

## Composition and Origin of Buried Ferromanganese Nodules from Central Indian Ocean Basin

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**Abstract** Five buried ferromanganese nodules were recovered at different depths of 167-169 cm (A), 172-174 cm (B), 228-230 cm (C), 328-330 cm (D) and 418-420 cm (E) in a 5 m sediment core from the siliceous sediment of Central Indian Basin (Lat 9°00' S, Long 76°00' E) at a water depth of 5260 m. These nodules were analysed for major, trace and rare earth element (REE) concentrations to understand their genesis and compare with the surface and buried nodules in the top 1 m of the sediment column from the same basin. Nodules A, B, C are of an early diagenetic (Mn/Fe ratio between 9.3 and 15.1), nodule D is of hydrogenetic (Mn/Fe ratio 1.6) and nodule E is of diagenetic (Mn/Fe ratio 3.0) origin. Total REE concentration ranges between 164 and 497 ppm (av-348 ppm) and is nearly 2 to 3 fold lower than the surface and buried nodules. REE are conveyed from the seawater to the nodules in association with a combined phase consisting of Fe - Ti - P. The shale (NASC) - normalized REE pattern displays a small convex pattern with a positive Ce-anomaly indicating an oxidized environment while, the presence of positive Eu-anomaly in nodules A, B and C probably suggest an aeolian dust. These buried nodules show a moderate middle and heavy REE enrichment (strong in nodules B and C) compared to light REE, but fractionation between middle and heavy REE is not very clear. It appears that not much significant post-depositional changes have occurred in these buried nodules.

**Keywords:** Buried Fe-Mn nodules, Chemical composition, Genesis, REE patterns, Central Indian Ocean Basin

### INTRODUCTION

Ferromanganese nodules generally occur at the sediment surface despite the slower growth rates of nodules (few mm / Ma) than the accumulation rate of associated sediment (few mm / ka). The possible mechanism for retaining the nodules at the sediment surface could be due to reworking of sediment by benthic organisms (Glasby et al 1982, Sanderson, 1985). Alternatively, due to small density difference between the nodules ( $1.96 \text{ g/cm}^3$ ) and associated sediment ( $1.33 \text{ g/cm}^3$ ) only a small upward force is enough to maintain nodules at the sediment - water interface (Glasby and Read, 1976). The nodules that are left behind during uplift are kept buried in the sediments (von Stackelberg, 1984). Usui and Ito (1994) suggested that nodules can be buried when upward lifting force exerted on nodules does not change significantly and when the sedimentation rate is greater than 5 m / Ma. Horn et al (1972) made a study on the occurrence and abundance estimation of buried nodules in the top few meters of sediment. Buried fossil nodules were observed at a few hundred meters below sea floor in DSDP/ODP cores (Glasby, 1978, Usui and Ito, 1994). However, occurrence of buried nodules in these cores were

suspected to be derived from the slumping of the upper sedimentary layer during drilling operations (McManus et al 1970, Cronan, 1973). Previous reports from the Central Indian Ocean Basin (CIOB) in the Indian Ocean, on buried nodules in the top 20 cm (Banerjee et al 1991) and top 1 m of sediment core (Pattan and Banakar, 1993) reveal that they are of hydrogenetic origin. However, there are no reports on the occurrence of buried nodules beyond 1 m depth of sediment column. Recently, the authors have recovered five buried nodules at different depths such as 167-169 cm (A), 172-174 cm (B), 228-230 cm (C), 328-330 cm (D) and 418-420 cm (E) in a 5 m long sediment core. The objective of the present study is to understand the genesis of buried nodules and compare their elemental concentrations with the surface and buried nodules in the top 1 m of sediment column from the same basin.

### MATERIALS AND METHODS

During *A. A. Sidorenko* (AAS-40) cruise, a 5 m long sediment core (GC-03) was recovered from the siliceous sediment in the CIB (Fig 1) at a water depth of 5260 m.

