

INTERNAL MICROFEATURES OF MANGANESE NODULES FROM THE CENTRAL INDIAN OCEAN

J.N. PATTAN

National Institute of Oceanography, Dona Paula, Goa 403 004 (India)

(Received April 13, 1987; revised and accepted September 22, 1987)

Abstract

Pattan, J.N., 1988. Internal microfeatures of manganese nodules from the Central Indian Ocean. *Mar. Geol.*, 81: 215–226.

The internal features of manganese nodules from abyssal hills ranging in height from 600 to 880 m and the nodules from abyssal plains in the Central Indian Ocean have been studied. Nodules from the abyssal hills show mainly parallel laminations whereas nodules from the abyssal plains show prominent, well-developed columnar structures. Features such as botryoids and fractures filled with Fe- and Mn oxides are more common in the nodules of abyssal plains whereas the clay content and clastic grains are more common in abyssal hill nodules. Compositional studies of layers within the nodules show that Mn, Ni, Cu and Zn increase from the nucleus to the outer layer, while Fe and Co are inclined to decrease. The innermost layer adjacent to the nucleus is hydrogenetic (Mn/Fe ratio of <1.5) and contains phillipsite, quartz and feldspar, while the outer layers are early diagenetic (Mn/Fe ratio of 4.2–5.4) and contain mainly todorokite with minor δMnO_2 , phillipsite and quartz. A mixing model shows that the contribution of interstitial water to the outer diagenetic layers was about 75% and that of sea water was about 25%.

Introduction

The internal features of manganese nodules are complicated with a varied texture, mineralogy and composition. The geochemistry of manganese nodules from the Indian Ocean was studied by Cronan and Tooms (1969), petrography and electron microprobe studies were carried out by Dunham and Glasby (1974), Siddiquie et al. (1978) studied mineralogy and geochemistry, Mallik (1980) examined the macro- and micromorphology, and internal growth features and ore microscopy were studied by Ghosh (1982). More recently Kari-siddaiah (1985) has reported on the mineralogy and composition of nodules from the southern part of the Carlsberg Ridge. In this study, manganese nodules are studied from seamounts with heights of 600–880 m and from

plains with depths varying from 5000 to 5400 m. The locations of these samples are shown in Fig.1. This investigation was undertaken to understand the environmental conditions and to investigate the different sources of supply for different layers of the nodules.

Methods

Manganese nodules were collected from the Central Indian Ocean as a part of the National Institute of Oceanography surveys of manganese nodules. Polished nodules were studied under reflected light using a Carl-Zeiss Jena ore microscope and subsequently, part of the same section was examined using a scanning electron microscope (Camebax No. 571 SEM) for detailed studies with magnifications ranging from 400 to 2000 \times .

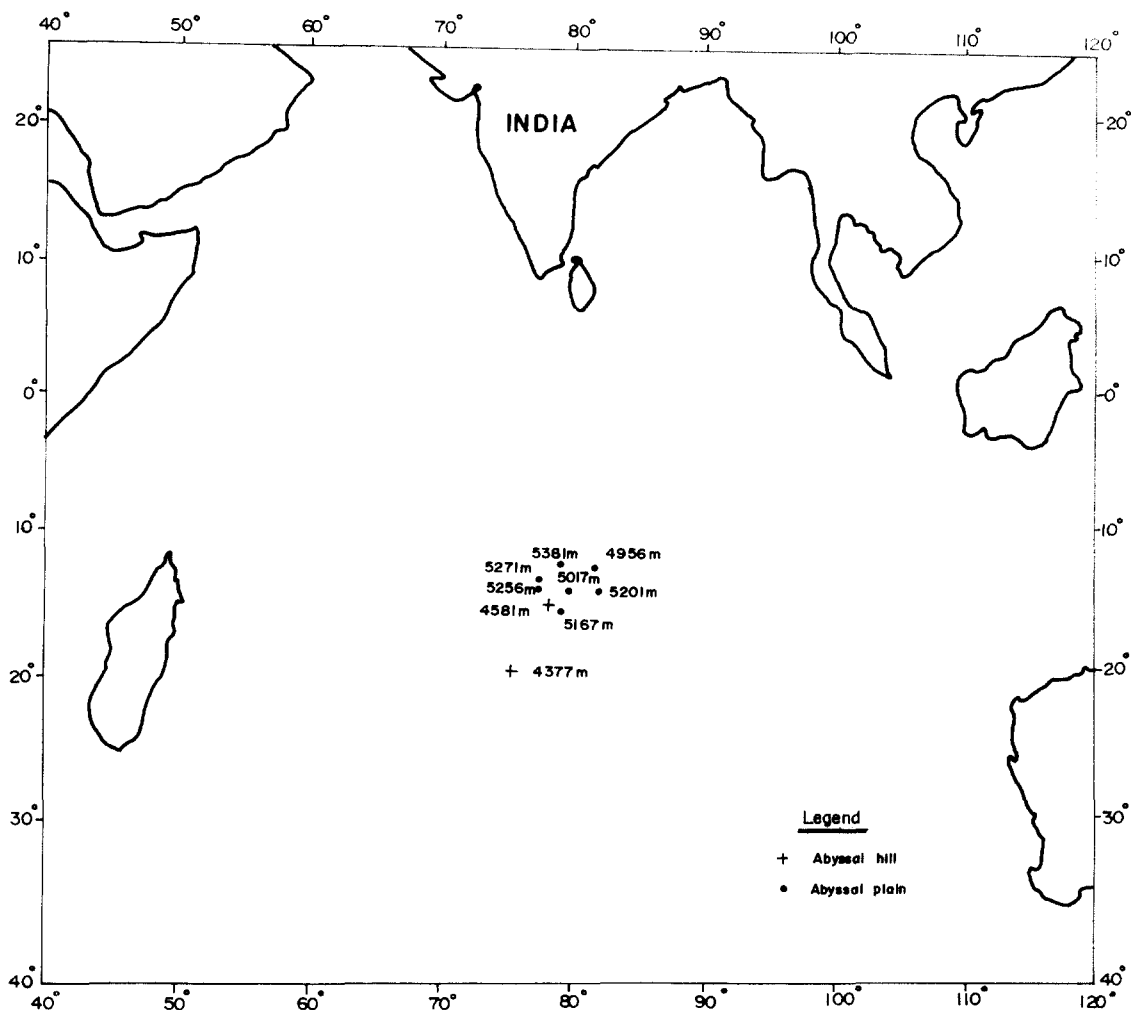


Fig.1. Sample locations with water depths in the Central Indian Ocean.

