GEOCHEMISTRY OF RARE EARTH ELEMENTS AND TRACE METALS ALONG THE WESTERN CONTINENTAL SHELF OF INDIA

Thesis submitted to the
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
in Partial Fulfilment of the
Requirements for the Degree Of

Doctor Of Philosophy
In
Chemical Oceanography
Under the faculty of Marine Sciences

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MAY 2004

May, 2004

CERTIFICATE

This is to certify that the thesis titled "Geochemistry of Rare Earth Elements and Trace Metals along the Western Continental Shelf of India" is an authentic record of the research work carried out by Siby Varghese under our supervision and guidance in the National Institute of Oceanography, Regional Centre Cochin, in partial fulfilment of the requirements for PhD degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any university.

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Preface

Rare earth elements (REEs) are in high demand on a global perspective, and the main reservoir of these elements is believed to be the ocean floor. A lot of studies on REEs are going on throughout the world for its quantification and exploitation. Even though, some preliminary attempts have been made in selected areas for the quantitative study of REEs in the EEZ of western continental shelf of India, no comprehensive work has been reported so far. In this context, this work has been initiated to study the distribution of REEs and other major and trace elements, and its geochemical behaviour in the EEZ of the marine environment.

REEs in the sedimentary phases are increasingly being used as indicators of several geological and oceanographic processes; hence the study of REEs is relevant. These elements form a very coherent group, although two elements cerium and europium may develop anomalies due to changes in their oxidation states. Most of the REEs exist in +3 oxidation state, while Ce and Eu changes their oxidation state in certain geochemical conditions. The distribution of uranium and thorium ant its geochemical properties along the west coast of India also have been addressed in this study.

In the present study, surface sediment samples were collected from the western continental shelf of India to estimate the distribution pattern and geochemical behaviour of REEs, major and trace elements. Bottom water samples were also taken at each station, and analysed for temperature, salinity and dissolved oxygen. Surface sediment samples were collected from the Kerala coast during pre monsoon and post monsoon to examine the seasonal variations of REEs and trace elements. Sediment cores were taken from the Andaman Backarc basin to study the downcore variation of REEs and other trace elements and to see the signatures of hydrothermal influences through REE fractionation indices.

The thesis is divided into six chapters. First chapter covers a brief introduction about rare earth elements and its chemical properties, the occurrence and abundance of REEs, its behaviour in the oceanic system under two different phases; such as seawater and sediments. The survey of previous works and the aim and scope of present study is also mentioned in this chapter.

Second chapter deals with the description of study area, sampling locations and procedures and various analytical methods adopted for the work. Variations of hydrographic parameters such as, temperature, dissolved oxygen and salinity of bottom waters and textural characteristics of sediments are also given.

Third chapter deals with the distribution and geochemical behaviour of REEs, uranium and thorium in the sediments of western continental shelf of India. The anomalous properties of cerium and europium, fractionation indices and element excess studies are also described in this chapter. The behaviour of Ce and U in the oxygen minimum zone is also addressed in this chapter.

Fourth chapter gives the distribution of major elements such as, Al, Fe etc. and trace elements such as Ni, Cu, Co, Sc, V, Ba, Zr, Hf etc. The relationship between organic carbon and bottom water dissolved oxygen, enrichment factors of the elements and upper continental crust normalisation of the elements are also given in this chapter. The statistical techniques such as correlation matrix and factor analysis used in this study are also given in this chapter.

Fifth chapter explains the seasonal variation of rare earth elements and trace metals along the Kerala coast during pre monsoon and post monsoon season. Comparison of coastal sediments samples with the offshore samples of Arabian Sea is also given in this chapter.

Sixth chapter deals with the concentration and down core variation of REEs and trace elements in the sediment cores taken from the Andaman Backarc basin. The hydrothermal and detrital sources of the sediments are explained with the use of inter-elemental ratios and discrimination plots. Mass accumulation studies of the sediment samples are also given in this chapter.

The summary given at the end of the thesis explains the distribution and geochemical behaviour of rare earth elements and trace elements in the western continental shelf of India. The seasonal behaviour of REEs in the coastal area and the hydrothermal-detrital sources of sediments in the Andaman basin are also given. This study contributes significantly to the national database of REEs and trace elements on the western continental shelf of India and Andaman Backarc basin.

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1.1 Rare Earth Elements

The Rare Earth Elements (REEs) from lanthanum to lutetium (atomic numbers 57-71) are members of Group IIIA in the periodic table and all have very similar chemical and physical properties.

Atomic No	Elements & Symbol	Atomic weight	Electronic Configuration
57	Lanthanum, La	138.90	[Xe] $5d^1 6s^2$
58	Cerium, Ce	140.12	[Xe] $4f^1 5d^1 6s^2$
59	Praseodymium, Pr	140.90	[Xe] $4f^3 6s^2$
60	Neodymium, Nd	144.24	[Xe] $4f^4 6s^2$
61	Prometheum, Pm*	145	[Xe] $4f^5 6s^2$
62	Samarium, Sm	150.4	[Xe] $4f^6 6s^2$
63	Europium, Eu	151.96	[Xe] $4f^7 6s^2$
64	Gadolinium, Gd	157.25	[Xe] $4f^7 5d^1 6s^2$
65	Terbium, Tb	158.92	[Xe] $4f^9 6s^2$
66	Dysprosium, Dy	162.5	[Xe] $4f^{10} 6s^2$
67	Holmium, Ho	164.93	[Xe] $4f^{11} 6s^2$
68	Erbium, Er	167.26	[Xe] $4f^{12} 6s^2$
69	Thulium, Tm	168.93	[Xe] $4f^{13} 6s^2$
70	Ytterbium, Yb	173.04	[Xe] $4f^{14} 6s^2$
71	Lutetium, Lu	174.97	[Xe] $4f^{14} 5d^1 6s^2$

[Xe] = configuration of xenon: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Table 1.1 Atomic weight and ground state electronic configurations of rare earth elements. (* Does not exist in nature).