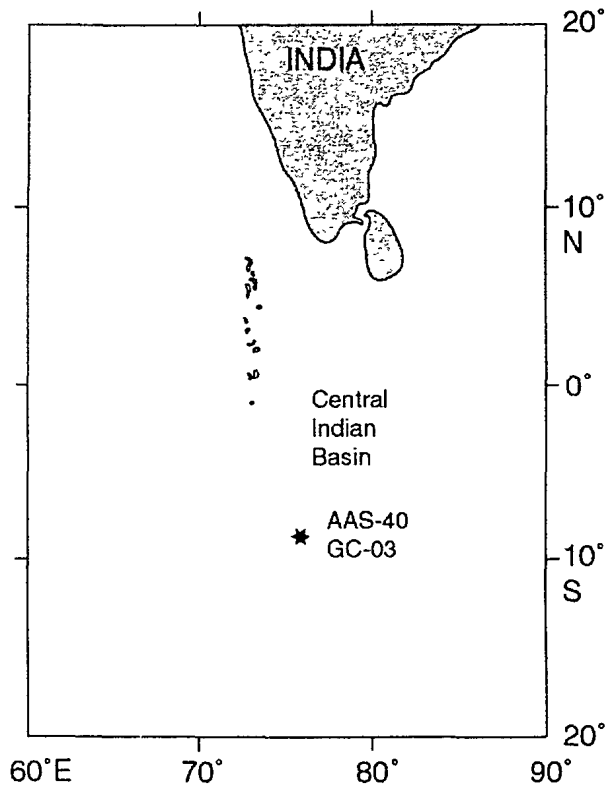


Fig.1. Map showing location of a sediment core (AAS-40/GC-03) where buried nodules were recovered at different depths.

(Lat: 9°00' S; Long: 76°00' E). Five buried nodules were recovered in this sediment core at different depths and their details are presented in Table 1 and shown in Fig.2. These buried nodules were washed, dried and only the oxide layers were powdered in an agate mortar. The powdered nodule layers were digested in a teflon beaker with an acid mixture of HF, HCl<sub>4</sub> and HNO<sub>3</sub>. Major elements were analysed

Table 1. Description of buried nodules at different depths in a sediment core

S. No.	Buried depth (cm)	Referred as	Description of buried nodule
1	167-169	A	5 cm x 2.5 cm, elliptical, rough surface texture
2	172-174	B	3 cm x 2.5 cm, elongated, rough surface texture
3	22G-228	C	2 cm x 2 cm, spheroid, rough surface texture
4	328-330	D	1.5 cm x 1 cm, elongated, mixed of smooth and rough surface
5	418-420	E	2 cm x 0.5 cm, elongated, mixed of smooth and rough surface

by Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) and trace and rare earth elements with Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) (for analytical details see Balaram and Saxena, 1988). To check the accuracy, international reference standard materials (P-1 and A-1) were used and the results are found to be within the acceptable limits.

## RESULTS

The elemental concentrations of the buried nodules are presented in Table 2 along with the mean concentration of surface (Jauhari and Pattan, 2000) and buried nodules in the top 1 m (Pattan and Banakar, 1993) from the same basin for comparison. Fe content of nodules A, B and C is low and ranges between 1.73 and 2.95 wt% whereas nodules D and E have high content of 8.49 and 6.25 wt% respectively. Similarly, Ti (0.10 to 0.14 wt%) and P (0.05 to 0.06 wt%) contents of nodules A, B and C are lower than nodules D

