

Relationship between Size and Geochemistry of Polymetallic Nodules from the Central Indian Ocean Basin : Significance in Selection of High Grade Nodules

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ABSTRACT

Morphological, mineralogical and geochemical studies on nodules of different sizes collected from the Central Indian Ocean Basin (CIOB) show two suits of nodule formation by oxic diagenetic and hydrogenous process resulting into distinct properties. The smaller nodules are higher in grade (Cu+Ni+Co %), Mn and Zn contents and suggest their formation at shallower depths by diagenetic process and transportation later to deeper depths. Larger nodules, in contrast, are poor in grade and higher in Fe, Co and moisture contents and indicate their formation at deeper depths by a hydrogenous process. N/n (size of nodule/nucleus) ratios and nucleus size increase with increase in nodule size, supporting the view that smaller and larger nodules were formed differently at different places. Among nodules of other sizes, only medium sized ones of 3-4 and 4-5 cm are higher in grade and their exploitation seems to be economical.

INTRODUCTION

Polymetallic nodules in the Central Indian Ocean Basin (CIOB) have been the subject of attention since the last decade due to their economic potential. Detailed studies on CIOB and the Carlsberg Ridge (CR) nodules by several workers have documented highly variable nature of compositions ranging from regional [6,8,36] to micronodule [32] and intranodule [11,39] variations. Nodules collected from different parts of the Pioneer Areas A and B differ largely in shape, size, texture [21, 40], microfeatures [28] and mineralogy [16,31]. Studies have also shown that diagenetic and hydrogenous processes are primarily responsible for the formation of CIOB nodules and micronodules which is revealed by the variation in the bulk chemical composition and Mn/Fe ratios [1,3-5,12,13,22].

Interaction of pore water during early diagenesis of nodules has been stated to be responsible for the growth of nodules [25] and sedimentary terrigenous flux has

been traced up to 8° in southern latitudes [26]. A major part of the central portion of the CIOB consists of siliceous sediments where high grade nodules are embedded [38]. Siliceous sediments are surrounded in the north by terrigenous sediments, calcareous in the west and pelagic (red clay) in the south. It has been shown that the high grade nodules are less abundant [37] in the Indian Ocean as well as in the Pacific Ocean [19,20]. Radiochemical [2] and morphometric [18] studies revealed the influence of seabed topography on the distribution of nodules at local and regional scales [17,23,29, 35].

Seabed topography in the CIOB is continuously undulating with ± 100 m and the average water depth is 5000 m. CIOB was tectonically disturbed in the past which is revealed by the presence of seamount chains [24] and fracture zones along 73° [15,33]; 75° 45' and 79° [14]; 83° and 89° E [34]. Comparative studies on ferromanganese oxides from the seamounts, ridge and basins in the CIOB showed compositional variation with respect to water depth [30].

Bulk rare earth element (REE) studies on the sediments [27] showed fractionation of REE with respect to sediment type. REE studies on nodules [41,42] showed variation of REE abundance with respect to nodule size. Work attempted on compositional variation with respect to nodule morphology showed systematic decrease in the proportion of certain transition elements with increase in nodule size [41 - 43]. In this paper, an attempt has been made to document the relationship between size and geochemistry of CIOB nodules, and probable reasons for such variations are discussed.

MATERIALS AND METHODS

Polymetallic nodules were collected by boomerang grabs during 1st, 2nd and 4th cruises of the chartered vessel *D.S.V. Nand Rachit* in 1989. Samplings were mainly from the Pioneer Area A. A total of 41 nodules were selected randomly; these were of different sizes. Comparative studies were carried out on individual nodules and then by grouping under four subgroups according to their sizes using the maximum diameter. Each subgroup was thus separated from the other by 1 cm. Nodules of < 1, 1-2 and > 6 cm diameter were not available for the study.

Principal manganese oxide and other accessory mineral phases were identified on X-ray diffractogram (XRD) obtained on Philips X-ray diffractometer (model 1729) with $\text{CuK}\alpha$ radiation and scintillation detector. The concentrations of Mn, Fe, Cu, Ni, Co and Zn in nodules of different sizes were determined on Philips PW 1480 sequential X-ray fluorescence analyser (XRF) using press pellets and Rhodium X-ray tube, where linear calibration curve was obtained after correcting the inter-element (matrix) effects using α - factors and the de Jongh (DJ) in X 44 software.

