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OCEANS : GEOCHEMISTRY AND MINERAL RESOURCES *

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Abstract

With increased exploitation of the onshore mineral resources, oceans, that cover almost 71% of earth's surface and known as storehouse of minerals, provide a suitable alternative. Amongst the various underwater mineral resources, placer deposits, phosphorites, manganese nodules and encrustations, metalliferous sediments and hydrothermal sulphides are well studied.

A variety of mineral deposits are known to occur within the EEZ of India. These include placer deposits along the East and West Coasts of India, phosphorite deposits off Goa and off Chennai, hydrothermal sulphides in the Andaman Basin. The polymetallic nodules from the Central Indian Ocean Basin have been studied in detail and as a result India was recognized as a pioneer investor. Further, India became the first country to have been allocated exclusive rights of exploration in the pioneer area in the Central Indian Ocean Basin.

Presently world wide some of the near-shore deposits are being exploited. However, the mining for other mineral resources on the continental margins as well as in deep sea is currently uneconomical. With further depletion of onshore resources and advancement in technology, the mining of these resources may also become a reality in the near future.

Keywords : Oceans, Mineral resources, Placer deposits, Manganese nodules, Geochemistry.

1. Introduction

Much of our industry and commerce depends on non-renewable resources. With ever increasing industrial activity, on land resources are on way of exhaustion necessitating search for offshore resources. The three major oceans, i.e., Pacific, Atlantic and Indian Ocean occupy (up to 80°S) an area of $176888 \times 10^3 \text{ Km}^2$, $98013 \times 10^3 \text{ Km}^2$ and $77700 \times 10^3 \text{ Km}^2$, respectively. First comprehensive understanding of the oceans was possible due to the successful voyage of 'HMS Challenger' that encircled the world during 1872-1876 and collected precious information about the sea floor whose description was carefully recorded by John Murray, a Canadian born Scott. The 'Deep Sea Drilling Project (DSDP)' under which the 'Glomar Challenger' drilled holes of kilometer long on the floor of all the oceans provided compelling evidences about the evolution of the Earth, particularly the sea-floor spreading and continental drift. Such efforts are continued presently under 'Ocean Drilling Programme (ODP)' using the deep sea drilling vessel 'JOIDES Resolution'. Serious attention to deep-sea minerals has been paid since last 50 years after pioneering work of John Mero on manganese nodules. By now, hundreds of the

research vessels belonging to various countries of the world have gathered enormous data on oceans providing fairly good idea about the oceanic processes, ocean geochemistry and its mineral resources.

'Geochemistry' of the oceans is controlled by the interactions between fluxes derived from Lithosphere, Hydrosphere and Atmosphere in the oceanic environment (Fig. 1) working as an 'unified chemical system'. Further, this system is also influenced by various oceanographic parameters such as chemical, physical, biological, geological etc. Eventually this system, wherever suitably balanced, results in the formation of mineral resources on the ocean floor. The objective of the present paper is to describe these processes. Processes leading to the formation of hydrocarbon resources (including gas hydrates), however, are not considered here.

2. Sea Floor Physiography

Physiographically, the seafloor is divided into continental shelf, continental slope continental rise, abyssal regions and deep sea starting from coast to deep sea (Fig. 2). One of the most interesting

* Keynote Address

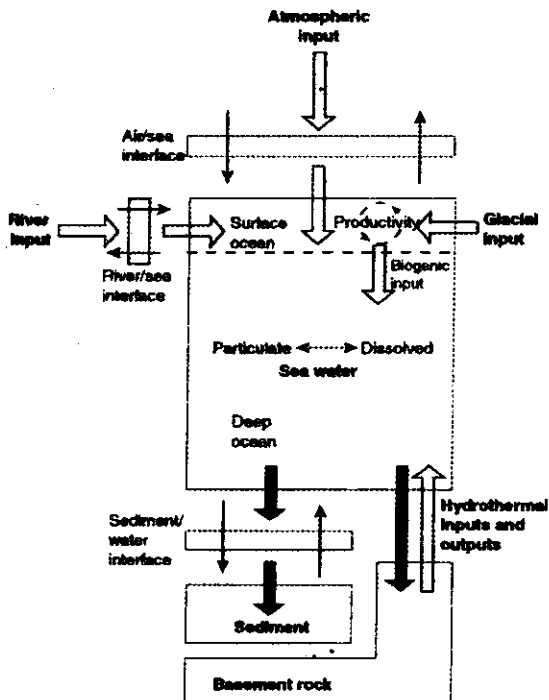


Fig. 1. Material fluxes to the oceans (modified after R. Chester, 2000.)

features of the deep ocean floor topography is the presence of mid-oceanic ridge system passing through floors of all the three oceans, i.e., Indian Ocean, Atlantic Ocean and Pacific Ocean. It is a chain of mountains about 66,000 km long with an average elevation of about 3,000 m above the sea floor. This ridge system is responsible for the sea-floor spreading and plays a significant role in metallogeny of deep sea floor.

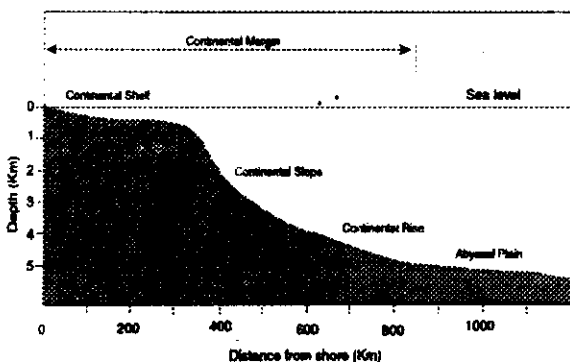


Fig. 2. The physiographic units of the sea floor.

3. Sediment Distribution on the Ocean Floor

The sediments on the ocean floor are classified into six broad categories (Fig. 3). The regions around the continents are covered by the terrigenous sediments, formed by weathering and erosion of land areas and transported to the oceans by rivers, glaciers and wind, which occasionally extend up to the deep sea particularly in the regions of the large deltas off the major river mouths. They comprise gravels, sands, silts and clays. Biogenic sediments are made up of the microscopic remains of planktonic marine organisms that secrete skeletons either of calcium carbonate or silica. These are generated by the surface water productivity and cover large areas where there is no dilution by terrigenous sediments. The siliceous group of organisms (radiolarians and diatoms) results in deposition of siliceous sediments. The red clays that are usually brown due to Fe coating but are popularly known as red clays occupy a large area on the deep-sea floor. The sediments deposited in the open ocean and beyond the influence of processes along continental margins are called pelagic sediments. Glacial sediments occupy large area around Antarctic and are obvious product of weathering of landmass of Antarctica.

4. Sampling of the sea-floor

Large number of devices are used for sampling of the sea floor. These include grabs, spade corer, box corer, gravity / piston corer, variety of dredges etc. The surface seabed samples collected provide the information about the on-going physico-chemical processes at sediment-seawater interface while the sediment cores provide valuable information about the paleo-environment of deposition. Other type of gadgets used are those which are dropped to the seafloor from a vessel and these return to the surface after collection of sample due to buoyancy after offloading the dead weights. These include boomerang grabs and boomerang corers. Underwater photographs also provide valuable information about the nature of the sediments on the floor. Other devices such as remotely operated vehicles and manned submersibles are highly useful for exploring the deep sea mineral deposits.

