CHAPTER 1

INTRODUCTION
Ferromanganese crusts (Fe-Mn crusts) have been known to the scientific world since the expeditions of H.M.S. Challenger in 1872-1876. Subsequently, some incidental recoveries of Fe-Mn crusts from the Pacific Ocean seamounts and ridges have been made while exploring for Fe-Mn nodules (Cronan, 1977). The scientists of Federal Republic of Germany, on board R/V Sonne, carried out first systematic studies of the seamount Fe-Mn crusts in 1981. The samples of Fe-Mn crusts for their studies were from the seamounts of Mid-Pacific and Line Islands region (Halbach et al., 1982; Halbach et al., 1983). Thereafter, in 1983 and 1984, United States (US) Geological Survey undertook detailed investigation on the occurrences of Fe-Mn crusts in the regions of Necker Ridge (Hawaii), Mid-Pacific Mountains, and Line- and Marshall-Islands utilizing research vessel R.V.S.P. Lee (Hein et al., 1985a; 1985b; Schwab et al., 1985). Since then many countries mostly associated with Fe-Mn nodule exploration activities in the past such as US, Germany, Japan, China, France, Russia, and India are actively involved in Fe-Mn Crust research and exploration.

1.1. Global occurrences of seamount Fe-Mn crusts

Even though the Fe-Mn crusts have been reported from almost all seamounts in the Pacific Ocean, detailed studies have been carried out mostly on the samples from EEZ of Micronesia, Marshall Islands, Kiribati, Hawaii, Johnston Islands and Mid-Pacific Mountains. The Fe-Mn crusts from the Central Pacific and French Polynesia were found to host most promising grade in terms of Mn (23 %), Co (1.2 %), Ni (0.60 %), and Pb (0.26 %) contents (Hein et al., 1987). Based on geologic, oceanographic and geochemical criteria, Hein et al. (1992) have ranked the resource potential of Pacific-Rim nations and islands in decreasing order as Micronesia > Johnston > French Polynesia > Kiribati > Hawaii > Tuvalu > Kingman/Palmyra > Howland/Baker Islands.
The Fe-Mn crusts from Atlantic are least studied for their economic potential in spite of being the region of several palaeoceanographic studies to understand the deep-ocean circulation patterns. In the Atlantic Ocean, the Fe-Mn crusts are not as abundant as in Pacific. Higher rate of sediment input is a main reason for less abundant Fe-Mn nodules and crusts in the Atlantic (Horn et al., 1972; Cronan, 1975; 1977). The western Atlantic receives large discharge of sedimentary load brought by world’s largest river Amazon, while the eastern Atlantic receives large dust input from African deserts (see Abouchami and Zabel, 2003). This set up is more or less similar to that found in northern Indian Ocean deep-sea fans, which have attained sedimentary thickness over 10 km due to large in put of continental detritus. It is well known that the formation of Fe-Mn nodules is ubiquitous in regions of extremely low sedimentation such as those far removed from the landmass. Similarly the seamount Fe-Mn crusts normally form on hard surfaces where sediment-particle rain is significantly lower and is continuously washed by currents. Such natural set-up is not evident in most part of the eastern- and western-Equatorial Atlantic. However, accumulation of Fe-Mn crusts and nodules have been found on the Blake Plateau, where the Gulf Stream maintains an environment that inhibits clastic sediment deposition (Manheim, 1972; Pratt and McFranklin, 1966). Occurrences of Fe-Mn crusts are also found on the Mid Atlantic Ridge, aseismic ridges, and on the continental shelf (Glasby, 1977). Toth (1980) described the chemistry of few Fe-Mn crusts from the Atlantic. Even though most of the Fe-Mn crusts he described were of hydrothermal origin, he noticed cobalt contents up to 0.35 % in few purely hydrogenetic Fe-Mn crusts from Mid Atlantic Ridge. The Fe-Mn crusts from Krylove Seamount in the Eastern Atlantic have a mixed hydrothermal and hydrogenetic origin (Varentsov et al., 1991). Goddard et al., (1987), have given the chemical and mineralogical composition of Fe-Mn crusts from the Sierra Leon Rise, equatorial Mid Atlantic Ridge and New England
seamount chain. They noticed comparatively higher Co values (up to 1%; average 0.58% ) in Sierra Leon Rise Fe-Mn crusts. Compared to the Pacific seamount Fe-Mn crusts Atlantic Fe-Mn crusts have lower metal content. Their average Mn and Fe concentrations are < 20% and the Mn/Fe ratios are less than unity. The average Co concentrations of different Atlantic Fe-Mn deposits are not more than 0.5% (Goddard et al, 1987; Koschinsky et al., 1995; Varentov et al., 1991; Xavier 1982). The Atlantic Ocean Fe-Mn crusts are mostly used for the isotopic studies such as Pb, Nd, Sr etc., to understand the past-ocean conditions.