Using a dentist's drill, samples for geochemical analyses were taken from different layers of the polished section. Finely powdered samples were weighed into 0.05 g batches and transferred to a teflon bomb to which 6 ml of hydrofluoric acid and 1 ml of aqua regia were added, and kept in an oven for 2 h at 110°C. 5.6 g of boric acid were then added and diluted to 100 ml with distilled water. Elemental analyses were carried out on an ASS Perkin Elmer model 5000. The reproducibility of data is $\pm 5-6\%$.

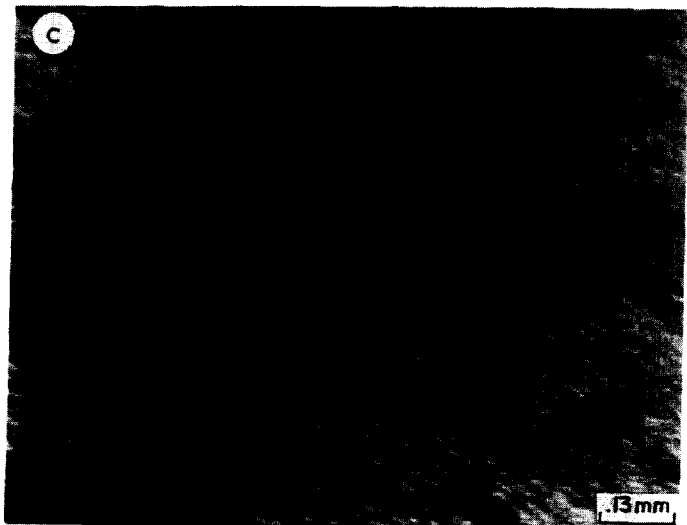
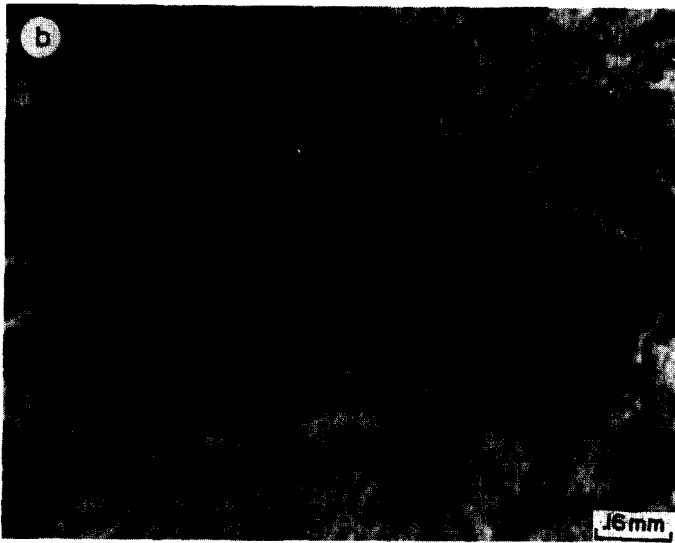
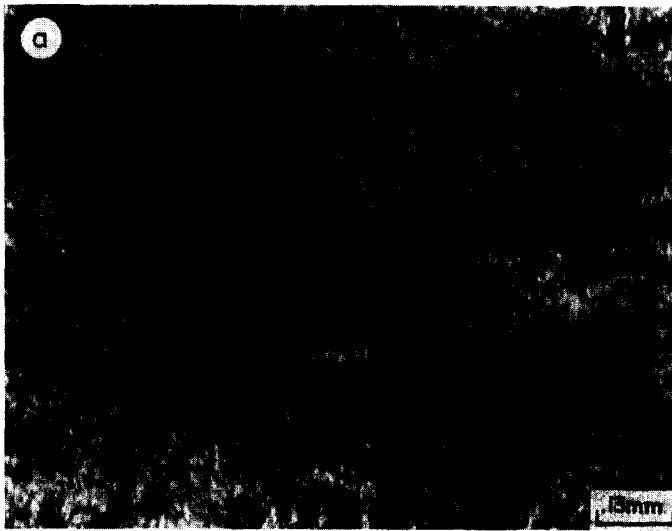
The mineralogy of individual layers was determined with a Philips X-ray diffractometer scanning from 8 to 69° at 2° 2 θ /min using a nickel filter and CuK α radiation.