They form a very coherent group, although two elements Ce and Eu may develop anomalies due to changes in their oxidation states. Pm, a lanthanide between Nd and Sm which can be produced by nuclear reactions, does not exist in nature in significant concentrations.

It has been found convenient to divide the REEs into two sub-groups: those from La to Sm (ie, lower atomic numbers and masses) being referred to as the Light Rare Earth Elements (LREEs) and those from Gd to Lu (higher atomic numbers and masses) being referred to as the Heavy Rare Earth Elements (HREEs). Very occasionally, the term Middle Rare Earth Elements (MREEs) is loosely applied to the elements from about Pm to about Ho.

Yttrium (Y, z =39) is also a member of group IIIA and shows similar chemistry to that of the REE, and is sometimes included with them in descriptive accounts. The term 'lanthanons' (abbreviated Ln) is applied to the sixteen elements in the group La to Lu plus Y. The significant growth of interest in the geochemistry of REE has come about because of the realization that the observed degree of REE fractionation in a rock or mineral can indicate its genesis, and accurate elemental analysis is now possible eventhough these elements occur at very low concentration (Henderson, 1984).

1.2 Chemical properties

REEs are difficult to separate because of their chemical similarity. The chemical similarity is with regard to the electronic configuration of the atoms and ions of the individual elements (Möller, 1968)

Lanthanum has an outer electronic configuration in the ground state of $5d^1$ $6s^{2\cdot}$ but the next element, Ce has an electron in the 4f sub-shell (Table 1.1). The following elements have the electrons entering the 4f sub-shell, until at ytterbium the 4f sub-shell is filled. The 4f electrons are well shielded by the eight electrons in the $5s^2$ and $5p^6$ sub-shells, so that they are not significantly involved in chemical reactions. Hence, any difference in the number of electrons in the 4f sub-shell does not lead to much difference in chemical behaviour, nor to significant ligand field affects. The REEs, therefore, tend to occur in any natural forms as a group rather than singly or as a combination of a few of their number (Henderson, 1984).

The REEs occupy a wide variety of co-ordination polyhedra in minerals, from six fold to twelve fold or even higher co-ordinations. The smaller REE ions can occupy six fold (CN = 6) co-ordination sites but do so only rarely in minerals. A correlation between co-ordination and ionic radius is observed, ie, the larger ions will tend to occupy larger sites and vice versa. Most of the REEs show a constant valency of three in their chemistry and geochemistry, while Ce and Eu exist in different oxidation states.

Lanthanide Contraction: The REEs exhibit a gradual and steady decrease in their atomic volumes with increase in atomic number as a result of imperfect *shielding of one electron by another in the same sub-shell, so that the effective nuclear charge acting on each 4f electron increases with increasing atomic number, thereby leading to a reduction in the size of the 4f sub-shell. This reduction is referred to as the lanthanide contraction and is reflected by* a steady decrease in ionic radius of the REE with increase in atomic number.

1.3 Occurrence and Abundance

The lanthanides were originally called rare earth elements. The word 'earth' was used because they occurred as oxides (which in early usage meant earth) and the word 'rare' was used because their occurrence was believed to be very scarce. Now many more elements occur even more rarely than lanthanides. Hence, although they are not abundant by any means, they are not considered to be rare in the sense in which this word was used before. The most commonly occurring lanthanide is Ce which constitutes about $3x10^{-4}$ percent of the earth's crust. For example, Ce is more abundant than tin in the earth's crust. Even the scarcest rare earths are more abundant than the platinum group elements. They are much more abundant than Au (4 ppb), Ag (70 ppb) and U (ppm) in the crust (Möller, 1989). Neodymium is more abundant than lead.

The rare earth elements are estimated to form about 0.02% of the earth's upper crust by weight. They occur in high concentrations in a considerable number of minerals. Although, REE contents vary with different rock formations, in general, it has been observed that the more basic (or alkaline) rock contain lesser amounts than do the acidic rocks.

1.3.1 Rare earth minerals

The concentration of the REEs during igneous rock formation (particularly granites and nepheline syenites) and in pegmatites leads to the crystallization of many rare earth minerals. Among the more important are the following: Yttrofluorite (CaF_2,YF_3), Bastnaesite $(CeF)CO_3$, Allanite (Ca,FeCeAl) silicate, monazite $(LREE,Th)PO_4$, etc. The principal source of the REEs is the mineral monazite, occurring in beach sand deposits.

Recovery of the rare earths is a by-product of the extraction of thorium. (Taylor, 1972).

Yttrium occurs in highest concentration in rare earth minerals that concentrate HREEs. The major source of Y is also monazite sand present in the beach sands. The accessory monazite originally present in granitic rocks resists weathering and is concentrated by sedimentary processes. (Kay, 1972).

1.4 Lanthanides in nature

REEs are strongly electropositive and so most of their chemistry is characteristic of ionic bonding than covalent contribution. Most of the REEs show a constant valency of three in their chemistry and geochemistry. Although, the regular oxidation state is 3+ in nearly all the mineral species, +2 oxidation state may be shown by Eu and Yb, and of +4 by Ce and Tb. The multiple oxidation states of these elements are partly due to the enhanced stability of half filled (Eu $^{2+}$ & Tb^{4+}) and completely filled (Yb^{2+}) 4f sub-shells, while Ce^{4+} has the electronic configuration of the noble gas Xenon. In natural systems Eu^{2+} and Ce^{4+} exists and Tb^{4+} has not been recorded in any mineral or natural aqueous medium. The existence of Yb^{2+} would require extremely reducing conditions; hence under the usual conditions prevailing in the crust, Yb is trivalent. Hence geochemically only the cations Ce^{4+} and Eu $^{2+}$ represent other important oxidation states.