RESULTS

Sampling locations are shown in Fig.1, where the water depth ranged from 4600 to 5400m and the average depth was 5103 m. Morphological studies show that a majority of the nodules have rough-granular surface texture and their occurrence (8.82-35.30%) dominates over smooth textured nodules (2.94-8.82%). Further, study of nodule types shows that ellipsoidal nodules are predominant. Nodule types can be arranged in descending order with respect to nodule size. In 2-3 cm size nodules, equal number of ellipsoidal and spheroidal nodules are present, whereas in 3-4 cm size, ellipsoidal type nodules are more than discoidal > smooth/rounded/irregular biological types. Nodules of 4-5 cm size are mostly spheroidal or irregular; other types are: long-elongated > discoidal/irregular/spheroidal type. In further longer size nodules (5-6 cm), irregular type dominates over intergrown and long-elongated types, whereas spheroidal and ellipsoidal types are nearly absent. Nodules belonging to 3-4 cm size have maximum nodule types (16) than those of 4-5 cm size (11 types). Nodules of 2-3 cm size have four types, whereas those of 5-6 cm size have minimum number of types (3). The total percentage of occurrence of smooth surface nodules is quite small (< 6%), whereas that of biological types (such as shark tooth, etc.) is rare (< 3%).

The relationship between nucleus (core) and nodule size shown in Figs 2 and 3 reveals that the larger nodules have a larger nucleus. Similarly Fig.4 shows the relationship between average N/n (size of nodule/size of nucleus) and nodule size, indicating that N/n ratio increases with increase in nodule size.

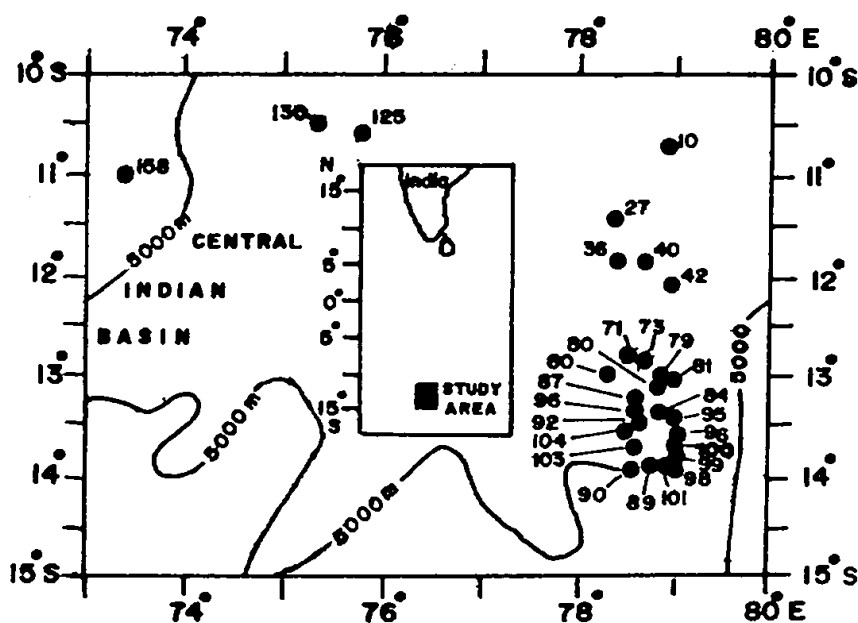


Fig.1 — Sample locations in Central Indian Ocean Basin

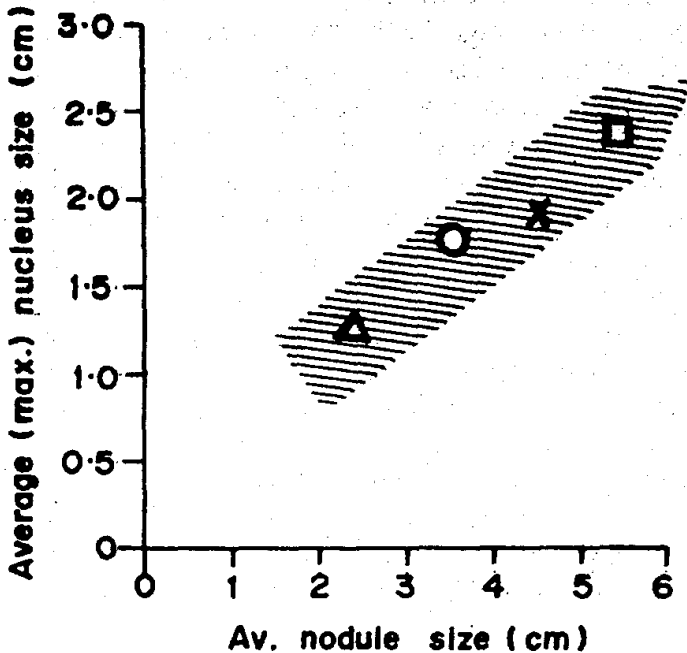


Fig.2 — Relationship between nodule size and average nucleus size

Todorokite occurs as the principal manganese phase for nodules belonging to 3-4 and 4-5 cm sizes, whereas others have δ -MnO₂ (vernadite) phase. Quartz and philipsite are the major accessory minerals among others. Todorokite peak height decreases systematically from smaller (2-3 cm) to larger (5-6 cm) size nodules (Fig.5). This observation is similar to those reported earlier [40,41].