On the other hand, Pacific seamounts host extensive deposits of Fe-Mn crusts with exceptionally high content of Co and Pt as compared to deep-sea nodules formed in the same region. The Central-Pacific Ocean Fe-Mn crusts are widely studied for their economical potential. From Figure 1 it is evident that Central Pacific seamounts invariably contain extensive Fe-Mn crusts enriched with cobalt (hereafter referred as "Cobalt Crusts", i.e., Co content > 1%). Many of the most economically promising
Cobalt Crust deposits are located in the Central Pacific (Marshall Island, Federated States of Micronasia, Johnston; Hein et al., 1992).

1.2. Mechanism of formation of Fe-Mn crusts

Two main metal-resources of deep-sea that have been found to be economically potential and studied worldwide during the last few decades are Fe-Mn nodules and Fe-Mn Crusts (mostly Cobalt-Crusts). The Fe-Mn crusts are polymetallic oxyhydroxide deposits that cap almost all seamounts of the world oceans. Fe-Mn crusts of the Pacific Ocean seamounts have been extensively studied as compared to Atlantic or Indian Ocean deposits. These seamount Fe-Mn crusts attracted the attention of many explorers and researchers due to; a) their high cobalt (Co) content (Cronan et al., 1976; Toth, 1980; Cronan et al., 1982; Halbach and Puteanus, 1984; Aplin and Cronan, 1985; Hein et al., 1988) and b) their potential as faithful repositories of past oceanographic conditions. The Co content varies from 0.2 % to 2.3 % with averages ranging between 0.3 % and 0.8 % for various parts of the Pacific Ocean (Hein et al., 1999 and references there in).

The formation processes of oceanic Fe-Mn deposits other than hydrothermal iron-stones are of two types. They are hydrogenetic and diagenetic types defined by source of metals to form oxyhydroxides. Metal-ions to the abyssal Fe-Mn nodules are contributed both from underlying sediment pore-water (diagenetic) and from overlying seawater (hydrogenetic) (Halbach et al., 1981; Dymond et al., 1984). Where as, in the seamount Fe-Mn crusts the metal contribution is mainly from the seawater (hydrogenetic). This difference in the formation of abyssal Fe-Mn nodules and Fe-Mn crusts reflect in their major element composition in general and Co, Ni and Cu contents in particular. The diagenetic contribution is normally reflected by enrichment of Mn over Fe (Mn/Fe > 2.5) and enrichment of Cu and Ni over Co (Cu+Ni >1.5 % and Co < 0.2 %). On the other hand, purely hydrogenetic nodules and seamount crusts contain near equal proportion of
Mn and Fe. The hydrogenetic Fe-Mn crusts formation can be distinguished further from hydrogenetic nodules from their very high content of Co (>0.5 %) and very low Cu and Ni (<0.5 %) (see Halbach et al., 1982). However, most of the Fe-Mn nodules found on the seafloor are of either diagenetic or mixed types (hydrogenetic + diagenetic). This is because it is hard to expect sediment on which the nodules are emplaced to be free from metal contribution through diagenetic remobilization of elements within upper sub-oxic sediments.

The seamount Fe-Mn crusts are considered as counterparts of the abyssal Fe-Mn nodules. Even though they possess similar compositions, there are distinct differences in their form and formations. Fe-Mn crusts are accreted as layers over sediment free substrate rocks, where as Fe-Mn nodules usually nucleate around volcanic, biogenic, detrital etc material. Even the shark teeth have been found to nucleate Fe-Mn nodule growth (Banakar and Sudhakar, 1989). The Fe-Mn crusts on seamount or other elevated seabed areas are known to contain higher concentrations of Co than typical abyssal nodules (Halbach and Fellerer, 1980). The contribution of metals from the substrate rocks in the formation of Fe-Mn deposits has been ruled out (Hein and Morgan, 1999), because, once a molecular layer of Fe-Mn oxide forms, the direct contact between the substrate rock and subsequently deposited oxide layers is eliminated.