Ce, independent of the other lanthanides exhibits an active redox - driven geochemistry in natural waters and sediments. Infact, oxidation of Ce^{3+} into Ce^{4+} in the seawater and its incorporation in the Mn oxides/hydroxides has been used as an explanation for the impoverishment of Ce in sedimental apatites of marine origin. Ce is also affected by its multiple oxidation state like Fe, Mn, U, V and Cr. Seawater is typically depleted in Ce when compared to ferromanganese nodules, which often exhibit Ce enrichment. Calculation of Ce and Eu anomaly compared to their strictly trivalent neighbors is useful to identify the oxidation - reduction reactions of Ce and Eu from other processes affecting their oceanic distribution (De Baar et al. 1985).

Reduction of Eu is noticed in magmatic processes. Europium redox changes [Eu (II)/Eu(III)] are restricted to the high temperatures and pressures associated with the formation of minerals and rocks and hydrothermal waters (Henderson, 1984, Henderson and Pankhurst, 1984, Taylor and McLennan, 1985). The most notable Eu anomalies are associated with hydrothermal waters venting to the seafloor. These venting waters are characterized by large positive Eu anomalies as a result of water/basalt reactions (German et al, 1990, Klinkhammer et al, 1994).

1.5 Oceanic system

The oceanic system, which covers about 70% of the earth crust, contains four major constituent sub systems- the seawater, suspended/ particulate material, sediment and the biota. All the naturally occurring elements are considered to be present in this oceanic system in almost all possible chemical forms, distributed in varying concentrations in these sub-systems. Inflow of element is either in the dissolved form or in particulate/ suspended form. Sediment, which acts as the sink and reservoir, plays the key role in removal. The biogeochemical processes such as acid-base reactions, oxidation–reduction reactions, complexation reactions, adsorption processes at interfaces, the precipitation and dissolution of solid phases and the distribution of solutes between aqueous and non-aqueous phases regulate the bioavailability of the element in the system. The suspended material moves through the ocean system and subject to change in composition as a result of processes such as aggregation, disaggregation, scavenging, decomposition and dissolution (Chester, 1990). In surface waters, total suspended material concentrations are higher, and more variable in coastal and estuarine regions, than they are in open ocean. Near shore sediments are strongly influenced by the adjacent landmasses while deep sea sediments are influenced by the reactivity between particulate and dissolved components within the oceanic water column.

1.5.1 REE supply to the Oceans

Martin et. al. (1976) showed that the REEs mainly enter the oceans incorporated in particulate material, only a few percent of the supply are dissolved. The REE content of this detrital material are similar to those of sediments ie, LREE enriched relative to HREE and having flat pattern without marked depletion or enrichment of any particular REE (Høgdahl, 1970, Martin et al, 1976). This similarity indicates that any fractionation of the REE which may occur during weathering and erosion is obliterated during transport. It also suggests that detrital material, once introduced into the marine environment, accumulates there to form sedimentary deposits without undergoing significant changes in its REE contents (Henderson, 1984).

Compared to dissolved MREEs, LREE and HREE are slightly enriched (Høgdahl, 1970, Martin et al, 1976). The LREE enrichment reflects the greater abundance of these REE in the continental crust, but the HREE enrichments reflects the ability of these elements to form soluble complexes, (eg. Goldberg et al, 1963). Martin et al (1976) have suggested that upto 50% of dissolved REEs may be removed from solution during its transportation through estuaries into marine environment due to processes such as absorption by plankton (Turekian et al, 1973) and co-precipitation with oxyhydroxides (Aston and Chester, 1973).

1.5.2 REEs in seawater

The oceans are heterogenous both on small and large scales with respect to REEs concentration, because the residence times of REEs are shorter than the mixing time of the oceans (~1000yrs). The REEs are minor constituents of seawater, having concentrations of only a few nanograms per litre. Unlike river water, seawater is markedly depleted in Ce. Goldberg (1961) proposed that Ce^{3+} in the oceans is oxidized to Ce^{4+} and is precipitated from solution as CeO_2, while the other REEs remain in the 3+ state and are lost from solution without discernible fractionation of other individual REE. This fractionation of Ce is due to its rapid removal, relative to the other REEs, from the oceans, as indicated by the residence times of the REEs (Table 1.2). Carpenter and Grant (1967) also supported that Ce^{3+} rapidly forms colloidal Ceric hydroxide in seawater with a pH of 8 or more.

Element	Conc. (ng/l)	Residence time (yr)
La	3	440
Ce	1	80
Pr	0.6	320
Nd	3	270
Sm	0.05	180
Eu	0.01	300
Gd	0.7	260
Dy	0.9	460
Ho	0.2	530
Er	0.8	690
Tm	0.2	1800
Yb	0.8	530
Lu	0.2	450

Table. 1.2. The concentrations (Brewer, 1975) and residence times (Goldberg et al., 1963) of the REE in seawater.

Three major sources which could supply REEs to the present ocean system are:- the dissolved load from rivers (eg. Goldstein and Jacobsen, 1988), hydrothermal alteration of the oceanic crust (Michard and Albarede, 1986) and sediments undergoing diagenesis. But the diagenetic REE flux is small relative to other two sources (Elderfield and Sholkovitz, 1987). Goldberg et al (1963) found that the concentrations of REEs in deep waters were markedly greater than those of the surface waters. Høgdahl et al (1968) also supported that there is a strong relationship between REE patterns and water masses. Piepgras et al (1979) confirmed this by looking at the differences in the isotopic compositions of Nd in different water masses.

Various biogeochemical processes must remove the REE from seawater and control the REE concentrations in seawater. The possible processes could be simple inorganic precipitation, the incorporation of REE in biogenic material or hydrogenous minerals, halmyrolitic reactions between seawater and lithogenous material and lastly interaction between seawater in hydrothermal solutions and the igneous oceanic lithosphere at ocean ridges (Fleet 1984).