Data on chemical composition, grade, Mn/Fe ratio and moisture content of 41 different sized nodules are presented in Table 1. Ranges are quite large (Table 2) and the averages are closer to the averages for NE Pacific Ocean nodules [9]. Comparatively, Pacific Ocean nodules have a much higher Co content and CIOB nodules are higher in Mn, Fe and Mn/Fe ratios. This is further evident from Fig.6 where the histograms display variation in the chemical composition of every element with respect to nodule size. The relationship between composition and nodule size shows that nodules belonging to 3-4 cm size have higher percentages of Cu (1.37), Ni (1.24), Zn (0.18), combined Cu+Ni+Co (2.7) and Mn/Fe ratios (5.06) than the others. Co content is higher (0.12%) in 2-3 cm nodules and Mn and Fe contents are higher (26.73%) and 8.87% respectively) in 4-5 cm nodules.

Inter-element relationships for the entire data for 41 nodules (Table 3) show very strong correlation of Mn with Cu (0.84), Ni (0.78), Zn (0.97), combined Cu+Ni+Co (0.85) elements and Mn/Fe ratios (0.89). Conversely, Fe and Co show a strong negative correlation (-0.88) with Mn. On the other hand, Fe correlates

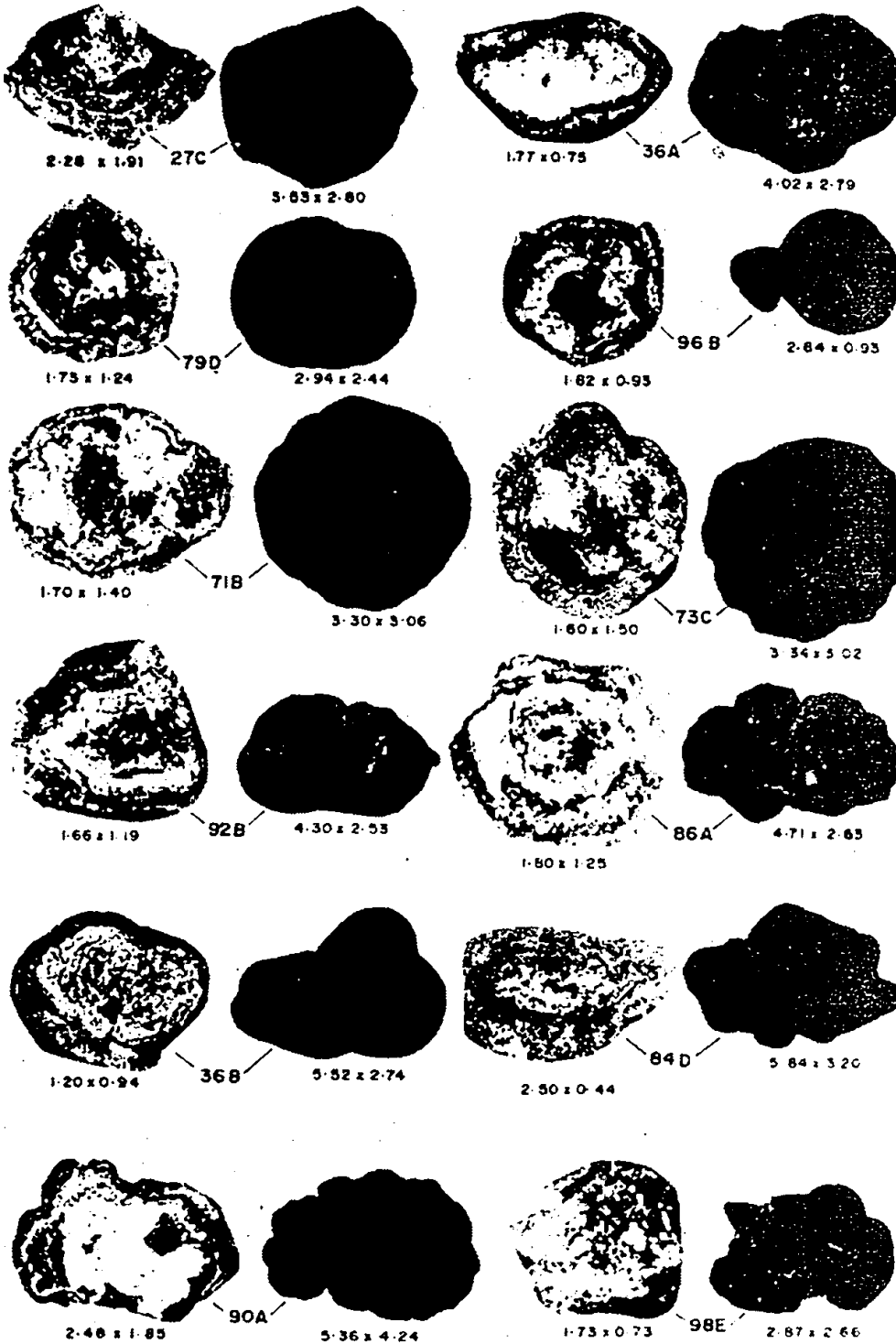


Fig.3 — Comparison between nucleus and nodule size (Note the bigger nucleus in larger nodules)

