

# Processes of formation of ferromanganese manganese nodules and crusts

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Manganese geochemistry and its oceanic cycling assume importance in view of the fact that it is the tenth most abundant element in the Earth's crust. It occurs in two valency states whose stability lies within the limits of the natural importance. Oxides of manganese also have high adsorption capacity. Therefore, they can easily adsorb divalent cations such as Ni, Cu and Zn from natural waters. Iron is the fourth most abundant element in the Earth's crust and this element occurs in two oxidation states and can similarly adsorb cations. Thus, both can migrate under the influence of redox gradients. Fractionation between this pair can probably occur in anoxic and high temperature conditions.

In balancing the Mn between different oceanic reservoirs, Goldschmidt in 1954 has pointed out that absolute masses of some metals in the ocean exceed their supply from continental rock weathering over geological time. The computation results also revealed that elements such as chlorine, sulfur, bromine, iodine, molybdenum were "excessive." According to various calculations made later, dissolved manganese supply to the ocean from various sources is 2.2-4.0 million tons annually; 0.7-7.4 million tons of manganese sink to the ocean bottom annually; 0.5-10 million tons of hydrothermal manganese are supplied to the ocean annually. In an alternate estimate, the supply of labile and dissolved manganese to the ocean is 0.2-0.4 million tons yearly through river discharge; 0.05-0.3 million tons yearly by atmospheric material; 1-10 million tons by hydrothermal material; and 0.4-4 million tons yearly through diagenetic cycling. The amplitude of minimum-maximum estimates is 1.2-14.7 million tons per year. The formation of manganese nodules in the deep oceans would probably account for largest sink of Mn.

Manganese nodules or polymetallic nodules are concretions composed mainly of three phases viz., iron oxyhydroxides, manganese oxyhydroxides and aluminosilicates. Iron and manganese oxyhydroxides dominate over the aluminosilicate fraction with most of the transition metals are co-hosted by these two phases. Manganese nodules are reported from the shallow and deep-seas in variety of physiographic settings such as the abyssal basins far removed from terrestrial sources, seamounts, abyssal hills, plateaus, mid-oceanic ridges etc. Nodules contain many metals well above the crustal abundances and hence aptly called polymetallic nodules.

## Morphology

Nodules vary in size, shape and surface texture. Size could vary between 1 to 8 cm with predominant size lying between 2-6 cm. Several morphological schemes have been proposed to describe the surface features. External shape, surface constitution together with the mineralogy reflect different sources of metals and growth environment. Size is an important factor with respect to the relationship between age and abundance per unit area. Nodules tend to become asymmetrical in shape with increase in size. While the primary morphological feature is spheroidal, other morphological types can include subspheroidal, ellipsoidal, elongated, triangular, flat, cubical, angular, discoidal etc. Coalesced nodules can also occur with the varying nature of coalescence. Some can be hip-jointed, with a thin veneer of Fe-Mn oxide layer; while others can be joined over a larger area and therefore merged into each other. Secondary morphological features such as lobation and faceting is also seen in irregularly shaped nodules.

Nodule surface texture can be smooth or rough and gritty. It is usually considered that the smooth surfaced nodules result from the hydrogenetic precipitation, while the diagenetic precipitation lead to the rough surfaced nodules. In discoidal nodules, an equatorial rim can separate the top and bottom, with tops being smooth in texture and the bottoms being rough. Some of the nodules can have granular appearance. The irregular nodules with knobby or gritty surfaces can occur in the abyssal hill area. Nodules with knobby surfaces can have white filamentous serpulid-type biological growth on them. Botryoidal and nodules with very rough surfaces commonly are rich in Ni and Cu along with Mn.



