concentration, solid Mn phase and micronodule abundance from the coarse fraction suggest that micronodules are one of the major component controlling the REE distribution in a sediment column.

Rare Earth Elements (REE) are useful tracers to understand the depositional environments of sediments and sedimentary rocks¹. Siliceous ooze from the Central Indian Basin (CIB) generally has higher REE abundance than the calcareous ooze but lower than red clays and show positive Ce/Ce^* anomalies. Tlig & Steinberg⁶ showed that coarse fraction of the Indian Ocean sediment have negative Ce/Ce^* anomalies due to biogenic component and finer fraction have positive Ce/Ce^* anomalies due to clays and oxyhydroxides. Based on the behavior of redox sensitive metal (Mn) and micronodule abundance (number of micronodule per gram of dried sediment) and their size in the sediment cores from CIB suggested top oxic, intermediate suboxic and subsurface maxima in the upper a meter sediment column⁷⁻⁹. The present study is made to understand the influence of oxic and suboxic environments and factors controlling the REE distribution in a sediment core from the CIB.

Materials and Methods

A 36 cm long sediment box core was retrieved onboard M.V. Skandi Surveyor cruise 11 (stn No.657) from 14° S latitude and 76°E longitude at a water depth of 5050m from a siliceous ooze area (Fig.1). Sediments were made salt free, dried and powdered. Bulk digestion and REE separation of the sediments were carried out according to the

procedures of Jarvis & Jarvis¹⁰. REE were analyzed on a Perkin Elmers, Plasma-400 sequential ICP-AES. International sediment standard (BCSS-I) was used for the accuracy and it was $\leq \pm 10\%$. Synthetic REE standards were used to check the recovery efficiency and it was $\sim 95\%$.

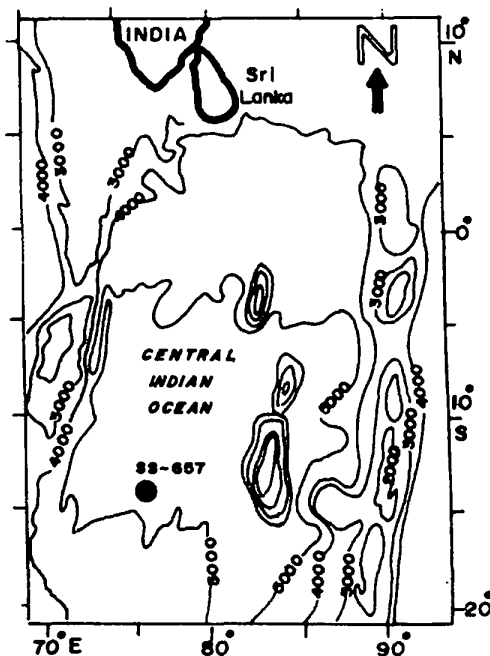


Fig.1—Location of sediment core SS-657.

Results and Discussion

Total REE concentration in the sediment core varies from 155 to 217 ppm (Table 1). REE content is higher in the upper oxic zone, lower at intermediate suboxic zone and increases with the depth again (Table 1 and Fig.2). The distinct variation in total REE concentration with depth suggest upward diffusion of REE from suboxic to more oxidizing zone when the REE carrier phase such as oxyhydroxides dissolve at intermediate

depth. Though micronodules constitute around 10 to 20% (by wt) of the bulk sediment but contain higher REE concentration (406–815 ppm)⁴. Dissolution of micronodules at intermediate depth of the core is observed by their lower abundance and smaller size⁹ resulting in the release of associated REE to pore waters. The diffused REE migrate upwards and are adsorbed by the oxyhydroxides in the upper oxic zone. The higher solid Mn phase, micronodule abundance and total

Table 1—Rare earth elements (ppm) concentration in the sediment core from the Central Indian Basin