1.5.3 REE contents of sediments and sedimentary rocks

The REE contents of sediments and sedimentary rocks naturally reflect the mineral contents of these deposits and hence the processes by which the minerals formed and were incorporated into the deposits. The chondrite normalized pattern of REE abundance in the sediments indicate that the LREE are enriched compared to HREE (Fleet, 1984). REE contents of most sediments and sedimentary rocks are similar in the relative abundance of individual elements although they differ in absolute concentration. (Balashov et. al (1964) and Spirn (1965).

REEs are useful tracers of various geological and oceanographic processes (Piper, 1974, Murray and Leinen, 1993). The REEs in sediments are likely to be influenced by (1) particulate supply from the adjacent land masses (Piper, 1974, Mc Lennan, 1989) (2) biogenic sedimentation from overlying seawater (Murphy and Dymond 1984) and (3) oxygenation conditions in the water column (Liu et al. 1988).

1.6 Previous works

After the pioneering work of Minami (1935) on REEs in sedimentary environment (Paleozoic and Mesozoic European and Japanese shales) several fundamental studies by Haskin and Gehl (1962), Balashov et al, (1964), Spirn (1965) have established that the REE contents of most shales are very similar in being enriched in the LREE relative to the HREE, when normalized to chondrite (Fleet, 1984). Haskin et al (1966) and Sholkovitz, (1990) reported that shale- normalized terrigenous input patterns from land to sea display no significant Ce anomalies.

McLennan (1989) studied about the influence of provenance and sedimentary processes on REEs in the sedimentary rocks. Murray et al (1991) studied REEs in Japan sea sediments along with diagenetic behaviour of Ce/Ce*. By investigating total REEs abundances and relative fractionations they studied the relative effects of paleo-oceanographic and paleogeographic variations, sediment lithology and diagenetic process on the recorded REEs chemistry of Japan sea sediments. Nath et al (1992) studied REEs patterns of Central Indian basin sediment related to their lithology. The bulk distribution of REEs and relative cerium fractionation in different surface sediments such as terrigenous, siliceous, calcareous and red clay has been studied in relation to bottom water conditions.

Pattan et al (1995) studied the distribution of major, trace and rare earth elements in surface sediments of the Wharton basin and observed that REEs in this sediment reflecting a combination of surface water properties and diagenetic processes. Ross et al (1995) studied about the REE geochemistry in sediments of the upper Manso river basin and observed a strong HREE enrichment and a positive Eu anomaly from the REE normalized patterns. This high HREE enrichment is associated with high pH systems while the feldspars and their secondary products, which are both enriched in Eu, might be the cause of the Eu anomaly.

Nath et al (1997) studied about the trace and rare earth elemental variation in Arabian Sea sediments through a transect across the OMZ. They analyzed sediment samples beneath the intense OMZ (<0.2 ml/l) and away from the OMZ (1-2 ml/l), but Ce anomaly showed not much significant differences between these two sets of sediments. Nath et al (2000) studied about the influence of provenance, weathering and sedimentary processes by analyzing rare earths, major and trace elements of the fine grained fraction of the bed load sediments from Vembanad lake. REE fractionation studies and discrimination plots indicate felsic source rock characteristics for these sediments.

1.7 Aim and Scope of present study

The distribution and biogeochemical reactivity of trace elements in the seawater system has attracted many, and considerably good amount of works have been reported also. A survey of the literature points out that the studies on REE, so far reported, mainly concentrates on the behaviour of these elements in other oceanic systems, rather than Indian Ocean scenario. In the case of western continental shelf of India, no comprehensive attempt to identify and assess the distribution or reactivity of the REE has been reported. Considering the global demands of REEs as a mineral resource and its high abundance along the west coast of India, especially in the beach sands of Kerala, this region demands a serious comprehensive and systematic exploration to unravel its provenance and distribution in the EEZ region. The study is to proposes and generate a databank on the rare earth elements in the EEZ of west coast of India. Seasonal surface sediment samples were collected from the Kerala coast (from off Alleppey to off Mangalore) to examine the seasonal variations of REEs and trace elements and also to compare the coastal distribution dynamics with that of the continental shelf.

The Andaman Sea, which is reported as hydrothermally active, represents an area, which attracts special attention in the REEs investigations. So, this area is also being selected as a part of this work to see the signatures of hydrothermal influences through REEs fractionation indices.

The detailed objectives of the study are:

1) To estimate distribution pattern of REEs, Th and U in the sediments along the Eastern Arabian Sea
2) To study the behaviour of Eu and Ce with respect to their neighbouring elements in view of their occurrence in multiple oxidation states, in the study area.
3) Inter-element relation of rare earth elements with other major elements diagnostic of redox, provenance and other geochemical processes
4) To study the north-south variation of REEs along the western continental margin and relate them to local geological and oceanographic processes

5) To study the depth wise variation of sedimental REEs from near shore areas (30m) to offshore depths (200m)

6) To study the seasonal variability of REEs and trace elements along the Kerala coast with an intention to link the coastal vulnerability with the REE distribution at coastal and offshore shelf margin.

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7) To study the downcore variation of REEs and other trace elements in the sediment cores and to investigate their accumulation with respect to other major elements such as Mn.

8) To decipher the hydrothermal signatures from the REEs fractionation indices and to compare the behaviour of Ce with that of Mn in view of their similar geochemical properties in order to understand the mechanism of Mn enrichment in sediments

9) To estimate the proportion of REEs and other trace elements contributed by hydrothermal processes vis-a vis the terrigenous source such as Irrawadi River.

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Chapter 2

MATERIALS AND METHODS

2.1 Description of study area

The study region identified is the EEZ of west coast of India and Andaman Backarc basin.