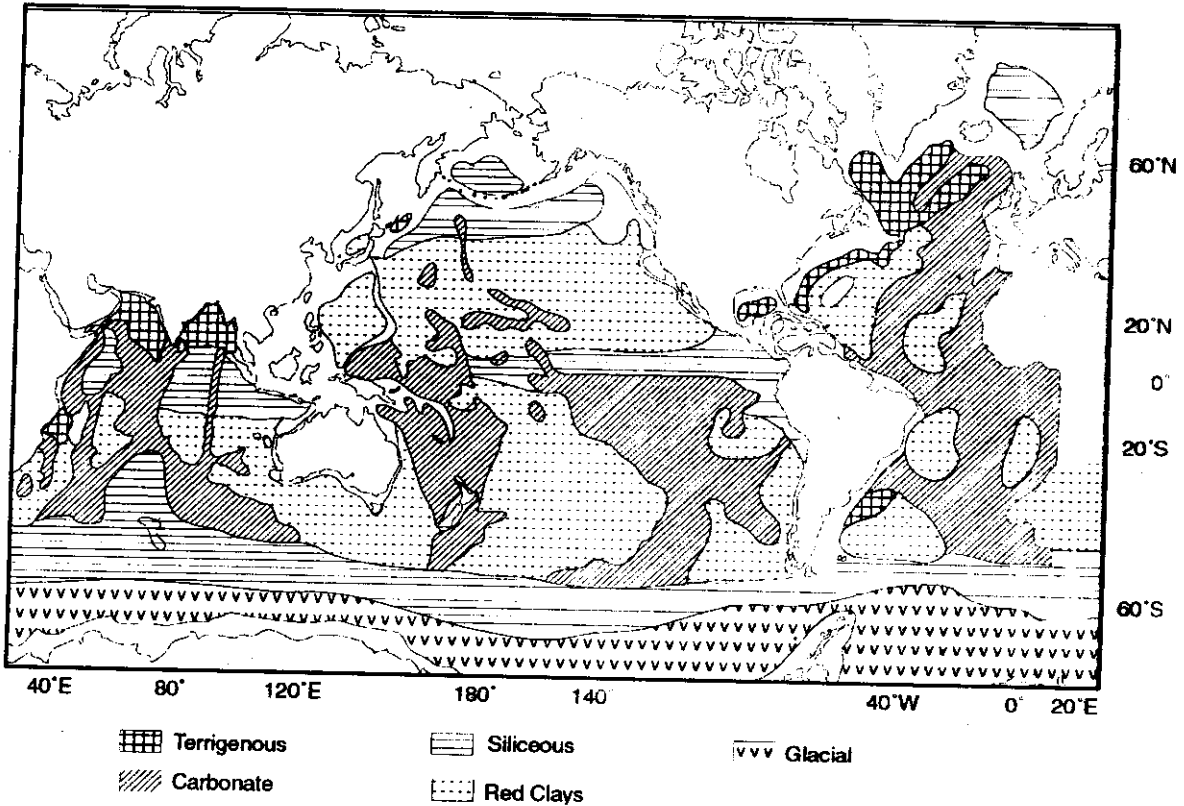


Fig. 3 The distribution of sediments on the ocean floor (modified after Davies and Gorsline, 1976).

5. Marine Mineral Resources

5.1 Placers Deposits

The subaqueous mechanical concentrations of detrital minerals that have been transported from land to the site of deposition in solid form are known as placers and aggregates. The sea level fluctuations during glacial and interglacial periods influence the segregation of such placers.

Important placer deposits are gold, platinum, diamond and other resistant minerals like cassiterite, ilmenite, rutile, zircon, monazite, garnet, magnetite and corundum. Emery and Noakes (1968) have classified the placer minerals into "heavy" heavy minerals with specific gravity of 6.8 – 21, "light heavy" (minerals with specific gravity of 4.2 – 5.3) and gems (with specific gravity from 2.9 – 4.1). Gold, platinum and cassiterite are important heavy heavy minerals. Ilmenite, rutile, zircon and monazite are important light heavy

minerals and the diamonds are the most important gem placer minerals.

The placer mineral deposits generally occupy a narrow strip along the coast on the beaches and ancient placers occur on fossil submerged beaches or in drowned valleys far out on the continental shelf and on raised beaches on land.

The worldwide distribution of the placer minerals is shown in Fig. 4. In North America, important among them are the platinum placers in the Goodnews – Chagvan area of Alaska (Moore and Welkie, 1976). Particulate gold off the seaward Peninsular Alaska and off Nome; Light heavy minerals off Florida and South Carolina. In Africa, diamonds are exploited from the raised beach sands (Murray, 1969) and in offshore areas of South-West Africa (Archer, 1973). Ilmenite and associated minerals have been reported off both East and West Africa (Bell, 1977). The cassiterite deposit of Indonesia, Malaysia and Thailand in South East Asia are

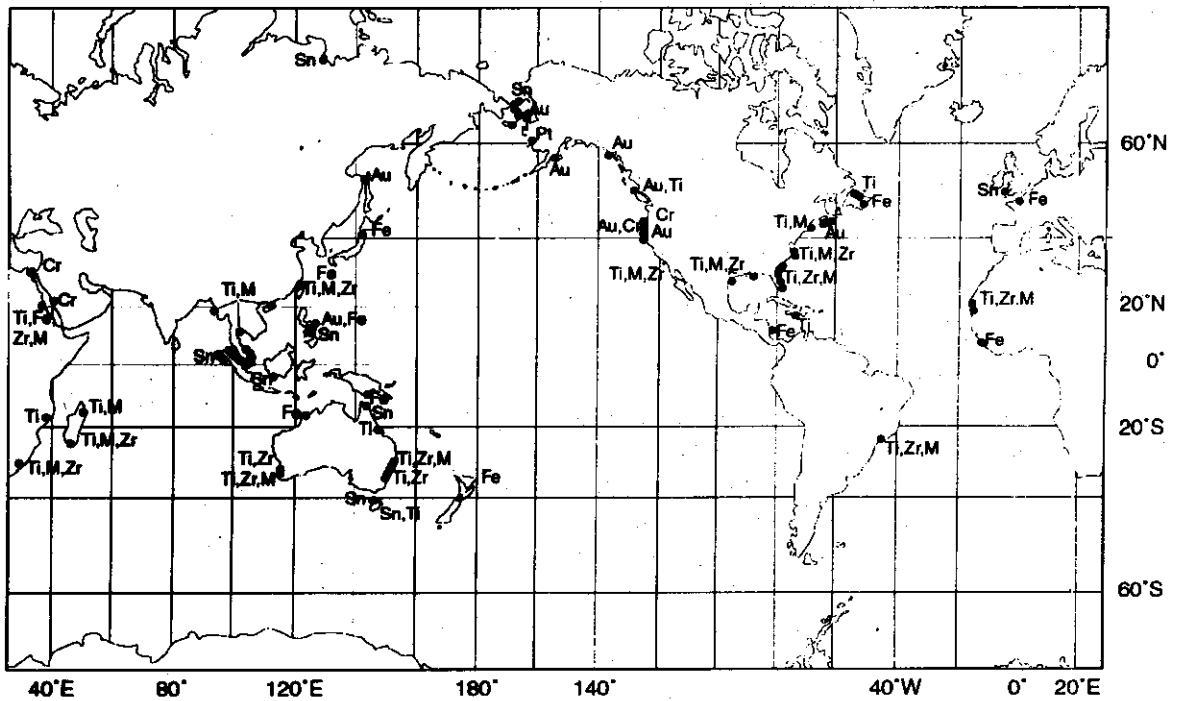


Fig. 4 Worldwide distribution of the Placer deposits (modified after Cruickshank, 1974, The Open University, 1977).

world's most important placer deposits (Aleva, 1973). Rutile and zircon have been produced from the beaches of Sri Lanka. In Australia, rutile, zircon and monazite sands occur on beaches in Queensland and New South Wales (Dunham, 1969). Around Banbury in Western Australia, heavy mineral beds up to 8 m thick and dominated by ilmenite occur at present sea levels and higher. Rutile and zircon bearing sands and gold and tin on beaches and in the offshore area have also been found off East Australia (Jones and Davies, 1979). Several million tonnes of titanomagnetite on the west coast of the North Island and economic ilmenite placers along with smaller deposits of gold, rutile, monazite and zircon as well as garnet, cassiterite and iron have been reported of the coasts of New Zealand (Summerhayes, 1967).

