

Ferromanganese micronodules from Bengal Fan

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Abstract

The occurrence of ferromanganese micronodules, hitherto unreported from any fan-valley system of the world, has been recorded from over 0.22 million km² area located in the middle fan region of the Bay of Bengal. Their abundance is higher in the eastern bay than in the western bay. Botryoidal and spheroidal are the two dominant morphological forms observed in the eastern and the western bay respectively. The bulk chemical analysis of the micronodules reveals that they have 24.1 per cent Mn, depleted Fe (1.10%), Ni (0.089%), Zn (0.150%) and Co (0.01%), and a Mn/Fe ratio of 21.1. Todorokite in association with quartz, feldspar and phillipsite is observed in the nodules. The preliminary results suggest that Mn released from the smectite clay mineral and early diagenesis are the responsible for their formation.

KEY WORDS ferromanganese micronodules, Bay of Bengal, morphogroups, and chemical composition

Introduction

Ferromanganese micronodules are generally distributed in the upper few cm surfaces of the sediment column of deep sea sediments. Based upon the mass balance equations, a negative correlation between rate of sedimentation and formation and abundance of these nodules has been established (Bender *et al.*, 1966, 1970; Hishida and Uchio, 1981; Stoffer *et al.*, 1984). Occurrence of micronodules (Bender *et al.*, 1970; Roy *et al.*, 1990) is, so far, unknown in a site having a high terrigenous input, particularly in the fan-canyon system. The present work is based upon the study of 13 box cores, and documents the first reported occurrence of ferromanganese micronodules from the middle fan region of the Bay of Bengal. This study consists of determination of spatial abundance, morphogroups, bulk mineralogy and chemical composition of these micronodules.

Methodology

The box cores collected during the 31st and 72nd cruises of the O.R.V. SAGAR

KANYA from the middle fan region having active channel and levees (Fig. 1) are utilized for the present study. The surfaces of cores (0-10 cm; salt freed, dried at 60°C) were subjected to grain size separation at one phi intervals using standard methods (Folk, 1966). The separated >45 µm fractions (sand and coarse silt) were examined under a binocular microscope and the abundance of the micronodules was obtained in >45 and 63 µm fractions of the 10 g dried samples. A minimum of 300 grains were counted in each sample to calculate the abundance of various morphogroups. Due to practical constraints (small quantity of available micronodules), chemical analysis of the bulk micronodules have been carried out on 100 mg of dried powdered micronodules after digesting them in aqua regia on a ICP-AES PLASMA-400. The accuracy of the results of the chemical analysis was checked against the standard SDO 1-3 and was found to be better than 5 per cent. The concentrations of the metals are presented on CaCO₃ free basis. Bulk mineralogy on the handpicked, powdered micronodules was obtained, using a Phillips Diffractometer Model PW 1840 (using a Ni filtered Cu K α radiation). For detailed morphological studies, about 100 micronodules were