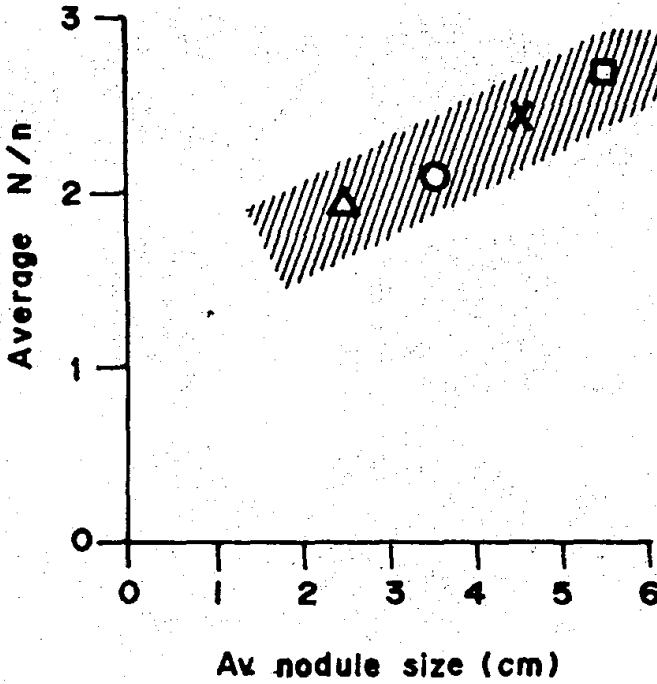


Fig.4 — Relationship between nodule size and average N/n ratio

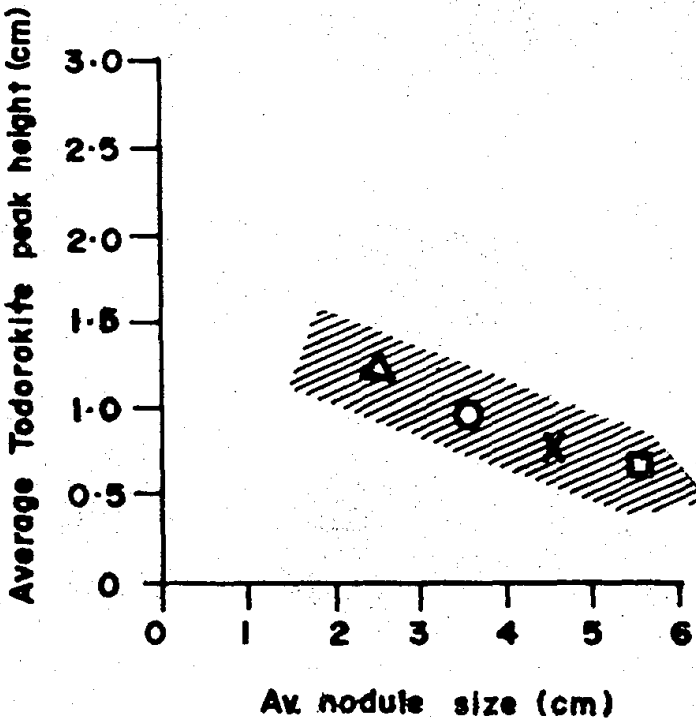


Fig.5 — Relationship between nodule size and todorokite peak height

Table 1 — Chemical Composition of Nodules from Central Indian Ocean Basin

Sr. no.	Size (cm)	Sample no.	Mn(%)	Fe(%)	Cu(%)	Ni(%)	Co(%)	Zn(%)	Cu+Ni+Co (%)	Mn/Fe(%)	Moisture (%)
1	2-3	79D	28.33	06.97	1.15	1.34	0.10	0.17	2.58	4.06	12.53
2		89B	20.11	13.77	0.31	0.73	0.24	0.09	1.28	1.46	10.37
3		92B	32.76	06.14	1.36	1.22	0.07	0.22	2.65	5.33	12.99
4		96B	31.59	05.80	1.88	1.30	0.07	0.21	3.26	5.45	10.11
5		98E	17.01	10.90	0.33	0.73	0.12	0.10	1.17	1.56	12.33
6	3-4	27C	29.40	05.45	1.98	1.48	0.07	0.18	3.54	5.39	11.55
7		60E	24.42	10.35	0.83	1.11	0.14	0.13	2.08	2.36	15.95
8		71B	34.08	04.54	2.03	1.28	0.06	0.24	3.38	7.50	12.42
9		73B	32.11	05.10	1.69	1.27	0.07	0.22	3.03	6.29	13.75
10		73C	33.34	05.16	1.47	1.25	0.07	0.23	2.79	6.45	14.41
11		79A	27.97	04.29	1.18	1.23	0.06	0.17	2.47	6.52	10.13
13		80A	19.63	12.91	0.34	0.77	0.14	0.10	1.24	1.52	15.18
14		80D	21.42	12.77	0.36	0.84	0.16	0.10	1.35	1.68	17.50
15		81B	31.62	03.95	1.38	1.52	0.07	0.20	2.97	8.01	15.59
16		92E	31.87	05.65	1.98	1.23	0.07	0.21	3.28	5.64	13.68
17		95B	27.59	07.72	0.92	1.12	0.07	0.16	2.12	3.57	11.21
18		95C	28.63	06.41	1.44	1.19	0.08	0.18	2.71	4.47	13.49
19		96D	29.91	05.71	1.26	1.17	0.07	0.19	2.50	5.24	11.53
20		95E	29.34	06.07	1.72	1.35	0.09	0.18	3.16	4.83	11.62
21		99E	25.14	05.61	1.15	1.09	0.07	0.18	2.31	5.19	11.43

Contd.

Table 1 — Chemical Composition of Nodules from Central Indian Ocean Basin — Contd.