5.2 Barite

Barite ($BaSO_4$) is widespread in marine sediments, mostly in association with biogeneous remains and occurs in the form of nodules, fecal pellets, euhedral crystals and microcrystalline aggregates. While it only averages about 1% by

weight or less in deep-sediments as a whole, Arrhenius and Bonatti (1965) have reported concentrations of as much as 10% on calcium carbonate-free fractions in some Pacific deep-sea sediments. Localized surface occurrences of barite concretions containing over 75% of $BaSO_4$ were reported off Sri Lanka by Jones (1887), and Sverdrup et al. (1942) have reported similar concretions off Indonesia and Southern California. In addition to biogenic source, barytes can also form by the hydrothermal source and is an important constituent of hydrothermal sulfide chimneys (Rona and Schott, 1993).

5.3 Phosphorites

Phosphorites have been described as sedimentary deposits composed mainly of phosphate minerals (Pettijohn, 1957). Its principal mineral is a variety of apatite called carbonate fluorapatite or francolite. Collophane is the term used to describe optically isotropic fine-grained phosphorite under the microscope. Apatite can occur in a variety of forms in the marine environment including fish debris, reptile and mammal bones, shells,

coprolites, microcrystalline aggregates in nodular, pelletal, oolitic or laminar forms, and carbonate and wood replacements (Gulbrandsen, 1969). In shallow marine environments, strontianite is most commonly present as pellets or nodules.

Submarine phosphorites generally occur in water depths of less than 1000 m on continental shelves, offshore banks or marginal plateaux (Fig. 5). They are also found on some oceanic seamounts in association with calcareous and volcanic rocks (Baturin and Bezrukov, 1979). Their greatest abundance is off the western margin of the continents, which are the areas of intense upwelling and high biological productivity. In such localities, the modern phosphorites are being formed by the release of phosphorus during decomposition of organic material. The released phosphorus reaches its supersaturation in the interstitial waters ultimately resulting in authigenic precipitation (Burnett, 1974). Alternatively, the phosphate ion from the interstitial waters causes the replacements in calcareous substrate forming the phosphorite mineral

(Manheim and Hess, 1981; Slansky, 1986). The areas recognized for modern phosphorite formation are the shelf off Peru - Chile in the east Pacific having P_2O_5 content between 12 and 28% (Veeh et al., 1973; Burnett, 1977; Manheim et al., 1975), and the inner shelf off South-West Africa (Baturin, 1971, Price and Calvert, 1978) with P_2O_5 concentration ranging from 5 to 33% (Veeh et al., 1974). According to Slansky (1986), the ideal environment for the formation of submarine phosphorite is the mildly oxidizing- mildly reducing conditions which are present at the interface of oxic-suboxic (OMZ) waters in the world oceans. Phosphorites also occur some eastern continental margins such as off the Blake Plateau, off south-eastern north America (Manheim et al., 1978) and east of New Zealand (Pasho, 1976). Cretaceous and Tertiary phosphorites outcropping on the Morocco-continental shelf have been reported by Summerhayes, (1970).

The formation of carbonate fluorapatite $[(Ca_{10}(PO_4)_6CO_3F_{2-3})]$ involves substitution of CO_3^{2-}

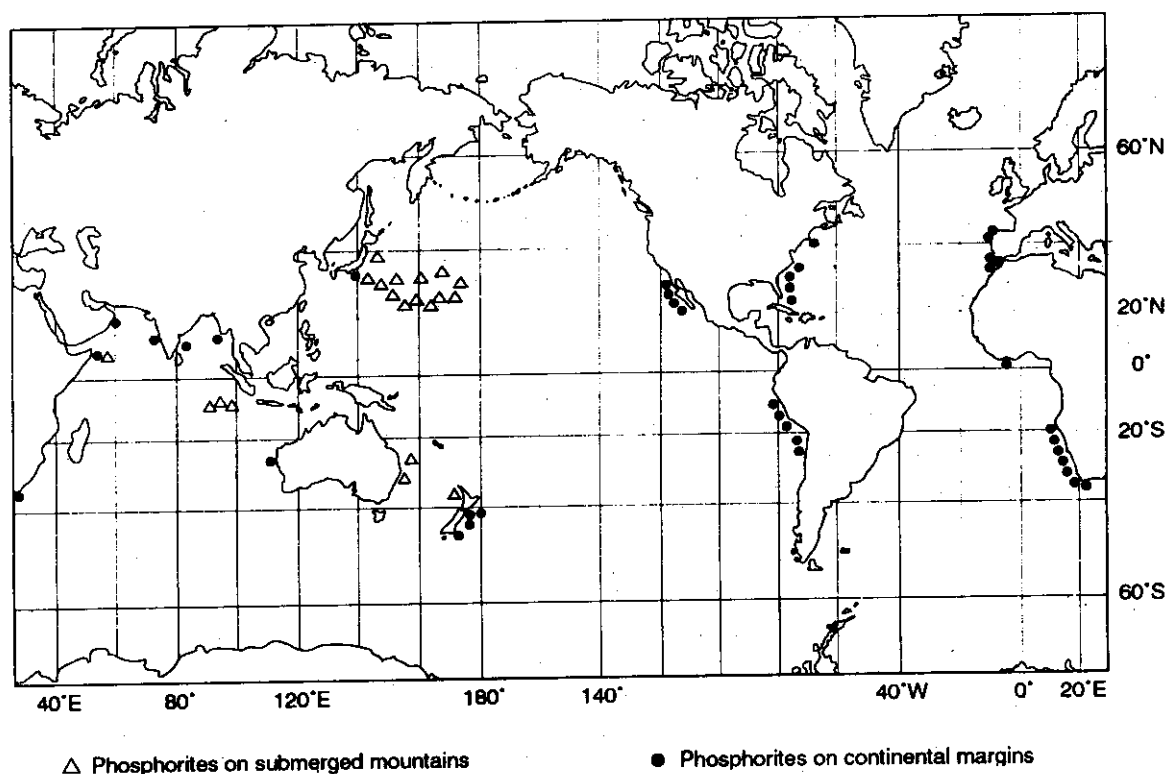


Fig. 5 Worldwide distribution of the Phosphorite deposits (modified after Baturin and Bezrukov, 1979).

by PO_4^{3-} groups. The imbalance of charge consequent on CO_3^{2-} substitution for PO_4^{3-} on one to one basis (Altschuler et al., 1958; Price and Calvert, 1978) is compensated by the introduction of F⁻ (Gulbrandsen et al., 1966) and possibly OH⁻ (Altschuler et al., 1958; Price and Calvert, 1978). Other possible substitutions are Na⁺ for Ca²⁺ and SO_4^{2-} for PO_4^{3-} (Altschuler et al., 1958; Gulbrandsen et al., 1966). The average P_2O_5 values in submarine phosphorites are between 20 and 30% (Mero, 1965).