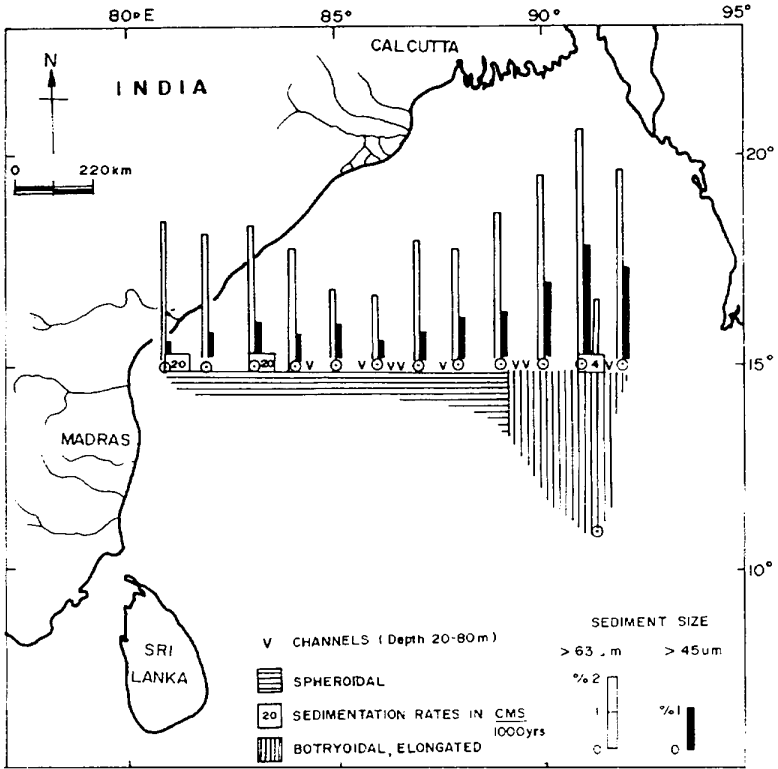


Fig. 1 - Location of the sampling stations, surface abundance of micronodules in 45 and 63 μ size and spatial distribution of morphogroups in the study area. Holocene rates of sedimentation based on earlier studies are also shown.

studied under a Cameax Scanning Electron Microscope (Model 571).

Results and discussions

The occurrence of the micronodules in the study area has been recorded over a 1100 km and 400 km along EW and NS transects respectively (about 0.22 million km^2). There is a marked change in their spatial abundance. The eastern bay has higher abundance of micronodules (>9%; Fig. 1) than the western bay (3%; Fig. 1). The morphology of these micronodules is also variable. A botryoidal-elongated morphology, cemented nodules, and occasionally mammillary

forms (Fig. 2a-c) are observed in the eastern bay. The morphology of the micronodules in the western and central regions is, however, dominantly spheroidal (Fig. 2d); botryoidal, elongated or cemented morphogroups are conspicuously absent.

X-ray diffraction studies of the bulk micronodules (Fig. 3) indicate that todorokite is the dominant manganese mineral phase in all the 9 samples analyzed from eastern, central and western bay. MnO_2 phase was conspicuous by its absence (Fig. 3). Associated mineral phases are quartz, feldspar and phillipsite. Similar association of the minerals was also observed in the micronodules of the Central Indian Basin (CIB) and Pacific (Stoffers *et al.*, 1984; Roy *et al.*, 1990; Banerjee and Iyer, 1991).