The Fe-Mn crusts can also form by hydrothermal activity. The precipitation of metals from the hydrothermal fluids readily forms oxide and sulfide minerals. They are generally known as ironstones. Those deposits are usually associated with active plate margins and in the vicinity of hydrothermal vents. The hydrogenetic seamount Fe-Mn crusts differ in minor and trace element compositions from hydrothermal deposits mainly in Co content. Seamount Fe-Mn crusts are usually enriched in Co and Co-enrichment is characteristic of hydrogenetically precipitated Fe-Mn oxides (Halbach et al., 1984;
A near unity Mn/Fe ratio of the hydrogenetic Fe-Mn crusts is also a criterion to distinguish the hydrogenetic Fe-Mn crusts from the hydrothermal oxide deposits, where the Fe/Mn ratios in latter reach very high values (up to 40).

Essential requirements for formation of the hydrogenous Fe-Mn crusts are:

1) Sediment free hard substrate
2) Fairly oxic ambient water
3) Adequate availability dissolved Mn.

The exact mechanism of precipitation of metal oxides is still not clearly understood. However, a plausible explanation given by Burns and Brown (1972) is that the Fe-hydroxide forms the primary layer during the hydrogenetic accretion of the Fe-Mn crusts, which subsequently catalyses the oxidation of Mn. Later, Koschinsky and Halbach (1995) gave a colloidal precipitation model for the hydrogenetic precipitation of Fe-Mn crusts (Figure 2). Their model consists of two stages: in the first stage, Mn$^{2+}$ rich water from the Oxygen Minimum Zone (OMZ) is mixed with oxygen-rich deep water, and oxidized to Mn (IV) and other metals such as Fe, Ti, Al, and Si form oxide and hydroxide colloid. These form mixed colloidal phases and scavenge trace metals by surface adsorption processes, which are dominated by Columbic- and chemical- interaction between colloidal surfaces and dissolved metal species. In the second stage the colloidal phases precipitate on the substrate rocks of the seamounts as ferromanganese oxide encrustations, incorporating the sorbed heavy metals into the mineral phases. The slow growth rate allows the minor elements to be scavenged on to the initially deposited Fe-Mn oxide layer (Koschinsky and Halbach, 1995), which is controlled by their concentration in seawater, surface charge and area of the colloidal particles (Halbach et al, 1983; 1989). This processes is autocatalytic and trace metals and ferromanganese
compounds precipitate onto the Fe-Mn crust surface, releasing and incorporating ions from the water column. The slower the growth rate, more trace metals that can be adsorbed (Halbach et al., 1983; Hein et al. 1987).

Figure 2. Schematic model showing physico-chemical processes proposed for the formation of seamount Fe-Mn crusts (Koschinsky and Halbach 1995). Upper panel shows the physical processes and the lower panel exhibits major chemical interactions between various element species during formation of the Fe-Mn crusts. It is evident from the figure that the surface charges of Fe-Mn and Fe-Ti colloidal particles play vital roles in scavenging many minor elements from the seawater to incorporate into the seamount Fe-Mn crusts.

The Fe-Mn crusts occur in a wide range of water depths from 400-4000 m. But they are most common at water depths of 1000-3000 m along the flanks of the seamounts. The Cobalt Crusts occur at water depths of 800-2500 m. Where as the thickest crusts are
commonly found at water depths from 1500 to 2500m over the Pacific Ocean Seamounts. The most probable areas of Fe-Mn crust occurrence have been identified as volcanic edifices that are older than 20 myr (Hein et al., 1987). They also precipitate along the submerged slopes of the island arcs and atolls. Thick Fe-Mn crusts have been reported from basal slopes of seamounts located at water depths as deep as 5200 m in the Central Indian Ocean (Banakar, 1988, Ph.D. Thesis; Banakar and Borole, 1991). However, those Fe-Mn crusts are not Co-enriched and show chemical characters typical of hydrogenetic Fe-Mn nodules. Usually Fe-Mn crusts accrete on any hard substrate irrespective of the composition of the substrate rocks. No specific substrate rocks have been found unique for the Fe-Mn crust accretion. It appears that hard substrates act simply as electron sink during the autocatalytic oxidation of metal-ions. Even though the thickness of the Fe-Mn crusts depends on the stability conditions of the substrate rocks, viz., basaltic substrates hold thicker crusts than comparatively low stability limestones (Hein et al., 1988). But under typical environmental conditions limestones also act as excellent substrates for the Fe-Mn crust growth (Banakar et al., 1997).