2.1.1 The Arabian Sea

The Arabian Sea covers an area of about 3,863,000 km^2 and is surrounded by arid landmasses to the west and north and by coastal highlands of western India to the east. There is no outlet to the north, but the basin waters and sediments are influenced by inflow from Persian Gulf and the Red Sea and by exchange across the equator (Wyrtki, 1971). The Indus, Narmada and Tapti rivers are the major sources of terrigenous sediments to the Arabian Sea. The Indus fan, formed by the sediments brought by Indus River, is one of the largest submarine fans in the world.

Oceanographic setting

The Arabian Sea has a negative water balance, since the evaporation far exceeds precipitation and run off. The Arabian Sea experiences extreme in atmospheric forcing that leads to the greatest seasonal variability observed in any ocean basin. Monsoons are the seasonally reversing winds, which bring rain to the Indian subcontinent and cause upwelling along the continental margins. This seasonal reversal of the wind direction between summer and winter drives the southwest (SW) and northwest (NW) monsoons in the Indian Ocean and precipitation over south Asia.

The surface circulation in the Arabian Sea is modulated by the seasonal variation of the monsoonal wind system. Wyrtki (1971) and Hasternath and Greishar (1991) reported about the seasonal reversals of the surface wind fields over the tropical Indian Ocean and these reversals have profound impact on the seasonal variation of the surface current system. The large excess of evaporation over precipitation and runoff results in high surface salinities in the Arabian Sea. During the summer monsoon (June-Sept) the low level southeasterly trade winds of the southern hemisphere extend across the equator to become southerly or southwesterly in the Northern Hemisphere.

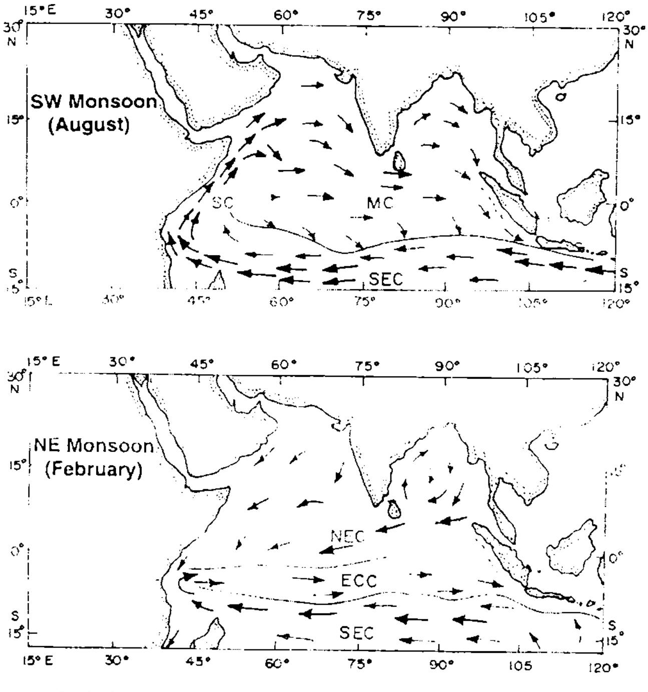

Fig. 2.1 Surface circulation in the Indian Ocean during the SW monsoon and NE monsoon period (after Wyrtki, 1973). MC - Monsoon Current, SC - Somali Current, SEC - South Equatorial Current, NEC - North Equatorial Current, ECC - Equatorial Counter Current

The generalized surface circulation in the Northern Indian Ocean is shown in (Figure 2.1). The frictional stresses of these in turn drive the Somali Current (SC), the westward flowing South Equatorial Current (SEC) and the eastward flowing southwest Monsoon Current (MC) (Figure 2.1)

Oceanic circulation during the NE monsoon season is relatively weak and is characterized by the North Equatorial Current (NEC), an eastward flowing Equatorial Counter Current (ECC) and a moderately developed anticyclonic gyre.

Geologic setting

The geomorphology and geology of the western continental margin of India have become better known only after the International Indian Ocean Expedition (1962-1965). The western continental shelf of India is wide off the river mouths becoming narrower south eastwards and narrowest on the SW margin. The width of the continental shelf is about 130 km off Ratnagiri and narrows down to 80 km off Cochin (Rao and Rao, 1995). It is again wider (120 km) at the southern tip of India, off Cape Comorin. Accordingly, the width of the inner shelf also varies; it is relatively wide and extends upto 60m water depth in the northern part and narrows down to 30m water depth in the southern part (off Cochin). The shelf break occurs at about 120m in the northern part and at about 80m in the southern part (referred from Thamban, 1998).

Nair and Pylee (1968), Hashmi et. al (1982) reported that two distinct sediment types occur on the western continental shelf of India: modern clastic clays on the inner shelf and relict sandy sediments on the outer shelf. The surficial sediments of this region can be further divided into terrigenous, biogenic and chemogenic sediments (Rao and Wagle, 1997). Terrigenous sediments mostly occur as sands in the near shore (upto 10-12 m water depth) followed by a zone of silty clays on the inner shelf between Saurashtra and Quillon. The outer shelf sediments are Holocene carbonate sands between Ratnagiri and Mangalore and are terrigenous sands between Mangalore and Cochin. Biogenic sediments are again predominant on the continental shelf between Quillon and Cape Comorin (Thamban, 1998). Chemogenic sediments are phosphorites and authigenic green clays.

2.1.2 The Andaman Backarc basin

The Andaman Basin extends from Myanmar in the north to Sumatra in the south and from the Malay Peninsula in the east to the Andaman and Nicobar Island in the west. This typical backarc basin incorporates both a spreading ridge and strike-slip faults. The Andaman basin is a region of geologic and tectonic importance between the southern extension of the Himalayas and Indonesia. The recent volcanic eruptions in 1991,1993 and 1995 at the Barren Island, which is a part of the Andaman Arc system, suggest that the region is tectonically active. (Chernova et al, 2001). Deeper parts surrounded by Malay continental margin, Irrawadi delta and eastern slope of Andaman Nicobar ridge form Central Andaman Basin (CAB). Important physiographic features in the CAB are Central Andaman Trough, Sewell Seamount and Alcock Seamount (Rao et al, 1996). The bathimetry of the basin significantly controls the sediment deposition. Curray et al (1979) reported a spreading centre in the Central Andaman Trough.