Interval cm	La	Ce	Nd	Sm	Eu	Gd	Dy	Yb	Lu	Tot. REE	Ce/Ce*	La/Yb _n	La/Sm _n	Sm/Yb _n
0-4	34.6	94.1	41.7	11.3	2.7	10.3	10.3	4.8	0.8	210	1.17	0.62	0.56	1.11
4-6	32.6	95.2	43.4	10.6	2.2	11.2	7.1	4.2	0.6	207	1.18	0.66	0.56	1.19
6-8	32.3	94.0	42.1	9.9	2.2	11.1	7.0	3.8	0.6	203	1.20	0.72	0.59	1.23
8-10	30.9	97.0	37.9	10.4	2.5	10.7	6.5	3.9	0.6	200	1.33	0.68	0.54	1.25
10-12	26.9	78.8	33.5	8.6	2.1	9.2	5.6	3.5	0.6	169	1.22	0.65	0.57	1.15
12-14	24.5	72.5	30.4	8.7	1.9	8.5	5.1	3.1	0.5	155	1.25	0.67	0.50	1.33
14-16	27.3	82.3	37.2	8.7	2.2	9.1	5.9	3.8	0.6	177	1.21	0.61	0.56	1.08
16-18	32.5	89.6	37.9	9.5	2.3	10.1	6.5	4.2	0.6	193	1.20	0.66	0.62	1.06
18-20	31.7	84.2	35.0	8.9	2.1	10.1	5.7	4.0	0.6	182	1.19	0.68	0.65	1.04
20-24	31.3	87.4	37.5	9.3	2.2	9.8	6.1	3.9	0.6	188	1.20	0.69	0.61	1.12
24-26	32.2	87.8	37.9	10.8	2.2	9.9	6.1	3.9	0.7	191	1.18	0.70	0.54	1.30
26-28	35.0	85.7	45.9	11.9	2.6	12.2	7.4	4.8	0.8	206	1.00	0.62	0.53	1.17
28-30	37.9	91.4	46.1	12.3	3.0	13.0	7.7	5.1	0.9	217	1.04	0.63	0.56	1.13
30-32	35.6	86.9	47.8	11.2	2.9	12.1	7.3	4.8	0.8	209	0.99	0.63	0.57	1.10
32-34	34.3	84.7	45.6	11.4	2.8	12.0	7.4	4.6	0.8	203	1.01	0.63	0.54	1.16
34-36	31.8	85.0	39.1	11.4	2.8	11.9	7.3	4.6	0.8	194	1.13	0.60	0.50	1.16

Ce/Ce* - Ce-anomalies. n - North American Shale Composite value

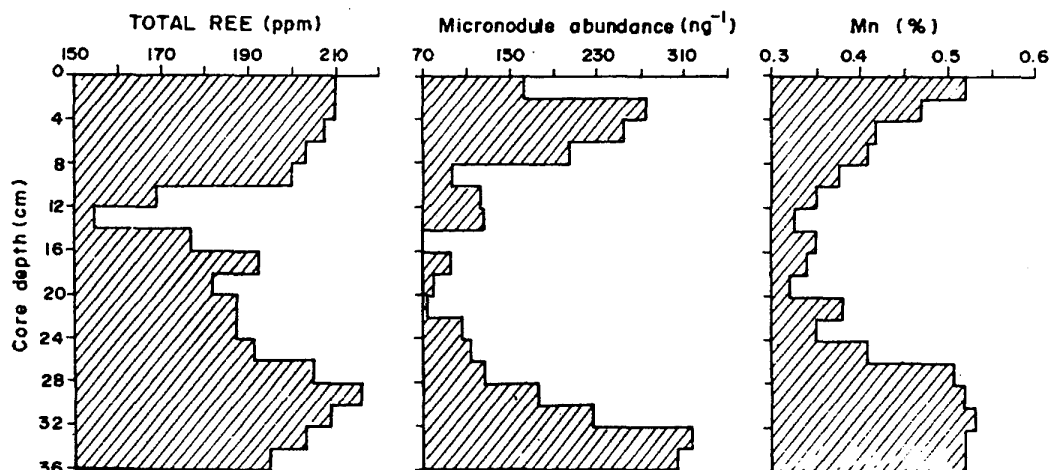


Fig.2—Distribution of REE content, micronodule abundance in the coarse fraction ($+63 \mu$)⁹ and solid Mn phase¹⁵ in the sediment core.

REE content at subsurface depth could be due to non-steady state diagenesis where excess oxygen diffuses downwards to oxidize Mn^{2+} deeper in the sediment core¹¹. Similar subsurface Mn spikes were also noticed in the eastern equatorial Atlantic sediments by Froelich *et al*¹¹. Based on pore water REE and trace metal data the behavior of REE has been related to redox cycling of Mn and Fe within

the sediment column¹². Dissolved REE concentration in the sediment pore waters decreases with increasing depth suggesting REE removal during diagenesis¹³. The vertical distribution of REE in seawater have suggested deep water enrichment which might be due to part of REE flux from pore waters released during early diagenesis¹⁴. The REE and solid Mn phase

