

Geochemical behaviour of ferromanganese nodules from the central Indian ocean basin

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ABSTRACT

The fact that deep sea ferromanganese nodules and encrustations are an important source of industrial metals like nickel, copper, cobalt and manganese was established some three decade back^[1] but since then many investigations have been carried out in order to determine the quality of the composition and the coverage density in the nodules field so as to locate areas suitable for deep sea mining. They represent the largest group of ferromanganese deposits. Although such deposits occur in all the oceans but they have been reported mainly from the Pacific and to some extent from the Indian ocean. The Pacific has the mining sites mainly in the north and equatorial part because the southern parts are less deeper and are above the Carbonate Compensation Depth (CCD). The geological and oceanographic environments in these parts are very much similar to the Central Indian Ocean Basin, it is therefore expected that the central part of the Indian Ocean contains large deposits of ferromanganese nodules. However, this part of nodule bearing areas exhibit a considerable variation in the density of occurrence, i.e. kg. of nodules per sq. km. A complex interplay of factors like the degree of oxidation of the depositional environment, abundance of nucleating agents, proximity of source of elements, sedimentation rates in the area, bottom current activity and existence of benthic organisms, biological productivity in surface waters and many other yet unidentified phenomena determine nodule density.

The nodules are mainly authogenic and diagenetic therefore, the forces acting at the interface between them and the solutions from which these deposits precipitate are unquestionably important and possibly dominating factors in the growth of these deposits in various environments, but the nature and characteristics of these forces in determining where ferromanganese deposits will form and what composition will result is still to be traced. The only established observation is that such nodules contain appreciable quantities of first

row transition metals such as Cu, Ni, Co and Zn, besides Fe and Mn, though considerable variations exist among them.

The present study reveals that the trace element variations in the ferromanganese deposits from the Central Indian Ocean Basin have been related to the underlying sediment types which are the immediate source of metals for nodule growth. The concentrations of Mn, Cu and Ni are higher in the nodules occurring in Siliceous Sediments whereas those of Fe and Co are higher in the nodules occurring in the Red Clays. The geochemical statistical parameters reveal that (i) Ni and Cu are associated with Mn whereas (ii) Co with Fe, in both sediment types. However, the degree of correlation between all the elements is higher in the nodules from Red Clay sediments compared to the Siliceous Ooze area nodules.

The variations in the Mn/Fe ratio reflect variability in the composition of bottom water which in turn influences the type of underlying sediments and supply of metals to the deposits. The higher concentrations of Mn, Ni, and Cu in the nodules from Siliceous Sediment reflect the influence of early diagenesis of the biogenic components, whereas the higher Fe and Co contents in the nodules occurring in Red Clay areas have been because of their precipitation as authogenic oxyhydroxides.

Key words : Geochemical behaviour, Ferromanganese nodules, Indian ocean nodules.

INTRODUCTION

The ferromanganese deposits in the deep sea represent an important class of authogenic mineral deposits forming at the present time. They will certainly be a viable commercial source of metals in the next decade because they contain metals of vital interest to modern industry.

Nodules were first discovered in the Pacific Ocean by the HMS Challenger expedition in 1872-76. Since then they have been found widely distributed on the deeper parts of the seafloor throughout the world where the rate of sedimentation is very low. The nodules are potato like nodular deposits of manganese and iron oxides formed around a nucleus which acts as a core for the formation of the concentric nodule layers. The nucleus may contain weathered basaltic grain, clay or phosphatic material, dead animal remains or even the iron pieces of the sunken ships which clearly indicate that they are of the recent origin.

Their size is extremely variable, ranging from 0.5 cm to 25 cm in diameter but most commonly they average at 2 cm-4 cm. The largest nodule ever recovered weighed about 800 kg and was found entangled in an undersea telegraph cable while being salvaged about 500 km east of the Phillipines. Their shape is

also quite variable such as spheroidal to oblate, discoidal or prolate. But mostly they are asymmetrical, however perfectly symmetrical nodules are rare and nearly spherical shapes have been observed in smaller nodules (< 2 cm diameter) and in buried nodules recovered in cores. The shape of the nodules is determined by their growth pattern and is a reflection of gross internal structures and the proximity of the nodule to the mud water interface.

