

Geochemistry of deep-sea sediment cores from the Central Indian Ocean Basin

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Four sediment cores from the Central Indian Ocean Basin (CIOB) were studied to characterise the coarse fraction ($< 63 \mu$), transition metal and major oxide contents. Transition metals (Mn, Cu, Ni, Zn) show enrichment towards the surface, thought to be of diagenetic origin. Metals are supplied by upward migration from a suboxic to anoxic zone at an intermediate depth of 12-35 cm below the sediment-water interface in all the cores. Buried maxima in transition metal concentration at depth of 26-55 cm below the sediment-water interface may represent relict enrichments formed prior to the formation of suboxic to anoxic zone. R-mode factor analysis suggests that detrital and diagenetic/hydrogenous components are the two main sources of elements in these sediments. The terrigenous index factor $[Al]/(Al + Fe + Mn)$ showed its maximum influence as far south as $14^{\circ}S$ from approximately 140 to 100 ky BP (last interglacial maxima). This might be related to discharge of large quantity of sediments by Ganges and Brahmaputra rivers during intensive monsoon in the Asian sub-continent during that period.

The process of ferromanganese nodule growth by early diagenetic remobilization of metals to the sediment-water interface is well established^{1,2}. The process of diagenesis in marine sediments may be recognized by studying the concentration profiles of redox-sensitive metals in sediment cores. Post-depositional remobilization of transition metals in deep-sea sediment cores from the Pacific²⁻⁵, Atlantic⁶ and Indian⁷ oceans was reported. Some of the sediment cores from the present work have been analysed for pore-water nutrients⁸ and oxidation states of manganese⁹ (O/Mn). The Ganges-Brahmaputra input into the Central Indian Ocean Basin (CIOB) has been recognized from clay mineral distribution^{10,11} and from surface sediment compositional data¹². Detailed clay mineralogy of piston cores and ODP Leg 116 in the northeastern Indian Ocean suggests that weathered origin of clay minerals are from the denudation of the Himalayas¹³⁻¹⁵. The objectives of the present work are to study the distributional pattern of the coarse fraction, transition metals and major oxide contents in sediment cores and their implications in understanding the growth of ferromanganese nodules. Further, an attempt has been made to trace the influence of subsurface terrigenous input to the CIOB.

Materials and Methods

Four sediment cores (Table 1) were retrieved

during different cruises from Central Indian Ocean Basin (Fig. 1). Cores 247 and 54 were from the northern part of the basin near to a terrigenous influenced material from Ganges-Brahmaputra river and were devoid of manganese nodules and sediment texture is silty clay to clayey silt. Cores 226 and 657 were from the southern part of the basin and are associated with siliceous sediments where manganese nodules are present at the sediment surface and sediment texture is clayey silt. Core lithology shows that cores top ($\sim 0-10$ cm) and the

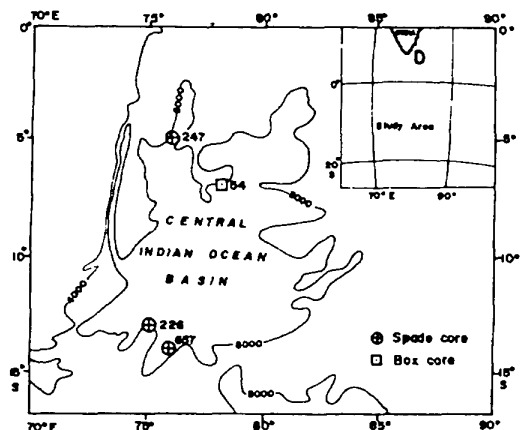


Fig. 1—Schematic map showing the location of sediment cores

Table 1—Details of the sediment cores from Central Indian Ocean Basin

Core no	Lat. (S)	Long. (E)	Water depth (m)	Type of corer	Core length (cm)
SK/247	5° 00'	76° 00'	5170	Spade	36
NR/54	7° 00'	78° 15'	5200	Box	70
SK/226	13° 08'	75° 01'	5270	Spade	30*
SK/657	14° 00'	76° 00'	5050	Spade	36*

* Manganese nodules present on the core top

base have moderate to dark brown sediment and at intermediate depth (~10-20 cm) show intercalations indicating bioturbation except core 54. The sediment cores were subsampled at 2 cm intervals and core logging was done immediately after collection. In the laboratory, the sediments were oven dried (100°C), washed to remove salt and the coarse fraction (> 63 µm) was obtained by sieving 8-10 g of dried sediment. Digestion of bulk sediments was carried out; and Si, Al and Ti were analysed in spectrophotometer¹⁶ (Beckman U-6). Sediments were digested¹⁷ and analysed for Ca, Mg, Na, K, Mn, Fe, Cu, Ni and Zn using atomic absorption spectrometer (Perkin Elmer-5000). USGS rock standards (DNC-1, BIR, W-2) were used as standards. The precision of the data is ± 2.5 to 5.4% for the elements analysed. R-mode factor analysis was also made¹⁸.