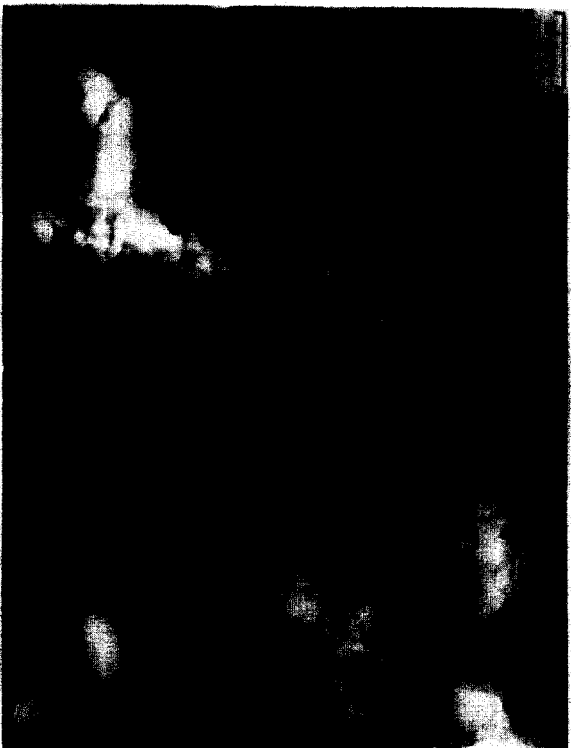
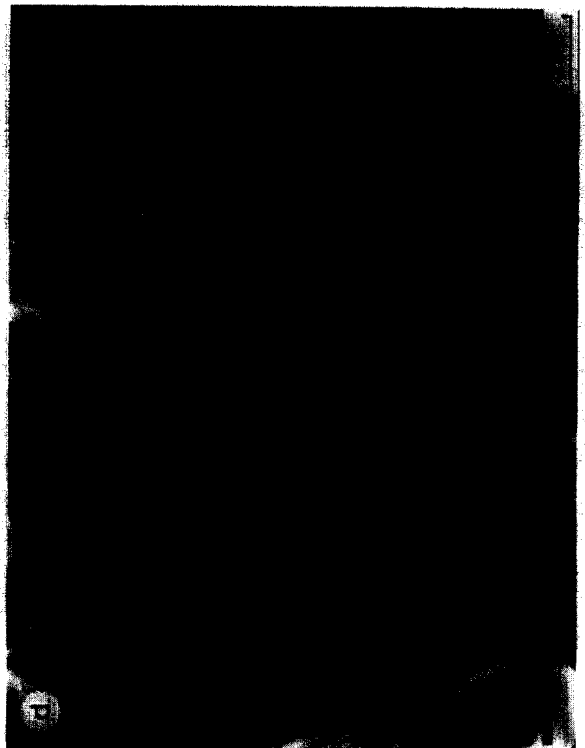
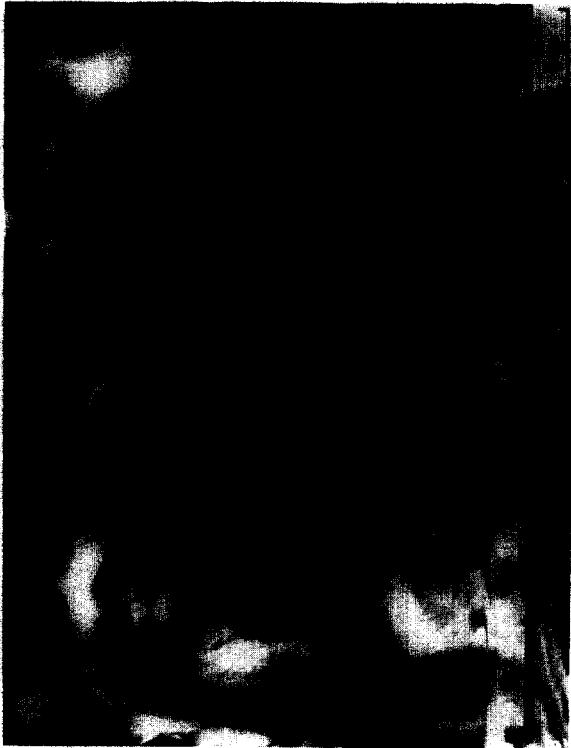
Results and discussion

Ore microscopic study

Under the ore microscope, nodules from abyssal plains show a prominent well-developed columnar-cusped texture (Figs.2a and

Fig.2. Polished sections of a manganese nodule. a and b. Abyssal plain nodule showing columnar texture. c. Abyssal hill nodule showing parallel laminations.