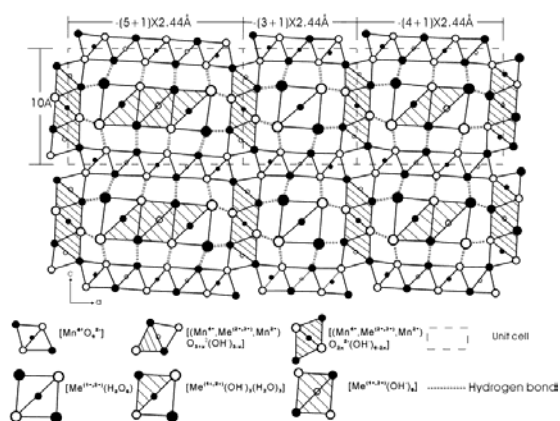
Fig. 1. Different morphological types of nodules.

## Mineralogy

Manganese nodules contain primarily 3 mineral phases viz., Mn oxides, Fe oxides and the aluminosilicates. Mn oxides tend to incorporate cations such as Ni, Cu, Zn, whereas Fe oxides mainly host anionic species of elements P, As, V, Mo, W, and more importantly cobalt and the rare-earth elements. Aluminosilicates on the other hand consist of elements such as Si, Al, Ti and Cr.

Three types of Mn oxide minerals occur in both the manganese nodules and crusts. They are todorokite,

birnessite and vernadite, which are alternatively called as busserite/10 Å manganate, 7 Å manganate and  $\delta\text{MnO}_2$  respectively. Mn oxide minerals are extremely fine-grained with their sizes ranging between 100-1000 Å. These minerals are crypto crystalline and the X-ray diffractograms using Cu as a target lacks clarity. However, using Fe and Co targets usually can result in clear diffractograms. Todorokite is a large tunnel-like structure (see the figure below) based on  $\text{MnO}_6$  octahedra.



**Fig. 2.** The model for the structural frameworks of marine diagenetic 10 Å manganates (Highly hydrated  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions can enter the walls of the tunnel to stabilize the structure (Jiang et al., 2007 – Deep-Sea Research I, 54:84-93).

$\text{FeOOH}$  minerals present in manganese nodules are also extremely fine-grained and are X-ray amorphous. Goethite may be present in some of the nodules. It was also suggested that  $\text{FeOOH}\cdot x\text{H}_2\text{O}$  is epitaxially intergrown with  $\delta\text{MnO}_2$ . Because of the fine-grained nature of minerals hosted by oxyhydroxides, Techniques such as XAS (X-ray absorption spectroscopy) and the electron diffraction would be useful to study their structures.

It is usually presumed that the todorokite is the predominant in nodules formed through hydrothermal and diagenetic processes and the presence of  $\delta\text{MnO}_2$  is attributed to the formation through hydrogenetic processes.

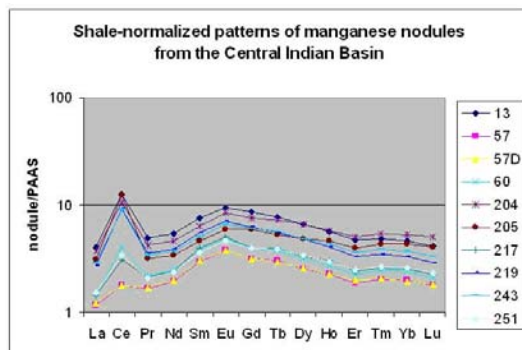
## Chemical composition

As mentioned in the Introduction, manganese nodule and crust matrix has 3 major compositional phases viz., Mn-oxyhydroxides, Fe-oxyhydroxides and aluminosilicates. Nodules and manganese crusts are exceptionally different in composition from other geological material in having most of the elements much above the values of upper continental crust. Chromium however is not enriched like other transitional metals. Most of the metals are fractionated between the major