Results and Discussion

Coarse fraction—The coarse fraction (> 63 µm) of the sediment cores (Fig. 2) comprises radiolarians (> 95%), micronodules, fish teeth, volcanic glass, detrital quartz and rarely corroded foraminifera tests. A few of the radiolarian and fish teeth were coated with stains of ferromanganese oxide. The coarse fraction content (wt%) varies from 0.13 to 4.75%. Core 247 has the lowest coarse fraction content (0.11 to 0.42%) and core 54 has a low coarse fraction (<2%) component throughout its length except between 30-35 cm where it is maximum (3.92%). It may be due to high terrigenous input. In the southern part of the basin, core 226 has a fluctuating (1.6 to 3.5%) coarse material and core 657 has a maximum (4.18%) content at 18-20 cm depth. The low coarse fraction (av. 0.77%) content in the northern cores (247 and 54) may be due to clay supplied from Ganges and Brahmaputra rivers, while in the southern cores high content of coarse fraction (av. 2.43%) may be due to higher biogenic productivity. Marchig and Gundlach¹⁹ observed maxima in the coarse fraction content in the top of the cores and a gradual decrease with the depth of cores

from the Central Pacific which is in contrast to the present study. Core 226 shows the presence of pumice at intervals 10-12, 18-20 and 26-28 cm indicating a possible submarine volcanic source. The small cavities and pores in the pumice were invariably filled with micronodules. These infillings might be due to later diagenetic precipitations of ferromanganese oxyhydroxides.

Transition metals—The distribution of transition metals (Mn, Cu, Ni, Zn and Fe) in the sediments are shown in Fig. 2. The enrichment of transition metals observed at the top of the cores (except for Fe in the core 247) indicates oxic diagenesis¹ which may be due to the dissolution of manganese oxides at depths resulting their migration upwards by diffusion and then reprecipitation in well oxygenated conditions at the sediment-water interface³. Ferromanganese nodules collected from the top of sediment cores 226 and 657 has high contents of Mn (25-35%), Ni and Cu (1-1.5%) and low Fe (2.5-7.5%) and Co (0.05-0.15%)⁹. This indicates influence of diagenetic process in their origin. Higher biogenic silica (25-35%) in CIOB²⁰ reacts with Fe-oxyhydroxides to form Fe-rich montmorillonite²¹, releasing Mn, Cu and Ni which may be incorporated into the nodules, thus causing the enrichment of these metals in the nodules. Cores from the northern part of CIOB (247 and 54) have comparatively low transition metal contents at the core top (0.2 cm) (Fig. 2) than at the greater depths. This suggests probably the diagenetic process might have been hindered by terrigenous input from Ganges and Brahmaputra rivers¹²⁻¹⁴. Minimum solid phase transition metal contents are encountered at intermediate depths (12-35 cm). This indicates suboxic to anoxic zone. Interestingly, core lithology at this depth is mostly bioturbated⁸. Previous studies on these cores have shown low nitrate content, high organic carbon⁸ and comparatively lower manganese oxidation state⁹ at this depth. High organic carbon (0.4-0.6%) at intermediate depths might be the driving force for the transition metal remobilization. In the surface oxidized zone, Mn, Ni, Cu and Zn contents show 2-4, 2, 2-4, and 2-10 fold increase over their concentrations in the suboxic to anoxic zone respectively. The thickness of surficial oxidized zone varies from 14 to 30 cm below the sediment-water interface. The subsurface enrichment of transition metal (except Zn) at 26 to 55 cm below the sediment-water interface (except in core 247) may represent a period of diagenetic enrichment preserved within the sediment column prior to the formation of suboxic to anoxic zone after burial.

