# On the occurrence of manganese micronodules in the deep-sea sediment west of Lakshadweep Ridge, Arabian Sea

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**Sediment cores collected from the eastern Arabian Sea, west of Lakshadweep Ridge at water depths of 2800–4400 m, have indicated the presence of manganese micronodules over an area of 0.08 million sq km. These nodules occur sparsely in the sediments between 10 and 50 cm below the seafloor. The host sediment is composed of brown to dark brown pelagic clay of 5 to 20 cm thick. The nodules occur as thin coatings and infillings of Mn-hydroxide mainly over planktonic foraminiferal tests. The micronodules do not exceed 0.5% by weight of the host sediment but are abundant in the coarse fraction (> 53 µm), constituting 2.6 to 24%. Birnessite is the main Mn-hydroxide mineral in the nodule. Chemical data suggest that micronodules are Mn-rich, and are generally Fe-depleted with Mn/Fe ratio varying between 4.76 and 80. Micronodules have highly variable trace element concentrations. In contrast to micronodules of Central Indian Basin, the present nodules are depleted in trace elements, though both have more or less comparable Fe–Mn abundance.**

Occurrence of ferromanganese micronodules in surface and sub-surface sediments has been described from both marine and lacustrine regimes the world over. The formation of both macro and micronodules demands several favourable conditions such as low sedimentation rate, an oxidizing environment, presence of nucleating material, influence of microbiotic activity and the availability of elements for precipitation from lithogenous component and/or pore water. These conditions facilitate the growth of colloidal aggregates of Mn–Fe oxides and hydroxides ranging from microscopic specks to macroscopic concretions[1]. While authigenising Mn and Fe, the nodules also incorporate traces of Ni, Cu, Co, Pb, Zn, noble metals, elements of platinum group and REE.

The basic difference between manganese macro- and micronodule is their size; the latter is commonly smaller than 1 mm and the former can be as large as a few cm (ref. 2). Micronodules from the Pacific are relatively well documented. The distribution of Fe, Mn, Cu, Ni and Co in coexisting Mn-nodules and micronodules from the world's oceans indicates that in about 60% of the coexisting pairs, micronodules are found to show relatively low Ni, Co and Cu and a low Mn/Fe ratio[3]. The morphology characteristics[4] and geochemistry[5–7] of micronodules from the Pacific have been extensively studied. Micronodules of the Central Indian Basin (CIB) have also been studied in recent years. Their distribution, morphology and geochemistry have been dealt by many workers[8–10]. Occurrence of micronodules has been recently reported from Bay of Bengal also[11,12].

The present work is based on preliminary studies of core samples collected from the western part of the Lakshadweep Ridge (LR) during cruises of *RV Samudra Manthan* (RVSM) of the Geological Survey of India between 1986 and 1993. Many of these cores collected from depths of 2800–4400 m have indicated the presence of manganese micronodules in the sub-bottom sediment layer. This layer is composed of brown to dark brown pelagic clay and forms the host sediment. Possibly this is the first report of the occurrence of micronodules from this part of Arabian Sea. The objective of the paper is to present basic data on mode of occurrence, morphology and geochemistry of these micronodules and discuss their probable origin.

Sub-bottom samples of 27 RVSM gravity and piston cores (Figure 1) were partly used for the present study. About 25–30 g of the host sediment was treated with 50 ml of 15% $H_2O_2$ for 15–20 min to rapidly separate the micronodules from the matrix. $MnO_2$ of the sediment being a natural catalyst splits $H_2O_2$ into $H_2O$ and $O_2$ (ref. 13). The reaction is exothermic and the intensity of heat and fumes generated is an indication of the abundance of micronodules in the sediment. After gently stirring and washing, the slurry was wet-sieved using + 230/270 ASTM sieve to separate the coarse fraction,