Sr. no.	Size (cm)	Sample no.	Mn(%)	Fe(%)	Cu(%)	Ni(%)	Co(%)	Zn(%)	Cu+Ni+Co (%)	Mn/Fe(%)	Moisture (%)
22		100B	29.59	05.73	1.38	1.18	0.08	0.19	2.64	5.12	12.12
23		100D	30.44	05.06	1.74	1.32	0.07	0.19	3.13	6.01	13.36
24		103B	31.86	06.05	1.52	1.23	0.10	0.21	2.85	5.27	16.28
25		103E	32.56	05.63	1.77	1.26	0.07	0.22	3.10	5.78	14.13
26		104E	30.76	06.79	1.64	1.27	0.08	0.20	3.00	4.53	14.64
27	4-5	10E	29.09	07.74	1.22	1.26	0.06	0.18	2.54	3.76	14.22
28		36A	27.85	08.09	1.44	1.38	0.09	0.16	2.91	3.44	14.21
29		40C	28.55	07.74	1.38	1.27	0.10	0.17	2.75	3.69	14.20
30		42C	25.66	12.75	0.80	1.18	0.08	0.14	2.07	2.01	10.61
31		86A	29.35	05.54	2.05	1.24	0.07	0.18	3.36	5.30	13.92
32		87E	23.20	10.96	0.46	0.90	0.15	0.12	1.51	2.12	17.38
33		101E	28.01	07.53	1.17	1.14	0.10	0.17	2.41	3.72	14.90
34		125E	27.67	06.45	1.61	1.44	0.07	0.16	3.12	4.29	15.30
35		130C	29.00	06.48	2.01	1.61	0.07	0.17	3.69	4.47	15.13
36		158A	23.74	10.61	0.56	0.99	0.10	0.12	1.64	2.24	16.82
37		158D	21.93	13.69	0.33	0.80	0.12	0.11	1.26	1.60	21.03
38	5-6	36B	28.31	06.98	2.15	1.29	0.08	0.17	3.52	4.05	13.65
39		84D	24.31	09.58	0.52	1.12	0.13	0.12	1.77	2.54	18.98
40		90A	27.19	08.27	1.02	1.07	0.11	0.16	2.20	3.29	15.05
41		90C	25.94	08.79	1.01	1.11	0.13	0.14	2.25	2.95	15.92

strongly with Co (0.79) and moisture content (0.56). Plots in the variation diagrams (Fig.7) also confirm the association and relationships of the above elements. The concentrations of Cu, Ni, Zn, grade (combined Cu+Ni+Co%) and Mn/Fe ratios increase and those of Fe, Co and moisture decrease with increase in Mn content (Fig.7).

