

# Mineralogy and Chemistry of Manganese Nodules from the southern part of Carlsberg Ridge

S. M. KARISIDDAIAH

National Institute of Oceanography, Dona Paula, Goa, India

## Abstract

Petrographic study indicates that the nucleus of nodules is generally composed of clay, volcanic glass, basalt fragments, and earlier nodules. Polished sections indicate typical collomorphic globular segregations and partly crystalline oxides of todorokite. Scanning electron micrographs indicate that they are made up of small and large botryoids; and occasional platelets of todorokite, within cavities formed due to post depositional recrystallization. X-ray diffraction patterns do not show any peaks of todorokite due to poor crystallinity, while  $\delta$ -MnO<sub>2</sub> is seen in all the nodules studied. The nodules analysed show: Mn 15.01-21.40%, Fe 10.07-20.10%, Cu 0.07-0.32%, Ni 0.32-0.57%, Co 0.07-0.21%, and also have a Mn/Fe ratio less than 2. The nodules are of hydro-genetic, secondary origin, source being volcanogenic.

## INTRODUCTION

The Indian programme for the exploration of manganese nodules was initiated by *R. V. Gaveshani* during cruises 86 and 87 in Jan.-Feb., 1981, when the vessel carried out extensive studies of manganese nodules in the North Western Indian Ocean. The present paper is based on the detailed study of the mineralogy and chemistry and origin of the nodules collected during these cruises from the south-western Carlsberg Ridge.

## MATERIALS AND METHODS

The samples of polymetallic nodules collected by *R. V. Gaveshani* during cruises 86 and 87 from the southwestern Carlsberg Ridge form the material for the present study. These nodules were collected by free fall grabs and dredges from nine stations (Fig. 1) ranging in depths from 3600 to 4500 m. The seabed is composed of calcareous oozes. Thin and polished sections of selected nodules were prepared and studied under Carl Zeiss Jena Polarising/ and Reflecting Microscope. Fresh, broken, unoriented peanut size samples were cleaned ultrasonically and mounted on SEM stubs and coated with gold-palladium, and scanned under ISI 40/3A Electron Microscope. X-ray diffraction studies were carried out by a Siefert Iso Debyelex 2000 Diffractometer (at 40 kV and 20 mA) using CuK $\alpha$  radiation and Ni-filter. The scan speed was 2° per minute with a time constant of one second. Chemical analyses of the nodules were carried out using Metrohm Herisau Polarometer with a Polarecord E 506, and titration methods.

## RESULTS

Nucleii of the nodules mainly consist of clay, volcanic glass, basalt fragments, and fragments of earlier nodules. A detailed examination of the basaltic nucleus reveals the presence of laths of plagioclase and pseudomorphs of olivine, and porphyritic texture, suggesting that these are altered olivine basalts.

The internal structures and textures of the manganese nodules are variable and complex. Crystallinity of the oxide phases is recognized by their anisotropism

