I. INTRODUCTION

1.1 General

Ferromanganese oxide deposits cover an area of about 10-15 million square kilometers in the Indian ocean (Siddiquie et al, 1978) and is the major authigenic mineral found on the ocean floor. These deposits occur as nodules and encrustations. They are the oxyhydroxides of Fe and Mn with trace and noble metals like Ni, Cu, Co, Pb, Zn, V, Mo, Au, Ag, Pt, Pd etc. Ferromanganese nodules (hereafter referred as nodules) have been accreting around any available nucleating agent like basaltic fragments, clay particles, animal bones etc., while the ferromanganese encrustations (hereafter referred as encrustations or crusts) are the accretions of above mentioned oxyhydroxides on large outcrops of oceanic basalts, compact and hard sediment grounds. Nodules and sediments have totally different depositional history which is discussed in the later chapters.

Central Indian Ocean Basin (hereafter referred as CIOB) has the richest abundance of these deposits. CIOB covers an area of 8 million sq.km and almost all the seafloor area is covered by nodules encrustations and other Fe-Mn oxide deposits with varying abundance and grade (Ni+Cu+Co). This variation has been revealed by the extensive exploration work carried out by National Institute of Oceanography under the financial support of Department of Ocean Development, Government of India.
Though the nodules and encrustations of Pacific Ocean have been studied extensively for understanding their genesis since their discovery (Goldberg and Arrhenius, 1958), those of Indian Ocean have been limited. Geochemical work on record for Indian Ocean nodules are (Mero, 1965; Cronan and Tooms, 1967; 1968;1969; Glassby et al, 1974; Siddiquie et al, 1978; Frazer and Wilson, 1979; Colley et al, 1979; Supriya Roy, 1981; Karisiddiaiah, 1985; Roonwal, 1986; Ahmed and Hussain, 1987 and Jauhari, 1987). The detailed studies for nodules of the various basins of the Indian Ocean was first done by Cronan and Moorby (1981). The interelemental relationship of CIOB nodules was studied by Jauhari (1987) and morphology of the nodules by Mukhopadhyaya (1987). As far as the radiochemical and growth rate studies of Indian Ocean Fe-Mn oxides (nodules and crusts) are concerned, only a limited amount of work is on record (Reyss and Lalou, 1981; Sharma and Somayajulu, 1983; Banakar and Borole, in press).

Nodules and encrustations cover a seafloor area of about 20% over the world oceans and their growth rate is controversial. One school (Ku and Broecker, 1966; Somayajulu, 1967; Ku, 1977; Moore et al. 1981; Krishnaswami et al. 1982; Sharma and Somayajulu, 1982; 1983; Mangini et al. 1986) believes in slow growth of the order of a few mm/ m.y. and the other (Arrhenius, 1967; Lalou and Brichet, 1972; Lalou et al. 1973; 1976) believes in rapid growth of the order of few tens to
few hundreds of mm/ m.y. The source of metals for nodule growth is either the overlying water column or the underlying sediments or both and in certain cases, the submarine volcanic activity. The most commonly occurring deep sea ferro-manganese nodules are shown to be the authigenic precipitates from the overlying water column (hydrogenous) and grow very slowly of the order of a few mm/10^6 y and hence are the best repositories to preserve the signatures of the past few million years of oceanic environmental changes and episodes (Bhat et al. 1970; Somayajulu et al. 1971; Sharma and Somayajulu, 1987). As one studies a nodule or a encrustation from its surface toward nucleus (DEPTH PROFILE), can trace back the history of their growth or the oceanic environments within the limits of dating intervals.

Nodules are not only the source for academic interest but also for the economic interest. They serve as the future resources of trace metals like Ni, Cu, Co and Mn (Mero, 1965). In the CIOB the combined Ni+Cu content is quite above the cutoff grade of 2.0% and abundance more than 5 kg/m^2 in considerable area, thus enabling India to acquire the Exclusive Right for exploration and mining over an area of 150,000 sq. km (UNCLOS document, 1987).