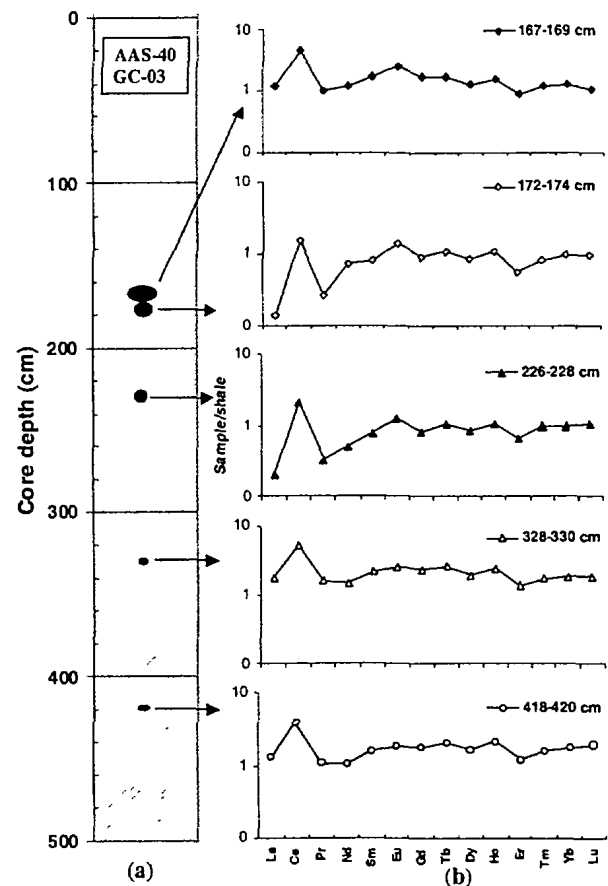


Fig.2. (a) Occurrence of buried nodules at different depths in a sediment core. (b) Shale (NASC)-normalized REE pattern of buried nodules.

(0.35 wt%; 0.078 wt%) and E (0.22 wt%; 0.075 wt%). On the contrary, Mn content is high in nodules A, B and C (26.05 to 27.52 wt%) as compared to nodule D (13.34 wt%) and E (18.75 wt%). Copper concentration is seen to follow the Mn trend. Thorium content shows considerable variation ranging between 4.24 and 48.4 ppm and behaves similar to Fe content. The total REE concentration ranges between 164 and 497 ppm with a mean of 348 ppm. Nodules B and C have lowest REE concentration close to shale (NASC) values. The shale-normalized REE patterns show a positive Ce and Eu-anomalies.

## DISCUSSION

The occurrence of larger buried nodules in the upper part and smaller nodules in the lower part of the sediment core suggest size of nodules decreases with the core depth (Table 1). Surface texture of nodules A, B and C is rough, whereas, nodules D and E are mixed with both rough and smooth surface. The source of Fe in the nodules is mostly from the hydrogenetic precipitation from the seawater. Very low concentration of Fe in nodules A, B and C suggests that these nodules might have been buried rapidly and thus

Table 2. Major, trace and REE concentrations in the buried ferromanganese nodules at different depth in a sediment core from Central Indian Ocean Basin