phases. While the Mn-oxyhydroxides and Fe-oxyhydroxides host most of the economically important metals, aluminosilicates basically host rock-forming elements. Ni, Cu and Zn are known to be associated with todorokite which has Mn in divalent state. In contrast, Co is associated with  $\delta\text{MnO}_2$ -rich nodules. Al, Si, Ca and K are generally believed to be bound to accessory minerals (quartz, feldspars, clays and zeolites). They may vary in nodules depending on the amount of detrital material present. However, inter-elemental relation have shown that Ca and Na may also be accommodated in Fe-Mn minerals. While the amorphous Fe-oxyhydroxides are the main Fe-bearing phase, a part of Fe may also be bound to silicates such as clay minerals, fragments of weathered basaltic rock and volcanic glass grains. A top-bottom fractionation is seen between several elemental phases in nodules with morphological differences between the top and bottom. While the tops are smooth and rich in Fe-oxyhydroxide phase (alongwith other elements such as Co, Pb), the bottom portions are rough and host predominantly the Mn-group of elements (Cu, Ni, Zn etc.). As the Mn and Fe oxide phases account for about 80% of the nodule composition, Mn/Fe ratios are used to identify the relative contribution of hydrogenous

and diagenetic sources. Ternary plots involving Mn, Fe and Cu+Ni+Co at three axes have been extensively used to distinguish the hydrogenetic from diagenetic nodules.

Rare-earth elemental abundances in manganese nodules and crusts show a clear authigenic signature with a middle REE enrichment. Typically, nodules have positive cerium anomaly compared to its trivalent neighboring REEs (Fig. 3), which has been explained as due to the oxidation of cerium to its tetravalent while its precipitation. Strontium, neodymium and hafnium isotopes of manganese nodules have shown them to have seawater signatures.



**Fig. 3.** Typical shale-normalized patterns of manganese nodules with a distinct positive Ce anomaly and with a middle REE hump (unpublished data of Nath, Makishima, Nakamura et al.).

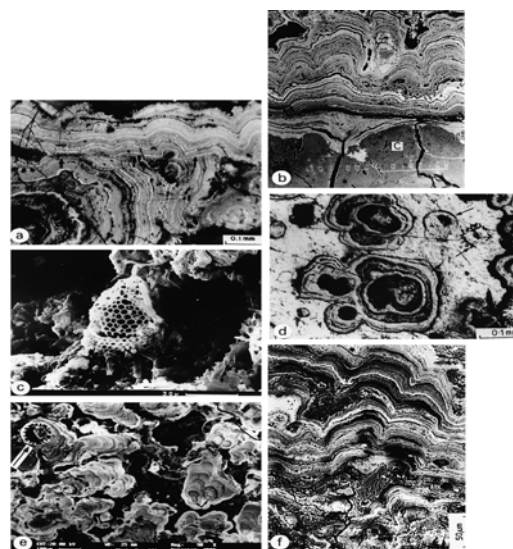
### Internal structures

The internal features of manganese nodules are complicated with a varied texture, mineralogy and composition. The internal structures can be mainly studied using the polished sections of ferromanganese nodules and crusts employing mainly the ore microscopy and the scanning electron microscopy (SEM). The internal features often display complex textures characterized by irregular, often concentrically banded zones of microlayers of different reflectivity. Reflectivity changes are caused by the relative content of Fe and Mn, the oxyhydroxides of these elements constituting the main minerals. Mn-rich layers are usually lighter in color compared to the Fe-rich dark layers. The internal structures alongwith the external morphological features can be linked to their origin.

Hydrogenetic nodules consist of grey colored material that shows no bireflectance or anisotropy. The smooth surfaced nodules when cut to normal to the growth axis show rounded protrusions or concentric lamination suggesting the growth pattern. Each thin lamination may represent a period of uniform hydrogenetic growth. Individual laminae would show compositional variations, probably representing the character of the depositional environment at the time of

the lamina formation. Intimate association of  $\delta\text{MnO}_2$ , amorphous Fe-oxyhydroxides and amorphous aluminosilicates is event from the chemistry of internal structures. Brightness in terms of higher reflectivity may be indicative of  $\delta\text{MnO}_2$  content. The colloform structures of hydrogenetic origin show roundish patterns of laminated oxide material without many pore spaces indicating quiescent conditions during accretion. Sometimes, the colloform structures grade into columnar type, indicating a change in the accretionary environment. Nodules from the Mascarene and Seychelles Basins have shown a change in texture from colloform to brushed appearance and further to columnar type textures and were attributed to the difference in supply rate of oxyhydroxide colloidal flocs from the water column. Different hues and reflectivities in the individual microlamella may reflect microenvironmental fluctuations.