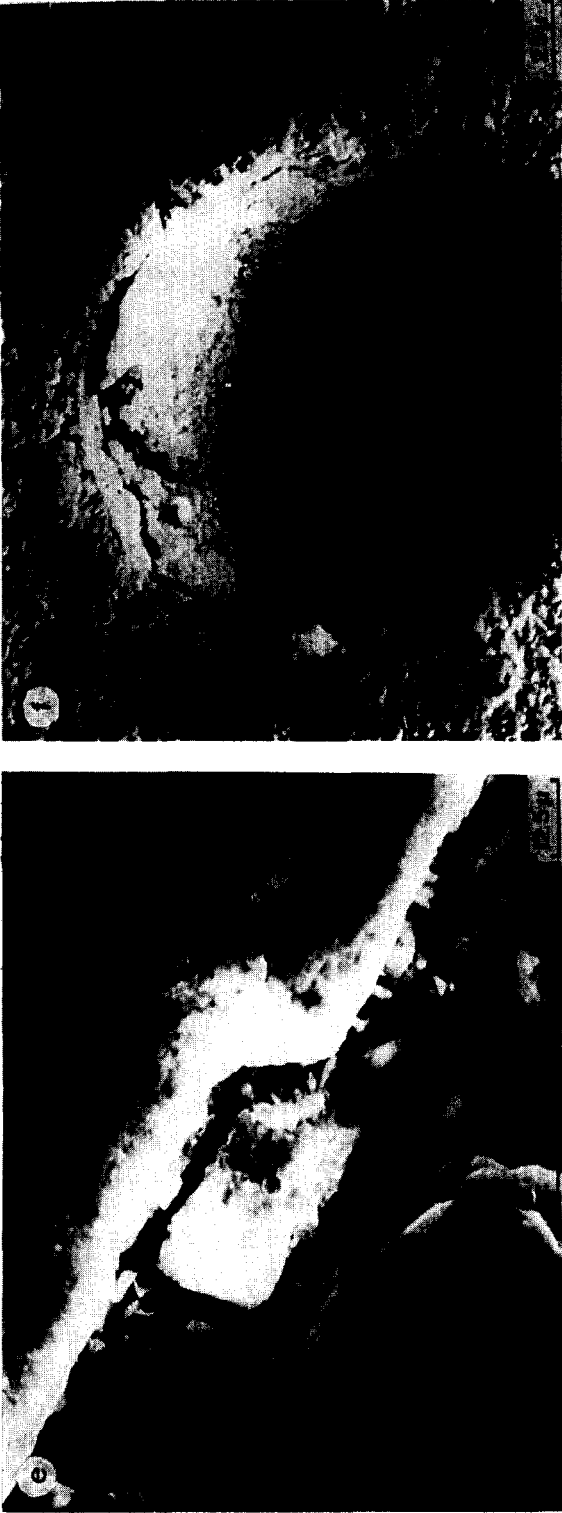


Fig.3. Electron micrographs showing structures of manganese nodules. a. Columnar texture with cross-cutting fractures. b. As above, under higher magnification. c. Electron micrograph showing variation in botryoids size. d. Cauliflower-like structure. e. Well-developed crystal in a fracture. f. Nodule in which a cosmic spherule is embedded.

b). This elliptical columnar texture shows a colloform nature and consists of subconcentric laminae which progressively widen outward and bifurcate. Columnar textures are the cross sections of minute botryoids which have been formed from interstitial waters. Heye (1978) suggested that the cusped pattern is related to the growth rate. In columnar textures, white or light grey laminae are the Mn oxides while dark grey layers are the Fe oxides. Occurrences of these alternate laminae of Mn- and Fe oxides are attributed to two different sources, i.e., seawater in the case of Fe-rich layers and interstitial water in the case of Mn-rich layers.

Further, nodules show diagenetic features such as fractures filled with Mn- and Fe oxides which are obviously from the underlying sediment. Abyssal hill nodules show parallel laminations (Fig.2c). A clay content and clastic grains were noted to be more dominant in nodules from the abyssal hill region.

SEM observations

Manganese nodules from abyssal plains show concentric growth or a cusped structure with alternate layers of Fe- and Mn oxides (Fig.3a). A single cusped (Fig.3b) shows variation in microlaminae thickness from 0.1–6.5 μm . These individual laminae are truncated and show crenulations with a number of cross-cutting fractures. The thickness of laminae is greater at the crest (6.5 μm) and gradually decreases along the limbs (0.1 μm). The variations in microlaminae are responsible for different mineral phases of the Mn- and Fe oxides. Heye (1975) noted that smooth parallel laminations represent slow growth rates, whereas cusped textures indicate a fast growth rate. On the other hand, Margolis and Glasby (1973) suggested that straight laminations represent relatively fast growth rates and that cusped structure indicates a slower accretion, i.e., precisely the opposite observation. The interiors of the nodules show aggregates of both small and large botryoids (Fig.3c) which are made up of flocculated material.

This flocc-like material represents amorphous Mn- and Fe hydroxides (Fewkes, 1973). Cauliflower-like structures (Fig.3d) can be observed and may have been formed from dehydration of todorokite during storage (Usui, 1979).

A well-developed crystal (Fig.3e) is present in a fracture which indicates diagenetic changes in the manganese nodules, this post-depositional diagenesis and recrystallisation process possibly having occurred inside the nodule.

Smooth, spherical cosmic spherules are embedded in the nodules (Fig.3f). Nodules from the abyssal hills show parallel laminations for which the source may be seawater. Further, widely spaced isolated botryoids not showing much variation within the manganese nodules were observed.

The back-scattered electron (BSE) study from the cusped structure shows that Cu, Ni and Fe are following a cusped trend, whereas Mn is not following any trend and is uniformly distributed in the manganese nodules. Using this method, Dunham and Glasby (1974) found that Mn, Cu, Ni, Fe and Co follow a specific trend in some deep- and shallow-water manganese nodules.

Compositional variation within nodules

The location of concentric layer samples along the structure within the manganese nodules is shown in Figs.4a and b. Compositional data within the nodules and correlation coefficients for metal concentrations are given in Tables 1 and 2 respectively. The nodule I-EN (depth, 5256 m) is elliptical in shape with a rough surface texture, having a long axis of 9.4 cm and a short axis of 5.4 cm, whereas nodule I-CN (depth, 5271 m) is circular having a diameter of 5.5 cm and again, a rough surface texture. Both nodules are from the abyssal plains.

There is a positive correlation between Mn and Ni, Cu and Zn and Fe and Co, and a negative correlation between Mn and Fe. Figure 5 shows that Mn, Ni, Cu and Zn increases from the nucleus to the outer layer,

TABLE 1

Chemical composition from inner layer to outer layer within manganese nodules of the Central Indian Ocean

Sample and layer No.	Mn (wt.%)	Fe (wt.%)	Cu (wt.%)	Ni (wt.%)	Co (wt.%)	Zn (wt.%)	Mn/Fe
I-CN							
A-I	26.10	6.2	1.14	1.10	0.04	0.10	4.20
A-II	26.10	6.2	1.16	0.89	0.03	0.10	4.20
A-III	26.10	4.8	1.27	0.87	0.03	0.10	5.43
A-IV	07.45	6.0	0.39	0.26	0.02	0.03	1.24
Core	03.72	6.8	0.22	0.12	0.01	0.03	0.54
B-I	32.88	6.0	1.23	1.31	0.06	0.15	5.48
B-II	34.91	6.6	1.69	1.13	0.06	0.15	5.29
B-III	33.89	5.8	1.62	1.08	0.04	0.13	5.84
B-IV	07.79	7.8	0.39	0.26	0.01	0.06	0.93
I-EN							
A-I	33.55	6.6	1.55	1.16	0.07	0.12	5.08
A-II	21.69	16.8	0.35	0.33	0.18	0.05	1.29
A-III	15.59	12.4	0.37	0.45	0.13	0.05	1.25
B-I	32.54	6.8	1.41	1.06	0.06	0.13	4.78
B-II	22.37	16.8	0.40	0.40	0.18	0.09	1.33
B-III	14.23	14.0	0.30	0.35	0.12	0.05	1.01
Core	01.65	9.0	0.07	0.07	0.00	0.03	0.18
C-I	27.45	13.8	0.83	0.89	0.13	0.08	1.98
C-II	23.05	16.4	0.50	0.49	0.16	0.08	1.40
C-III	16.94	19.0	0.30	0.29	0.16	0.05	0.89
D-I	30.50	5.8	1.31	1.02	0.07	0.12	5.26
D-II	19.66	14.0	0.40	0.37	0.12	0.05	1.40
D-III	21.69	15.2	0.38	0.44	0.16	0.05	1.42