Oceanographic setting:

The Andaman Sea is a partly isolated water body and is influenced by the large quantity of fresh water run off from the Irrawady and Salween rivers. The Irrawadi River is the major source of sediment to the Andaman basin. The sediment deposition is controlled by the bathymetry of the basin (Rao et al, 1996). The rate of sedimentation is 0.7-1.7 cm/ 1000 year

(Neprochnov, 1964). The anthropogenic factor in the region is insignificant. The Andaman Sea, similar to the adjoining Bay of Bengal, experiences the semi-annually reversing SW monsoon (June- Sept) and NE monsoon (Dec-Feb) resulting in seasonal changes in surface circulation and productivity. In spite of large fresh water discharge, the nutrient concentration in the Andaman Sea is only modest (Venkatesan et al, 2003).

Geomorphology:

Andaman Nicobar Ridges are divided into four groups by transecting channels, the great channel, Ten Degree Channel and Preparis channel from south to north. The Andaman and Nicobar islands are fringed by coral reefs and the shelf is relatively wider (10-50km) on the western side than on the eastern side (<10km). The continental shelf is 170km wide off the Irrawadi (Ayeyarwady) delta. The Andaman Sea is 1200km long, 650km wide and has an area of 800,000km^2 and its physiographic features (elongated sea mounts such as Alcock Seamount and Sewell seamount, Sea highs, Invisible bank and Narcondam Barren Basin, Central Andaman Trough) are aligned north south, parallel to the rift valleys. Rudolfo (1969) suggested that the Andaman basin is dominated by complex structures and is either tensional in origin or has resulted from the combined tensional and strike-slip movements. Seamounts are the products of volcanism along the fissures of the continental slope faults. The entire margin of the Andaman basin showed sub-recent to recent emergence, as evidenced by numerous raised beaches and reefs in the Andaman and Nicobar islands. Western Malaya has emerged about 17m (Rudolfo, 1969).

Surficial sediments:

The terrigenous sediments contributed by rivers are the most predominant source of sediment in the Bay of Bengal and the Andaman Sea. Rudolfo (1969) made detailed study on the sediments of the Andaman Basin and described seven provinces of sediments. The sediments of the delta province are silty clays. The outer delta shelf sediments (>60m) are relict and enriched with feldspar, quartz and mollusc fragments and foraminifera. The Mergui terrace is surfaced with muddy sands with abundant quartz (80-90%) and traces of feldspar. Homogenous silty clay dominates the central portion of the Andaman basin. Rudolfo (1969) studied on the clay mineralogy of the Andaman Sea and reported that the Andaman- Nicobar Ridge sediments are kaolinite- poor (<10%). Illite percentage ranges between 10 and 20% over the entire basin. High montmorillonite (60-75%), followed by kaolinite and minor chlorite-derived from the Irrawadi river-are the dominant clay minerals in the deltaic sediment and in the deep western and central parts of the Andaman Basin clays.

Biogenous sediments in the Bay of Bengal and the Andaman Sea are mostly carbonates. The $CaCO_3$ distribution in the surficial sediments of the eastern margin of India indicates that the modern sediments are $CaCO_3$ poor (Subbarao, 1956).

Hydrothermal deposits:

Backarc basins are considered to be favorable for the formation of hydrothermal minerals. The Andaman Sea is an example of trench-arc-backarc system, where an underthrusting of the Indian lithospheric plate is taking place below the southeastern Asian plate. The west Andaman fault probably defines the boundary of the volcanic arc. The dredge samples from different physiographic features of the backarc basin consist of massive and vesicular basalt and vein type metal sulphide (pyrite and chalcopyrite) particles indicating hydrothermal activity in the basin (Rao et.al. 1996). Mitra and Bandyopadhyay (1996) have also reported hydrothermal activity in the Andaman Sea.

2.2 Sampling

The surface sediment samples were collected from the western Indian continental shelf using Van veen Grab, under MR-LR benthic program (sponsored by DOD; New Delhi). The sediment cores were taken from the Andaman Backarc basin using spade corer. Bottom water samples were also taken at each station, and analysed for temperature, salinity and Dissolved oxygen. Surface sediment samples were collected from 7 transects along the Kerala coast from off Alleppey to off Mangalore to see whether seasonal variations are observed for REEs and trace elements.

2.2.1 Arabian Sea

The study region includes 29 sample locations from 7°- 22°N and 68°-77°E, which comprises 13 transects from the west coast of India. The location map of the stations is given in the figure 2.2.

With respect to the depth of these stations, they are grouped into 3 sets, viz. 30m stations, 100m stations and 200m stations. These transects are:

1) off Cape Comorin: In this transect, 3 surface sediment samples were collected at 30m, 100m and 200m water depths. This transect is in

7.5 °N latitude and 77.3°E longitude. This area is recognized as no clay zone (Rao and Wagle, 1997).

2) off Trivandrum: In this transect, 2 sediment samples were collected from 30m and 100m water depths. This transect lies in 8.5 °N latitude and 76.8°E longitude.
3) off Quilon: Three surface sediment samples were collected from this transect at water depths of 30m, 50m and 100m. The geographic location is 9°N latitude and 76.3°E longitude.
4) off Cochin: Three surface sediment samples were collected from this transect at water depths of 30m, 100m and 200m. The geographic location is 9.9°N latitude and 76°E longitude.
5) off Calicut: In this transect, 2 sediment samples were collected from 30m and 100m water depths. This transect lies in 11.3 °N latitude and 75.5°E longitude.
6) off Cannanore: In this transect, 2 sediment samples were collected from 30m and 200m water depths. This transect lies in 11.9 °N latitude and 75°E longitude.
7) off Mangalore: Two surface sediment samples were collected from this transect at water depths of 30m and 200m. The geographic location is 12.8°N latitude and 74.6°E longitude.
8) off Marmagao: Two surface sediment samples were collected from this transect at water depths of 30m and 200m. The geographic location is 15.4°N latitude and 73°E longitude.

