

Size, surface texture, chemical composition and mineralogy interrelations in ferromanganese nodules of central Indian Ocean

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Fiftyseven ferromanganese nodules, classified into 3 size class (< 4, 4-6 and 6-8cm diam.), from the siliceous sediments of central Indian Ocean were analysed for transition metals and representative sample from each size class for mineralogy. Smaller (< 4 cm diam.) nodules are invariably rough and very rough and spherical; they have higher concentration of Mn, Ni and Cu. The intensity of todorokite reflection decreases in higher size (> 4 cm diam.) class. These observations suggest that the smaller nodules appear to have been influenced more by diagenetic processes than the larger nodules.

Heterogeneity in distribution and chemical composition of ferromanganese nodules of the world Oceans are well known. Heye¹ has noticed relationship between size and chemical composition of nodules in a small area of Pacific Ocean. The present study on 3 size classes of ferromanganese nodules from central Indian Ocean with variation in their surface texture is made to understand the relationship between size, mineralogy and chemical composition.

Materials and Methods

The study area is covered by siliceous sediments of the central Indian Ocean (lat. 13°S and long. 78°E). Extensive dredging was carried out onboard *M V Skandi Surveyor*. From different dredge hauls 57 nodules were randomly selected representing 3 size class (< 4, 4-6 and 6-8 cm diam). The aliquots were digested in a mixture of hydrochloric, hydrofluoric and perchloric acids (5, 2.5 and 5 ml respectively) on a sand bath and subsequently analysed for Mn, Fe, Ni, Cu and Co on AAS (Perkin Elmer-5000) alongwith USGS-A(1) and NIO-2388 nodule standards. The accuracy of the results is $\pm 5\%$ for the elements analysed. Mineralogy has been studied for representative sample from different size class on Philips X-ray diffractometer using Ni filter, CuK α radiation with a scanning speed of $2^\circ 2\theta \text{ min}^{-1}$.

Results and Discussion

Transition metal concentrations for nodules analysed are presented in Table 1. Mn content is higher (~ 30%) in smaller nodules (< 4 cm diam.) and decreases (~ 23%) in larger (> 4 cm diam.). On the other hand Fe increases with size. Ni and Cu also show an

Table 1—Transition metal concentrations in ferromanganese nodules of 3 size classes

Sr. No.	Surface texture	Concentration (%)					
		Mn	Fe	Co	Ni	Cu	Mn/Fe
< 4 cm diam. class							
1	r	28.26	6.38	0.14	1.32	1.29	4.4
2	r	28.85	6.25	0.13	1.26	1.21	4.6
3	vr	30.76	5.86	0.12	1.26	1.29	5.3
4	vr	30.80	5.83	0.13	1.31	1.31	5.3
5	r	29.45	7.75	0.15	1.15	1.17	3.8
6	vr	32.45	6.05	0.13	1.35	1.47	5.4
7	s	26.98	5.73	0.13	1.10	1.23	4.7
8	r	29.42	7.13	0.14	1.21	1.29	4.1
9	vr	30.08	5.63	0.12	1.20	1.38	5.3
10	r	29.29	6.63	0.14	1.22	1.39	4.4
11	vr	30.30	5.89	0.12	1.41	1.42	5.1
12	r	27.64	6.23	0.14	1.22	1.32	4.4
13	r	28.74	5.64	0.12	1.17	1.31	5.1
14	r	29.96	7.15	0.14	1.22	1.34	4.2
15	r	30.16	6.01	0.12	1.29	1.33	5.0
16	r	33.61	8.40	0.15	1.10	1.11	4.0
17	r	29.63	6.73	0.13	1.19	1.28	4.4
18	r	29.27	6.15	0.12	1.20	1.30	4.8
19	s	27.94	9.18	0.16	1.06	1.10	3.0
20	r	29.13	6.37	0.13	1.26	1.12	4.6
21	r	29.35	6.19	0.13	1.29	1.24	4.7
22	r	29.27	5.89	0.13	1.31	1.29	5.0
23	r	27.68	7.84	0.13	1.12	1.20	3.5
24	s	26.96	7.10	0.12	1.14	1.17	3.8
25	r	27.65	6.14	0.14	1.15	1.14	4.5

contd

Table 1—Transition metal concentrations in ferromanganese nodules of 3 size classes—*contd*