whereas Fe and Co show more of a tendency to decrease. Nickel- and Cu-rich bands reaching concentrations of 2.83% are present in the outermost layers of the nodules. The Mn/Fe ratio for the inner layer, adjacent to the nucleus, is less than 1.5, indicating a hydrogenetic source (Halbach et al., 1981). The outer layers have Mn/Fe ratios between 4.2 and 5.4 which indicate an early diagenetic nature (Halbach et al., 1981). Based on Mn/Fe ratios, hydrogenetic and early diagenetic layers within the nodules are shown in Figs. 4c and d. The low Mn/Fe ratio (< 1.5) and the somewhat higher Co content in the inner layers (I-EN, layers II and III and I-CN, layer IV) indicates a seawater contribution. High Mn/Fe ratios (4.2–5.4) in the outer layers (I-EN, layer I and I-CN, layers I, II and III) reflect an interstitial water contribution. These variations in source

suggest that rates of accretion and environmental conditions during formation of the layers were different. In nodule I-EN, the outer layers are diagenetic except at the protruding face, C. This face is hydrogenetic in origin (Mn/Fe ratio, 1.9) and corresponds to the top of

TABLE 2

Correlation coefficients for metal concentrations within the manganese nodules (from Table 1)

	Mn	Fe	Cu	Ni	Co	Zn
Mn	1.00	—	—	—	—	—
Fe	-0.21	1.00	—	—	—	—
Cu	0.86	-0.64	1.00	—	—	—
Ni	0.91	-0.53	0.95	1.00	—	—
Co	0.17	0.90	-0.32	-0.19	1.00	—
Zn	0.91	-0.49	0.94	0.95	-0.15	1.00

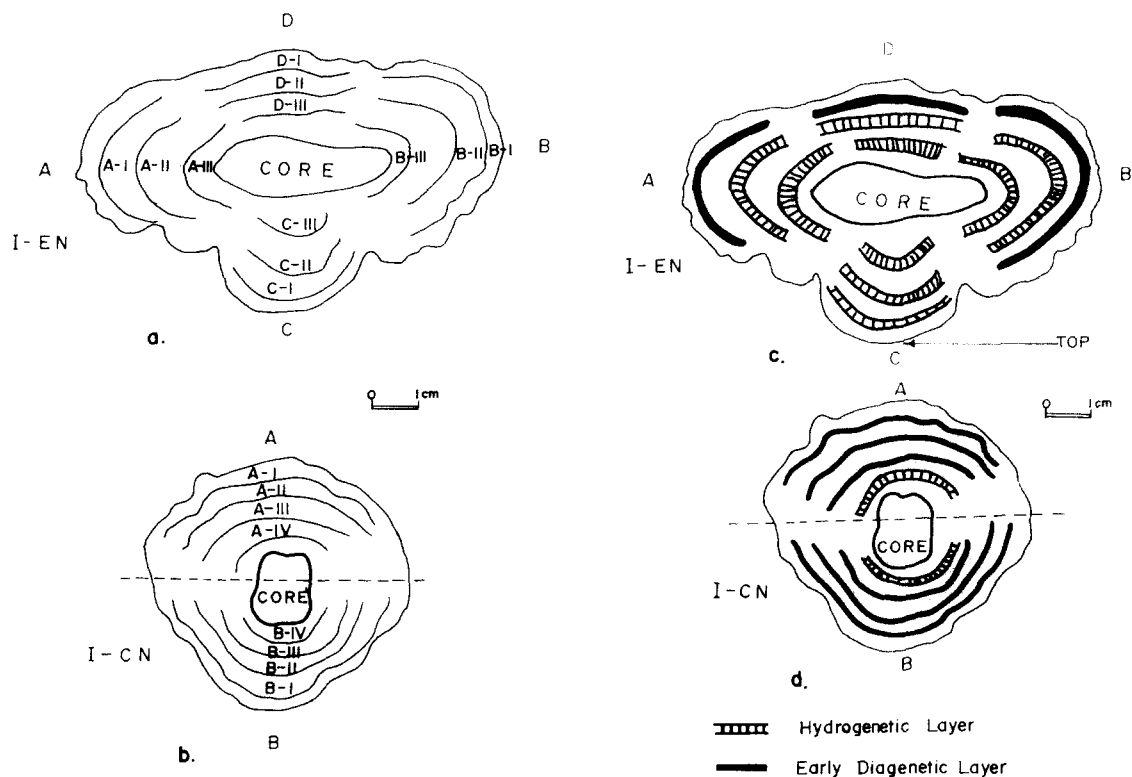


Fig.4. a and b. Location of concentric layer samples within the manganese nodules. c and d. Hydrogenetic and early diagenetic layers.

the nodule. This origin is confirmed by high Co (0.16%) and Fe (19%) contents compared to the outer layers.

Burns and Burns (1977) found birnessite, todorokite and δMnO_2 in manganese nodules. Mineralogical studies show that the outer layers (I-CN, layers A-I, II and III and I-EN, layer D-I) are dominantly composed of todorokite with a small amount of δMnO_2 (Figs.6a and b).