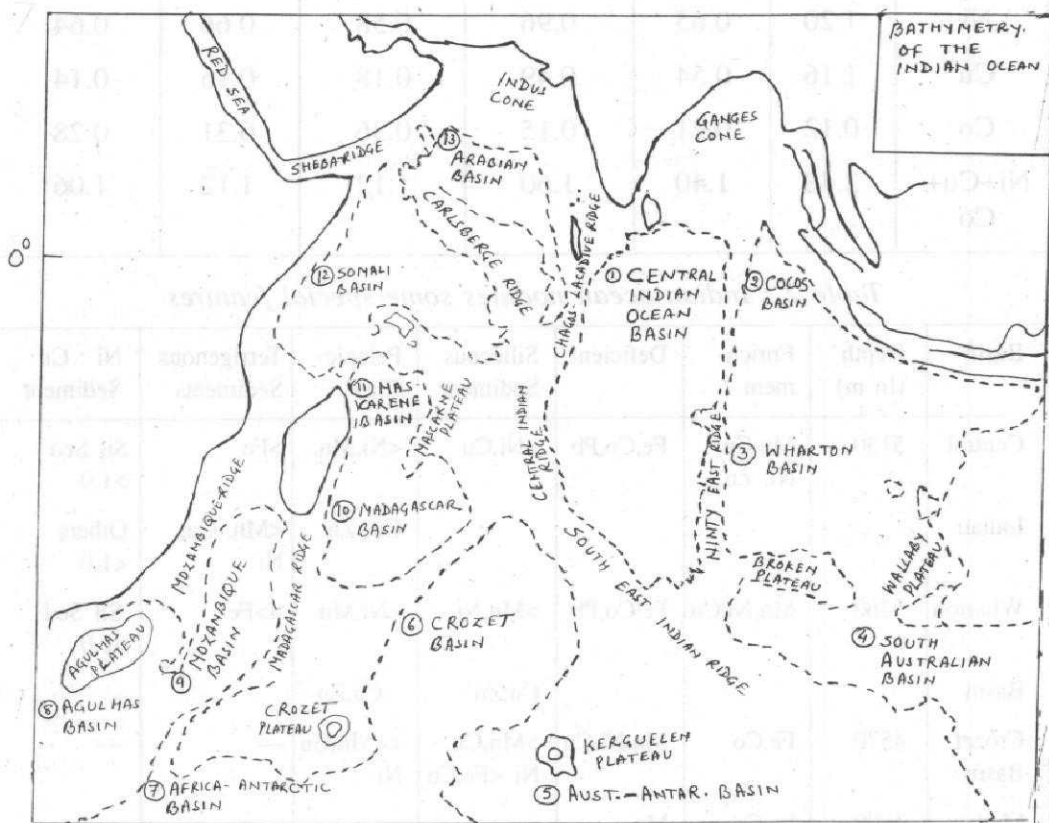


Fig. 1 : Bathymetry of the Indian ocean

Indian Ocean Nodule

Because of the bathymetric complexity of the Indian Ocean (Fig. 1), its nodules do not show much regional variation as in the Pacific but are often sharply differentiated from basin to basin,^[2]. Mineralogically, todorokite occurs principally in nodules that occur in basin areas, whereas delta MnO_2 occurs principally in ferromanganese encrustations and is more common in elevated areas. The average metal concentration of nodules from the different basins of the Indian Ocean is given in Table 1 and some special parameters are given in Table 2.

Table 1 : Average metal concentration of nodules from the Indian ocean

Wt.% of the Metals	Central Indian	Wharton Basin	S.Australia Basin	Seychelles Region	Agulhas Plateau	Moxambal Basin
Mn	26.10	19.80	22.60	25.00	15.90	20.40
Fe	7.60	11.20	10.90	16.50	14.10	18.90
Ni	1.20	0.65	0.96	0.58	0.66	0.64
Cu	1.16	0.54	0.49	0.18	0.15	0.14
Co	0.12	0.21	0.15	0.36	0.31	0.28
Ni+Cu+Co	2.48	1.40	1.60	1.12	1.12	1.06