1.3. Chemical Composition of Fe-Mn crusts

The Fe-Mn crusts contain metal oxides and hydroxides of transition metals like Mn, Fe, Co, Cu, Ni, Pb, V, Mo, etc. In addition to Co, the Fe-Mn crusts are also a potential source for Pt, Mn, Tl and Te. The Fe and Mn together constitute 30 % to 50 % volume of the Fe-Mn crusts. Their ratio commonly varies between 0.4 and 1.2 (Hein, 2000). The Fe-Mn crusts are enriched with Co, Ni, Pb, Zn, rare earth elements (REE) and platinum group elements (PGE) by several orders of magnitude over their seawater concentrations. The Co and Pt are most potential element of economical importance found in Fe-Mn crusts. In general the global ocean seamount Fe-Mn crusts show widely varying Co and Pt contents. The Co ranges from 0.2 % to 2 % and Pt from 200 ppb to
1500 ppb. The highest average value of Co is reported for the Fe-Mn crusts from French Polynesia (1.2 %), where as, other seamount averages are normally between 0.5 % and 0.7 % (Hein et al., 1992). In some Fe-Mn crusts the high concentration of Ni, Ti, Zn, Pb Ce, in addition to Co and Pt are the result of a combination of their substitution in the Fe- and Mn-phases and their higher oxidation potential (Hein et al., 1988). The REE also show enrichment in Fe-Mn crusts much beyond the average shale-composition. The Marshall Island Fe-Mn crusts exhibit so far known highest enrichment of Ce (up to 0.11 %) in the Pacific crusts. On the global scale, the most enriched Ce (up to 0.4 %) is found in the Fe-Mn crusts of the Afanasiy-Nikitin Seamount (this study and also see Rajani et al., 2005). The shale normalized-Ce is expected to show positive anomaly within Fe-Mn crusts, as the crust formation is an oxidative process. The REEs in the Fe-Mn crusts are derived from seawater, which intum is supplied from fluvial and eolian input from continental sources. The concentrations of strictly trivalent REEs appear to increase in Fe-Mn crusts with increasing water depth of occurrence (Aplin, 1984; De Carlo and McMurtry, 1994). The PGE is another minor group of elements that contributes to the overall chemical composition of the Fe-Mn crusts. All PGEs (Pt, Rh, Ru, Ir) except Pd are enriched several times in Fe-Mn crusts over their abundances in the Earth’s crust and Fe-Mn nodules. Most PGEs commonly correlate inversely with water depth of occurrence of the Fe-Mn crust (Halbach et al., 1984).

1.4. Mineralogy of Fe-Mn crusts

The X-ray diffraction (XRD) analyses of Fe-Mn crusts have shown that the vernadite (Fe-rich $\delta$MnO$_2$) forms the dominant mineral phase. The todorokite, a dominant mineral phase in most of the diagenetic and mixed type Fe-Mn nodules, rarely dominates in Fe-Mn crusts. The X-ray amorphous Fe-hydroxide (FeOOH $\times$ nH$_2$O) is second
dominant phase present along with $\delta$ MnO$_2$. Other common secondary minerals include quartz, feldspar, barite, calcite etc. These secondary minerals are mostly derived from the continental detritus and settling biogenic products. They are trapped in the Fe-Mn crust along with accreting colloidal authigenic Fe-Mn oxides. A detailed account of secondary material trapped in the nodules and crusts is available in Banakar and Tarkian (1991). In certain cases the Fe-Mn crusts contain distinct phosphatic layers, which are composed of calcium fluorapatite (See Puteanus and Halbach, 1988). The presence of phosphatic material within the Fe-Mn crust indicates rapid changes in the depositional environment between oxic and sub-oxic.