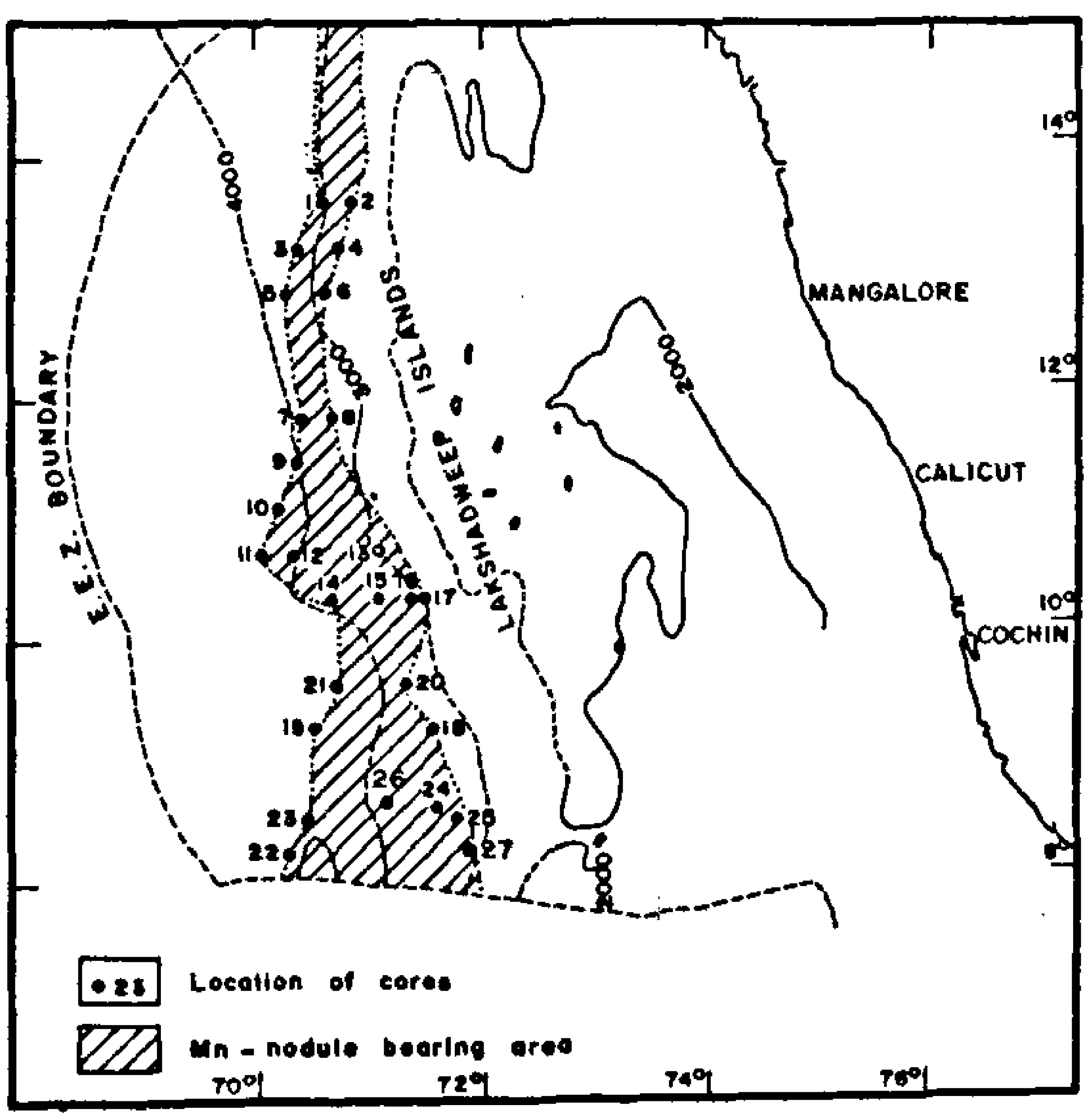


Figure 1. Map of the eastern Arabian Sea showing manganese micronodule-bearing area with locations of gravity cores.

which was dried, and then treated with 20 ml of 10% acetic acid for 10–15 min to remove the uncoated carbonate tests. The concentrate thus obtained was dried, weighed and examined under microscope to find the non-carbonate impurities. In few cases, the coarse fraction was subjected to heavy liquid separation using bromoform (sp. gr. 2.8). The thinly or partially coated micronodules floating in the heavy liquid were collected to study their morphology. Siliceous tests and detrital minerals in the concentrate were less than 1%.