Element	167- 169 cm	172- 174 cm	226- 228 cm	328- 330 cm	418- 420 cm	Mean (n=5)	Nodules from top 1 m sed. core*	Surface Nodules #
Mn (%)	26.05	27.52	27.28	13.34	18.75	22.56	25.84	24.2(1119)
Fe (9b)	1.73	2.95	2.12	8.49	6.25	4.31	10.32	7.10(1119)
Ti (%)	0.10	0.14	0.12	0.35	0.22	0.19	0.34	0.43(37)
P (%)	0.051	0.056	0.050	0.078	0.075	0.063	0.19	0.17(33)
Sc (ppm)	—	419	481	169	101	293	—	—
V	1297	961	692	592	687	846	—	—
Cr	24.46	33.52	31.27	27.96	27.66	28.97	—	—
Co	270	700	580	1480	1080	822	1570	1100(1108)
Ni	5110	7210	6500	3490	9470	6356	10206	11000(1108)
Cu	13560	14380	14410	4050	4300	10140	8062	10400(1108)
Zn	450	630	660	370	770	576	1111	1200 (676)
Ga	19.73	27.85	29.52	20.39	32.34	25.97	—	—
Rb	26.10	182	159	53.54	28.75	89.88	—	—
Sr	598	649	556	602	514	584	—	679 (37)
Y	23.68	12.55	15.11	34.59	31.25	23.44	105	102(22)
Zr	62	573	487	359	171	330	—	—
Nb	24.60	15.69	11.58	17.37	12.00	16.25	—	—
Mo	782	753	733	418	634	664	527	570 (22)
Cs	1.07	0.65	0.81	1.01	1.01	0.91	—	—
La	38.60	4.52	6.53	56.63	41.88	29.63	126	132(37)
Ce	329	110	154	385	281	252	551	528(11)
Pr	7.83	2.05	2.52	12.48	8.81	6.74	~	33 (37)
Nd	35.64	24.13	16.93	48.52	35.15	32.67	144	147 (37)
Sm	9.49	4.55	4.46	12.19	8.92	7.92	31	33 (37)
Eu	3.05	1.75	1.61	3.06	2.30	2.35	74	8(33)
Gd	8.71	4.57	4.22	11.88	9.11	7.7	31.9	34(11)
Tb	1.41	0.98	0.90	2.20	1.72	1.44	—	5(37)
Dy	7.05	4.94	4.95	11.01	9.29	7.45	26.3	27 (33)
Ho	1.59	1.07	1.14	2.47	2.20	1.69	4.9	5(33)
Er	3.04	1.99	2.16	4.60	4.23	3.2	13.2	13(11)
Tm	0.58	0.44	0.46	0.88	0.84	0.64	—	2(11)
Yb	3.77	2.96	3.08	5.66	5.51	4.2	11.1	12(33)
Lu	0.54	0.45	0.49	0.85	0.85	0.64	1.8	2(37)
Hf	1.09	12.17	11.62	8.11	4.19	7.44	—	—
Ta	0.33	0.50	0.87	0.82	0.55	0.62	—	—
Pb	1116	800	—	914	1032	966	832	712(12)
Th	9.95	4.24	6.11	48.40	33.76	23.12	—	—
U	1.89	3.04	2.67	2.67	2.24	2.5	—	—

\* - Pattan and Banakar -1993, (n= 9). # - Jauhari and Pattan -2000. Value in the parenthesis is number of samples analysed. — data not available. Sc and downwards all values are in ppm.

were exposed for a short time to scavenge Fe from the seawater or might have been diluted by detrital material. On the other hand, nodules D and E appear to have been exposed for a longer time to seawater resulting in higher concentration of Fe (Table 2). Nodules A, B and C have higher Mn content than nodule D and E (Table 2) which might have been supplied from the underlying sediment pore water through diagenesis. As expected, Fe and Mn show an inverse relation ( $r = -0.97$ ). The Mn/Fe ratio of these nodules varies considerably from 1.6 to 15.1. Nodules A, B and C are of early diagenetic (Mn/Fe 9.34 to 15.1), nodule D (Mn/Fe 1.6) and E (Mn/Fe 3.0) are of hydrogenetic and diagenetic origin respectively. Previous studies of nine buried nodules in the top 1 m sediment column (Mn/Fe ratio  $< 3$ ) are inferred to be of hydrogenetic origin (Pattan and Banakar, 1993). Mn shows a positive correlation with Cu ( $r = 0.96$ ), Mo ( $r = 0.91$ ) and Ni ( $r = 0.89$ ), but the low content of Ni compared to Cu in these nodules is difficult to explain (Table 2). The presence of a combined colloidal Fe-Ti-P phase in these buried nodules ( $r = 0.98$ ) is similar to the earlier reports (Glasby et al. 1987; Pattan and Banakar, 1993). Fe, Ti and P content of these buried nodules are depleted nearly two fold while, Mn and Cu are in a similar range to that of surface and buried nodules from the same basin (Table 2).