As mentioned in Section 1.3, various elements are incorporated into the Fe-Mn crusts from the ambient water by adsorption on to different precipitating and settling particle phases. Hein et al., (1992) have identified five phases within the Fe-Mn crusts viz., $\delta$MnO$_2$ (primary authigenic phase) characterized by high content of Mn, Co, Ni and Pb; Fe- oxyhydroxide (primary authigenic phase) including authigenic Fe-silicates, characterized by high Fe, Si and As contents, alumino-silicates (secondary detrital minerals) characterized by high Si, Al, Cr, Ti and K; biogenic-phosphate (secondary biogenic phase) characterized by high P and Ca, and biogenic non-phosphate (other settling particles) characterized by high Cu, Ni, Ba, Zn and Cd. The sequential leaching experiments indicated that the $\delta$MnO$_2$ is most important minor and trace metal bearing phase that enriches Co, Ni, Cd, Tl, Ba, Zn, and Cu. Similarly, the Fe-hydroxide phase also enriches several minor metals such as Pb, Mo, V and minor portions of Cu and Zn (Koschinsky and Halbach, 1995). That is, the Mn- and Fe-oxides together host majority of minor elements present in Fe-Mn crusts. Based on detailed statistical analyses, Wen et al., (1997) have grouped the elements of Fe-Mn crusts from Central Pacific in to hydrogenetic group (Mn, Ni, Co, Cu, Ce, Zn), biogenic group (Ba, Zn, Cu, Pt, Fe),
detrital group (Al, Si, Fe), and apatite group (Ca, P, REE). These previous investigations clearly indicate that the seamount Fe-Mn crusts although considered as pure hydrogenetic material, do contain a mixture of biogenic and detrital fractions. The researchers have utilized these different fractions to unravel the past oceanic environment under which the Fe-Mn crusts have accumulated.

1.5. Dating of Fe-Mn crusts

Several methods have been proposed to date Fe-Mn crusts. They range from biostratigraphic through isotopic. The comparison of $^{87}$Sr/$^{86}$Sr in Fe-Mn crusts to that of $^{87}$Sr/$^{86}$Sr isotopic evolution in seawater has also been used to date the crusts (Futa et al., 1988; Hein et al., 1993; Burton et al., 1997). Most popular methods are those using radioactive tracers incorporated into Fe-Mn crusts during their accretion. The U-Th disequilibrium series has been used successfully to date upper few mm (i.e., up to ~0.5 Ma) of Fe-Mn crusts (Abouchami et al., 1997; Banakar and Borole, 1991; Bollhöfer et al., 1996; Chabaux et al., 1995; 1997; Eisenhauer et al., 1992; Segl et al., 1984). The calcareous biostratigraphy (Cowen et al., 1993), magnetostratigraphy (Joshima and Usui, 1998) and cosmogenic $^{10}$Be (Frank and O’Nions, 1988; Koschinsky et al, 1996; Ling et al., 1997; McMurtry et al., 1994; O’Nions et al., 1998; Segl et al., 1984; Somayajulu, 1967) have been other techniques so far utilized to date Fe-Mn crusts. The $^{87}$Sr/$^{86}$Sr ratio was found inappropriate method for age determinations of the Fe-Mn crusts as the ratios showed post-formation exchange with younger seawater isotopic ratios (Ingram et al., 1990; VonderHaar et al., 1995). The uranium-thorium isotopes have provided precise growth rate estimates, but are restricted to only ~500 kyr. Cowen et al, (1993) attempted to use coccolith imprints to calculate the age and growth rates of Fe-Mn crusts. Joshima and Usui (1998) have developed magnetostratigraphy in conjunction with isotopic
method for precise age estimation. The cosmogenic $^{10}$Be isotope is the only precise and accepted direct method available presently to date Fe-Mn crusts which have accreted in the last $\sim$15 myr.