Sr. No.	Surface texture	Concentration (%)					Mn/Fe
		Mn	Fe	Co	Ni	Cu	
< 4 cm diam.class							
26	vr	29.84	6.04	0.13	1.28	1.31	4.9
27	r	26.96	7.10	0.12	1.14	1.17	4.5
28	r	27.24	5.87	0.14	1.19	1.14	4.6
29	s	27.89	8.36	0.15	1.08	1.05	3.3
30	r	28.24	6.02	0.12	1.22	1.24	4.7
31	vr	29.00	5.78	0.12	1.22	1.27	5.0
32	vr	30.76	5.86	0.12	1.26	1.29	5.3
33	vr	30.80	5.83	0.13	1.31	1.31	5.3
34	vr	29.52	6.06	0.13	1.22	1.24	4.9
Mean		29.22	6.50	0.13	1.21	1.25	4.6
±SD		1.51	0.89	0.01	0.08	0.09	0.06
4-6 cm diam. class							
1	s	26.82	6.56	0.12	1.09	1.18	4.1
2	s	26.82	6.96	0.11	1.10	1.19	3.9
3	s	27.55	6.75	0.14	1.18	1.26	4.1
4	r	27.98	7.43	0.14	1.18	1.24	3.8
5	s	26.88	8.41	0.14	1.15	1.14	3.2
6	r	28.17	8.09	0.13	1.20	1.19	3.5
7	vs	22.50	10.00	0.14	0.98	0.97	2.3
8	vr	29.09	6.56	0.12	1.13	1.23	4.4
9	vs	23.09	6.71	0.11	1.03	1.09	3.5
10	r	26.09	6.12	0.12	1.09	1.06	4.1
11	r	27.60	6.91	0.15	1.15	1.15	4.0
12	r	27.60	6.96	0.13	1.20	1.27	4.0
13	vr	28.63	5.88	0.11	1.16	1.24	4.8
14	s	26.21	7.95	0.13	1.06	1.02	3.3
15	vs	26.60	11.90	0.18	0.81	0.65	2.2
Mean		26.7	7.54	0.13	1.10	1.12	3.7
±SD		1.87	1.58	0.01	0.10	0.15	0.7
6-8 cm diam. class							
1	s	25.50	8.50	0.14	1.03	1.08	3.0
2	s	24.65	7.13	0.14	0.98	1.01	3.5
3	r	26.98	8.12	0.14	1.05	1.12	3.3
4	vs	22.29	8.95	0.15	0.89	0.89	2.5
5	vs	19.21	11.25	0.16	0.69	0.66	1.7
6	s	26.69	8.49	0.13	1.07	1.07	3.1
7	vs	29.26	8.37	0.14	0.80	0.75	2.3
8	s	21.01	6.60	0.11	0.96	0.87	3.2
Mean		22.94	8.42	0.13	0.93	0.93	2.8
±SD		2.91	1.38	0.01	0.13	0.16	0.6

Surface texture: vr = veryrough, r = rough, s = smooth and vs = very smooth

enrichment in the smaller nodules, whereas Co does not show any relation with size. Average Mn/Fe ratio is maximum in < 4 cm nodules (4.58), decreases in 4-6 cm class (3.68) and is minimum in 6-8 cm nodules (2.83). The interelemental association of Mn, Ni and Cu are strongly positive ($r > 0.9$) while, Fe correlation with Mn, Ni and Cu is negative ($r > 0.7$). These observations are similar to those reported for world ocean nodules. Mn/Fe ratio (Table 1) indicates that, nodules studied have been accreting under the early diagenetic influence². To find out the relation between size and surface texture nodules were classified into 4 categories [very rough(vr), rough(r), smooth(s) and very smooth(vs)] based on visual observation, (Fig. 1). Smaller nodules (< 4 cm) are spherical in shape without any mammillaries and as size increases nodules become elliptical to discoidal and sometimes irregular in shape. Mn and Fe (average) concentrations of nodules of < 4 cm diam. are quite similar to those of rough (r) and very rough(vr) surface textured nodules while concentrations of nodules of > 4 cm diam. are similar to those of smooth(s) and very smooth(vs) nodules (Table 2). Hence, surface texture can be related to size alongwith the intensity of early diagenetic influence.