1.2 CIOB

The CIOB extends from 0°S to 25°S and 70°E to 90°E. It is bordered by Indian subcontinent on north, ninety east
1. RVG-S-134.10D. (nodule)  
2. F-VIII-380 (encrustation)  
   GR-1-2A (encrustation)  
   F-123F (Fe-Mn oxide on shark tooth)  
   118A. (Fe-Mn oxide on shark tooth)  
3. SS-X-657. (oriented nodule)  
4. SK-XVI-176. (oriented nodule)  
5. SS-XL-663x (encrustation)  
6. SS-126. (nodule)  
7. SK-148 A&B. (nodules)

Figure 1. Location map of the ferromanganese oxide deposits (nodules and encrustations) studied.
ridge on east, Chagos Laccadive ridge on northwest, Carlsberg and Mid-Indian ridge on west and South Australian ridge on south. The average depth of CIOB is ~4800 m and varies between 4000 m and 6000 m (Fig. 1). There are a few isolated seamounts ranging in their relief between 200 m and 900 m. The major area of CIOB is an abyssal plain (Fairbridge et al., 1966). The abyssal plains of CIOB are believed to be developed by the Ganges fan turbidity currents which distribute the sediments to the far south (Venkataramnam and Hayes, 1974). The entire equatorial current system predominates the circulation system in this area particularly the south equatorial currents are conspicuous (Kinne, 1970).

Four sedimentary facies are reported in CIOB. Terrigenous sediments dominating above 5°S latitude; siliceous sediments between 5°S and 15°S latitudes with isolated patches of calcareous sediments within; pelagic sediments south of 15° latitude which are borderied by calcareous sediments on west of 72°E longitude (Fig. 2). The origin of terriginous sediments is due to the turbidities of Indus, Ganges and Brahmaputra fan; Siliceous sediments due to the settling siliceous skeletal bodies of the organisms like radiolarians and diatoms; pelagic sediments due to settling of clay particles brought down under suspension and calcareous facies due to biological activity in the proximity of continental margins and shallow waters above the limit of CCD.
Figure 2. Distribution of surface sediment types in the Indian ocean (Udintsev et al., 1975).
1. Terrigenous sediments; 2. Pelagic clay;
(taken from Cronan & Moorby, 1981)
I have studied the nodules and encrustations along with a few conspicuous Fe-Mn oxide depositions on biologically introduced hard parts like shark teeth and animal bones and a few buried nodules. These specimens are from the three sedimentary facies except terrigenous facies (Fig 1).

1.3 Genesis of marine Fe-Mn nodules and encrustations

After the discovery of nodules during 1873-1876 Challenger expeditions, Murray and Renard (1891) for the first time proposed that, the elements in nodules were derived from submarine volcanism and/or from continental runoff. Considerable variation in their chemical composition, morphology, internal structure etc prompted Bonatti et al (1972) to attribute nodule accretion and metal accumulations to multiple sources.

Presently we have four theories for explaining the genesis of marine Fe-Mn oxide deposits (nodules and encrustations):

a) Hydrothermal origin (Murray and Renard, 1981): The source of metals are supposed to be the hydrothermal solutions ejected by submarine volcanic activity. Such deposits are characterised by high concentration of Fe over Mn with low trace metal contents. This theory later supported by Bonatti and Nayudu (1965).
b. **Hydrogenous origin** (Goldberg and Arrhenius, 1958): In this case the overlying water column is the source of the metals. The inorganic precipitation of Fe and Mn hydroxides with simultaneous scavenging of trace metals in colloidal state accrete around any available nucleating materials to form nodules and encrustations. These deposits are characterised by Mn/Fe ratios less than 5 and relatively higher concentrations of trace metals (Bonatti et al. 1972).

q. **Diagenous origin** (Murray and Irvine, 1894): The upper few cm thick sedimentary column is the source of metals for these deposits. The Mn in its dioxide phase, in the reducing environment, reduced to lower valency states and pass in to solutions of the upper few cm thick sediment layer (pore waters) and remobilize and migrate upwards in the sedimentary column and gets reoxidised and precipitate as dioxide around a nucleus to give rise to concentrically layered nodules or enters the intermediate layers of todorokite lattice (Halbach et al, 1982). These deposits are characterised by very high Mn/Fe ratios (>5) and Mn/trace metal contents (Bonatti et al. 1972).

d. **Biogenous origin** (Graham, 1959; Ehrlich, 1972): This theory considers the origin of Fe-Mn oxide deposits due to organic rather inorganic processes. The microbes extract trace metals from sea water, oxidize them through enzymetic reactions in which peptones act as catalytic agents and
oxidised metals accrete around a nucleus. The microrzs
extract these metals for their energy source.