The total REE concentration of the buried nodules ranges between 164 and 497 ppm with an average of 348 ppm. This is nearly a 2-3 fold lower when compared to surface and buried nodules (Table 2). Nodules B and C have REE concentration similar to shale (NASC) except for an enrichment of Ce and Eu. This suggests that the detrital material within the oxide layers has diluted REE in these two nodules. This is confirmed by a 2-4 fold enrichment of detrital elements such as Sc, Zr and Rb compared to nodules A, D and E (Table 2). REE in the nodules are supplied by the seawater through a combined phase consisting of Fe-Ti-P ( $r = 0.9$ ) (Glasby et al. 1987; Pattan and Banakar, 1993). The negative correlation of REE with Mn ( $r = -0.9$ ) suggests that there is no diagenetic supply of REE into these nodules (Nath et al. 1992; Pattan and Banakar, 1993). The shale-normalized REE patterns of all the nodules show a moderate positive Ce-anomaly while, nodules A, B and C show a weak positive Eu-anomaly (Fig.2). Further, nodules B and C shows that light REE such as La, Pr and Nd (except Ce) are even lower while middle and heavy REE's have concentration slightly more than the shale values. This suggests that REE are mostly supplied from the detrital

source in addition to the small contribution from the seawater in these two nodules.

Ce-anomaly has been calculated using the formula  $\log [Ce_{(n)}/(2/3 La_{(n)} + 1/3 Pr_{(n)})]$  where 'n' is shale value (Elderfield et al. 1981). Nodules exhibit a positive Ce-anomaly varying from 0.49 to 0.91 suggesting an oxidized environment (Goldberg, 1961). This is similar to the earlier reports from the CIB (Nath et al. 1992; Pattan and Banakar, 1993; Banakar and Jauhari, 1994; Jauhari and Pattan, 2000). The presence of Eu-anomaly could be due to hydrothermal or aeolian input (Elderfield, 1988). Nodules A, B and C shows a presence of Eu-anomaly (Fig. 2). The Eu-anomaly caused by the hydrothermal influence is characterized by a strong negative Ce-anomaly, high REE and trace element concentrations. The absence of negative Ce-anomaly, comparatively low REE and trace element concentration suggests Eu-anomaly in these nodules (A, B and C) is caused by aeolian dust. This indicates a strong wind carrying aeolian dust was active during the deposition of top ~3 m of sediment column in the CIB. Europium, compared to other REE members shows a moderate positive correlation with Fe-Ti-P ( $r = -0.4$ ), which confirms an additional source other than seawater. The shale-normalized REE patterns show a small convex shape suggesting middle REE (MREE) enrichment because precipitation of oxyhydroxides has the capability of promoting MREE enrichment (Grandjean-Lecuyer et al. 1993). To understand the fractionation pattern, we have used the ratios of  $(La_n/Yb_n)$ ,  $(Sm_n/Yb_n)$  and  $(La_n/Sm_n)$  where 'n' is shale value. From these ratios it is clear that all the nodules show HREE enrichment over LREE, which could be due to retention of seawater pattern (Elderfield and Greaves, 1982) and MREE enrichment over LREE. Fractionation between MREE and HREE shows that two nodules (A and D) show MREE enrichment over HREE whereas the remaining three nodules (B, C and E) show HREE enrichment over MREE. This suggests that there is no clear fractionation pattern between MREE and HREE. Probably some of the REE might have been mobilized after their burial. Therefore, the above observations indicate that buried nodules have not been significantly subjected to post-burial depositional processes.