9) off Ratnagiri: In this transect, 2 sediment samples were collected from 30m and 200m water depths. This transect lies in 16.7 °N latitude and 73°E longitude.
10) off Mumbai: In this transect, 2 sediment samples were collected from 30m and 100m water depths. This transect lies in 18 °N latitude and 72°E longitude.
11) off Veraval: In this transect, 2 sediment samples were collected from 30m and 100m water depths. This transect lies in 20 °N latitude and 70°E longitude.
12) off Porbandar: Two surface sediment samples were collected from this transect at water depths of 30m and 200m. The geographic location is 21.5°N latitude and 69°E longitude.
13) off Dwaraka: Two surface sediment samples were collected from this transect at water depths of 30m and 200m. The geographic location is 22°N latitude and68°E longitude. This area is widely influenced by the Indus River.

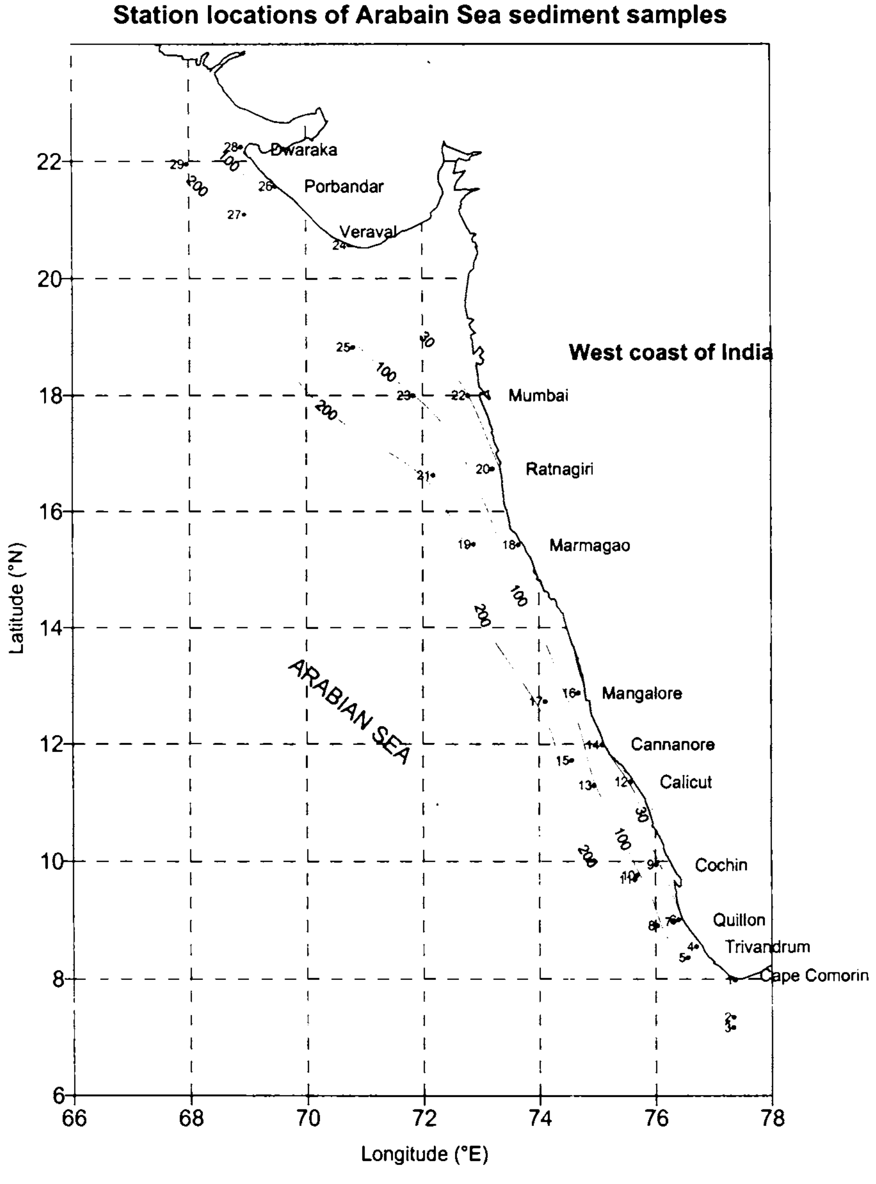

Figure 2.2. Station location of Arabian Sea sediment samples

2.2.2. Seasonal studies

Surface sediment samples were collected from 7 transects along the Kerala coast (off Alleppey to off Mangalore). The transects under study are:

1) off Alleppey: Three surface sediment samples were collected from this transect at water depths 5m, 10m and 40m during premonsoon and post monsoon. The geographic location is 9.49°N latitude and 76.3°E longitude.
2) off Cochin: Two samples were collected from this transect at water depths 5m and 40m during both seasons. The geographic location is 9.97°N latitude and 76.2°E longitude.
3) off Ponnani: Three surface sediment samples were collected from this transect at water depths 5m, 10m and 40m during premonsoon and post monsoon. The geographic location is 10.78°N latitude and 75.9°E longitude.
4) off Calicut: Three surface sediment samples were collected from this transect at water depths 5m, 10m and 40m during premonsoon and post monsoon. The geographic location is 11.16°N latitude and 75.7°E longitude.
5) off Cannanore: Three surface sediment samples were collected from this transect at water depths 5m, 10m and 40m during premonsoon and post monsoon. The geographic location is 11.8°N latitude and 75.38°E longitude.
6) off Kasargode: In this transect two sediment samples were collected from water depths of 5m and 10m. The geographic location is 12.48°N latitude and 74.97°E longitude.
7) off Mangalore: In this transect three surface sediment samples were collected from water depths of 5m, 10m and 40m. The geographic location is 12.94°N latitude and 74.78°E longitude.