The innermost layer does not show any manganese-bearing minerals but contains phillipsite, quartz and feldspar. Phillipsite and quartz are present in all the layers.

As shown by Piper and Williamson (1981), manganese nodules receive metals from both seawater and interstitial water. In this case excess Mn, Ni, Cu and Zn was calculated for the diagenetic layers according to the mixing model as described by Piper and Williamson (1981). For nodule I-CN, layer A-I, excess Mn,

Ni, Cu and Zn can be calculated by considering layer IV as zero because the Mn/Fe ratio is between 1 and 2:

$$\left[\text{Mn}_{\text{ex}} \right]_i = \left[\text{Mn}_{\text{tot}} \right]_i - \left[\text{Fe}_{\text{tot}} \right]_i \left[\frac{\text{Mn}_{\text{tot}}}{\text{Fe}_{\text{tot}}} \right]_{\text{IV layer}} = 19.3 \text{ wt.}\%$$

$$\left[\text{Ni}_{\text{ex}} \right]_i = \left[\text{Ni}_{\text{tot}} \right]_i - \left[\text{Fe}_{\text{tot}} \right]_i \left[\frac{\text{Ni}_{\text{tot}}}{\text{Fe}_{\text{tot}}} \right]_{\text{IV layer}} = 0.83 \text{ wt.}\%$$

Similarly, the values for Cu_{ex} and Zn_{ex} are 0.93 and 0.07 wt.% respectively. Excess Mn, Ni, Cu and Zn values for all the diagenetic layers are given in Table 3. The excess Mn, Ni, Cu and Zn contents in diagenetic layers are attributed to an interstitial water source. This mixing model study (from Tables 1 and 3) showed that nearly 75% of the contribution is from interstitial water and that 23% is from seawater. Graphs of the Mn_{ex} versus Ni_{ex} , Cu_{ex} and Zn_{ex} (Fig.7) show positive linear relationships.

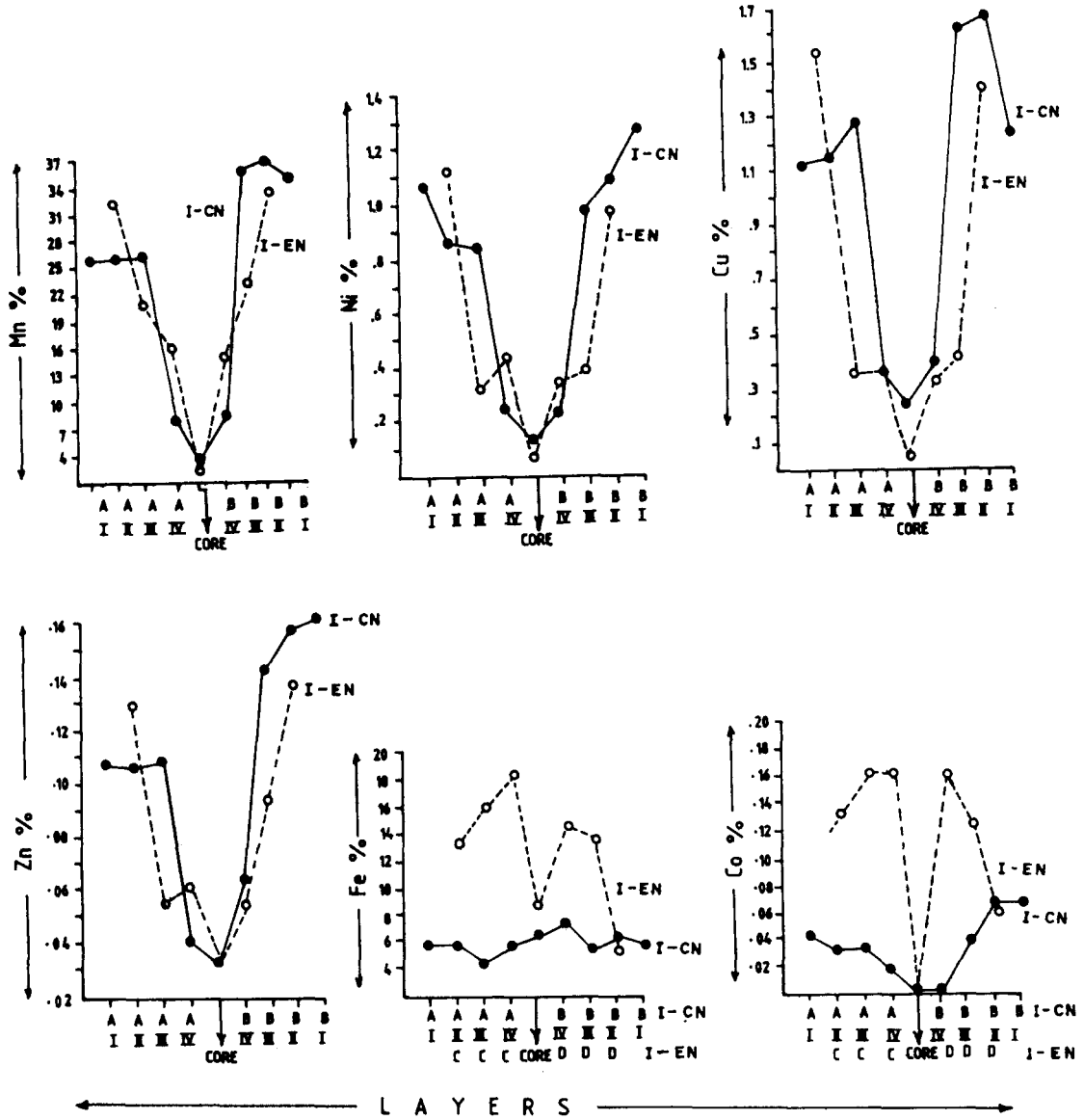


Fig.5. Variation of Mn, Ni, Cu, Zn, Fe and Co relative to the various nodule layers.