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## References

- BALARAM, V. and SAXENA, V. K. (1988) Determination of rare earth elements (REE) in standard geological reference samples by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using indium as internal standard. First International Conference on Plasma Source Mass Spectrometry, (Abstract), Durham University, United Kingdom, 12-16 Sept. 1988, p.44
- BANAKAR, V.K. and JAUHARI, P. (1994) Geochemical trends in the sediments and manganese nodules from the part of the Central Indian Basin. *Jour. Geol. Soc. India.*, v,43, pp.591-598.
- BANERJEE, R., IYER, S.D. and DUTTA, P. (1991) Buried nodules and associated sediments from the Central Indian Basin- *Geo-Mar. Lett.*, v.11, pp.103-107.
- CRONAN, D. S. (1973) Manganese nodules in sediment cored during Leg.16. Deep Sea Drilling Project. *Int. Rep. DSDP.5:* 605-608.
- ELDERFIELD, H., HAWKESWORTH, C.J., GREAVES, M.J. and CALVERT, S.E. (1981) Rare earth element zonation in Pacific ferromanganese nodules. *Geochim. Cosmochim. Acta*, v,45, pp. 1231-1234.
- ELDERFIELD, H. and GREAVES, M.J. (1982) The rare earth elements in seawater. *Nature (London)*, v,296, pp.214-218.
- ELDERFIELD, H. (1988) The oceanic chemistry of the rare earth elements. *Phil. Trans. Royal Society London*. A325., pp.105-126.
- GLASBY, G.P. (1978) Deep-sea manganese nodules in the stratigraphic record: Evidence from DSDP cores. *Mar. Geol.*, v.28, pp.51-64.
- GLASBY, G.R. and READ, A.J. (1976) Deep-sea manganese nodules. *In:* K.H. Wolf (Ed.), *Handbook of Strata Bound and Stratification Ore deposits*. Elsevier, Amsterdam, pp.295-340.
- GLASBY, G.P., STOFFERS, P., SIOULAS, A., THIJSSSEN T. and FRIEDRICH, G. (1982) Manganese nodule formation in the Pacific Ocean; a general theory. *Geo-Mar. Lett.*, v.2, pp.47-53.
- GLASBY, G.P., GWOZDZ, R., KUNZENDORF, H., FRIEDRICH, G. and THIJSSSEN, T. (1987) The distribution of rare earth and minor elements in manganese nodules and sediments from the equatorial and SW Pacific. *Lithos.*, v.20, pp.97-113.
- GOLDBERG, E.D. (1961) Chemistry in the oceans. *In:* M. Sears (Ed.), *Oceanography*. Amer. Assoc. Adv. Sci.. Washington, D.C., v.7, pp.583-587.
- GRANDJE N-LECUYER, P., FEIST, R. and ALBARERDE, F. (1993) Rare earth elements in old biogenic apatite. *Geochimica Cosmochimica Acta.*, v. 53, pp 2507-2514.
- HORN, D. R., HORN, B. M. and DELACH, M.N. (1972) Distribution of ferromanganese deposits in the world ocean. *In:* D.R. Horn (Ed.), *Ferromanganese Deposits on the Ocean Floor*. NSF. Washington, D.C. pp.9-18.
- JAUHARI, P. and PATTAN, J.N. (2000) Ferromanganese nodules from the Central Indian Ocean Basin. *In:* D.S. Cronan (Ed.), *Hand Book of Marine Mineral Deposits*, CRC Press, pp. 171-195.
- MCMANUS, D.A., WEESER, O., VON DER BORCH, C.C., VALUER, T. and BURNS, R.E. (1970) Regional aspects of Deep Sea Drilling in the northeast Pacific. *Int. Rep. DSDP.*, v.5, pp.621-636.
- NATH, B.N., BALARAM, V., SUDHAKAR, M. and PLUGER, W.L. (1992). Rare earth element geochemistry of ferromanganese deposits from the Indian Ocean. *Mar. Chem.*, v.38, pp. 185-208.
- PATTAN, J.N. and BANAKAR, V.K. (1993) Rare earth element distribution and behaviour in buried manganese nodules from the Central Indian Basin. *Mar. Geol.*, v.112, pp.303-312.
- SANDERSON, B. (1985) How bioturbation supports manganese nodules at the sediment-water interface. *Deep Sea Res.*, v.32, pp.1281-1285.
- USUI, A. and ITO, T. (1994) Fossil manganese deposits buried within DSDP/ODP cores, Legs 1-126. *Mar. Geol.*, v.119, pp.111-136.
- VON STACKELBERG, U. (1984) Significance of benthic organisms for the growth and movement of manganese nodules, Equatorial North Pacific. *Geo-Mar. Lett.*, v.4, p .37-42.

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