The constant flux of Co into Fe-Mn crusts and its inverse relationship with growth rates provided another possibility of dating (Halbach et al., 1983). Puteanus and Halbach (1988) have proposed for the first time an empirical relationship between the Co-content and growth rate specifically for the Co-rich Pacific Fe-Mn crusts after tuning the Co-model age estimates with measured $^{10}$Be ages. They developed an empirical relationship to estimate growth rate of each layer of the Fe-Mn crust as:

$$Growth\ rate\ (mm/\text{myr}) = 1.28/ [\text{Co} \% - 0.24].$$

This formula was found to be valid only for those Fe-Mn crusts having Co concentrations between 0.24 % and 2.0 % without intermittent phosphate mineralization.

Manheim (1986) and Manheim and Lane-Bostwick (1988) suggested an empirical relationship between Co-content and growth rate in various types of Fe-Mn crusts and nodules expressed as $Growth\ rate\ (mm/\text{myr}) = 0.68/\text{Co}_{\text{w}}^{1.67}$, where $\text{Co}_{\text{w}}$ is the detrital component corrected Co-concentration. This chronometry was well correlated with $^{10}$Be age profiles for Pacific Fe-Mn crusts and nodules (McMurtry et al., 1994). Klemm et al., (2005) dated a Fe-Mn crust from the Pacific by measuring its Os isotopes and comparing the record with seawater Os-curve. Frank et al. (1999) have proposed modified Co-model empirical relationship for world ocean Fe-Mn crusts and compared them with AMS $^{10}$Be-ages. Although they noticed that the consistency between $^{10}$Be-dates and corresponding Co-model dates was variable from ocean to ocean, the study enabled them to propose growth rate model for all ranges of Co-concentrations.

Irrespective of the dating tool, noteworthy fact is that, the estimated and measured growth rates of Fe-Mn crusts by several researchers have been few mm/myr. The range of
so far estimated growth rates for Fe-Mn crusts from all water depths of all oceans is between 1 mm/yr and 20 mm/yr.

1.6. Potential of Fe-Mn crust for palaeoceanographic studies

In addition to their economic importance, the seamount Fe-Mn crusts are considered as condensed stratigraphic sections. They have been effectively utilized for low-resolution palaeoceanographic reconstructions. As their growth rate is exceptionally slow (see section 1.5) they can preserve important long-term changes in ambient water conditions within a small thickness of oxide layer. Further, the Fe-Mn crusts also contain intimately intermixed silicate detritus components along with hydrogenetic oxide component. The former component is exclusively of continental origin. Therefore, its variation along the growth axis (layers) of Fe-Mn crust indicates the variation in terrigenous matter input to the ocean through several millions of years and hence is a potential tool to reconstruct continental weathering history (see Banakar et al., 2003). The Fe-Mn crusts accrete at considerably slower rates (by three orders of magnitude) than the sedimentation rates. For example the accretion rates of Fe-Mn crusts is generally few millimeters per myr (Banakar and Borole, 1991; Frank et al, 1999; Halbach et al., 1983; Hein et al., 1988; Manheim and Lane-Botswick, 1988: Segl et al., 1984) as against few mm per kyr abyssal sedimentation rate. Therefore, Fe-Mn crusts are well suited to study long-term changes in oceanographic parameters. A rough comparison is that a palaeocean record present in 1 km thick abyssal sediment may be traced in about 10 cm thick Fe-Mn crust. The only limitation of Fe-Mn crusts is that, they cannot be easily used for high time-resolution investigations such as climate change studies. However, few researchers have tried reconstructing past climate driven changes in oceanic chemistry using
specialized sampling of Fe-Mn crusts at few micron intervals (Abouchami et al., 1999; Claude et al., 2005; Christensen et al., 1997; Eisenhauer et al., 1992).

It has been shown that chemical and isotopic variations recorded by hydrogenetic Fe-Mn crusts have the potential to provide information on erosional input to the oceans and ocean circulation patterns, which in turn are related to climatic and tectonic events. Hein et al. (1992) made first attempt to interpret in details the palaeoceanographic events from petrography and mm-scale chemical variability in a Fe-Mn crust from the Horizon Guyot in the Central Pacific. Until that time such studies relied mostly on internal growth structures (Halbach et al., 1982; Kang, 1984; Mangini et al., 1986; 1990; Segl et al., 1984a; 1984b; Von Stackelberg et al., 1984). Another notable study was to reconstruct the tectonic history of the Himalayas utilizing Nd-Sr isotope systematics of the silicate detritus trapped within a Fe-Mn crust of the Central Indian Ocean (Banakar et al., 2003).