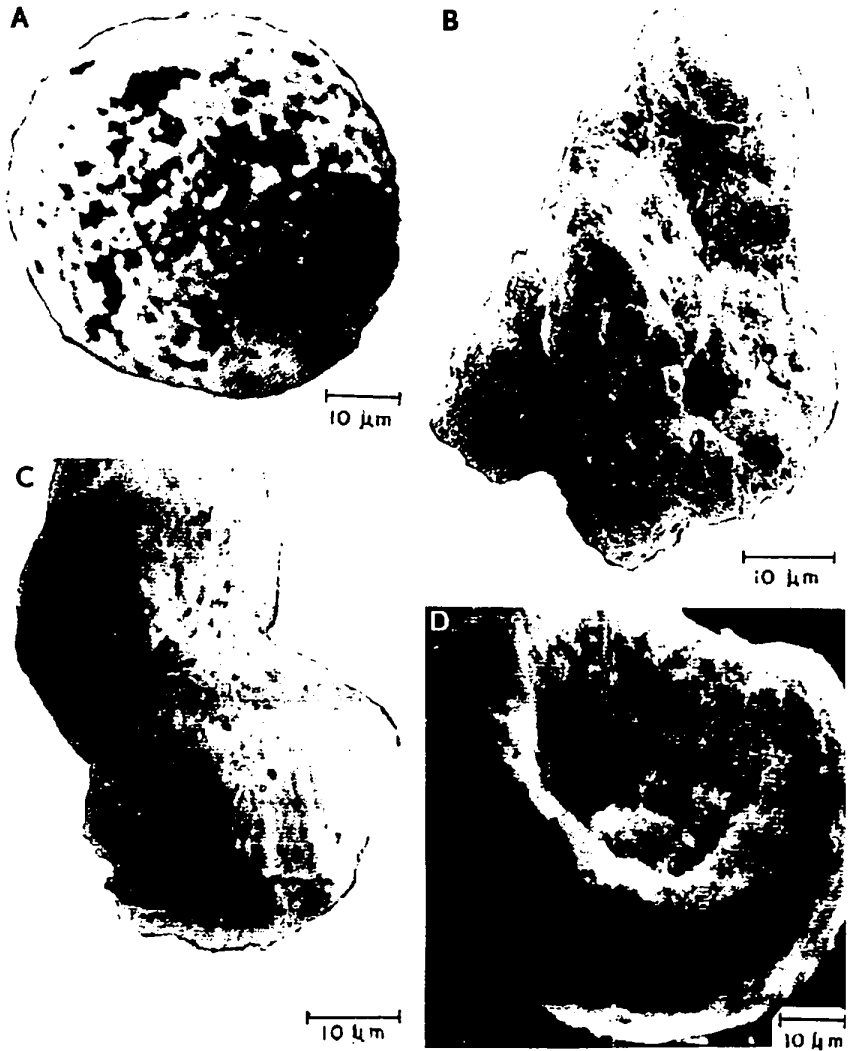


Fig. 2 - SEM microphotographs of the micronodules depicting different morphologies (A-C, from the eastern bay; D, from western bay; all at x 800).

The chemical composition of the bulk micronodules is presented in Tab. 1. The micronodules of the Bay of Bengal are enriched in Mn (24.1%), and depleted in Fe (1.10%), Ni (0.089%), Co (0.01%) and Zn (0.150%). The Mn/Fe ratio in the micronodules is 21.1. Compared to the deep sea micronodules of the other regions of the world

ocean, these micronodules are poorer in Mn, Cu and Ni, and have comparable value of Fe with those of CIB (Tab. 1). The micronodules of the Pacific Ocean, on the contrary, have 10 fold higher Fe and more Ni and Cu, resulting in a lower Mn/Fe ratio (Tab. 1). The important parameters which control the formation of the micronodules

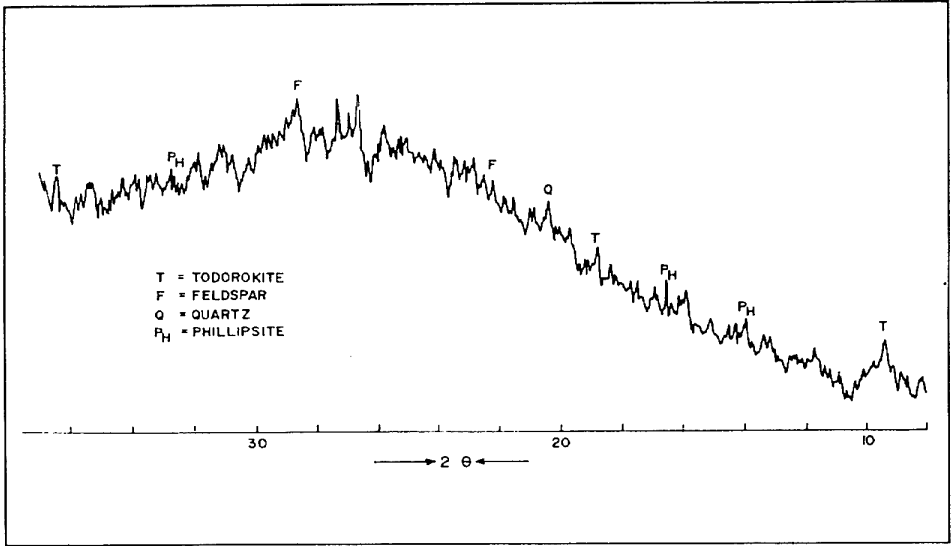


Fig. 3 - X-ray diffractogram of the bulk micronodules from the bay.

are: i) availability of Mn (believed to be contributed from hydrogenous, diagenetic or hydrothermal sources), ii) an oxidizing environment, iii) a low sedimentation and iv) availability of the seeding material (Bender *et al.*, 1966; Roy *et al.*, 1990). The observed presence of micronodules over a sizable area in the Bay of Bengal confirms that the environment for the formation of these micronodules is widespread, and suitable conditions do prevail despite the high rate of sedimentation in this region. This fact also reflects that the rate of sedimentation is not a limiting factor for their formation.