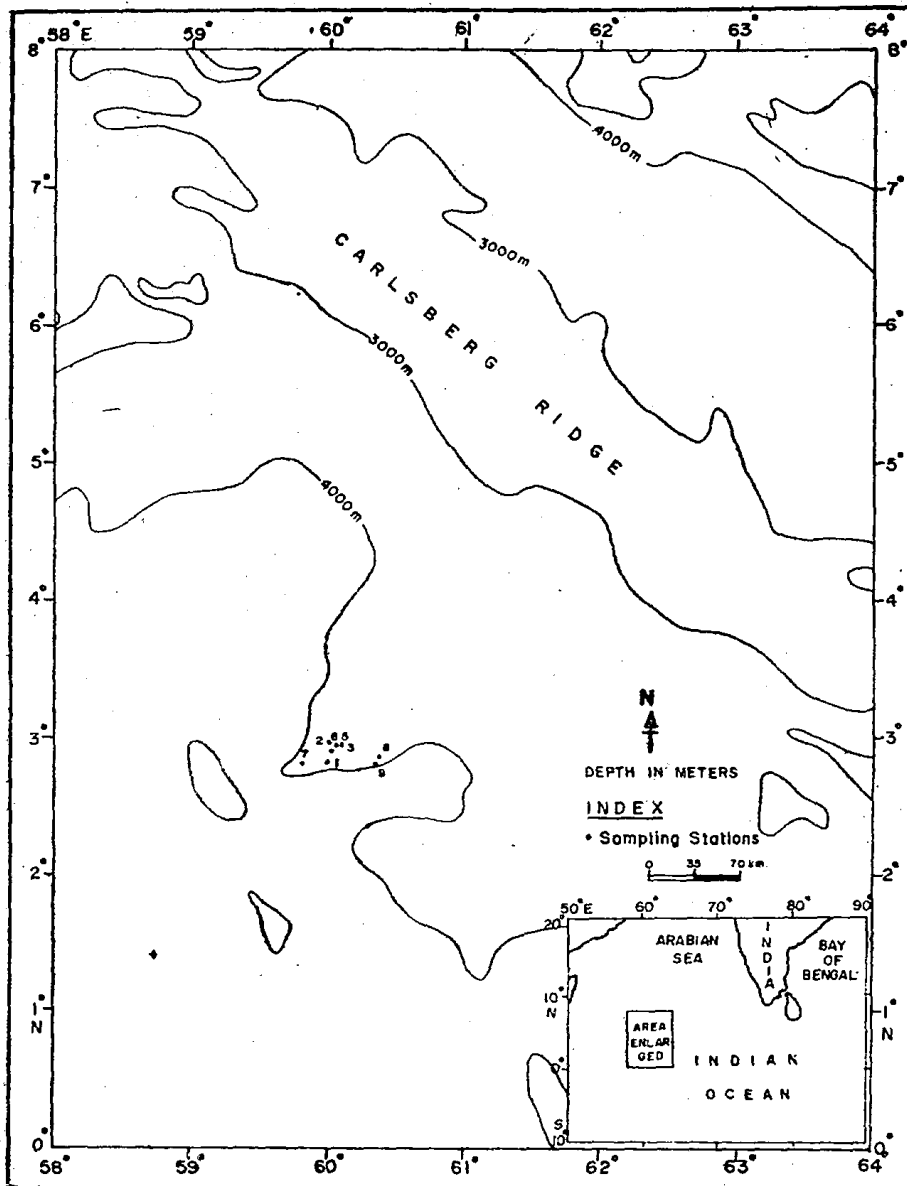


Figure 1. Map of the study area.

(Fig. 2) between crossed polarisers, and the amorphous iron-rich oxides are isotropic in polished sections. The partly crystalline oxides in the nodules studied are restricted to interstitial spaces (Fig. 3), secondary infillings (Fig. 4), veinlets within the nucleus, and pod-shaped bodies which are interlayered with other oxides in the overall concentric nodule structure. Ore microscopic studies of the polished sections, reveal collomorphic, dendritic, and massive, columnar, and laminated structures similar to those observed by Andrushchenko and Skornyakova (1969), and Sorem and Foster (1972). In polished sections, the concentric bands (Fig. 5)

represent thin layers of varying reflectivity, the more highly reflective layers being generally rich in manganese, than the poorly reflective ones (Cronan and Tooms, 1969). Irregularities in nodule growth, with cross-cutting layers indicate periods of non-deposition. Typical structures of easily recognizable collomorphic globular segregations (Fig. 6) of nodules are seen to persist throughout much of the nodule interior. Quite often globular segregations become linked into polygons or cusps (Fig. 7) elongated radially in the direction of the growth of the nodule. Well developed broadly concentric outer layers observed in some of the nodules are quite interesting, which may be attributed to post depositional rearrangement of ferromanganese nodules (Dunham and Glasby, 1974). The dendritic growth textures consisting of alternate laminae of bright grey and grey reflections as noticed by Halbach *et al* (1982) in the Pacific nodules, are also quite common. The typical pod of todorokite, as noticed in the present studies, is smooth and convex towards the outer centre, where many re-entrants in the oxide mass are occupied by finely divided material as well as microfossils (Figs. 8, 9) revealing that pods are of primary origin, developed partially or largely by post depositional replacement of other materials (Sorem and Fewkes, 1977).

Scanning electron microscope studies reveal that the nodules are made up of small and large botryoids, sometimes enclosing platelets of todorokite (Fig. 10) within cavities. Few SEM photographs reveal microlaminations that are believed to be primary structures, as they are laterally continuous around the nodule and remain uniform in both straight and cusped growths. The nodules from the southwestern Carlsberg Ridge, under SEM reveal certain rounded botryoidal features on the external surface resembling a heap of cabbages, loosely aggregated, suggesting that these textures are indicative of deposition by flocculation.