The chemical analysis was carried out on 12 out of 27 concentrates. About 0.1 g of the concentrate was treated with 5 ml aqua-regia and then with 1 ml of 40% HF. The solution was gently evaporated to dryness and 5 ml of concentrated HCl was added and again heated to dryness. After another addition of 5 ml of 1 : 1 HCl, the solution was gently warmed. Mn, Cu, Pb, Zn, Ni and Co were determined using AAS (Varian Spectr. AA 30) in air–acetylene flame whereas Fe was determined in nitrous oxide–acetylene flame. Necessary dilutions were made before feeding the solution into AAS. Calibration standards used were prepared from recommended metals/salts.

X-ray diffraction of one nodule sample (core no. 5057; location 26 in Figure 1) was carried out on Phillips APD refractometer using $CuK_\alpha$ radiation to know the mineralogical components of the nodule. Results were cross-checked using $FeK_\alpha$ radiation.

The micronodules are distributed over a length of approximately 800 km between 8° and 15°N latitudes and 69° and 72°E longitudes. The area of their distribution is narrow (~ 45 km) in the north but gradually widens towards south (~ 380 km) covering nearly 0.08 million sq km of the eastern Arabian Sea (Figure 1). The middle and lower parts of the slope and the areas fringing the abyssal plain show greater abundance of nodules.

Mn-micronodules occur at depths 10–50 cm below sea bed. The host sediment varies in thickness from 5 to 20 cm and is a distinct layer of brown to dark brown (10YR 5/3–4/3) pelagic clay. It occurs between pale brown hemipelagic clay above and olive grey calcareous ooze/hemipelagic clay below, indicating respectively oxic and reducing conditions. Preliminary studies reveal that the micronodules constitute not more than 0.5% by weight of the host sediment, but they are abundant in the coarse fraction (> 0.05 mm), constituting 2.6 to 24%. Interestingly, one core (No. 5050, location 27 in Figure 1) from far-south reveals the presence of fossil Mn-oxidation front even below 50 cm level. The litholog of a representative core (No. 2631, location 15 in Figure 1) from the central part is given in Figure 2.

The micronodules occur as jet black to brownish black coatings and infillings essentially over microforaminiferal tests, less commonly over skeletal tests of pteropods and radiolarians and rarely over glass shards. Authigenic coating over planktonic tests is the most dominant type. The nodules display spheroidal, elongated, botryoidal, tubular or pseudo-framboidal morphologies and commonly retain the shape of skeletal tests or substrate (Figure 3). Their size is generally < 0.25 mm, but larger ones are not infrequent. Pteropod-coated nodules can be even 2 mm long. Partial or incipient coating of the nucleii is seen more in the northern part of the area. The surface texture of the micronodules is characterized by irregular, gritty and at times smooth and polished appearance with bright lustre. Growth of secondary minerals over the nodule often masks its colour and texture.

XRD result suggests birnessite as the major mineral phase in the present micronodule. This is the intermediate variety of the common manganese hydroxides in Mn-nodules and normally forms under suboxic condition. Associated minerals detected are quartz, feldspar, chlorite and illite.