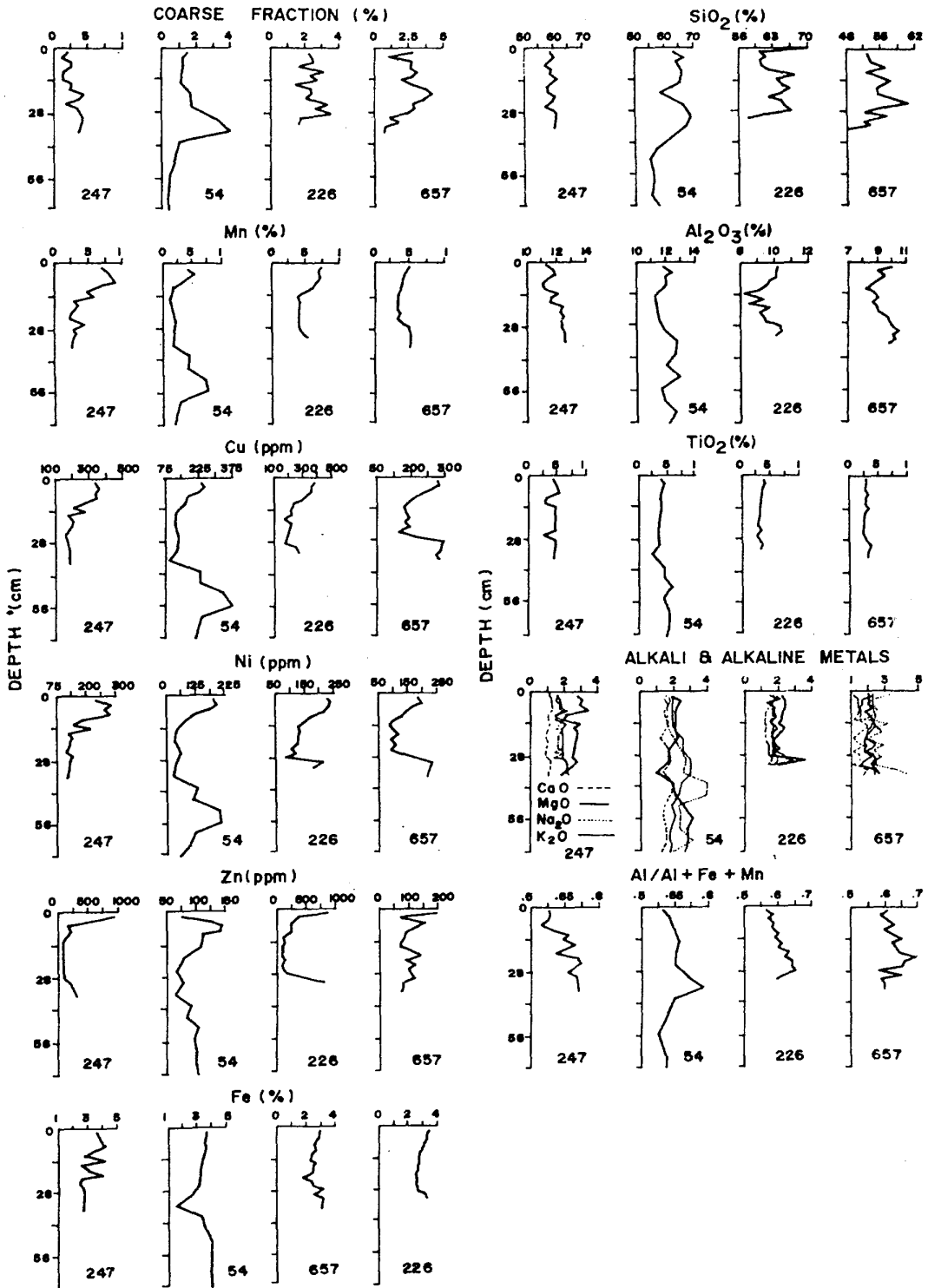


Fig. 2—Distribution of coarse fraction (%), Mn (%), Cu (ppm), Ni (ppm), Zn (ppm), Fe (%), SiO₂ (%), TiO₂ (%), Al₂O₃ (%), Alkali & alkaline earth metals (%) and Al/(Al+Fe+Mn) in the sediment cores (247, 54, 226 and 657)

The behaviour of Cu and Ni during early diagenesis is closely related to that of manganese²². The concentration profiles of Cu and Ni show similar trend to that of Mn throughout the core. The dissimilar behaviour of Zn compared to other transition metals at the lower levels of the sediment core is difficult to explain. Fe content varies from 1.85 to 4.27% and decreases from north to south. The higher Fe content (av. 3.31%) in the northern area may be due to supply of detrital material from distal Ganges deep-sea fan¹⁵. Fe in the southern area (av. 2.73%) was due to the presence of Fe-rich montmorillonite¹¹, which was formed by an interaction between iron-oxyhydroxides and biogenic silica during early diagenesis. The slight enrichment was observed in transition metals in southern than the northern cores. In the northern area, the environment is less oxidizing and have more clay supplies. In the south, environment is more oxidizing, low sediment accumulation rate⁷ (2 mm.ky⁻¹) and have high biological productivity²⁰.