The composition of minor and trace elements in the phosphorites is very variable. Carbonate fluorapatite lattice, adsorption phenomenon, organic matter, sulfides and detrital matter all play a variable role in this regard. A correlation between organic matter and Ni, Cu, Zn, Ag, Mo, V, Cr, Se and Cd has been reported. Environment of deposition also plays a vital role in composition of phosphorites. For example, if phosphorites are formed under reducing conditions associated sulfides are partly responsible for concentration of certain elements such as Ag, Pb, Cu, Zn, Cd, Mo and Se into the deposits. Several elements such as Ba, Mo, Sr, Y, Ni, Zn, U and rare earths are concentrated by their uptake into carbonate fluorapatite lattice (Price and Calvert, 1978).

5.4 Manganese nodules and encrustations

It was during the Challenger expedition (1873-1876) that the deep-sea potato-shaped concretions - manganese nodules - were first studied in detail. These are found in all the world oceans but in varying abundance (Fig. 6). Usually, the nodules occur carpeting the ocean floors but sometimes they are also found buried underneath the sediments. These nodules primarily consist of Fe and Mn oxides with higher concentration of certain trace elements (Table 1) along admixture of silicate and biogeneous material. Considering this a large number of studies have been carried out resulting in fairly good idea of their worldwide distribution and compositions.

Bonatti et al. (1972) classified the ferromanganese oxide deposits, on the basis of different sources of elements, into hydrogenous, hydrothermal, halmyrolytic and diagenetic

varieties. Hydrogenous deposits are defined as those which acquire their elements, by slow precipitation of elements from normal seawater. Hydrothermal deposits are defined as those in which the elements are supplied to the sea floor by hydrothermal activity in the areas of high heat flow associated with volcanism. Halmyrolytic deposits are defined as those in which the elements are at least in part derived from low temperature submarine alteration (halmyrolysis) of basaltic material on the sea floor. Diagenetic deposits are defined as those in which the elements are supplied partly by their post-depositional redistribution within the sediment column.

According to Murray and Brewer (1977), the removal of iron and manganese from seawater is dependent on the form in which the metal exists. Both elements can occur as colloids or associated with fine-grained clay minerals or as various solution species. Iron in oxygenated seawater is in the 3⁺ oxidation state, which is very insoluble and mostly present in a very fine particulate form indistinguishable from soluble iron by conventional filter techniques. Murray and Brewer (1977) report that most experimental work has tended to suggest that Mn in sea water is predominantly in Mn²⁺ state, the upper limit of solubility of which may be controlled by the formation of MnCO_3 .

Adsorption is a mechanism often proposed for extracting minor elements from seawater into forming ferromanganese oxides (Glassby, 1974). Goldberg (1954) suggested that elements were adsorbed either onto the particulate iron or manganese phases, depending on the relation between the charged densities of the adsorbing surface and that of the adsorbed ions. Opposite charges attract, so negatively charged MnO_2 would attract positively charged ions and vice-versa for positively charged Fe-oxides, MnO_2 being about 2-3 times more effective than iron oxide in this regard. Biological removal of metal from seawater and transporting them to seafloor is an important mechanism for the formation of nodules under areas of high biological productivity (Correns, 1941; Vinogradov, 1953).

Almost all ferromanganese oxide deposits contain a nucleus of one sort or another (Fig. 7),

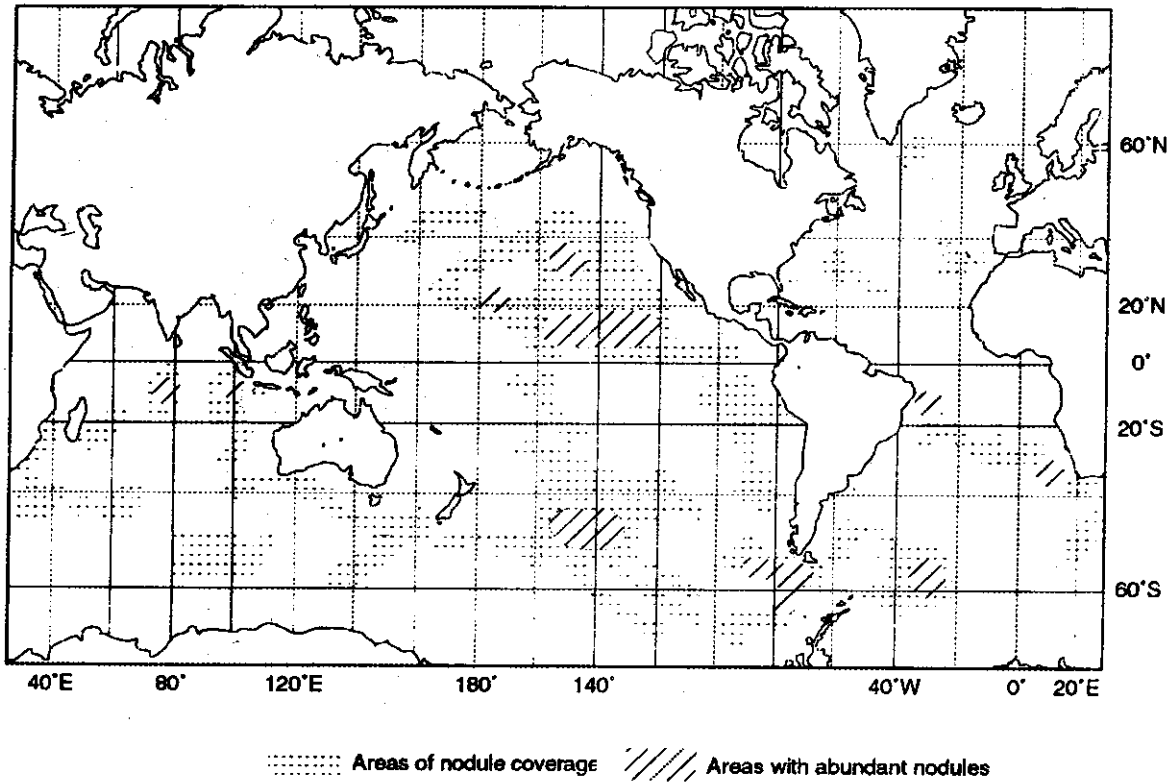


Fig. 6 Distribution of Manganese Nodules on the floor of the world oceans (modified after Rawson and Ryan, 1978, Cronan, 1980).

Table 1. Average elemental concentration (wt %) of manganese nodule from different oceans. From: Ghosh and Mukhopadhyay (1999).