The early diagenetic nodules consist of complicated internal structures with dendritic structures as the main internal structure. Coarse dendritic growth zones consist of alternating laminae of bright grey crystalline todorokite and dark grey amorphous iron oxyhydroxides. The interlaminated dendritic structure of microlayers of massive material and amorphous material is typical of early diagenetic nodules. However, massive layers were observed in the contact zone of multiple hydrogenetic nodules from the Mascarene Basin when coalesced together indicating the existence of conditions similar to the early diagenetic processes responsible for diagenetic nodules. Typically occurring internal structures in the Central Indian Basin are shown in Fig. 4.



**Fig. 4.** Internal structures within the nodules (a) Growth hiatus within a nodule marked by truncation of earlier interlaminae of todorokite (light grey) and vernadite (dark grey) followed by

development of laminations of the same minerals on the plane of erosion=nondeposition (indicated by arrows) (reflected light, oil immersion). (b) Laminated microstructure at the contact with the core (C) of the nodule grades gradually outward into dendritic (botryoidal) microstructure. Both microstructures consist of alternations of vernadite (dark grey) and todorokite (light grey) (reflected light, oil immersion). (c) Undissolved radiolaria (*Cycladophora davisiana*) and diatom frustules retained on the nodule surface (SEM). (d) Globular growth of todorokite (light grey molds) and vernadite (dark grey) around biogenic tests (since dissolved leaving black molds). The matrix is recrystallized todorokite. Arrows indicate traces of biogenic tests infilled by oxides (reflected light, oil immersion). (e) Growth of interlaminated todorokite (light grey) and vernadite (dark grey) around pre-existing biogenic tests (now molds; arrows) merging into dendritic microstructures with random growth directions (SEM). (f) Detrital mineral grain-rich (dark grey) laminae (concordant; upper part of the figure) disrupts (lower part of the figure) dendritic microstructure formed by todorokite (light grey) and vernadite (grey) (reflected light, oil immersion). Photographs and captions from Banerjee et.al., 1999, Marine Geology, v.157).

### Nuclei

One of the most striking features of manganese nodules is the concentric layered growth structures with a more or less distinct nucleus at its center. Nodules invariably contain atleast one nucleus, sometimes they are more than one. Nuclei are usually hard material, around which the growth layers of Fe-Mn oxides accrete. However, it is usually assumed that the chemical nature of the nucleus does not seem to affect the deposition of manganese or the composition of the manganese and iron phase of the nodule. Various kinds of material listed below can act as nuclei.

Primary material - 1) Clastic rock fragments of altered oceanic rock, 2) Pumice, 3) Consolidated clays, 4) Fragments of weathered and cemented ash and 5) Biogenic hard parts such as shark's teeth, whale bones (especially the ear bones).

Secondary material -Older nodule fragment

Sometimes the nodule nuclei is not seen with a naked eye as well with a microscope, probably because it is replaced by ferromanganese oxides. High metal grade manganese nodules in the Central Indian Basin predominantly have pumice as their nuclei and occur mostly close to seamounts. Globally, the volcanic rocks from the seamounts act as a nucleus. Therefore, the distribution of nodules is governed by the availability of nuclei. Multinucleated and coalesced nodules are common at the foothills of seamounts.

Colloidal particles of Mn and Fe oxides are usually seen on the rough side of biogenic material as well as the weathered rocks with a larger surface area. Formation of authigenic mineral phases such as phillipsite post-dates the accretion of Fe-Mn oxide layers within the nucleus. One of the nodules had a large phillipsite as its nucleus in one of the nodules from the Central Indian Basin. The shapes of many nodules seem to be controlled by the shape of the nucleus present in them.