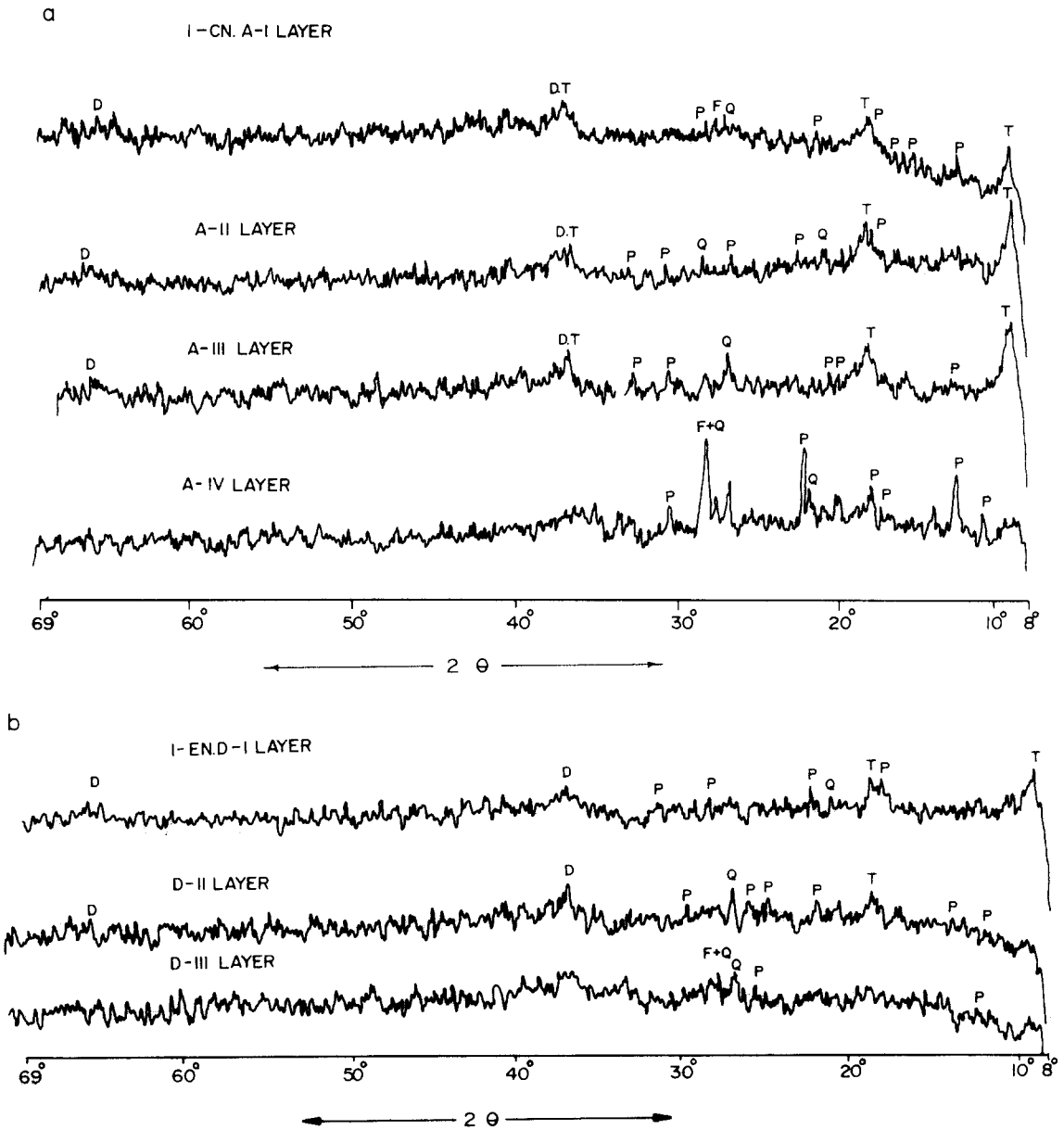


Fig.6. X-ray diffractograms of different nodule layers. a. Nodule I-CN. b. Nodule I-EN. T — todorokite; D — δMnO_2 ; P — phillipsite; Q — quartz; F — feldspar.