Element	Atlantic Ocean	Pacific Ocean	Indian Ocean	Average for all the three oceans
Mn	13.25	20.10	15.25	18.60
Fe	16.97	11.40	14.23	12.40
Ni	0.32	0.76	0.43	0.66
Cu	0.13	0.54	0.25	0.45
Co	0.27	0.27	0.21	0.27
Zn	0.12	0.16	0.15	0.12

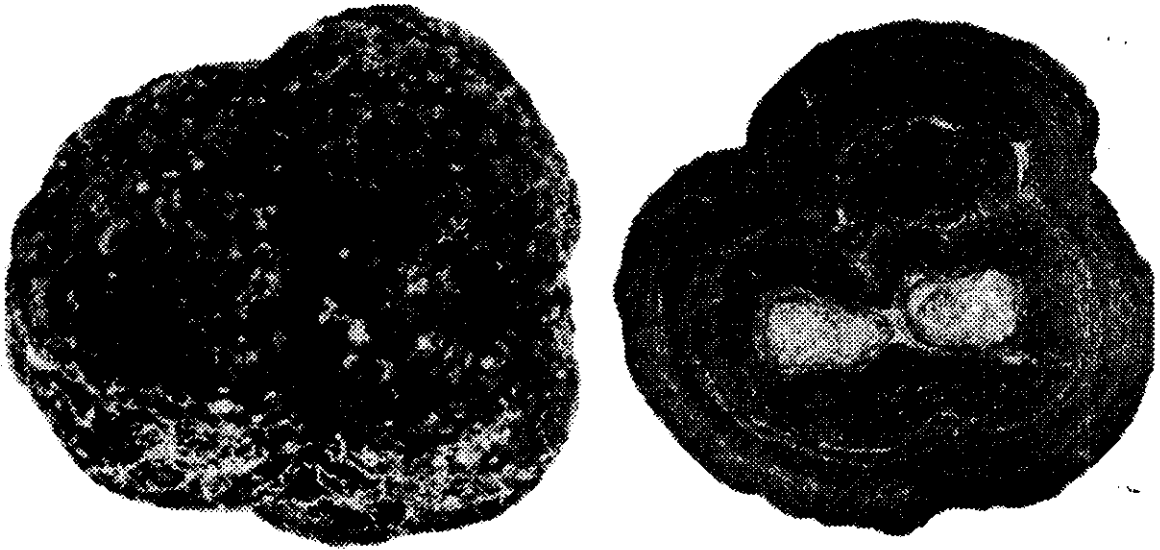
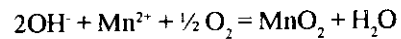


Fig. 7 (a) A normal view of Manganese nodule (b) Cross-sectional view of a manganese nodule showing nuclei (light colour) with concentric layers of Fe-Mn oxides. Both from Pacific Ocean from a depth of 5000 m (after Egiazarov and Ziyka, 1985).

which determines the shape of the early-formed concretions. Quantitatively, the most important nucleus on the deep sea floor is the volcanic debris of various types. Other nuclei commonly found in deep sea nodules are various organic remains such as shark's teeth, foram tests etc. The nodules have various shapes such as spherical, ellipsoidal, tabular, flatten, polygonal and tubercular. In their surface textures they exhibit mamillated appearance on which small tubercles are sometimes superimposed (Raab, 1972). Grant (1967) and Goode et al (1972) defined 'nodules' which have a single nucleus, relatively thick oxide coatings and oval in shape or flattened concretions as 'botryoids', the one which has single nucleus and relatively thin oxide coatings as 'crust' and those consisting of irregular masses composed of pebbles or similar objects, encrusted by thin ferromanganese oxide coatings as 'agglomerates'. The main factor determining the major morphological features of ferromanganese oxide concretions, particularly their shape, is the principal supply path through which they receive their constituents. Notwithstanding the general considerations regarding the element sources to ferro-manganese oxides already discussed, elements will be supplied to concretions either from overlying seawater or underlying interstitial waters.

The main feature of the internal structure

of nodule and encrustation is the concentric banding. According to Stumm and Morgan (1970), the oxidation of Mn^{2+} to MnO_2 is catalyzed by a reaction surface. The first transition metal oxide phase to precipitate is iron oxide - hydroxide ($FeOOH \cdot xH_2O$, goethite or amorphous iron oxide), which forms a surface (Goldberg and Arrhenius, 1958) particularly conducive to Mn oxide precipitation:



This chemistry, alternately, results in the growth of nodule. Nevertheless, the role of organic agencies and of bacteria is important in the formation of nodules. (Graham and Cooper, 1959; Greenslate, 1975 and others). Once in place, the Mn oxide surface is itself autocatalytic and effective in attracting subsequent Mn into the growth structure and also highly effective in attracting and sequestering other transition metals such as Ni and Cu.

The data on the bulk composition of manganese nodule are summarized in Table 1. In addition to the elements shown in the Table, several other elements are also concentrated in these nodules, sometimes enriched in comparison with their normal crustal abundance. Some elements such as Mn, Co, Mo, and Ti are concentrated about 100-fold or more in deep sea nodules. Ni, Ag, Ir, and Pb about 50-100 fold, B, Cu, Zn, Cd, Yb, W, and Bi about 10-50

fold while P, V, Fe, Sr, Y, Zr, Ba, La and Hg up to about 10-fold. There are two possible processes by which the elements are incorporated into the manganese nodule. This includes the substitution of Mn^{2+} ions by divalent cations such as Zn^{2+} , Ni^{2+} , and Cu^{2+} on the basis of ionic radii considerations (Burns and Burns, 1978) and substitution of Mn^{4+} by Co^{3+} (Burns and Burns, 1977) or as $Co^{3+} OOH$ for $Fe^{3+} OOH$ (Arrhenius et al., 1979). The second process is the adsorption of the metals. It is well known that hydrous manganese and iron oxides are characterized by high specific surface areas and are capable of strong interactions with cations in solutions (Stumm and Morgan, 1970).

Rates of growth of manganese nodules and crust have been measured with the help of natural radioisotopes, i.e., ^{230}Th , ^{231}Pa , ^{10}Be , K-Ar, fission track dating of nodule nuclei and hydration ring dating (Krishnaswami et al., 1972; Guichard et al., 1978). Accretion rates can vary from about 1 to 6 mm per million years; Changes in growth rate and in the composition and detailed structure of successive layers have been correlated with past climatic events, in particular the glacial fluctuations that commenced during late Tertiary times (the last 15 Ma or so). The highest growth rates were recorded for the period from about 125,000 years ago to the present; but there seems to be no hard and fast correlation between growth rate and climatic conditions.

5.5 Metalliferous sediments

Metalliferous sediments are the deposits rich in iron, manganese and several other elements found in association with submarine volcanic activity. These deposits are polygenetic in that they can derive their components from more than one source such as terrigenous, biogenic, authigenic, halmyrolitic, hydrothermal and magmatic.

By and large, the land-derived components (terrigenous) always contribute very little to these deposits. Biological contribution by decomposition of soft parts and dissolution of carbonates in deeper waters releasing their metal contents for incorporation into the metalliferous sediment is recognized. In general, the greater the surface biological productivity, the greater will be the transfer of metals

from surface waters to bottom waters. Hydrothermal leaching of crustal rocks by circulating high temperature seawater is well recognized (Corliss, 1971; Spooner and Fyfe, 1973, Bertine, 1974) wherein the acidic nature of waters result, in uptake of heavy metals into solution supporting the formation of metalliferous sediments. Alternatively, the carbonate rich emanations from the mantle enriched in Fe, Mn, P, Ba and U may play a major role in concentration of these elements in mid-ocean ridge sediments (Bostron, 1973). Evidence for supply of elements to metalliferous sediments seawater comes from similarity in isotope ($^{87}Sr / ^{86}Sr$ ratios) and REE concentration in metalliferous sediments and seawater (Dymond et al., 1973). Geochemical partition analyses of the East Pacific Rise (EPR) metalliferous sediments suggested precipitation of Mn, Co, Ni and Pb from seawater, possibly catalyzed by Fe oxides (Cronan and Garrett, 1973).

The most exciting submarine metalliferous sediment deposits are those formed by the role of brines. e.g., the highest grade metalliferous sediments in the Red Sea, in the Atlantis II DEEP. Experimental data show that brine is a more effective leaching agent of metals from rocks than normal seawater. Further, in the Atlantis II DEEP, the brines do protect the sulphides from oxidation and destruction by maintaining a reducing environment and, thus, are probably necessary for the long-term preservation of the deposits.