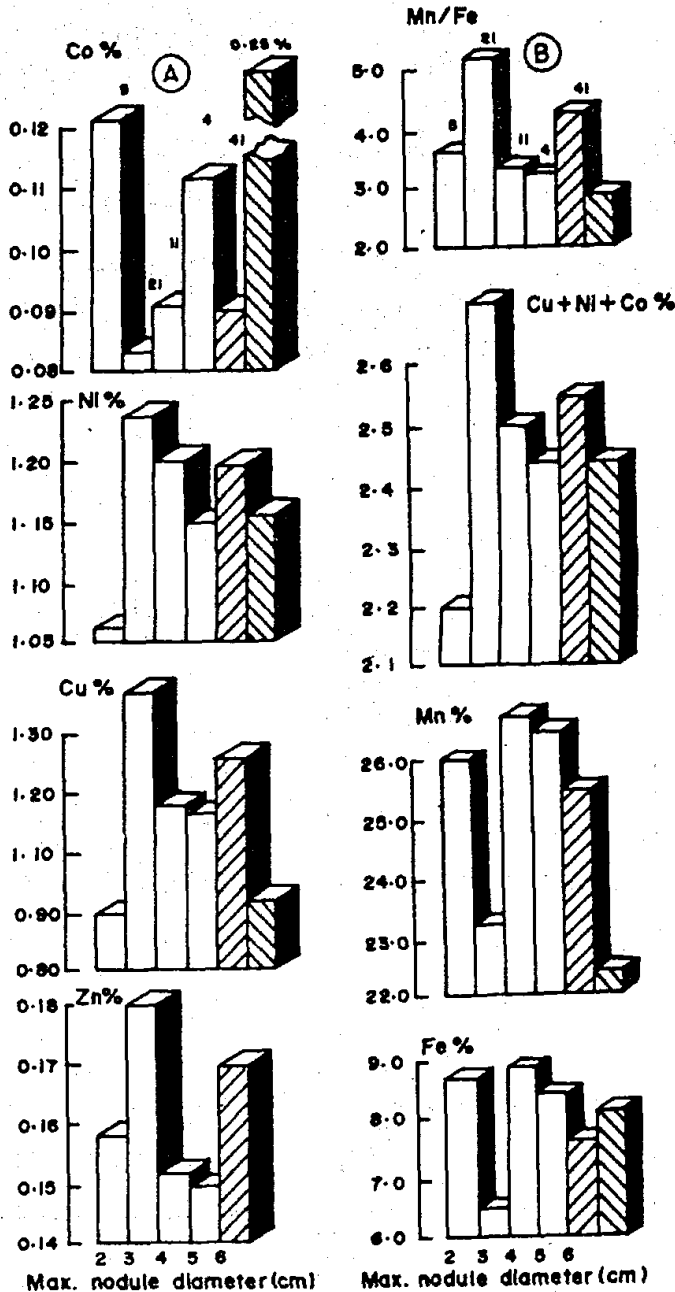


Fig.6 — Histograms showing A) compositional variation of Co, Ni, Cu and Zn with nodule size and B) compositional variation of Mn/Fe ratio grade (Cu+Ni+Co %), and Mn and Fe contents with nodule size [▨ = Av. this study; ▩ = Av. N E Pacific Ocean modules]