Chemical data of 12 samples are given in Table 1. The data suggest that Mn content is high, varying between 25.10 and 43.0% with an average of 35.83%. Fe varies from 0.53 to 5.27% with an average of 1.82%. The Mn/Fe ratio varies considerably from 4.76 to 80 with an average of 31.10. The trace element content is as follows; Cu: 178–1,100 ppm, Ni: 20–2,000 ppm, Zn: 28–350 ppm, Co: 10–300 ppm and Pb: 40–1,600 ppm. In general, higher Mn values are recorded from deeper areas. The chemistry of the present occurrence and that

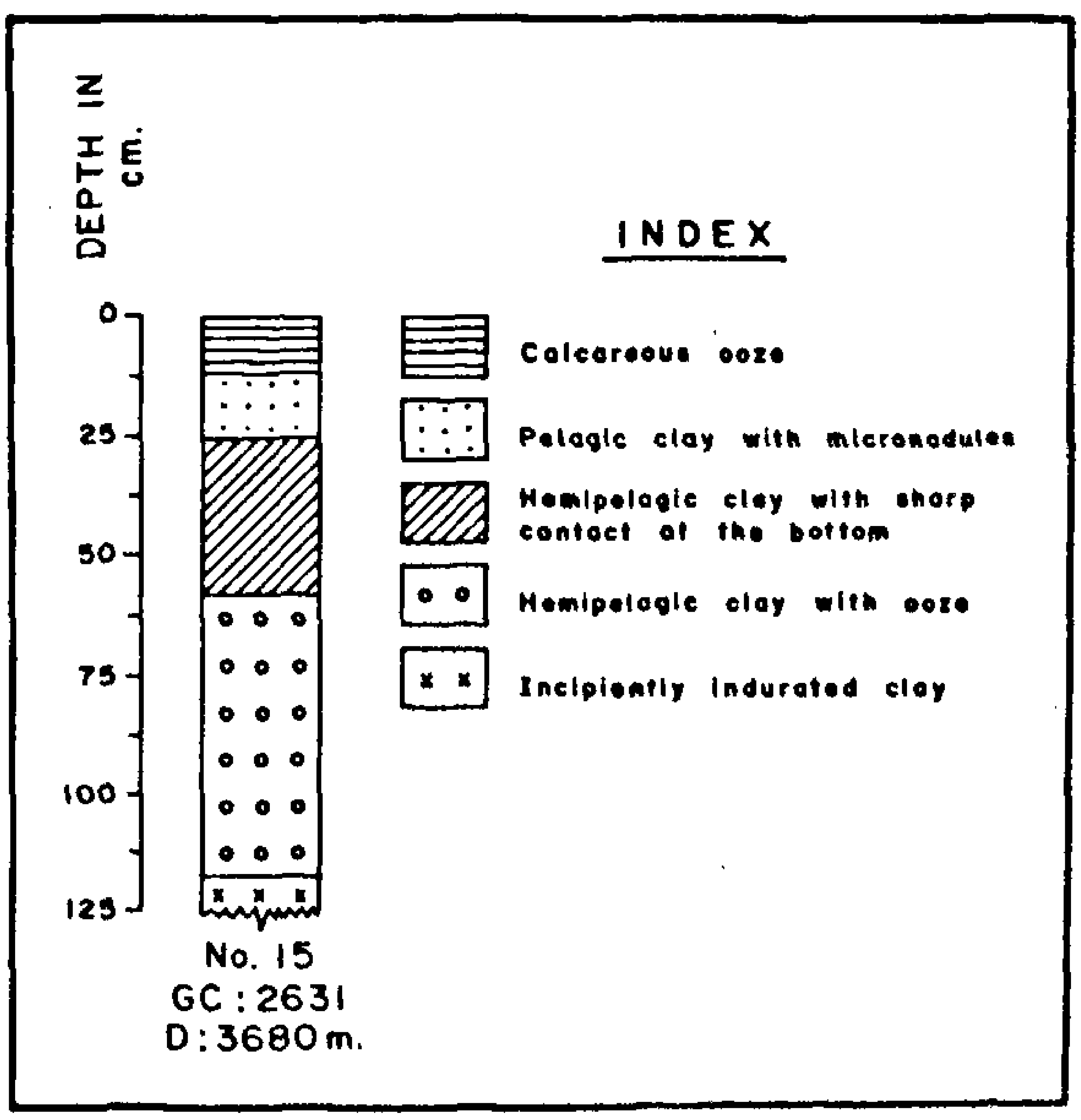


Figure 2. Litholog of a representative core showing Mn-micronodules-bearing horizon.