The metalliferous sediments in the Red Sea offer the greatest economic potential of any such deposits so far found. They occur in a number of deeps in the Median Valley of the Red Sea and are still in the process of formation. The characteristic features of the Red Sea sediments is the considerable diversity in chemical constituents that they often exhibit both vertically and laterally over relatively small distances. (Bischoff, 1969; Backer and Richter, 1973; and Bignell et al., 1976). Bischoff (1969) classified the Red Sea sediments into 6 major groups i.e. oxides, sulphides, sulphates, carbonates, silicates and normal sediments. Of these groups, the sulphides, oxides and silicates are those containing the largest metal enrichment. The sulphide group of sediments form the principal economic deposits and are divided into a) mixed sulphides of Fe, Cu and Zn, and b) pyrite. In the

Atlantis II Deep mixed sulphides exhibit concentrations of Zn, Cu and Fe over 10%, 2% and 15%, respectively (Bignell, 1975). It has been suggested that the sulphide in the Atlantis II Deep, brine was precipitated in the Deep, as increased concentration of free metal ions caused by dissociation of chlorite complexation. However, precipitation may also occur prior to discharge at temperatures as high as 150°C.

5.6 Hydrothermal sulphide

Analogue to the discovery of metalliferous sediments, the most significant was perhaps the discovery of polymetallic sulphide occurrences at 21°N EPR (East Pacific Rise) where ore-forming “Black Smokers” and venting fluids were actually observed. From economic point of view, compared to manganese nodules, these deposits are indeed rich in many metals by about 1000 times the mass per unit area. The majority of hydrothermal deposits are found in extensional tectonic settings (i.e., in rifts) on axis or near axis of the Mid Oceanic Ridges and in Back Arc Basins (Fig. 8). Mineralization at spreading ridges result from seafloor hydrothermal processes involving free circulation (convection) of seawater through

oceanic crust and its return to the seafloor with elevated temperatures of a few hundred degrees centigrade. The mixing of hot fluids with ambient seawater results in precipitation of sulphide minerals eventually forming hydrothermal vents or chimneys. The heat source is most commonly a magma chamber that may occur at depths varying from 1-10 km. The hydrothermal convection is also fuelled by anomalously high thermal gradient between the hydrothermal fluids and seawater. The percolating seawater enters high temperature environment at deeper depths, changes to a chemically modified hydrothermal fluid, and while the hot aqueous circulating fluid selectively alters, leaches, and dissolves many elements from the host oceanic crust, gets enriched in those elements (Pirajno, 1992) which include S, Fe, Mn, Cu, Zn, Cd, Pb, Ni, Co, and others. In this process, the hot fluid becomes acidic having abundant hydrogen sulphide and metals relative to normal seawater. During the reaction of the fluid and hot rock, magnesium gets totally removed from the circulating hydrothermal solution, while Ca, Be, alkalis (except Na), H₂, H₂S, CO₂, CH₄, helium (³He) contents increase. Some typical hydrothermal mineral phases are sulphides of Cu, Fe, Zn, with noble metals Ag, Au, Pt; sulphates of Cu, Fe, Zn,

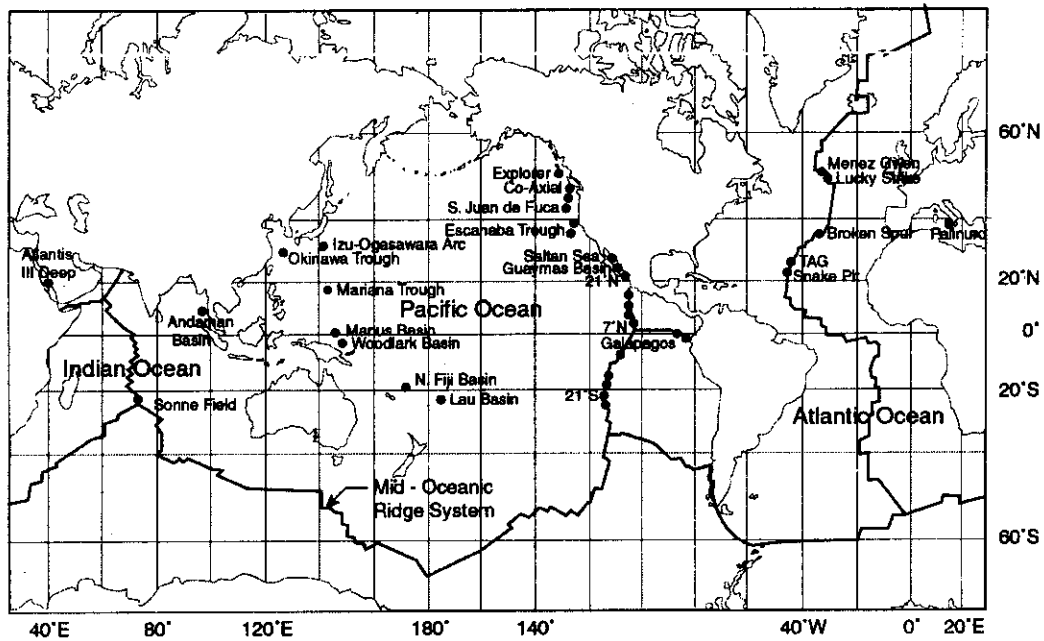


Fig.8 Worldwide distribution of Hydrothermal Sulfide deposits (modified after Herzig and Hannington, 2000).

Ba; Silicates of Fe, Al, Na, K; Oxides and hydroxides of Fe, Mn; and carbonates of Mn and Fe (Rona, 1984; Rona et al., 1986).

The smokers are of two types-White and Black. The white smokers (temperature 100-250°C) containing barite, silica, and some pyrite are discharged through chimney shaped edifices, at rates of tens of cm/second to precipitate, from white clouds, whereas, Black smokers, in contrast, consists of very hot (temperature 350-400°C) hydrothermal fluids gushing out from chimneys at faster rates of 2-3 m /second and precipitating sulfide minerals. The fastest forming chimneys are reported from EPR, growing at the rate of 8 cm in height and 2 cm diameter per day (Lalou et al., 1985). These black chimneys are concentric hollow spires up to 6 m high, with 1.5-10 cm in diameter. Walls of these chimneys are remarkably thin (varying between 12cm to as little as few mm, yet showing a temperature difference of 300°C or greater), and exhibit steep compositional gradient between inner and outer fluids. The result is that the inner channel in contact with hydrothermal solution is lined with chalcopyrite, while the outer layer in contact with sea water contains varying amounts of anhydrite, pyrite, marcasite, chalcopyrite, bornite, sphalerite and wurtzite (Lalou et al., 1985).

The hydrothermal deposits are explored using the most unequivocal indicators, concentration anomalies of helium, manganese and methane in the water column. A weak tracer of hydrothermal activity is the distinct positive Eu-anomaly (Michard, 1989). The presence of a certain group of biological organisms at deep sea also acts as a tracer of hydrothermal activity. These include mussels, giant clams, crabs, whelks, pink bythitid fish, tube worms and many species of limpets are known to thrive in areas of hydrothermal vents. These vent organisms utilize chemical energy through the process known as chemosynthesis.

The well-known example of hydrothermal activity along the fast-spreading ridge is the area between 9°S and 26°S along EPR (East Pacific Rise). The spreading rates here vary about 80 mm per year. The reported regions of intermediate-spreading

ridge where hydrothermal mineralisation occurs are the Galapagos spreading center, North East Pacific Rise, Gorda-Juan de Fuca-explorer ridge and the Guaymas basin (William et al., 1974; Heckinian and Fouquet, 1985; Rona and Schott, 1993; Schott, 1997). The slow spreading ridges where hydrothermal activities are reported are Gorda Ridge, Red Sea, Central Indian Ridge, and Mid-Atlantic ridge. Hydrothermal ferromanganese encrustations are also reported from Rodriguez Triple Junction in the Indian Ocean (Nagender Nath et al., 1997). Hydrothermal activities at convergent plate boundaries such as subduction zones are also well known, like those of Okinawa Trough, Mariana Trough, Loihi seamount, Lau basin, Papua New Guinea.