Contrasting morphogroups of micronodules have been observed in the areas characterized by high and low sedimentation rates (botryoidal, elongated and cemented morphogroups in the eastern and dominant spheroidal morphogroups with a complete absence of other types in the central and the western bay). Stoffers *et al.* (1984) have reported that the spheroidal morphogroups are produced by the deposition of Mn(IV) in biological tests which have been subsequently dissolved *in situ*. The treatment of about 100 micronodules with 5 per cent solution of acetic acid reveals the occurrence of

solution pits on the surfaces of 80 per cent micronodules in the central and western regions of the bay only. This implies that the spheroidal group is produced by precipitation of Mn(IV) in the carbonate tests, which are still a part of the micronodules in the western and the central bay.

Oxic environment is dominant at the sediment water interface or a few cm below sub-bottom, and gradually weakens with depth (Marchig and Gundalach, 1979). This environment in the upper few cm of the sediment column is a prerequisite for precipitation of Mn (IV) (Marchig and Gundalach, 1979; Stoffers *et al.*, 1984; Pattan, 1993). An early, deep burial of the micronodules associated with high sedimentation will subsequently move them from oxic to suboxic and then to the reducing environment, and will, therefore retard the precipitation of Mn (IV) released through diagenesis of deeper subsurface or available from hydrogenetic sources (Glasby, 1978; Marchig and Gundalach, 1979; Stoffers *et al.*, 1984; Roy *et al.*, 1990; Banerjee and Iyer, 1991; Pattan, 1993). Thus, following this analogy, an early, deeper burial of the micronodules in an area of high sedimentation should affect the precipita-

Tab. 1 - Average chemical composition of micronodules from Bay of Bengal, Central Indian Ocean Basin, Pacific and world oceans. Values are expressed in per cent. (Adapted from: +Pattan, 1993; # Stoffer *et al.*, 1981; * Poppe *et al.*, 1984).

Elements	Bay of Bengal	Central Indian Ocean Basin +	Pacific Ocean #	World Average *
Titanium	0.10	0.24	-	0.69
Manganese	24.10	36.02	19.81	16.18
Iron	1.10	1.39	10.97	6.47
Aluminium	2.04	0.96	-	1.47
Calcium	1.90	2.34	-	2.22
Magnesium	1.30	3.68	-	1.56
Nickel	0.08	1.44	0.42	0.48
Cobalt	0.01	0.15	0.12	0.30
Copper	0.05	1.69	0.43	0.25
Zinc	0.15	0.38	0.11	-
Mn/Fe ratio	21.90	25.99	1.80	2.50

tion of Mn (IV) or the growth of the micronodules. Also, in a region of slow sedimentation, accreting micronodules will spend more time in a favorable oxicsuboxic environment and will have an enhanced growth.

There is a large contrast in the rate of sedimentation in the Bay (Sarin *et al.*, 1979; Chauhan *et al.*, 1992; Fig. 1): the western and central regions are characterized by a very high sedimentation rate (20 cm/ky; Fig.1), and the burial of the micronodules is much faster in these regions than in the eastern bay which has five fold reduced sedimentation (4 cm/ky). The higher abundance of the micronodules, the presence of botryoidal and the cementation of micronodules in the eastern bay (rather an advanced stage of the micronodule growth) in the eastern region, outline the influence of a high sedimentation input on the growth of the micronodules. Therefore, it is suggested that the rate of sedimentation, though not a limiting factor for the formation of the micronodules, regulates the rate of accretion of Mn.