Recent studies²³ on micronodule abundance, size and their chemical composition showed that northern cores has lower abundance and smaller size than the southern cores. Further their abundance is higher in core tops and at the sub-surface levels and minimum at intermediate depths. Their size has linear relation with the abundance. Transition metal concentration and micronodule abundance in the sediment cores show similar trend suggesting micronodule may control the concentration of transition metals.

Detrital elements—In the deep-sea, silica is being supplied from land-derived quartz and biogenic material. Biogenic silica is mostly supplied from diatom, radiolarian, sponge and silicoflagellate remains. In the present cores, the SiO₂ content varies from 48 to 68% and does not show any trend except at intermediate depth where it shows a slight increase

(Fig. 2). This may be due to an increase in terrigenous input. Pattan *et al.*²⁰ reported that approximately 33% of total silica is of biogenic origin in cores 247 and 54, and this proportion increases to 50% in cores 226 and 657 and was attributed to the higher surface productivity and better preservation. The higher content of SiO₂ (core 226) at 8-10, 18-20 and 26-28 cm is due to the presence of pumice. Silica does not show any correlation with Al and Ti indicating dominance of biogenic source. Alumina is supplied mainly from land-derived aluminosilicates, although a small portion may be contributed from weathered basalts and hydrothermal sources^{24,25}. Alumina (Fig. 2) varies from 8 to 13% and is higher in northern cores (11-13%) than southern cores (8-10%). This indicates a decrease in terrigenous input towards the south. Al shows good correlation with Ti ($r = .74$) and Fe ($r = .50$), suggesting a detrital origin (Table 2).

Titanium is mostly immobile in the marine environment²⁶, and is of continental origin with a small amount of it is contributed from the oceanic weathering of basalts²⁷. TiO₂ content (Fig. 2) varies from 0.28 to 0.44% and decreases from the northern cores to the southern cores, indicating a reduced terrigenous input. Titanium shows very good correlation with Fe ($r = .72$) and Mg ($r = .69$). It does not show much variation with depth. The presence of higher values of TiO₂/Al₂O₃ at intermediate depth suggests increased supply of terrigenous material.

Alkali and alkaline earth metals—The alkali and alkaline earth metals (Fig. 2) are mainly associated with the clay fraction. The source of sodium in the marine environment is from continental weathering of rocks. The average Na₂O content in the sediments is 1.97%. In deep-sea sediments biogenically-derived calcium depends mainly on the position of the carbonate compensation depth (CCD). Other sources include clay minerals and feldspars. In the

Table 2—Correlation matrix for the elements analysed

	Si	Al	Ti	Mn	Fe	Ca	Mg	Na	K	Cu	Ni	Zn
Si	1.00											
Al	.20	1.00										
Ti	.03	.73	1.00									
Mn	-.21	-.13	.13	1.00								
Fe	-.06	.49	.71	.43	1.00							
Ca	-.11	-.17	-.10	.12	.02	1.00						
Mg	-.23	.29	.69	.33	.56	-.17	1.00					
Na	-.53	-.00	-.10	-.05	-.11	.50	-.11	1.00				
K	.21	.22	.01	-.25	-.20	.33	-.04	.39	1.00			
Cu	-.35	-.05	.29	.92	.55	.14	.46	-.01	-.35	1.00		
Ni	-.28	-.02	.29	.91	.50	.12	.50	-.05	-.25	.91	1.00	
Zn	.02	.01	.11	.42	.25	.01	.24	-.20	-.14	.47	.45	1.00

N=67, Level of significance at 99.9% is 0.38

present study, all the cores were retrieved at a depth of 5050–5270 m and are located below CCD²⁸. This results in low CaO concentrations (av. 1.88%). However, a few corroded foraminifera were observed in the coarse fraction. Magnesium is present in the lattice of montmorillonite. The average MgO in the sediment cores is 2.26% and it shows good correlations with Ti ($r = .69$) and Fe ($r = .57$). The MgO content also decreases from north (2.36%) to south (2.05%) across the CIOB. Clay minerals are also the main source of potassium²⁹. The average potassium content is 1.88%. All the alkali and alkaline earth metals do not show much variation with depth in all the cores, except for slight increases near the core base (cores 226, 657 and 54).