Most of the previous studies made by various workers
were directed to solve the origin of the deposits, but none
could evolve a cogent and universally acceptable theory.
However, the inorganic removal and precipitation of metals
either from sea water or from interstitial waters of sediment
column could explain the origin of these deposits with
minimum criticisms and doubts. I considered inorganic
processes are responsible for removal of metals from the
various sources for oxidising and accreting them to form a
nodule or encrustation. The present investigation is based
on this premise.

1.4 Removal of trace metals from oceanic environments

The principal metals in nodules and encrustations
are iron and manganese occurring as oxi-hydroxides. These two
phases act as the hosts for a suite of trace metals like
copper, nickel, cobalt etc., which are present in the sea
water. Although much is understood about the distribution of
these metals in oceanic environment, it is quite difficult to
estimate relative importance of the various mechanisms to
remove them from sea water to authigenic minerals like
nodules. Bender (1972) suggested four approaches to under-
stand the mechanism of trace metal removal;
a. Analysing the chemical compositions and accumulation rates of nodules. From this data the rates of removal of various metals by phases of interest can be estimated.

b. Study of distribution of elements having isotopic compositions which specify their sources, such as uranium, thorium, strontium, lead etc. These elements in sediments having the same isotopic compositions as in sea water are precipitated from sea water whereas other elements can be shown to have detrital or volcanic sources (Bender et al. 1970; Somayajulu et al. 1971).

c. The relative concentrations of REE are indicative of the various sources.

d. Analyses and comparison of trace metal concentrations and their variations in sea water and the geochemistry of underlying sediments yield valuable clues about the behaviour of these metals in ocean environments.

The studies on rates of manganese accumulation (Bender et al., 1970; Somayajulu et al. 1971) in pelagic sediments and as well as nodules indicated almost the same rate suggesting that, there are no special processes involved in enriching the Mn in nodules and the elements largely confined to authigenic phase (Somayajulu et al. 1971).

Nodules and crusts contain as much iron as manganese. Therefore, it is likely that Fe also plays an important role.
in enriching the trace metals in these deposits. Fe may serve as a catalytic agent for oxidation of Mn$^{+2}$ to Mn$^{+4}$ (Goldberg and Arrhenius, 1958). Both Fe and Mn in particulate form have been shown to be effective scavengers of Ni, Cu, Co, Pb etc. from sea water by Krauskopf (1956). Kester and Byrne (1972) studied various complexes of Fe which are expected to be in ocean water and concluded that, under the given pH range of sea water the most significant forms of dissolved Fe are Fe(OH)$_2^+$ and Fe(OH)$_4^+$. Thus the hydroxides of Fe are very important phases in sea water which remove most of the trace metals to underlying sediments and nodules.

1.5 Removal of U-Th series nuclides from oceanic environment

The addition of U-Th series nuclides to the oceanic environment takes place through the following four pathways.

a. rivers supply dissolved U and Ra and their daughter nuclides (alongwith $^{232}$Th) in particulate phases to the ocean.

b. the long lived parents like $^{238}$U and $^{232}$Th decay to Ra and Rn in the sediments and their daughters can be mobilized through sediment pore waters. Depending on the magnitude of interaction with the sediment particles, considerable amount of their daughter nuclides diffuse into the overlying water column.

c. introduction of $^{234}$Th, $^{231}$Pa, $^{210}$Pb etc., to the oceans takes place by insitu production of these nuclides in
coastal and open ocean waters by the decay of their soluble parents like U, Ra and Rn. Wind acts as one of the agents to introduce radionuclides to the ocean. $^{210}\text{Pb}$ produced in the atmosphere through the decay of Rn which has been emanating from continental rocks and soils gets scavenged from the atmosphere through precipitation. Thus $^{210}\text{Pb}$ produced in the atmosphere from Rn decay deposits on to the ocean surface.