Table 2 : Indian ocean nodules some special features

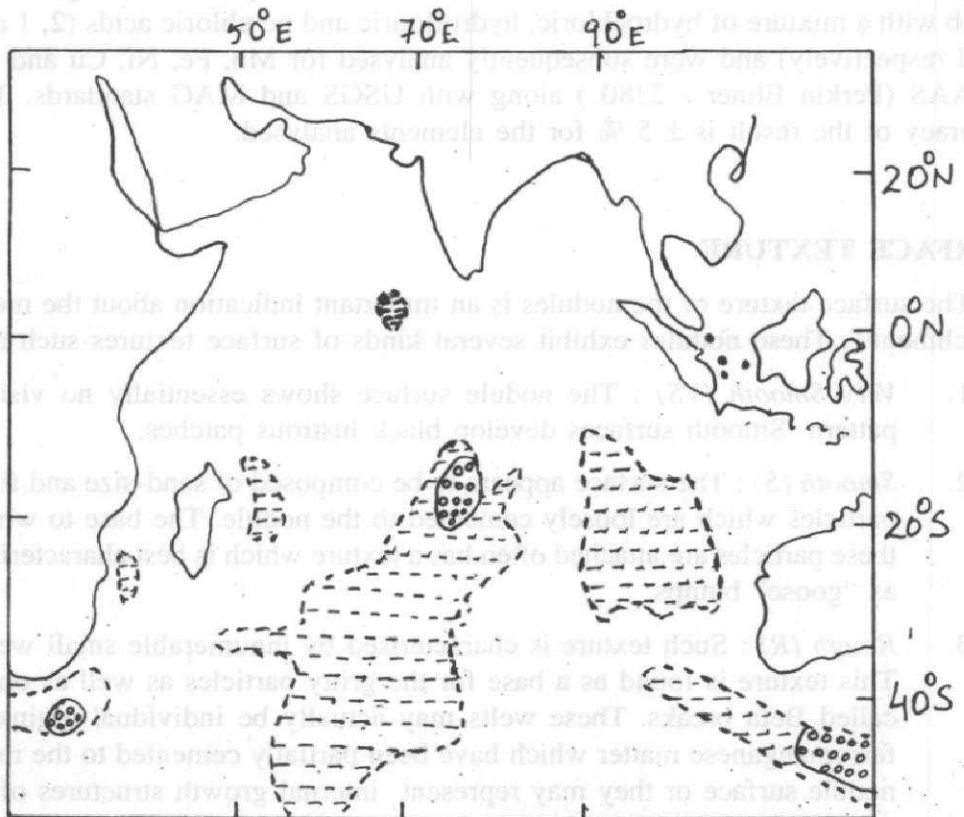
Basin	Depth (In m)	Enrichment	Deficient	Siliceous Sediment	Pelagic Clay	Terrigenous Sediments	Ni : Cu Sediment
Central Indian	5130	Mn,Cu, Ni, Zn	Fe,Co,Pb	>Ni,Cu	<Ni,Mn, Cu, Zn	>Fe	Sil Sed >1.0
Wharton Basin	5260	Mn,Ni,Cu	Fe,Co,Pb	>Mn,Ni, Cu,Zn	<Ni,Mn Cu,Zn	>>Fe	Sil Sed >1.0
Crozet Basin	4570	Fe,Co	Mn,Ni,Cu	>Mn,Cu, Ni <Fe,Co	<<Mn,Cu Ni	—	—
Mada-gascar Basin	4600	Fe,Co	Mn	—	—	—	—
Arabian Basin	4300	Fe	Mn,Ni,Cu	—	—	—	—

The most promising economic grade nodules in the Indian Ocean occur in the following basins which have been arranged according to decreasing values of (Mn+Cu+Ni) content.

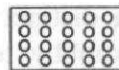
1. The Central Indian Ocean Basin (W of 90° E Ridge)
2. The South Australian Basin

3. The Wharton Basin (Keeling Basin, E of 90° E Ridge)
4. The Seychelles region (S Central Indian Ocean Basin - Crozet Basin)
5. The Agulhas Plateau region
6. The Mozambique Basin.

The other basins which are less important with respect to the metal concentrations have not been mentioned. Fig. 2 represents the nodule field area of the Indian Ocean.



Areas containing
nodules



Areas of nodules
with higher contents
of Ni, Cu and Co

Fig. 2 : Location of manganese nodule field in the Indian ocean

CENTRAL INDIAN OCEAN BASIN

Materials and Methods

The samples were carried on board by the "R V G A REAY -1" Cruise by extensive dredging and systematically operated Free Fall Boomerang Grab Sampler (Latitude 9-10 S and Longitude 77-78 E). From different dredge hauls and grabs 28 nodules were randomly collected and were studied for 2 size classes ($1 < 4$ cm and $2 > 4$ cm diameter). The other 18 nodules were provided by the NIO, Goa from the Red Pelagic Clay Sediments site of the Central Indian Ocean, which were also studied for the same size class. The aliquots were digested in bomb with a mixture of hydrochloric, hydrofluoric and perchloric acids (2, 1 and 2 ml respectively) and were subsequently analysed for Mn, Fe, Ni, Cu and Co on AAS (Perkin Elmer - 2380) along with USGS and MAG standards. The accuracy of the result is $\pm 5 \%$ for the elements analysed.