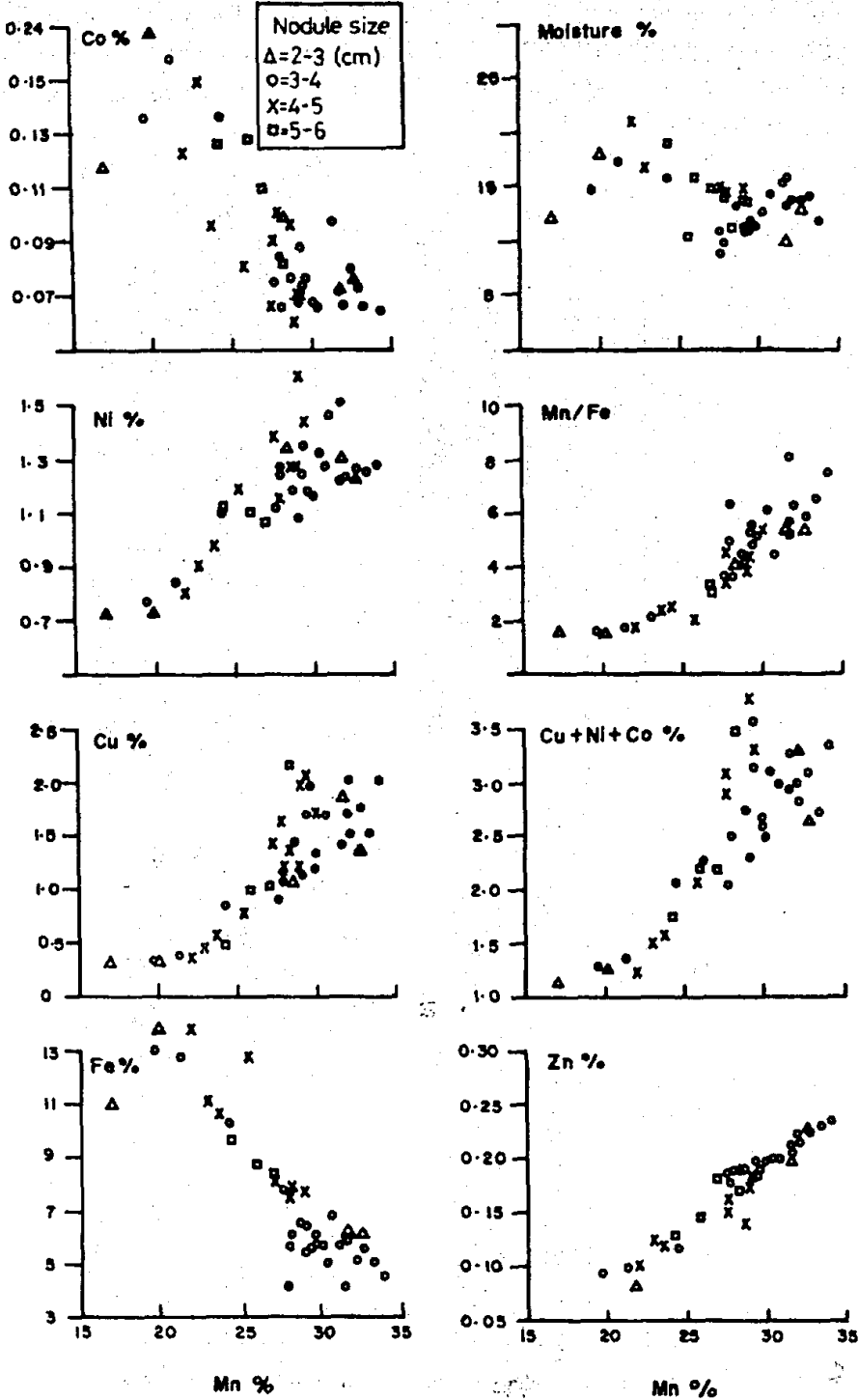


Fig.7 — Variation of Fe, Cu, Ni, Co, Zn, grade, Mn/Fe ratio and moisture content with Mn [Δ = 2-3 cm; O = 3-4 cm; X = 4-5 cm; □ = 5-6 cm]

DISCUSSION

It is clear from Fig.6 and Table 1 that the average chemical composition of a nodule is inversely related to its size. Compared to their larger components, the smaller nodules have a higher grade. Thus, it can be said that besides morphological characters, the smaller and larger nodules are distinct in their compositions. The two different suits of nodules, therefore, represent at least two different ways of formation, namely, by diagenetic and hydrogenetic processes, as described earlier [41].

Large variations in Mn/Fe ratios (1.46 to 8.01, Table 2) indicate multiple source and an early diagenesis [10, 39]. This is further evident from the large variation in

Table 2 — Range and Average Concentrations for the CIOB Nodules

	Min.	Max.	Aver.	SD
Mn(%)	17.01	34.08	27.68	3.89
Fe(%)	3.95	13.77	7.59	2.71
Cu(%)	0.31	2.15	1.26	0.54
Ni(%)	0.73	1.61	1.18	0.20
Co(%)	0.06	0.24	0.09	0.03
Zn(%)	0.09	0.24	0.17	0.04
Cu+Ni+Co(%)	1.17	3.69	2.54	0.69
Mn/Fe	1.46	8.01	4.23	1.69
Moisture(%)	10.11	21.03	14.06	2.51

Table 3 — Inter-element Relationship in the CIOB Nodules (entire data)

	Mn	Fe	Cu	Ni	Co	Zn	Cu+Ni+ Co	Mn/Fe
Mn								
Fe	-0.85							
Cu	0.84	-0.82						
Ni	0.78	-0.78	0.83					
Co	-0.75	0.79	-0.71	-0.73				
Zn	0.97	-0.88	0.81	0.69	-0.76			
Cu+Ni+Co	0.85	-0.83	0.99	0.90	-0.72	0.80		
Mn/Fe	0.89	-0.94	0.78	0.71	-0.73	-0.90	0.78	
Moisture	-0.42	0.56	-0.44	-0.41	0.61	-0.47	-0.43	-0.48
N = 41, r = 0.49, CL = 99.9%								