Factor analysis—R-mode factor analysis has been carried out for the whole area (Table 3) for all the elements analysed along with coarse fraction and terrigenous index factor $[Al/(Al + Fe + Mn)]$. Columns were standardized and normalized before matrix preparation. All 5 factors were rotated with varimax criterion. The percent variation of factors 1 to 5 are 31.9, 26.1, 15.4, 15.4 and 11.2 respectively. Factor 1 shows detrital influence with higher positive loadings on Al, Ti, Fe, Mg and negative loadings of coarse fraction (Table 3) and can be designated as detrital factor. A good correlation also exists between Ti, Mg, Al and Fe (Table 2). In Factor 2 Mn, Fe, Ni, and Zn show higher negative loadings and positive loadings of terrigenous index factor, suggesting hydrogenous/diagenetic nature. Mn shows good positive correlation with Cu ($r = .92$), Ni ($r = .92$) and

with Fe ($r = .43$). Factor 3 has positive loadings of Si and is attributed to biogenic source. Association of Ca, Na and K is in Factor 4, which indicates clay minerals influence. Cu alone shows highest positive loading in Factor 5. Detrital and hydrogenous/diagenetic are the main sources to these sediments.

Terrigenous influence—The $[Al/(Al + Fe + Mn)]$ ratio has been used in the past to trace terrigenous input to sediments²⁷. This ratio is expected to decrease with increasing distance from the continent. The ratio varies from 0.5 to 0.77 with the depth in the cores, and is lower (< 0.65) near top and base of the cores and reaches maximum (0.65 to 0.77) at intermediate depth (Fig. 2). The sediment accumulation rate for cores 247, 226 and 657 were 4.2, 2 and 2 $mm.ky^{-1}$ respectively^{30,31}. Core 54 has an accumulating rate of 2.5 $mm.ky^{-1}$ based on radiolarian stratigraphy³². The sediment accumulation rate decreases from north to south. The oldest sediments encountered at cores 247, 54, 226 and 657 are ~ 86, 280, 180 and 180 ky BP respectively. The depth intervals showing maxima in terrigenous input, together with their corresponding age and the sediment accumulation rates are presented in Table 4. The $[Al/(Al + Fe + Mn)]$ ratio reaches maximum in cores 54, 226 and 657 at intermediate depths. These correspond to ages of ~ 140 to 100 ky BP and coincide with the last interglacial maxima³³. Hence, minimum biogenic²⁰ silica noticed during this period might be due to dilution by the terrigenous input into CIOB. Core 247 is comparatively closer to the continent and has a higher sediment accumulation rate (4.2 $mm.ky^{-1}$)³¹. Increased terrigenous input was seen in this core from 30 ky BP onwards. Prell and Kutzbach³⁴ reported intensified monsoons in the Asian sub-continent between 125 to 75 ky BP, as a result, rivers like Ganges and Brahmaputra would be expected to have discharged a considerable amount of sediment into the CIOB. Venkatratnam and Biscaye¹⁰ identified a terrigenous influence upto 10°S, based on the clay mineralogy and noticeable

Table 3—R-mode factor loading matrix of geochemical data along with coarse fraction and terrigenous index factor for all the sediment cores

Variable	Factors				
	1	2	3	4	5
SiO ₂	-0.045	0.085	0.942	-0.038	0.013
Al ₂ O ₃	0.829	0.259	0.250	-0.144	0.206
TiO ₂	0.922	-0.126	0.069	-0.018	0.029
Mn	0.068	-0.756	-0.203	0.079	0.386
Fe	0.724	-0.558	0.012	0.007	-0.380
CaO	-0.202	-0.328	-0.126	-0.827	-0.125
MgO	0.702	-0.325	-0.216	0.158	0.025
Na ₂ O	-0.019	0.203	-0.645	-0.649	0.032
K ₂ O	0.060	0.358	0.166	-0.745	0.168
Cu	-0.027	-0.105	-0.028	-0.083	0.915
Ni	0.184	-0.631	0.173	-0.079	0.023
Zn	0.047	-0.513	0.114	0.133	0.434
CF*	-0.892	0.055	0.072	-0.145	0.053
TIF**	-0.056	0.888	0.232	-0.135	0.055
Variance (%)	31.97	26.06	15.38	15.42	11.17

*CF—Coarse fraction

**TIF—Terrigenous index factor

Table 4—Details of sediment accumulation rates, depth of maximum terrigenous input and its corresponding age in the sediment cores

Core no.	Sediment accumulation rate ($mm.ky^{-1}$)	Depth of maximum terrigenous input (cm)	Age corresponding to max. terrigenous input by BP
247	4.2*	24	57
54	2.5 \$	35	140
226	2.0*	28	140
657	2.0†	22	110

* = Borole³¹, \$ = Gupta³², † = Banakar³⁰

terrigenous influence upto 8°S from chemical analyses of surface sediments¹². In this study, subsurface maxima in terrigenous influence upto 14°S has been noticed approximately between 140 to 100 ky BP.

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