SURFACE TEXTURE

The surface texture of the nodules is an important indication about the metal enrichment^[3]. These nodules exhibit several kinds of surface textures such as :

1. *Very Smooth (VS)* : The nodule surface shows essentially no visible pattern. Smooth surfaces develop black lustrous patches.
2. *Smooth (S)* : The surface appears to be composed of sand-size and finer particles which are loosely cemented to the nodule. The base to which these particles are attached often has a texture which is best characterised as "goose" bumps.
3. *Rough (R)* : Such texture is characterised by innumerable small welts. This texture is found as a base for the gritty particles as well as on so called Beta breaks. These welts may actually be individual grains of ferromanganese matter which have been partially cemented to the main nodule surface or they may represent internal growth structures of an accreting manganese oxide band.
4. *Pisolitic or knobby or very rough (VR)* : These types of nodules develop a distinct equatorial zone often exhibiting a band characterised by a knobby texture. This zone appears to be composed of fused grains larger than 2 mm. The pisolitic band may face in any direction, either toward the gritty or toward the smooth surface of the nodule; it is however, always been confined to the equatorial zone of the nodule. Individual knob may reach as much as 2 cm in size.

RESULTS AND DISCUSSION

The transition metal concentrations of these nodules for the 2 sizes (< 4 cm and > 4 cm) along with their surface texture are presented in Table 3. It is evident from this table that the smaller nodules have higher concentration of Mn, Ni and Cu whereas the larger nodules have higher concentration of Fe. The concentration of Co does not match with any specific size class. Its value is almost constant in all the cases.

The interelement association of Mn, Ni and Cu are strongly positive ($r > 0.9$), whereas Fe correlation with Mn, Ni and Cu is markedly negative ($r > 0.7$). These observations match with those of the reported world ocean nodules^[4].

The higher Mn/Fe ratio (4.61 - 3.67 & 3.26 - 2.71 in the smaller and larger nodules of the Siliceous and Red Pelagic sediments respectively) indicate that the nodules have mixed origin, i.e. hydrogenetic as well as early diagenetic. Since the smaller nodules rest predominantly directly on the sediments or on the top layer of the sediments, the nodule growth is obviously caused by a supply of metals representing corresponding metal compounds in the near bottom sea water^[5,6]. Such type of nodule growth can be attributed to the hydrogenetic process which accounts for the accumulation by precipitation of colloidal particles in contact with near bottom seawater. Further, these nodules are supplied with metals from the interstitial water, i.e. they have been accumulated at early diagenetic conditions.

Table 3 also provides informations regarding average compositional ranges of nodules from 2 sedimentary facies of the Central Indian Ocean Basin, viz. Siliceous Sediment type and the Red Pelagic Clay type. The trace element variation in these nodules have been related to the underlying sediment types (diagenetic) which are immediate source of metals for nodule growth. The concentrations of Mn, Cu and Ni are higher in the nodules occurring in the Siliceous Sediments whereas those of Fe in the nodules occurring in Red Pelagic clays. This is because of the mobilization of trace metals from the decomposition of organic matter in the peneliquid layer of the Siliceous Sediments. The decomposition and gradual oxidation of relics of organic matter can produce a weak decrease of the redox values in pelagic sediments^[5,7-9]. Due to highly oxidising condition in deep seawaters, the redox values in the pore water of the peneliquid sediment layer are also relatively high^[5]. This geochemical fractionation separates Mn from Fe causing an upward migration of Mn ions^[10]. The dissolved Mn is reprecipitated at increasing redox values. The Siliceous Sediment is also conducive for the enrichment of Cu, and Ni because of the prevalent biogenic activity^[11]. Their enrichment depends upon the supply of metals available and on conditions in the

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Table 3 : Composition of 2 facis of nodules from the central Indian ocean basin for 2 size classes

Nodules from silicious sediments

(A) Less than 4 cm diameter class

S. No.	Surface Texture	Mn	Fe	Concentration, %			Mn/Fe
				Co	Ni	Cu	
1	R	28.20	6.10	0.13	1.30	1.28	4.63
2	R	28.70	6.30	0.14	1.28	1.21	4.56
3	VR	29.40	5.90	0.12	1.28	1.27	4.98
4	VR	30.28	5.80	0.12	1.40	1.39	5.22
5	VS(min)	26.35	7.00	0.14	1.15	1.18	3.76
6	VS	26.95	7.10	0.12	1.15	1.17	3.80
7	VR	30.18	6.01	0.12	1.30	1.35	5.02
8	VR	30.42	5.88	0.12	1.20	1.38	5.17
9	S	27.50	6.20	0.14	1.15	1.15	4.44
10	VR	29.20	5.94	0.13	1.28	1.20	4.92
11	VR	30.42	5.90	0.12	1.26	1.30	5.16
12	S	27.65	7.80	0.13	1.12	1.20	3.54
13	R	29.40	7.70	0.15	1.15	1.17	3.82
14	VR(max)	32.50	5.99	0.12	1.28	1.32	5.43
15	VR	30.20	6.11	0.12	1.26	1.34	4.94
16	S	26.90	7.10	0.12	1.15	1.16	4.40
Mean		29.02	6.43	0.13	1.23	1.25	4.61