Mn/Fe ratios in the study area where nodules have grown to different sizes with varying compositions. Therefore, variation in Mn/Fe ratio also supports the view that different sized nodules have formed differently at different places in various sedimentary environments. Formation of nodules by three different accretionary processes is obvious from Fig.8, where the plots spread from diagenetic to hydrogenous field. Those formed by oxic diagenesis are further distinguished in the diagenetic field [7]. It is, therefore, clear that all these processes were responsible for the formation of nodules, leading to distinguishable morphological, mineralogical and chemical properties. Owing to the fact that the different sized nodules occur close to one another on the seafloor, it is not reasonable to consider that the above processes were active either all at a time, alternatively or simultaneously in the area. This supports the previously proposed view that formation of different sized nodules took place separately in different areas [40,41]. Thus, larger nodules which are poor in grade and Mn and Zn content suggest their formation mostly from seawater and, therefore, have higher Fe, Co and moisture contents. Formation of smaller nodules by diagenetic process with an additional supply source (such as CCD) explains why they are higher in grade and Mn and Zn contents.

The CIOB area was tectonically disturbed in the past [14,15,33,34] and the downslope and currents could have been responsible for the movement of nodules

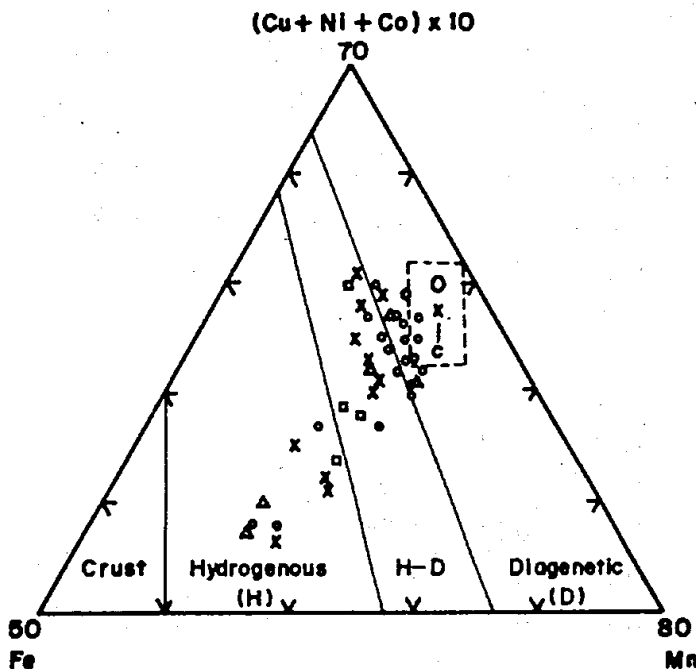


Fig.8 — Ternary diagram of Fe-Mn $(Cu+Ni+Co) \times 10$ for different sized nodules [Symbols as in Fig.7]

towards deeper depths to give rise to the present picture of association of different sized nodules on the seafloor. Presence of planktonic foraminifera (*Globorotalia menardii*) in the nucleus (1.03 × 0.77 cm) of sample 5A (4-5 cm size; 5300 m depth) supports this view. It is possible that initially the nucleus of this particular nodule was formed at a shallower depth and then it was transported to 5300 m depth due to the currents along the downslope, where it grew to 4-5 cm size slowly from the seawater (hydrogenous).

It can be inferred from the relationship shown in Fig.2 that the larger nodules were formed on a larger nucleus and *vice versa*. This further suggests that the smaller nodules did not grow to the larger sizes, which, in turn, means that the processes of formation of smaller and larger nodules were operated separately and that the larger nodules did not grow from smaller ones. Figure 4 further shows that the thickness of Mn-Fe oxide shell over the nodule during formation increased with increase in nodule size. It is clear that although a sufficiently large space for the formation of shell was available, the larger size nodules developed as poor grade. A similar correlation is evident from Fig.7, where plots scatter towards a higher Mn content.

Nodules of 3-4 and 4-5 cm sizes are economically important, as they have high grades (2.7 and 2.48 % respectively). Nodules of other sizes are lower in grade. This observation tallies with earlier reports [40,41,43] based on the study of 84, 91 and 613 different sized nodules covering a very large area in the CIOB. Such an extensive data on nodules with respect to size has not been reported from elsewhere.

CONCLUSION

- 1) Different sized nodules from the CIOB have distinct geochemical, mineralogical and morphological characteristics by which they can be distinguished as being of poor or high grades.
- 2) Poor grade nodules are hydrogenous and large in size and suggest their formation in deeper water.
- 3) There is evidence to support the view that the smaller nodules were formed at shallower depths and then transported into the deeper areas.
- 4) Average N/n ratio and nucleus size increase with increase in nodule size lending support to the view that smaller and bigger nodules were formed at different places by different accretionary processes.

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