Bulk chemical analysis of the micronodules indicates that they have a high Mn and a low Fe. Mn/Fe ratio of nodules has been used to stress the processes that contribute towards their formation (Roy *et al.*, 1990; Banerjee and Iyer, 1991). Marchig and Gun-

dlach, (1979), Dymond *et al.* (1984) and Roy *et al.* (1990), based upon the plots of Ni + Cu + Co x 10 and Mn/Fe ratio, have outlined the processes of their formation. The micronodules of study area have a ratio of 21.1 and occupy the diagenetic field in the ternary diagram of Ni + Cu + Co x 10, Fe and Mn (Dymond *et al.*, 1984; Roy *et al.*, 1990). This implies that the diagenesis has played a significant role for the formation of these micronodules. The micronodules of CIB, with similar Mn/Fe ratio and reported to be formed by early diagenesis (Pattan, 1993), also have a similar ratio. The micronodules from the Pacific (Tab. 1), which are, in addition to the diagenetic processes, also precipitated through hydrogenous and hydrothermal sources (Stoffers *et al.*, 1984; Burns and Burns, 1978), have much reduced ratios. Based upon limited preliminary results and available data, the process of formation of the micronodules of the bay appears to be early diagenesis.

In the micronodules, todorokite is the phase reported as a result of diagenetic remobilisation of Mn or its subsequent reprecipitation at the surface of the sediment column (Burns and Burns 1979; Stoffers *et al.*, 1981, 1984; Roy *et al.*, 1990). The results of the present mineralogical studies suggest

that todorokite identified by distinct reflections at 9.65 and 4.82 Å and weak reflections at 2.42 and 1.40 Å (Burns and Burns, 1979) is the major phase in the micronodules (Fig. 3). MnO₂ is conspicuously absent. The observed presence of this mineral, therefore, provides further evidence that the micronodules of the Bay of Bengal are formed during early diagenesis.

The release and remobilisation of Mn (II) from smectite is well documented (Kolla and Rao, 1990; Banerjee and Iyer, 1991). Smectite is the main clay mineral in the Holocene sediments of this area (Rao, 1983; Chauhan *et al.*, 1992). It is well established that Mn is associated with the smectite in the sediments of the continental margin of India (Rao, 1972; Mascarenhas *et al.*, 1985). Sclater *et al.* (1976) and Kalesha (1980) have also shown good correlation between the contents of Mn and smectite, and as such, a high concentration of Mn is observed in the regions enriched in this clay mineral. Under early diagenesis, the release and remobilisation of Mn (II) from this clay mineral have been documented (Kolla and Rao, 1990; Banerjee and Iyer, 1991). Thus, the main source

of Mn seems to be from the clay mineral smectite through diagenesis. In conclusion, it is inferred that the micronodules of the Bay of the Bengal are formed from diagenetic processes. The necessary Mn needed for the formation of these micronodules appears to be released from the diagenesis of smectite, a clay mineral present in significant amounts in the sediments of the bay.

Based upon the abundance of micronodules and distribution of botryoidal and spheroidal morphogroups, it is inferred that the formation of the micronodules is controlled by the availability of the manganese, but their growth depends mainly upon the sedimentation rate.