Local bottom topography, relief, geology, currents and sediment facies control the nature of the nucleus. Therefore, large local variations are seen in the seamount environment.



Fig. 5. Various types of nuclei occurring in the Central Indian Basin.

### Growth rate

Knowledge of growth rate is critical for any model describing the genesis and geochemistry of manganese nodules and crusts. Element concentrations in manganese nodules can be considered as a cumulative flux of metals from the seawater and the adjoining sediments. The accumulation flux of metals in nodules thus can be calculated as a function of growth rate, elemental concentration and the density of growth layers, and can be mathematically expressed as

$$F = \sum S(r) \cdot C(r) \cdot \Phi,$$

where S and C are the concentration and growth rates at a depth (r) and  $\Phi$  representing the density.

Deep-sea nodules and crusts are amongst the slowest growing minerals on Earth. The minimum growth rate can be as low as  $0.8 \text{ mm} \cdot \text{Ma}^{-1}$ . Several methods have been used with variable success. The methods used and their limitations are listed below:

1. K-Ar dating: It is the earliest method used and based on dating the volcanic material in the nucleus. This can give only a minimum age and does not account for the time gap between the nucleus age and the initiation time of oxide accretion.
2. Fossil assemblages: Paleontological methods were used employing calcareous nanofossils such as coccoliths, siliceous radiolarians and also the ichthyoliths. These methods were used with some success, but the hiatuses in the growth may not be discernable.
3. Radiometric dating: They are considered to be most reliable by many workers. Several isotopic pairs were used, such as (a)  $^{230}\text{Th}/^{232}\text{Th}$ , (b)  $^{231}\text{Pa}/^{230}\text{Th}$  and (c)  $^{10}\text{Be}$ .  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$  and  $^{10}\text{Be}$  have half-lives of 75 kyr, 32 kyr and 1.5 Myr respectively which enable them to date ~5 times their half lives. Thus the first two isotopic pairs can be used for dating the outer 1-2 mm only, while the  $^{10}\text{Be}$  method is the most suitable method which can date up to 10 Myr. A school of thought consider that the nodule/crust matrix is permeable for the diffusion of radionuclides and consider that the ages obtained are not reliable. However, growth models such as the (a) growth-decay-diffusion model, (b) the diffusion-decay model have been employed to circumvent this problem. Sr-isotope stratigraphy has been used with limited success in view of the lack of well defined seawater Sr curve for the Neogene period, as well as the continuous exchange of Sr isotopes from the seawater both by the Mn-oxides, phosphatic and detrital phases.

4. Empirical equations from the elemental data: Based on the comparison between the elemental composition and the radiometric dates, Mn/Fe ratios and cobalt content based chronometers have been used. Cobalt-chronometer has been particularly found to be useful and is increasingly being employed in dating the ferromanganese crusts.

### Genesis

Multi-accretionary processes are invoked to explain the formation of the manganese nodules. While several processes were invoked in the earlier days, to explain their formation, the schools of thought have converged now in invoking a multi-accretionary process involving the supply of nuclei from submarine volcanoes, hydrogenetic precipitation of metals, diagenetic cycling and supply of metals through sediment porewaters, and also involving chemical and microbial oxidation. Though, the precipitation mechanism involves supply from seawater and porewater, the metals in the seawater have 2 ultimate sources viz., terrestrial sources from freshwater discharges into the ocean or through airborne particles and the hydrothermal sources at the oceanic spreading centers. Some reports have suggested a direct biological role in view of the faunal traces associated with nodules.