Table 2—Average Mn, Fe and Mn/Fe variation in different surface texture nodules

Surface texture	Mean conc. (%)		
	Mn	Fe	Mn/Fe
Very rough (vr)	30.4	5.9	5.7
Rough (r)	29.6	6.4	4.6
Smooth (s)	26.3	7.5	3.5
Very smooth (vs)	22.2	9.5	2.4

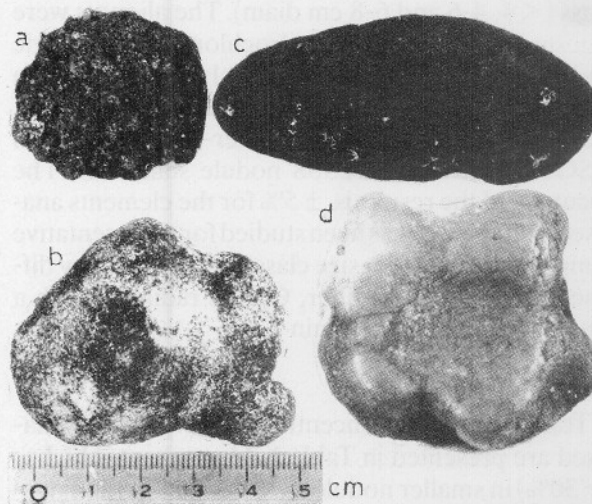


Fig. 1—Nodules showing different surface texture (a = very rough, b = rough, c = smooth, d = very smooth)

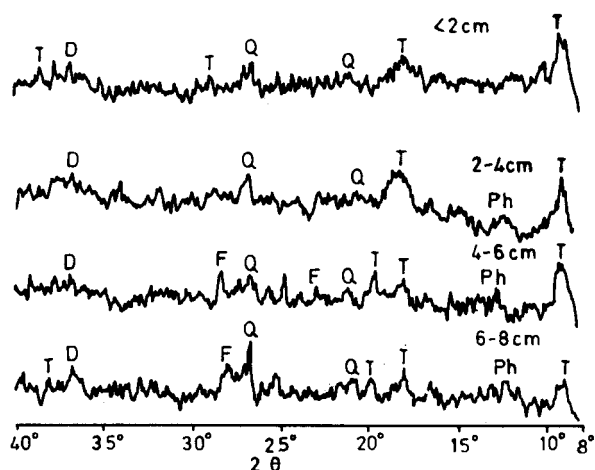


Fig. 2—X-ray diffractograms of different size nodules. (T = todorokite, D = $\delta\text{-MnO}_2$, Q = quartz, Ph = phillipsite and F = feldspar)

Mineralogy of different size nodules shows a decreasing intensity of todorokite reflections towards larger nodule and this decreasing pattern is associated with increasing intensity of $\delta\text{-MnO}_2$ (Fig. 2). Todorokite formation at lower Eh than $\delta\text{-MnO}_2$ can be directly related to the intensity of diagenesis in which todorokite and $\delta\text{-MnO}_2$ represent 2 end members of diagenetic and hydrogenetic accretion respectively.

The decreasing Mn/Fe ratio and intensity of todorokite towards larger nodules suggest that, the smaller nodules are prone to increasing influence of early diagenesis than the larger nodules. Higher concentration of Mn, Ni and Cu in the smaller and rough to very rough surface nodules may be due to their burial in the top layer of sediment column, while acting as wedge during biological upward pumping of larger nodules³.

The present study indicates that concentration of Mn, Ni and Cu increases towards smaller nodules (< 4 cm diam.) and hence these have more economic importance than the larger nodules (> 4 cm diam.) in the central Indian Ocean.

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