6. India's Offshore Mineral Wealth

India is bestowed with a coastline of about 6539 km and its continental margin comprising the continental shelf, slope and parts of the deep sea (upto 3000 m depth) covers an area of over 1.164 million sq km. The Exclusive Economic Zone (EEZ) of India, which extends to 200 nautical miles offshore, has an area of about 2.02 million sq km (Fig. 9), which is equivalent to about 2/3rd of area covered by its landmass. Three seas, the Arabian Sea in the west, the Bay of Bengal in the east, and the Indian Ocean in the south, adjoin the Indian coast.

Oceanographic investigations in India were initiated since India's participation in the 'International Indian Ocean Expedition (IIOE)' in mid-sixties listing naval vessels such as INS Darshak, INS Kistna. Those efforts have resulted in the establishment of a premier oceanographic institution in India, the 'National Institute of Oceanography (NIO)' in 1966. The first fully dedicated Indian oceanographic research vessel, 'R. V. Gveshani' was acquired by NIO in 1974. Subsequently, Department of Ocean Development (DOD) acquired a highly sophisticated multi disciplinary research vessel, 'ORV Sagar Kanya' (Fig. 10) in 1983. The 'Geological Survey of India (GSI)' also acquired a research vessel 'RV Samudra Manthan' in 1983. These organizations also acquired some coastal research vessels to augment their scientific

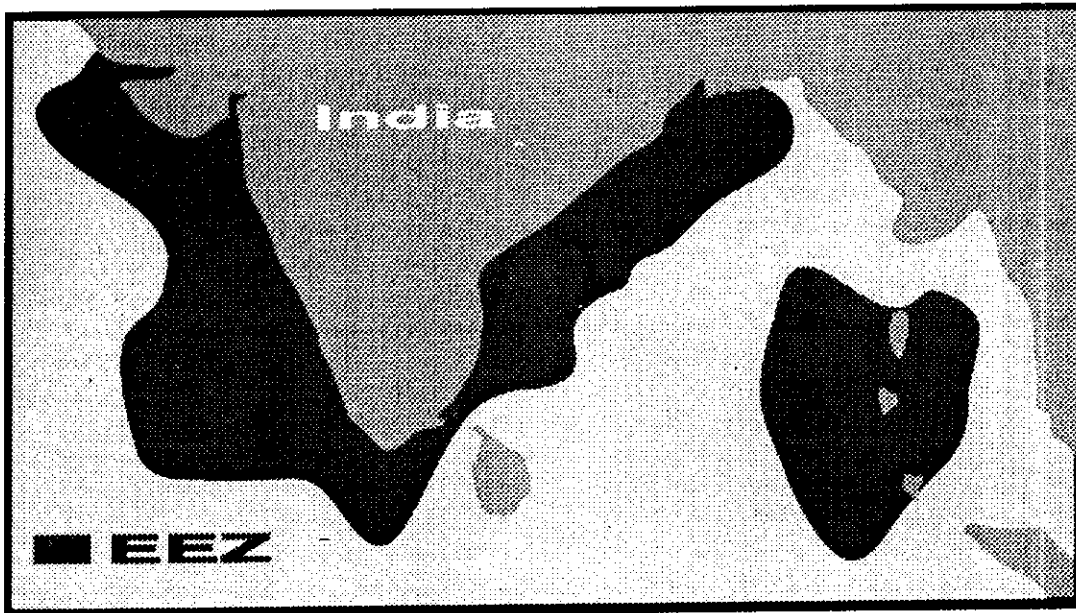


Fig. 9 The 'Exclusive Economic Zone' (EEZ) of India.

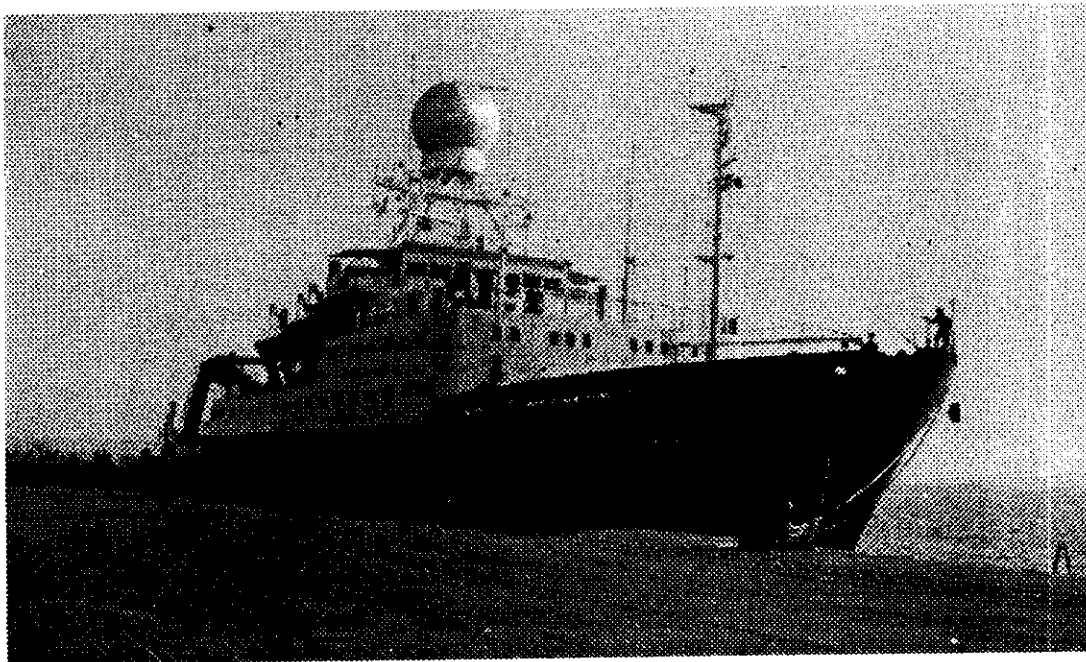


Fig. 10. The multidisciplinary oceanographic research vessel of India 'ORV Sagar Kanya' belonging to the Department of Ocean Development (DOD), Delhi.

fleet. Various research vessels of 'Oil and Natural Gas Commission (ONGC) also contributed to scientific advancement in oceanography. All these vessels have provided enormous information about the mineral resources within the EEZ of India and also from the Central Indian Ocean Basin.

Heavy mineral placer sands are reported to occur along several localities in the innershelf (within a water depth of 40 m) of Kerala, Maharashtra, Andhra Pradesh and Orissa (Siddique et al. 1984; Rajamanickam, 2000). All these placer deposits are composed of light heavy minerals (ilmenite, magnetite, zircon, monazite etc..) except for one occurrence of heavy heavy mineral (gold) in the nearshore sediments off Baypore, Kerala. Along the West Coast, the exploration for heavy minerals in the innershelf zone off Kerala has indicated the presence of 1.4 million tonne (mt) of ilmenite, 0.1 mt of rutile, 0.1 mt of zircon and 0.5 mt of sillimanite in Varkkela and Chavra sectors. In Maharashtra, 13 bays stretching for about 130 km along Ratnagiri coast have been surveyed where ilmenite and magnetite are major constituents of heavy mineral placers. These placers have ilmenite upto 64% and inferred reserves of ilmenite in sand covered zone upto 1 meter of sand thickness are to the tune of 12.5 million tonnes (Gujar et al., 1988). Along the east coast about 13.4 million tonnes of heavy minerals (ilmenite, garnet, sillimanite) are indicated off northern Andhra Pradesh, whereas 17.28 mt of ilmenite, 6.8 mt of sillimanite, 4.86 mt of garnet and 1.62 mt of monazite, zircon and rutile are reported along the Orissa coast.