The early diagenetic nodules grow in the peneliquid layer (top few cm) of pelagic sediments. Hydrated divalent cations such as Mn, Ni, Cu, Zn are supplied through the porewater. Precipitation of these metals in an oxic sediment environment will lead to todorokite rich nodules. Diagenetic nodule formation can be through oxic diagenesis (or low-grade early diagenesis) or suboxic diagenesis (higher grade diagenesis) depending upon the amount of organic matter supplied to the pelagic sediments. During the higher grade diagenesis, greater input of organic matter and its decomposition will lead to the reduction of solid Mn (IV) species to soluble  $\text{Mn}^{2+}$  and upward diffusion in porewater until it is available to the nodule formation. The most important factor controlling the supply of Mn for nodule accretion is the sedimentary flux of biogenic matter, which in turn is governed by the biological productivity of the ocean surface waters.

Hydrogenous nodules form by direct accretion of colloidal hydrous metal oxide from near-bottom sea water. This process is controlled by the colloidal chemical surface reactions.

## Cobalt rich ferromanganese crusts

Ferromanganese oxyhydroxide crusts are commonly found on the hard-rock substrates throughout the ocean basins mainly on the flanks and summits of seamounts, ridges, plateaus and abyssal hills which are free of sediment accumulation. Most of the ferromanganese encrustations on the seamounts and topographic highs, which are away from the spreading centers are formed from the slow precipitation of metals from the seawater. Mixed Fe and Mn colloids with adsorbed metals in the seawater precipitate onto hard rock substrates as poorly crystalline or amorphous oxyhydroxides probably through bacterially mediated catalytic processes. Cobalt enrichment may take place by oxidation from  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  on the crust surface. Mineralogically, they are similar to the hydrogenetic nodules.

Fe-Mn crusts with high Co content were mainly found in the Pacific such as seamounts of equatorial Pacific (EEZ of Federal States of Micronesia, Marshall Islands, Kiribati and U.S) and mid-Pacific seamounts. Compared to the 50,000 and odd seamounts in the Pacific, the Atlantic and Indian Oceans have fewer seamounts and crusts occurring in these two Oceans have a hydrothermal component, thereby reducing the possibility of cobalt adsorption. In the Indian Ocean region, the Afanasiy-Nikitin seamount in the Equatorial Indian Ocean has yielded ferromanganese crusts with Co contents up to 0.8%. A detailed exploration is needed to cover the entire seamount and evaluate the economic potential of this deposit.

### Economic value

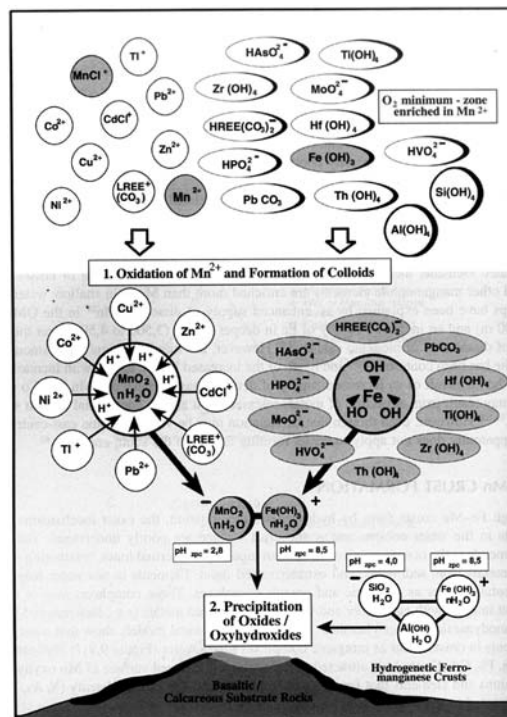
Cobalt in most of the crusts from mid-Pacific seamounts and seamounts in the EEZ of island nations range between 0.3 and 0.8%. In addition, platinum has been considered a potential by-product of Co mining of crusts and has a mean value for different areas of up to 0.8 ppm. Elements that are most strongly enriched over abyssal Fe-Mn nodules include Co, Pt, Pb, V, P, Ca, Ti, Sr, Te and REEs. Crusts have been considered an important potential resource for Co, Ni, and Cu. However, it has recently been determined that crusts contain other metals that may offer significant additional incentive for recovery. For example, Ti has the highest value after Co, Ce has a greater value than Ni, Zr is equivalent to Ni, and Te has nearly twice the value of Cu. This analysis assumes that economic extractive metallurgy can be developed for each of those metals. Traditional economic evaluation of crust and nodule mining for Cu, Ni, and Co indicates that crust mining would be competitive with nodule mining only at times when the price of Co is high. However, adding Ti, rare-earth elements, Zr, Te, and possibly other metals to the economic models could change this outlook.