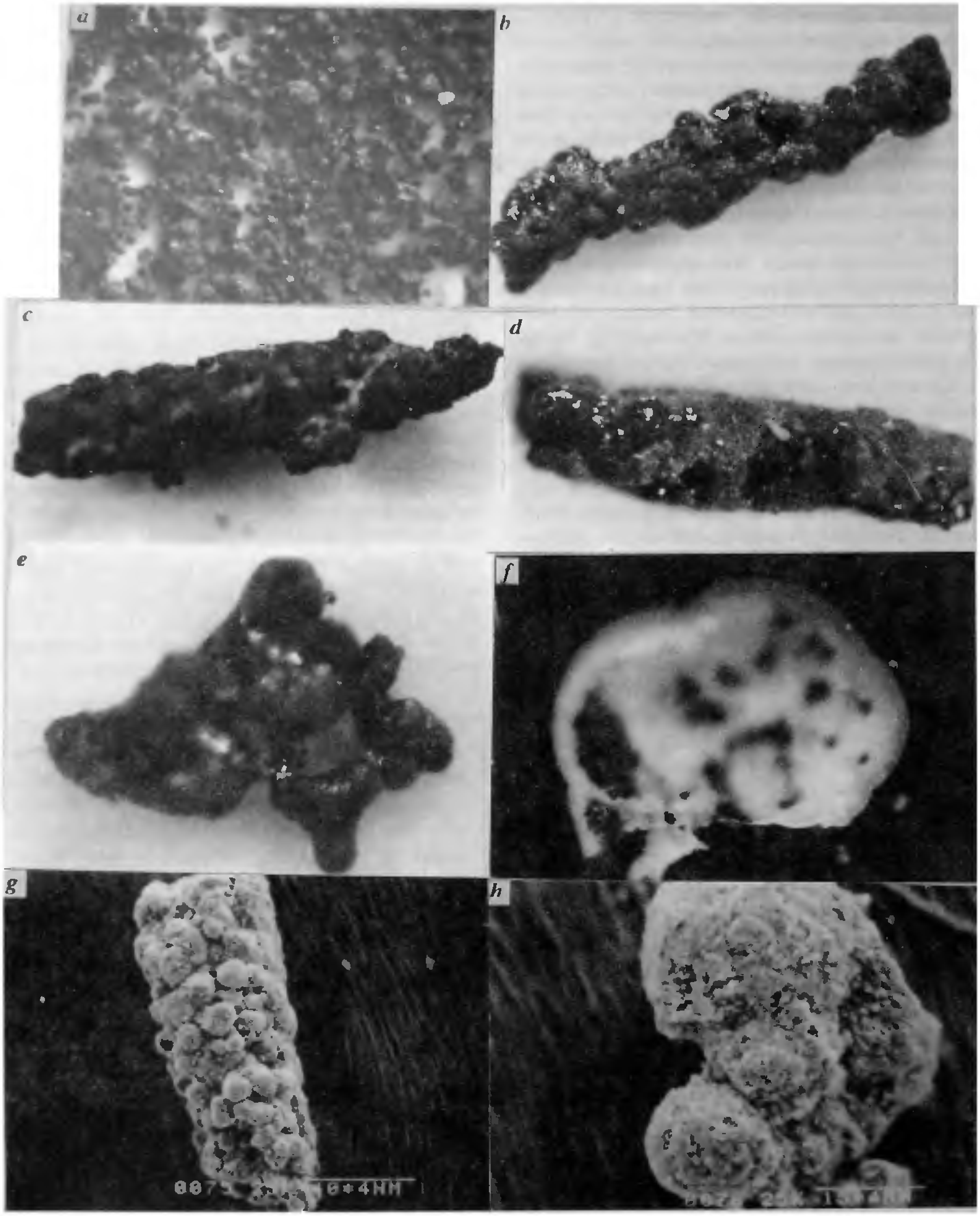

**Figure 3.** Photomicrographs of various types of Mn-micronodules: ***a***, spherical/tubular (assorted), scale (×80); ***b***, elongated botryoidal; ***c***, tubular; ***d***, tubular gritty; ***e***, semipolished and polished with luster, (***b*** to ***e*** scale (×250)); ***f*** incipient coating over *G. menardii*. SEM photos (×150): ***g***, fine hemispherical crystalline aggregates and ***h***, exhibiting poorly developed micro concretions.