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REFERENCES

- BANERJEE R. AND IYER S.D., 1991. Biogenic influence of the growth of ferromanganese micronodules in the central Indian Basin. *Mar. Geol.* 97, 413-421.
- BENDER M.L., KU T.L. AND BROECKER W.S., 1966. Manganese Nodules: their evolution. *Sci. N. Y.* 151, 325-328.
- BENDER M.L., KU T.L. AND BROECKER W.S., 1970. Accumulation rates of manganese in pelagic sediments and nodules. *Earth Planet. Sci. Lett.*, 8, 143-148.
- BURNS R.G. AND BURNS V.M., 1978. Postdepositional metal enrichment processes inside manganese nodules from north equatorial Pacific. *Earth Planet. Sci. Lett.*, 39, 341-348.
- BURNS R.G. AND BURNS V.M., 1979. Marine oxides. In: R.G. Burns (Ed.), *Marine Minerals*. Mineralogical Soc. America, 146.
- CHAUHAN O.S., MASCARENHAS A., PAROPKARI A.L. AND RAO CH.M., 1992. Late Quaternary sedimentation in the eastern bay of Bengal. In: B.N. Desai (Ed.), *Oceanography of the Indian Ocean*. IBH Publisher, Delhi, 479-486.
- DYMOND J., LYLE M., FINNEY B., PIPER D.J., MURPHY K., CONARD R. AND PISIAS N., 1984. Ferromanganese nodules MANOP site HS and R-Control of mineralogical and chemical composition by multiple accretionary processes. *Geochim. Cosmochim. Acta.*, 48, 931-949.
- FOLK R.L., 1966. A review of the grain size parameters. *Sedimentology*, 6/2, 73-93.
- GLASSBY G.P., 1978. Deep sea manganese nodules in the stratigraphic records: evidences from the DSDP core. *Mar. Geol.*, 28, 51-64.
- HISHIDA H. AND UCHIO T.J., 1981. Sedimentological, geochemical studies of micronodules and associated sediments in some piston cores in the north Pacific Ocean. *Fac. Eng. Univ. Tokyo*, 36 B, 522-563.
- KALESHA M., 1980. Clay mineralogy and geochemistry of Kakinada-Pentakota shelf sediments, east coast of India. Unpublished Ph.D thesis, Andhra University, Waltair, India, 275 pp.
- KOLLA V. AND RAO N.M., 1990. Sediment sources in the surface and near surface sediments of Bay of Bengal.

- Geo-Mar. Lett., 10, 129-136.
- MARCHIG V. AND GUNDALACH H., 1979. Diagenetic changes in the radiolarian oozes of the central Pacific and their influence on growth of manganese nodules. In: C. Lalou (Ed.), *La Genese des nodules de Manganese*. Coll. Int C.N.R.S., 55-60.
- MASCARENHAS A., PAROPKARI A.L. AND MURTY P.S.N., 1985. Geochemistry of the sediments of the eastern continental shelf of India. *Mahasagar Bull. Nat. Inst. Oceanography India*, 18, 1-25.
- PATTAN J.N., 1993. Manganese micronodules: a possible indicator of sedimentary environment. *Mar.Geol.*, 113, 331-344.
- POPPE L.J., COMMEAN R.F., COMMEAN J.A., MANHEIM F.T. AND ARNSEAVAGE P.J., 1984. Ferromanganese micronodules from the surficial sediments of Georges Bank. *J. Mar. Res.*, 42, 463-472.
- ROY S., DASGUPTA S., MUKHOPADHYAY S. AND FUKUOKA M., 1990. Atypical ferromanganese nodule from the pelagic areas of the central Indian basin, Equatorial Indian Basin. *Mar. Geol.*, 92, 269-283.
- RAO CH. M., 1983. Geochemistry of the sediments of the central western continental shelf of India. Unpublished Ph.D. thesis, Andhra University, Waltair, India, 343 pp.
- RAO D.P.N.V.N., 1972. Some aspects of sediments of Pulicat lake and continental shelf, east coast of India. Unpublished Ph.D. thesis, Andhra University, Waltair, India, 275 pp.
- SARIN M.N., BOROLE D.V. AND KISHNASWAMI S., 1979. Geochemistry and geochronology of sediments from Bay of Bengal and Equatorial Indian Ocean. *Proc. Indian Acad. Sci.*, 88A, 131-154.
- SCLATER F.R., BOYLE E. AND EDMOND J.M., 1976. On the marine geochemistry of nickel. *Earth Planet. Sci. Lett.*, 31, 119-128.
- STOFFERS P., GLASBY G.P. AND FRENZEL G., 1984. Comparison of the characteristics of manganese micronodules from the equatorial and south west Pacific. *TMPM Tschernak Mineral. Petrogr. Mitt.*, 33, 1-23.
- STOFFERS P., GLASBY G.P., THUISSEN T., SRIVASTAVA P.C. AND MELGUEN M., 1981. Geochemistry of co-existing nodules, micronodules, sediments and pore waters in five areas in the equatorial and southwest Pacific. *Chem. Erde*. 40, 273-297.