#### X-RAY DIFFRACTION PATTERNS

X-ray diffraction patterns of the powdered samples show  $\delta$ -MnO<sub>2</sub> in most of the nodules, and the diffractogram of each of the nodule is an almost straight line except for few diffused peaks of todorokite. Quartz, microcline, and orthoclase are the other mineral phases identified.

#### CHEMICAL COMPOSITION

Chemical analyses of the nodules (Table-I) reveal that Mn content ranges from 15.01 to 21.40 per cent, Fe 10.07 to 20.10 per cent, Cu 0.07 to 0.32 per cent, Ni 0.32 to 0.57 per cent, Co 0.07 to 0.21 per cent, and Mn/Fe ratio 0.91 to 1.30. Ni enrichment in southwestern Carlsberg Ridge nodules when compared to the ocean average, is normal whereas Cu enrichment is lower as compared to the nodules of the other Indian Ocean basins.

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#### EXPLANATION OF FIGURES

- Fig. 2. Photomicrograph of a polished section of partly crystalline todorokite, showing anisotropism. Nicols crossed.
- Fig. 3. Photomicrograph of a polished section of todorokite seen in an interstitial room.
- Fig. 4. Photomicrograph of a polished section of fine grained todorokite seen as secondary infilling into the silicate zone of the core material.
- Fig. 5. Photomicrograph of a polished section of columnar texture with concentric bands.