## Genesis

Though, the principal mechanism of formation is similar, the dominant controls on the formation of crusts are

- 1) element concentration in seawater
- 2) residence time of elements in seawater
- 3) element-particle reactivity
- 4) abundance and ratio of colloidal flocs in seawater
- 5) the colloid surface charge
- 6) types of complexing agents
- 7) redox state and pH conditions of bottom water
- 8) the amount of dilution by detrital minerals
- 9) the surface area available for metal adsorption etc

Partitioning of elements between the Mn and Fe phases occurs because of the sorption of cationic ocean-water species onto the negatively charged surfaces of Mn colloids and sorption of anionic and neutrally charged ocean-water species onto the slightly positively charged surfaces of Fe colloids. Many of the most highly enriched metals undergo an oxidation reaction after adsorption onto the Mn (Co, Ce, and probably Ti) and Fe (likely Te and Pt) oxide surfaces. A schematic model of processes responsible for formation of the crusts is given below



(source: Hein et al., 2000).

Fig. 6. Model of formation of cobalt rich manganese crusts.

### Paleoclimatic value

In addition to the economic value, the Fe-Mn oxide material capping the volcanic and biogenic substrates are storehouses of valuable climatic information. While a

six metre long sediment core from a deep-sea floor may yield information of ~ 1 to 1.5 million years of paleoclimate, crusts preserve a longer term climatic history in its oxide material. Oxide material slowly precipitates from seawater and is least altered diagenetically as the crusts are devoid of sediment cover. The structural, mineralogical, chemical and isotopic changes in the growth layers of the ferromanganese oxide material have helped in deciphering Quaternary climatic fluctuations, earth's orbital forcing mechanism, erosional episodes, evolution of bottom water sources, paleochemistry, deep-water circulation patterns of the past, past fluctuations in oxygen minimum zone etc. Further, the distribution of the long-lived radiogenic isotopes such as Nd, Pb, Be, Hf and Os in Co-crusts has been extensively used to study the patterns of deep ocean circulation and the provinciality of these crusts over the past few years. Most recently, supernova debris has been identified in a crust from the Pacific from the distribution of  $^{60}\text{Fe}$  in a well-resolved time profile.

#### *Constraints in mining the crusts*

Mining may be even more difficult than the manganese nodules. While manganese nodule are loosely lying in the sediments, ferromanganese crusts are embedded on to volcanic outcrops. Techniques such as hydraulic suction may not be sufficient, a combination of scraping and sucking mechanism will be necessary.

Oxide thickness varies for different locations, and spot sampling may not help in evaluating the thickness of entire ore body. The thickness on a single crust may vary from < 1 cm to 15 to 20 cm and therefore, it is going to be tougher designing a mining system with a flexibility in depth of scraping.

Most seamounts in the Indian Ocean are much below the OMZ, which is in contrast to Central and Equatorial Pacific, thereby reducing the chance of widespread occurrence of cobalt-rich crusts in the Indian Ocean. The seamounts closer to OMZ have been found to have thick cobalt content as a result of redox reactions at the OMZ boundary.

#### *Some outstanding problems*

- 1) Role of ferromanganese oxides in balancing the lithium in oceans
- 2) Tracing the diffusion of radionuclides within the nodule matrix
- 3) Hydrothermal influence on the composition of nodules
- 4) Link between the timing of nodule growth initiation and the large-scale tectonics

#### **Suggested Reading**

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