The radioactive decay of the nuclides added to the ocean produce several daughter nuclides which in turn are removed to the bottom sediments by the settling particles in the water column through adsorption. Precipitation of oxides and hydroxide phases of manganese and iron can scavenge dissolved radionuclides and incorporate these into sediments and authigenic minerals like nodules and crusts. In oxidizing aqueous environment (pH >6), the naturally occurring uranium isotopes are dissolved during the chemical weathering and form a stable uranyl complex $[\text{UO}_2(\text{CO}_3)_5]^{4-}$ which is introduced to the ocean through river waters. The considerable variation in the concentration of U in river waters was attributed to the localised man-made effects. The uranium concentration in open ocean has been studied by number of workers and indicate that, U is highly conservative in seawater and varies with only salinity. The concentration level of U in open ocean environment is $3.3 \pm 0.1$ ug/l (Turekian and Chan, 1971; Ku et al. 1977).
Within the limitations of uncertainties the oceans are believed to be in steady state with respect to uranium. The removal of U to various sinks takes place through organisms, precipitation of authigenic minerals like nodules etc. The calculated supply of uranium by earlier workers is between $1 \times 10^{10}$ g/y (Borole et al. 1982), while the removal to various sinks accounts to $2.2 \times 10^{10}$ g/y. Out of this total removal metalliferous sediments and ferromanganese oxide deposits take in ~6.4% i.e., $0.14 \times 10^{10}$ g/y.

Unlike uranium, thorium in marine environment is highly particle reactive since its residence time in the oceanic environment is < 100 y (Somayajulu and Goldberg, 1966; Kaufman, 1969). $^{232}$Th enters the open ocean mainly in detrital form. Several workers estimated the thorium concentration of the sea water and gave the upper limit as $0.08$ ug Th/1000 l (Cochran, 1982). Spencer et al (1978) and Brewer et al (1980) observed through the sediment trap experiments deployed at various stations in the Atlantic that, $^{234}$Th activity of the particles was almost constant with water depth indicating the removal of Th on to the particles by adsorption is balanced by its decay. On the other hand the activity of $^{230}$Th was observed to increase with depth. As the particles sink they scavenge more and more $^{230}$Th with depth and there is no availability of sufficient time for its decay during particle settling. Thus the relationship
between $^{230}$Th flux and water depth dependent solely on the $^{234}$U activity of the overlying water column which equals to $2.6 \ D \ \text{dpm/cm}^2/\text{y}$, where D is the water depth in km (Cochran and Osmond, 1976).

1.6 Accumulation rates of ferromanganese oxide deposits

Determination of growth or accumulation rates of nodules and encrustations give clue to their genesis. Hydrogenetic growth is slower in principle than diagenetic and hydrothermal growth, since the contribution of the metals to the oxide and hydroxide phases to be solely from overlying water column. On the other hand diagenetic supply of metals is too rapid in the underlying few cm thick upper layers of the sediment column (Bonatti et al, 1972). Moore et al (1981) have shown through their combined study of a MANOP site nodule that, the top of the nodule had been growing three times slower than its bottom. Earlier to these studies, Krishnaswami and Cochran (1978), suggested the possibility of growth of nodules only when it is exposed to the water column i.e., a nodule turns over or flips at every $10^4 - 10^5 \ \text{y span}$ and the growth is alternative to both sides.

The growth rate of nodule has been a controversial topic since last two decades. The commonly applicable methods like $^{230}$Th (excess), $^{230}$Th (ex)/$^{232}$Th activity ratio, $^{231}$Pa (ex.) have been questioned (Arrhenius, 1967; Lalou and Brichet, 1972; Lalou et al, 1976).
The criticisms made the radiochemists to look for the other long lived isotopes to extend the determination to the greater depths within the nodules. Thus emerged a new method two decades ago viz., cosmogenic Be-10 dating (Somayajulu, 1967). This isotope has comparatively a very long half life of 1,500,000 y and its long term constancy in the oceanic deposition rates (Ku et al, 1982). The growth rates derived from Be-10 studies gave comparable rates with the rates derived from U-Th series nuclides (Sharma, 1982). However the difference in growth rates between these two methods vary by a factor of 2 (Krishnaswami et al, 1982; Segl et al, 1984) and attributed to the changes in nodule growth rate with time. The concordancy in the growth rates (slow rate) by using these various nuclides of very large difference of half lives rules out the possibility of diffusion of these isotopes into the body of the preexisting nodule to give the exponential decay.

1.7 Objectives of the present study

The present study is undertaken to (i) estimate the growth rates of nodules and encrustations of CIOB and to unravel their growth and genetic history by radiochemical and geochemical studies. (ii) estimate the metal fluxes to the accreting body of the nodule and comparing with the other ocean nodules. (iii) to trace the paleoenvironmental episodes recorded in such deposits and reported elsewhere for the
Pacific. (iv) understand the behaviour of metals like Fe, Mn, Ni, Cu, and Co within the body of these deposits and to substantiate the radiochemical and geochemical data base for CIOB.