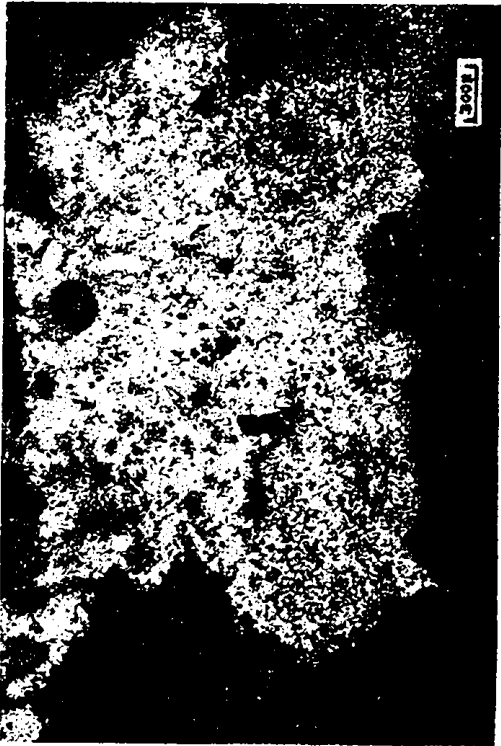


Fig. 2



Fig. 3



Fig. 4



Fig. 5

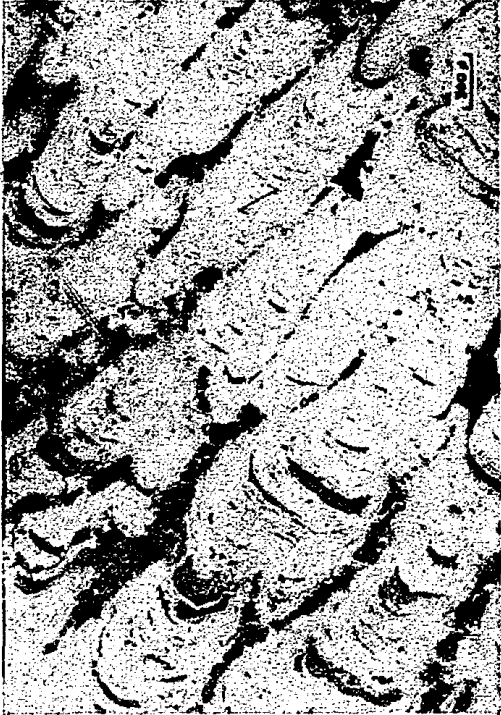


Fig. 7



Fig. 9

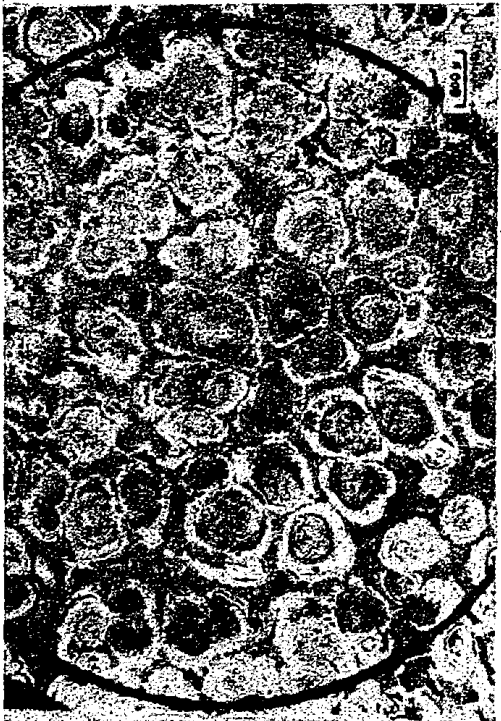


Fig. 6



Fig. 8

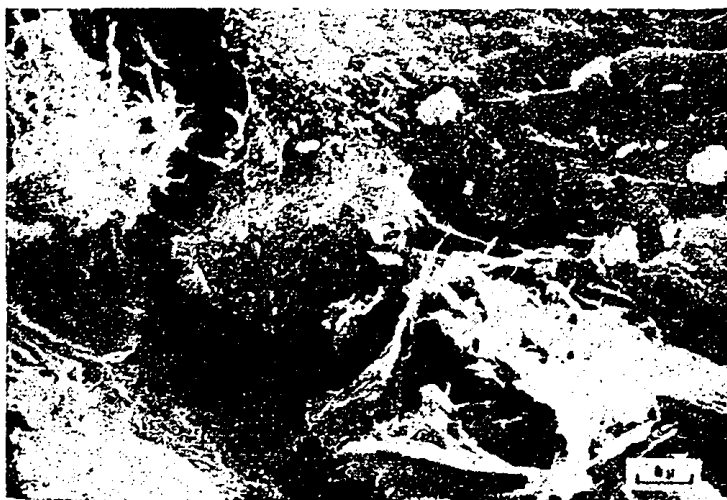


Figure 10. Electron micrograph of a nodule showing platelets of todorokite (white ones) within cavities.

#### DISCUSSION

Marine manganese nodules forming far from areas of high sediment input, and zones of high biological productivity, probably accumulated on highly oxidised sediments. Diagenetic recycling is limited. The association of alternate grey layers of  $\delta$ - $MnO_2$  and  $FeOOH \cdot H_2O$  in the manganese nodules can be ascribed to the phenomenon of hydrogenesis, wherein slow precipitation of hydrated metal oxides take place from near bottom sea water (Bonatti *et al* 1972). This study indicates the presence of  $\delta$ - $MnO_2$ - $FeOOH \cdot H_2O$ , and todorokite.  $\delta$ - $MnO_2$ - $FeOOH \cdot H_2O$  occurs as discrete microlayers, which cannot be seen, whereas todorokite is seen as platelets, secondary infillings, veinlets, pods, in interstitial spaces, and concretions. Burns and Burns (1978a, b) based on SEM studies have shown that post depositional recrystallization leads to the formation of authigenic todorokite inside manganese nodules. Similar processes may be responsible for the todorokite platelets enclosed in cavities which are seen in the nodules studied. Todorokite (from photomicrographs) formation also needs a supply of  $Mn^{2+}$  ions which may take place only under early diagenetic pore water conditions, where a slight decrease of redox potential may cause  $Mn^{2+}$  mobilization (Halbach *et al* 1982) needed for the formation of todorokite. Surface characters and internal structures do show the presence of

#### EXPLANATION OF FIGURES

- Fig. 6. Photomicrograph of a polished section of collomorphic globular segregations.
- Fig. 7. Photomicrograph of a polished section of collomorphic globular segregation linking into polygon or cusp.
- Fig. 8. High magnification photomicrograph of a polished section of foraminifera trapped in the layer of a manganese nodule.
- Fig. 9. Photomicrograph of a polished section of another broken foraminifera seen enclosed in the todorokite layer.

todorokite. X-ray studies do not reveal clearly the peaks of todorokite, perhaps due to poor crystallinity and complex behaviour of this mineral phase in regard to X-ray patterns. Submarine volcanism could be the source for the formation of manganese nodules.

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