of other known occurrences are given in Table 2 for comparison. Micronodules of the present area are broadly comparable to CIB micronodules in their Mn and Fe contents and Mn/Fe ratio. The trace element values in the latter[2], however, are significantly higher and the former is highly depleted of the same. In relation to the micronodules of Bay of Bengal[11,12], the present nodules have higher Mn and comparable Fe, Ni and Co contents.

Marine Mn-mineralization is controlled by three accretionary modes[11,12], viz. hydrogenous precipitation, oxic diagenesis and suboxic diagenesis. Triangular plots of Mn, Fe and (Cu + Ni + Co) × 10 contents of macro/micronodules have been used to delineate the environments of nodule precipitation[14,15,11]. The micronodules and Mn-coating of the present area fall within the suboxic environment (Figure 4). This is corroborated further by the disposition of the host sediment between lithologies indicative of oxic and reducing conditions. Similar sediments, with light coloured brown units above and olive coloured units below showing sharp colour boundary suggestive of an active oxidation front, have also been reported from the Madeira Abyssal Plain, N. Atlantic[16]. Brown colours in pelagites are commonly produced by concentrations of manganese hydroxides[17]. Higher Mn/Fe ratio implies an early diagenetic effect on nodule growth[2,9]. A transition from reducing condition

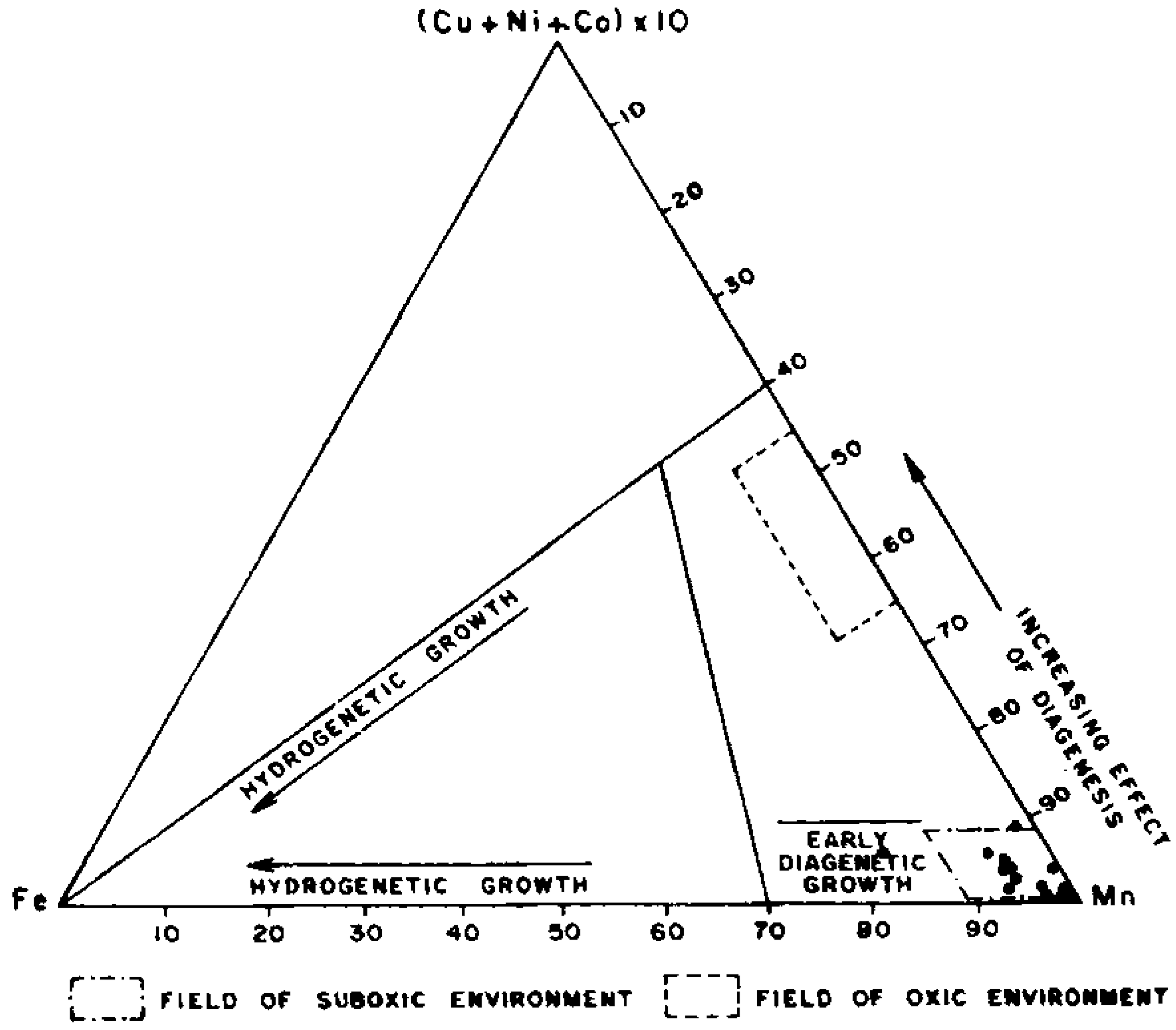