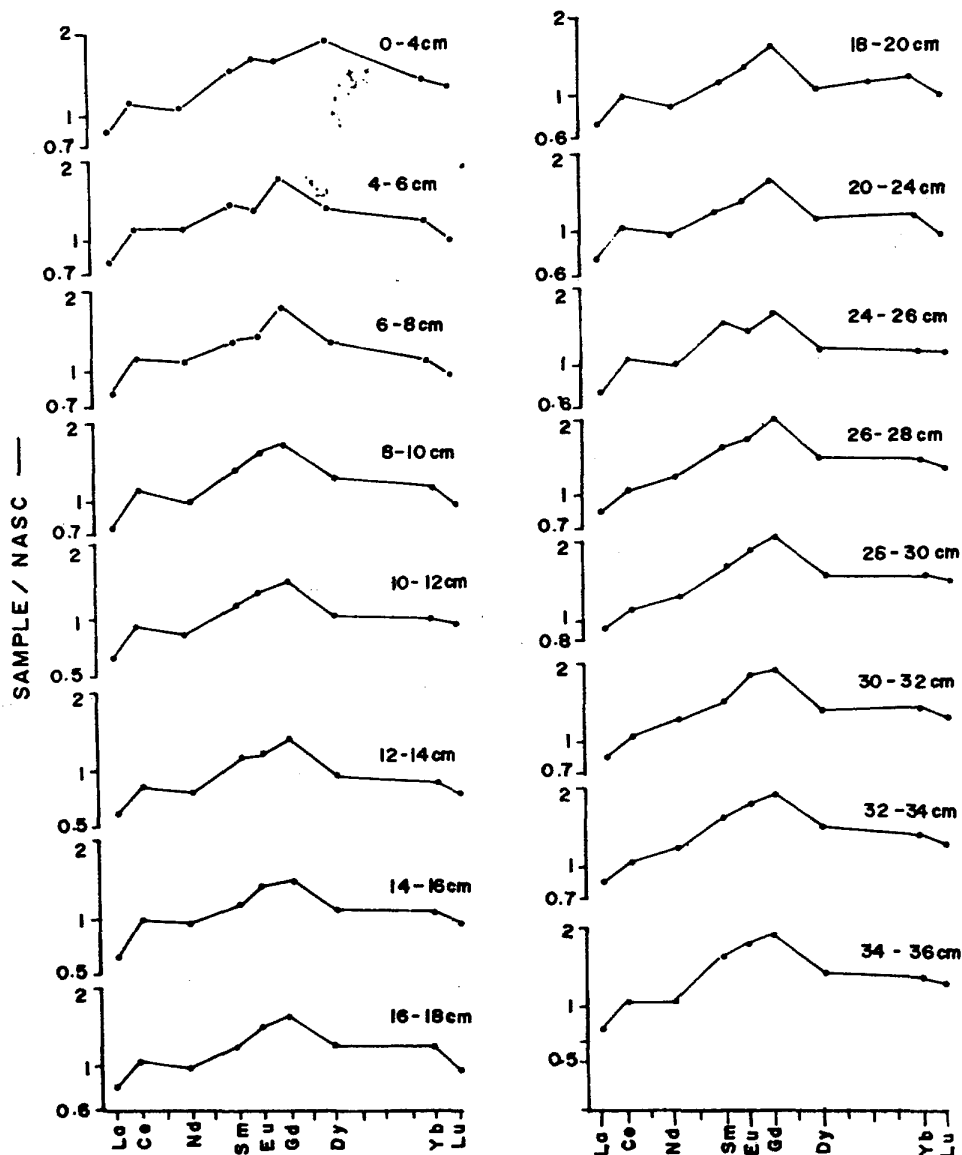


Fig.3—Shale-normalized REE pattern of sediment.

distribution pattern in a core is very similar because it is based on bulk sediment whereas micronodule distribution is not exactly similar to REE and Mn phase because micronodule abundance data is from coarse fraction ($+63\mu$). The similar depth distribution pattern of total REE, solid Mn phase and micronodule abundance suggest that micronodules are one of the major components controlling REE distribution in the bulk sediment.

Ce/Ce* anomalies are weak positive with a mean value of 1.2 and are similar to surface siliceous sediment from the same basin^{2,4,5}. The biogenic component in the siliceous sediment have negative Ce/Ce*^{6,15} anomalies hence, the positive Ce/Ce* anomalies in these sediments could be due to authigenic phase most probably oxyhydroxides. REE fractionation can be understood by normalizing REE concentration with North American Shale Composite (Fig.3) and by taking ratios of La/Yb_n, La/Sm_n and Sm/Yb_n. These ratios (Table 1) and shale-normalized patterns suggest enrichment of middle REE (MREE) over heavy REE (HREE) and light REE (LREE). These patterns are very similar to ferromanganese nodule and micronodule REE pattern from the CIB^{3,4,16,17} suggesting that the oxyhydroxide phase control the sediment REE pattern. The other components of the sediments such as siliceous ooze, zeolites and apatite have negative Ce/Ce* anomalies¹ and detrital clays have flat pattern¹ which are not observed in the present samples. Therefore, the influence of these components in the REE distribution may not be much significant. Though REE abundance changes with depth in the

sediment core their fractionation pattern remains same.

Acknowledgment

Authors are grateful to Dr. E. Desa, Director for the permission to publish and Mr.R.R.Nair for the encouragement. The financial support from Department of Ocean Development is acknowledged. This is NIO contribution No 2545.

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