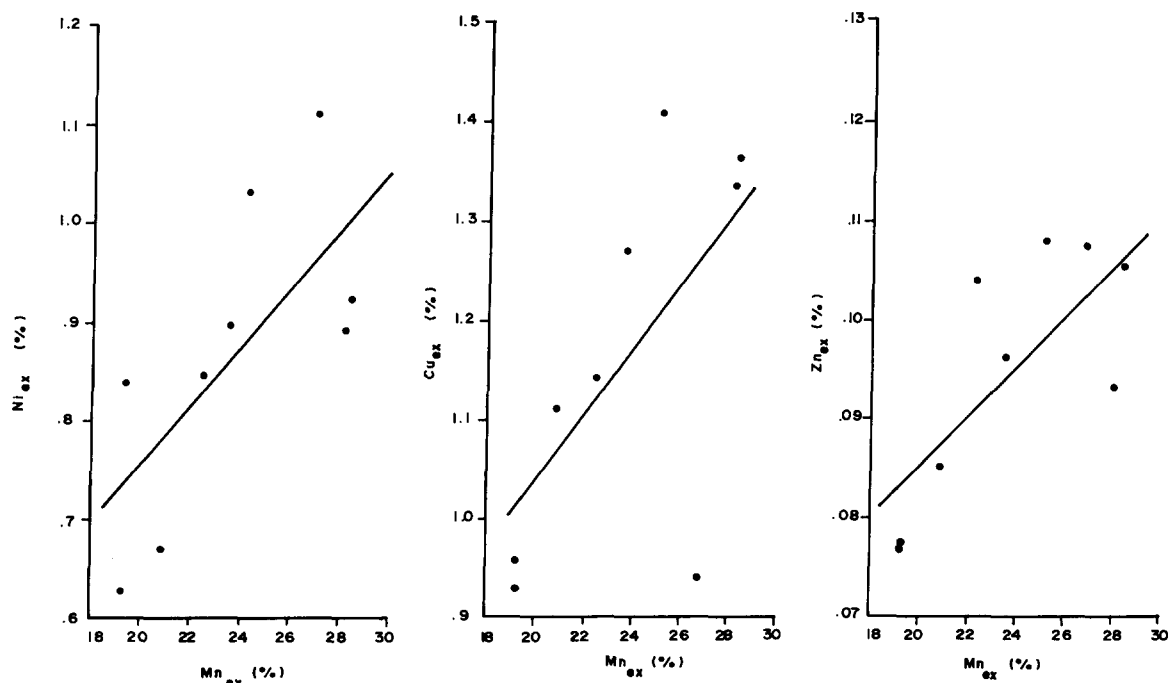


Fig.7. Graphs of the Mn_{ex} versus Ni_{ex} , Cu_{ex} and Zn_{ex} .

TABLE 3

Excess Mn, Ni, Cu and Zn from interstitial water in diagenetic layers within manganese nodules based on mixing model calculations (Piper and Williamson, 1981)

Sample and layer No.	Mn (wt.%)	Ni (wt.%)	Cu (wt.%)	Zn (wt.%)
I-CN				
A-I	19.30	0.83	0.93	0.07
A-II	19.30	0.62	0.95	0.07
A-III	20.80	0.66	1.11	0.08
B-I	26.88	1.11	0.93	0.10
B-II	28.32	0.91	1.36	0.10
B-III	28.10	0.89	1.33	0.09
I-EN				
A-I	25.04	1.03	1.41	0.10
B-I	25.49	0.89	1.27	0.09
C-I	22.36	0.87	1.14	0.10

Conclusions

(1) Manganese nodules from abyssal plains show a prominent well-developed columnar tex-

ture and nodules from abyssal hills show parallel laminations, this indicating different sources and environmental conditions of formation.

(2) Manganese, Ni, Cu and Zn increase from the nucleus to the outer layer of a manganese nodule while Fe and Co show more of a tendency to decrease.

(3) A positive correlation between Mn and Ni, Cu and Zn and Fe and Co, and a negative correlation between Mn and Fe holds good for the different layers.

(4) Compositional and mineralogical studies indicate that nodules were exposed to different source supplies during their growth history.

(5) A mixing model of seawater and interstitial water in manganese nodules indicates nearly 75% contribution in the diagenetic layers by interstitial water and 25% by seawater.

Acknowledgements

The author is grateful to the late Dr. H.N. Siddiquie, Director, for his guidance and en-

couragement. Thanks are due to Shri R.R. Nair, Assistant Director, and to M.V.S. Gupta and Dr. D.Z. Piper of the U.S. Geological Survey for critically reading the manuscript. Thanks are also due to D. Sridhar Iyer, the scientist in charge of the SEM laboratory who helped the author during the SEM studies, and to Shri G. Parthiban for his help in the chemical analysis. The research was carried out with financial support from the Department of Ocean Development under its programme on the manganese nodules survey.

References

- Burns, R.G. and Burns, V.M., 1977. Mineralogy. In: G.P. Glasby (Editor), *Marine Manganese Deposits*. Elsevier, Amsterdam, pp.185-248.
- Cronan, D.S. and Tooms, J.S., 1969. The geochemistry of manganese nodules and associated pelagic deposits from the Pacific and Indian Oceans. *Deep-Sea Res.*, 16: 335-339.
- Dunham, A.C. and Glasby, G.P., 1974. Petrographic and electron microprobe investigation of some deep and shallow water manganese nodules. *N.Z.J. Geol. Geophys.*, 17: 929-953.
- Fewkes, R.H., 1973. External and internal features of manganese nodules as seen with SEM and their implications in nodule origin. In: M. Morgenstein (Editor), *The Origin and Distribution of Manganese Nodules in the Pacific and Prospects for Exploration*. Hawaii Inst. Geophys., Honolulu, pp.21-29.
- Ghosh, A.K., 1982. Internal growth features of manganese nodules from the Indian Ocean. *Indian J. Mar. Sci.*, 11: 317-320.
- Halbach, P., Scherhag, C., Hebisch, U. and Marchig, V., 1981. Geochemical and mineralogical control of different genetic types of deep sea nodules from the Pacific Ocean. *Miner. Deposita*, 16: 59-84.
- Heye, D., 1975. Wachstumsverhältnisse von Manganknollen. *Geol. Jahrb., Reihe E*, 5: 3-122.
- Heye, D., 1978. The internal micro-structure of manganese nodules and their relationship to the growth rate. *Mar. Geol.*, 26: M59-M66.
- Karisiddaiah, S.M., 1985. Mineralogy and chemistry of manganese nodules from the southern part of Carlsberg ridge. *J. Geol. Soc. India*, 26(6): 402-406.
- Mallik, T.K., 1980. Macro- and micromorphology of some manganese nodules from the Indian Ocean. *Mar. Geol.*, 34: M45-M56.
- Margolis, S.V. and Glasby, G.P., 1973. Microlaminations in marine manganese nodules as revealed by scanning electron microscopy. *Geol. Soc. Am. Bull.*, 84: 3601-3610.
- Piper, D.Z. and Williamson, M.E., 1981. Mineralogy and composition of concentric layers within a manganese nodule from the North Pacific Ocean. *Mar. Geol.*, 40: 225-268.
- Siddiquie, H.N., Dasgupta, D.R., Sengupta, N.R., Shrivastva, P.C. and Mallik, T.K., 1978. Manganese iron nodules from the Indian Ocean. *Indian J. Mar. Sci.*, 7: 239-258.
- Usui, A., 1979. Nickel and copper accumulation as essential elements in 10-Å manganite of deep sea manganese nodules. *Nature*, 271: 411-419.