Figure 4. Plot of composition of micronodules from the area in Fe–Mn–(Cu + Ni + CO) × 10 triangular diagram. Most of the values fall in the field of suboxic environment.

**Table 1.** Mn, Fe, Cu, Ni, Zn, Co and Pb values with Mn/Fe ratio of 12 Mn-micronodule samples of the area with water depths

| Location no.*/ core no. | Water depth (m) | Sub-bottom depth (cm) | Mn (%) | Fe (%) | Mn/Fe | Cu (ppm) | Ni (ppm) | Zn (ppm) | Co (ppm) | Pb (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|
| 4/2948 | 2901 | 23–26 | 25.10 | 5.27 | 4.76 | 400 | 1500 | 200 | 10 | 250 |
| 6/2939 | 2874 | 32–35 | 30.16 | 2.17 | 13.90 | 300 | 1500 | 270 | 200 | 170 |
| 12/PC32 | 4048 | 15–23 | 31.00 | 0.60 | 51.47 | 900 | 2000 | 350 | 300 | 220 |
| 14/2630 | 3784 | 32–36 | 40.00 | 0.60 | 66.67 | 490 | 650 | 150 | 260 | 150 |
| 15/2631 | 3680 | 13–26 | 33.10 | 2.00 | 16.55 | 430 | 765 | 285 | 125 | 125 |
| 18/3951 | 3508 | 13–22 | 31.00 | 1.85 | 16.76 | 225 | 750 | ND | 250 | 220 |
| 19/3953 | 4246 | 21–35 | 41.18 | 2.30 | 17.90 | 1100 | 1200 | ND | 230 | ND |
| 21/4563 | 4371 | 22–40 | 42.41 | 0.53 | 80.00 | 178 | 190 | 76 | 60 | 40 |
| 22/5051 | 4321 | 27–40 | 43.00 | 1.20 | 35.83 | 320 | 750 | 300 | 175 | 1600 |
| 23/5055 | 4246 | 44–50 | 41.00 | 1.20 | 34.17 | 270 | 20 | 28 | 35 | 150 |
| 24/5059 | 3613 | 21–33 | 39.00 | 2.00 | 19.50 | 390 | 1100 | 165 | 120 | 190 |
| 25/5060 | 3363 | 23–36 | 33.00 | 2.10 | 15.71 | 190 | 500 | 200 | 190 | 170 |
| Average | | | 35.83 | 1.82 | 31.10 | 433 | 910 | 202 | 163 | 295 |

*Location no. is shown in Figure 1.