Rich calcium carbonate deposits from Lakshadweep group of islands are also thoroughly explored (Siddique and Mallik, 1975). Sewell (1938) has reported the occurrence of barium concretion in the bottom deposits of Laccadive sea but no details are given.

Occurrence of phosphatic deposits (Recent, Holocene and Late Quaternary) along the western and eastern margins of India are known. Paropkari et al. (1981) and Rao et al. (1987) reported recent phosphorites from the western margin of India and attributed their formation to authigenic precipitation as well as to the replacement of carbonate by phosphate. Rao and Lamboy (1996) have shown that the phosphate in phosphatized

limestones along the western continental margin of India occurs as a trapped siliciclastic material which has been subsequently phosphatised or is formed as direct microbial mediation of the substrate material. Recently, phosphorite concretions (Fig. 11) have been recovered in a core from a topographic high on the continental slope off Goa. These concretions consist of carbonate fluorapatite as main mineral phase with about 33% P_2O_5 (Rao et al., 1995; Rao and Rao, 1996). According to Rao and Rao (1996) these appear to have been formed 250,000 years BP. Vaz et al. (1999) reported occurrence of phosphorites along the eastern continental margin of India off Chennai which are composed of carbonate fluorapatite and calcite as major minerals and have 8-20% of P_2O_5 . These phosphorites range in age from Eocene even up to early Holocene. Similar studies by Rao et al (1998) have shown that the phosphorites off Chennai occur buried 20 cm under the clays, contain 9 to 31% of P_2O_5 and cover an area of approximately 636 sq km.

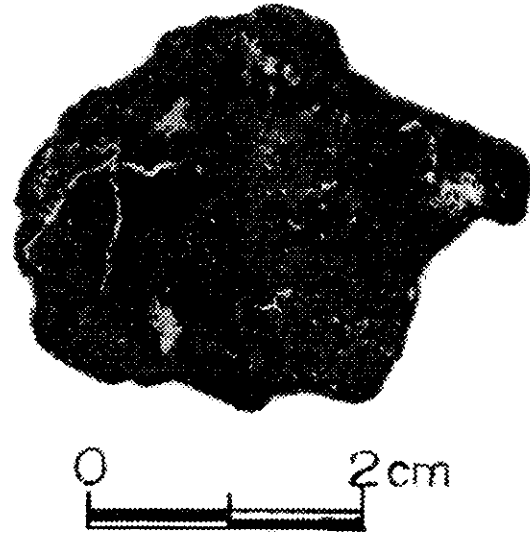


Fig. 11 Phosphorite concretion recovered from the marginal high off Goa, western margin of India (Photo courtesy V.P.C. Rao).

The preliminary geological and geophysical investigations in the Andaman Back-arc setting have indicated the occurrence of hydrothermal activity in the region (Rao et al., 1996). These indications are in the form of vent like features, broken parts of Chumney stature and rocks with disseminated and vein type of metal sulphides. Globules of pyrite

are also reported from active ridge sediment. The details like their extent, metal concentration etc., are yet to be investigated and its economic viability to be ascertained.

India has also surveyed a large area in the Central Indian Ocean basin (outside the EEZ) for polymetallic nodules as per the provisions under the International law of seabed authority. The region is covered by with abundant nodules occurrence (Fig. 12) with high trace metal concentrations (Table 2). Already a mine site has been leased and presently environmental impact assessment (EIA) stud-

ies by NIO are in progress. The area covered by the nodules in the Indian Ocean is 10-18 million sq km, with a reserve estimate of the order of 0.15 trillion tonnes. As a result of demarcation of about 3,00,000 sq. km. with an estimated total of nodule resource of 1335 million tonnes, India was recognized as a Pioneer Investor in April 1992. In August 1987, India became the first country to have been allocated exclusive rights for further exploration in the 150,000 sq. km. of the pioneer area in the CIOB (Central Indian Ocean Basin). Of this 75,000 sq km is relinquished back to International Seabed Authority and 75,000 sq km is remaining with India with exclusive

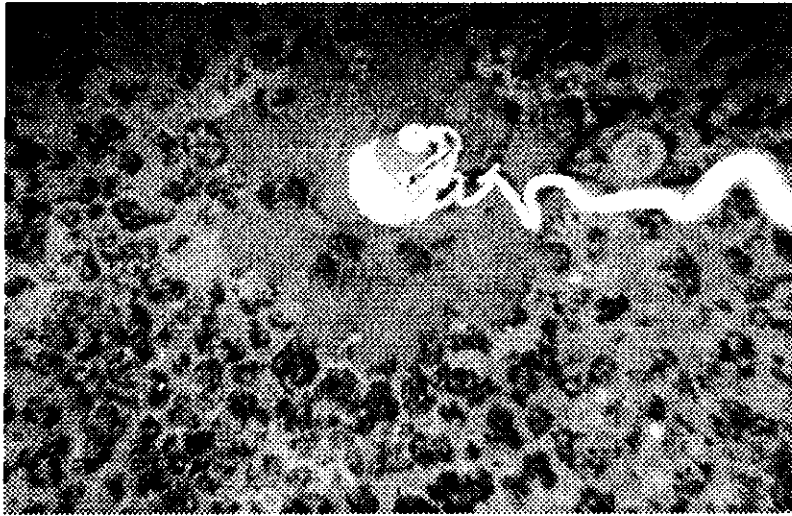


Fig. 12. Photograph showing Manganese Nodule abundance on the seafloor of Central Indian Ocean Basin (Photo courtesy V. N. Kodagali).

Table 2. Composition of the Ferromanganese nodules (in wt.%) from the Central Indian Ocean Basin (CIOB). (Data source: Jauhari and Pattan (2000).

Element	Max.	Min.	Mean	No. of samples analysed
Mn	48.6	6.50	24.4	1119
Fe	20.5	2.40	7.10	1119
Ni	2.21	0.18	1.10	1108
Cu	2.73	0.13	1.04	1108
Co	0.43	0.07	0.11	1108
Zn	1.14	0.02	0.12	676

mining rights. The Indian pioneer area has resources of 144 MMT of manganese, 0.85 MMT of Cobalt, 7.00 MMT of Nickel, and 6.5 MMT of Copper.

7. Mining Strategy

Each country has sovereign right over its EEZ, which is presently the area of 200 nautical miles from its coastline. Variety of mineral deposits occurs in the EEZ areas which can be explored and exploited by the countries within whose EEZ these deposits occur. Further, the exploration and exploitation of deep-sea mineral deposits (outside the EEZ of any country) is also possible following proper guidelines and instructions from International Sea Bed Authority under the Law of the Sea Convention. Nevertheless, offshore mining, both from EEZ and outside EEZ depends on various economic, technological and political factors. Presently, coastal placer deposits and various other mineral deposits on the continental margins are being exploited. But as the deep sea mineral deposits generally occur farther from the land and, therefore, their exploitation is expensive and presently uneconomical. However, the time is not too far that the exploitation of deep sea mineral resources will also become a reality with depletion of onland resources and advancement of technology.

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