(B) More than 4 cm diameter class

S. No.	Surface Texture	Mn	Fe	Concentration, %			Mn/Fe
				Co	Ni	Cu	
1	VS(min)	22.90	8.54	0.12	0.90	1.10	2.68
2	R	27.50	6.88	0.15	1.15	1.15	4.00
3	R	27.88	6.95	0.14	1.16	1.14	4.01
4	VR	29.19	6.72	0.12	1.13	1.20	4.34
5	VR(max)	29.40	6.75	0.14	1.14	1.16	4.36
6	S	26.20	7.90	0.13	1.10	1.05	3.32
7	S	26.80	8.40	0.13	1.14	1.08	3.19
8	S	26.70	6.99	0.11	1.10	1.20	3.82
9	R	26.10	8.00	0.13	1.20	1.19	3.26
10	R	27.50	6.99	0.13	1.20	1.25	3.93
11	S	26.50	8.35	0.13	1.12	1.07	3.17
12	R	27.40	6.95	0.15	1.14	1.13	3.94
Mean		27.01	7.45	0.13	1.12	1.14	3.67

Contd.....

Nodules from red pelagic clay
(A) Less than 4 cm diameter class

S. No.	Surface Texture	Concentration, %				Mn/Fe Cu	
		Mn	Fe	Co	Ni		
1	VS(min)	18.08	6.30	0.10	0.60	0.40	2.87
2	S	19.05	6.45	0.11	0.78	0.50	2.95
3	R	22.05	8.12	0.12	0.90	0.60	2.72
4	R	24.03	8.00	0.12	0.90	0.66	3.00
5	R	25.64	7.90	0.11	0.92	0.70	3.25
6	VR(max)	29.13	7.20	0.12	1.04	1.05	4.05
7	VR	26.12	7.00	0.11	1.19	1.05	3.73
8	S	20.11	6.00	0.10	0.80	0.69	3.35
9	VR	25.11	6.94	0.11	0.84	0.90	3.62
10	R	24.13	7.12	0.11	0.90	0.92	3.39
11	S	20.12	6.34	0.12	0.84	0.80	3.17
Mean		23.05	7.03	0.11	0.88	0.75	3.28

(B) More than 4 cm diameter class

S. No	Surface Texture	Concentration, %					Mn/Fe
		Mn	Fe	Co	Ni	Cu	
1	VS(min)	16.22	8.41	0.11	0.84	0.78	1.92
2	VR(max)	24.66	6.14	0.13	1.02	1.08	4.01
3	VR	24.42	7.15	0.14	0.90	0.85	3.42
4	R	22.12	6.90	0.12	0.84	0.80	3.21
5	R	20.85	7.00	0.11	0.80	0.84	2.98
6	S	19.74	8.44	0.12	0.68	0.72	2.34
7	R	18.10	7.42	0.12	0.80	0.74	2.44
Mean		20.85	7.35	0.12	0.80	0.74	2.90

enrichment of the particular mineral structures. The bond strength of divalent cations in the migration are :



Thus in these two facies of nodules the environment of deposition actually turns out to be much less significant than sediment type in accounting for variations in the Transition metals. Nodules richer in the transition metals are rough textured and apparently grow with the surface sediment layer and account for their diagenetic growth.

CONCLUSION

The main parameters of determining the environment of growth of deep sea nodules are

- (a) the local sedimentation rate
- (b) the sedimentary facies related to CCD and biological productivity in surface waters
- (c) the relative topography and
- (d) the bottom current activity.

The variation of these parameters result in the mixed type of nodule growth:

Hydrogenetic - caused by direct precipitation of colloidal compounds from near bottom seawater, which leads to nodule substance in δMnO_2 and $\text{FeOOH} \cdot x \text{H}_2\text{O}$.

Early diagenetic - caused by remobilization of metals and subsequent precipitation in the peneliquid layer which leads to nodules richer in Mn, Ni and Cu content. Todorokite is the main mineral phase in this case. The main factor controlling the intensity of early diagenesis is the supply of organic matter in oceanic surface waters. The variations in the Mn/Fe ratio reflect variability in the composition of the bottom water which in turn influences the type of underlying sediments and supply of metals to the deposits.

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