**Table 2.** Average chemical composition of micronodules from Arabian Sea, Bay of Bengal, Central Indian Ocean Basin, Pacific Ocean and World Oceans

| Element | Arabian Sea (LR) | Bay of Bengal* | Indian Ocean# | Pacific Ocean+ | World average@ |
|---|---|---|---|---|---|
| Mn | 35.83 | 24.10 | 35.02 | 19.81 | 16.18 |
| Fe | 1.82 | 1.10 | 1.38 | 10.97 | 6.47 |
| Cu | 0.04 | 0.01 | 0.16 | 0.12 | 0.30 |
| Ni | 0.09 | 0.08 | 1.44 | 0.42 | 0.48 |
| Zn | 0.02 | 0.15 | 0.37 | 0.11 | – |
| Co | 0.02 | 0.01 | 0.16 | 0.12 | 0.30 |
| Mn/Fe | 4.76–80 | 10.55–25.42 | 5–101 | 1.95–5.37 | .. |

*Chauhan *et al.*[12]; #Pattan[2]; +Stoffers *et al.*[7]; @Poppe *et al.*[21].

below to oxic condition above is thus indicated by the dark brown pelagites in the present case. It is, therefore, inferred that micronodules of the study area have formed under suboxic conditions with diagenetic mobilization of Mn from the deeper levels and its precipitation at upper levels in the sediment column. This is in contrast to the oxic environment suggested for the formation of micronodules of CIB and for some occurrences in Bay of Bengal[12,2,11]. As in the present case, a few sub-bottom occurrences in the latter, however, have formed under suboxic condition too[11].

The sedimentation rate in the Arabian Abyssal Plain is 2–3 $cm/10^3$ yr (ref. 18). Higher rates of 4.6 to 9.8 $cm/10^3$ yr recorded from the northern Arabian Sea[19] are probably due to the influence of Indus discharge. The waning influence of Indus influx in the south might be another factor responsible for the abundance of micronodules in the southern part and their near-absence in the abyssal plain further west. Another critical feature is that on the western side the abyssal plain had received maximum turbiditic discharge from the Indus during the last glacial peak and on the eastern side forming the western slope of LR the sediments were contemporaneously laid at very slow rate. This must also have favoured nodule growth in the western slope of the LR but not far west in the abyssal plain.

Bioturbation by benthic organisms is cited as another reason for generating the oxidation processes or the means of Mn and Ni supply to the red clays of south Pacific[20]. In this process the burrowing activity is considered to provide furrows and pellets for Mn coating. Ni enrichment is attributed to precipitation by organic processes. Indications of intense bioturbation are seen in the present cores suggesting that elemental concentration by burrowing mechanism is a distinct possibility.

In conclusion, Mn-micronodules and coatings occur extensively in the slope region, west of the Lakshadweep Ridge at water depths of 2800–4400 m. They are usually found in the 5 to 20 cm thick dark brown pelagic clay host sediment which is interbedded with light coloured inhomogeneous sequence of hemipelagic clay/calcareous ooze. The sediment commonly lies 10–50 cm below the seabed. The abundance of the micronodules in the host sediment varies greatly between 2.6 and 24% by weight of the $>0.05$ mm fraction, but not exceeding 0.5% of the total sediment.

Birnessite is the dominant mineral in the Mn-micronodules. The nodules are rich in Mn (35.83%) and are in general Fe-depleted (1.82%) with Mn/Fe ratio averaging 31.10. They have highly variable content of common trace metals, viz. Cu, Ni, Co, Pb and Zn. Based on lithological characteristics, chemistry and mineralogy it is inferred that these nodules have been formed under suboxic condition with early diagenetic effect. The nodule growth is enhanced further by low rate of sedimentation and was possibly aided by bioturbation.

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