1.7. Economic potential of seamount Fe-Mn crusts

The exceptionally slow growth rates, high porosity (>50%) and large specific surface area (300m^2/g) of the colloidal particles forming the Fe-Mn crusts effectively allow for the adsorption of large quantities of economically important minor metals from the seawater. As noted in earlier sections, the occurrence of these deposits is ubiquitous under favorable conditions. They occur as continuous slabs over the seamounts. The chemical processes involved in genesis and growth of Fe-Mn crusts have been shown to enrich particularly Co and Pt metals. Therefore, Fe-Mn crusts could be considered as future resources of Co and Pt. Further, recent studies have indicated that Fe-Mn crusts also contain other valuable metals such as Ti, Ce, and Te, which may offer significant additional incentive for recovery of the seamount Co-enriched Fe-Mn crusts. Presently available rough estimates indicate that the submerged seamounts under the seas host over
2 trillion tonnes of Fe-Mn crusts enriched with Co and Pt. The world’s land reserves for Co metal are limited and its supply has been largely governed by geopolitical scenario in the past. As the Co-metal is finding increasing applications in high-tech industries appears to be one of the most important component of the Fe-Mn crusts.

The Co has several strategic and irreplaceable industrial applications. It is a silvery metal with close packed hexagonal crystal structure. Its physical properties are, density = 8.85 g/cm³, melting point = 1493°C, boiling point = 3100°C, atomic number = 27, valency = +2 & +3. The multiple valency of Co makes it one of the most redox-sensitive elements and hence readily oxidized to immobile state on Fe-Mn colloidal surfaces. This property is largely responsible for its enrichment in these deposits. The Co retains its strength even at very high temperatures, and hence is being used extensively in superalloys, surface coatings, high-speed steel, high-temperature cutting tools, cemented carbides etc. It can retain ferromagnetic property up to a temperature of 1100°C, which is highest for any other metals. Therefore, it is used in manufacturing of Alnico magnets, recording tapes, alloys for spacecraft etc. The Co in conjunction with silica produces intense deep blue colour and hence is used in manufacturing of paints and enamels. The Co as acetate is an effective catalyst, hence extensively used in oil refineries. These are some of the presently known usages of Co metal indicating its possible versatility in future.

Although Co is one of the abundant metals in Earth’s crust (33rd in order of abundance), it is highly scattered. Exploitable concentration is found in several countries, out of which, 17 countries presently produce this metal either from its own land resources (12 countries) or by refining imported slag and scrap (5 countries). The Co is mostly associated with Cu, Ni, and As ores. In 2003 nearly 40% of the world production came from Ni-ores. Presently the world production of Co stands at around 42000 tonnes, and
current land deposits are estimated to last for over 100 years. The Co mining is active in Australia, Brazil, Belgium, Canada, China, Cuba, Morocco, Zambia, South Africa. India is one of the countries that refined nearly 500 tonnes of Co during 2004 from imported slag concentrates from Congo and Cuba. In most of the cases Co is produced as byproduct of Ni and Cu mining. The pure (99.8\%) Co metal price rose to as high as ~28 $ per lb (60 $ / Kg) in recent past and is again low at ~US$ 15/lb (Source: www.thecdi.com; Banakar et al., Co-Crust Project Phase I Report, 2005).

1.8. Objectives of the present study

The economic as well as palaeoceanographic importance of the Fe-Mn crusts are well established. But, compared to the Pacific Fe-Mn crusts Indian Ocean Fe-Mn crusts are least studied. Among that only a couple of studies are available on the Afanasiy-Nikitin Seamount (ANS) Fe-Mn crusts (Banakar et al.,1997; 2007; Parthiban and Banakar, 1999; Rajani et al., 2005). Therefore, my present aim is to look in to the chemistry of ANS Fe-Mn crust to understand the genetic and palaeoceanographic implications. Broad objectives of the present study are:

1) Detailed study of the compositional variations of ANS Fe-Mn crusts to understand their genesis.

2) To understand the long-term (myr time-scale) evolution of oceanic processes and continental weathering utilizing the compositional variations in ANS Fe-Mn crusts through time.