2.2.3 Andaman Sea

Three Spade cores were taken from the Andaman Backarc Basin. The location of the cores is given in the figure 2.3. The details of the cores are:-

SPC-1: The core taken was of 28cm length from the Andaman basin of water depth 3040m and sub sampled to 14 sections of 2cm interval. The geographical location of this core is 11.17°N latitude and 94.73°E longitude.

SPC -2: The core taken was of 18cm length at a water depth 3150m and sub sampled to 9 sections of 2 cm interval. The geographic location of this core is 10.58°N latitude and 94.72°E longitude.

SPC -5: This core is of length 30cm and was taken at water depth of 3124m. The core was sub sampled to 15 sections of 2cm interval. The geographic location of this core is 10.32°N latitude and 94.39°E longitude.

2.3 Details of Analytical Procedure

2.3.1 Dissolved Oxygen

Dissolved oxygen estimation was carried out by Winkler's titrimetric method (Grasshoff et.al, 1983). The oxygen present in the water sample is immediately fixed with Winkler A (Mn2+ solution) and Winkler-B (alkaline KI). After acidification, the Iodine released is estimated by sodium thiosulphate using starch as indicator. From these titre values, dissolved oxygen in the water samples was calculated.

2.3.2 Sediment analysis

2.3.2.1.Textural analysis

The sediment samples were dried in a hot air oven at 95°C. The percentage of sand, silt and clay portions of this dried material was determined by pipette analysis (Krumbein and Petti John, 1938).

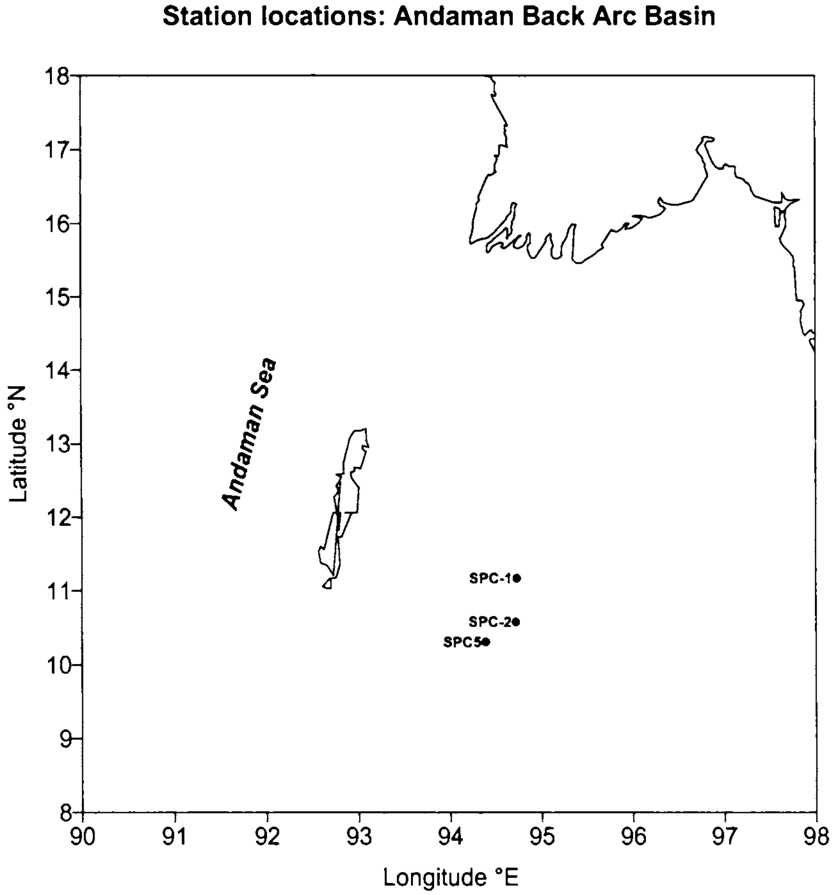

Figure 2.3. Sediment core locations in the Andaman Backarc basin

40g wet sediment was added with 10ml 1N HCl to remove all the carbonates. After washing, the residue was treated with H_2O_2 (15%) and kept overnight to remove organic matter. The solution was slightly warmed and washed with distilled water (3 times). This residue was kept in oven for drying. 10g of dried sediment was taken in a 500ml beaker and added with 7.5g Sodium hexa metaphosphate. To this 200ml distilled water was added and kept overnight. Using a rod with rubber cork, the sample was pressed and stirred. The sample was sieved using a sieve of mesh size 63µ pouring water through a funnel into a 1000ml measuring jar and the volume was made upto 1000ml. The residue left in the sieve is sand/grains. This sand material was transferred to a petri dish of known weight, and the percentage of sand can be calculated form this weight. The filtered portion obtained in the measuring jar was stirred using a hand stirrer. 20ml of sample at 10cm depth was taken using a marked pipette and poured into a small beaker of known weight. After oven drying, the weight of material in the beaker was calculated. The percentage of sand, clay and silt were calculated using the formula:

$$\text{sand}(\%) = \frac{(\text{Final wt. of dish - Initial wt. of dish})}{10} \times 100$$

$$\text{clay}(\%) = \frac{(\text{Final wt. of beaker Initial wt. of beaker}) - 0.15 \times 1000 \times 100}{20 \times 10}$$

silt (%) = 100- (sand % + clay %). The precision of analysis was calculated by duplicate measurement.

2.3.2.2 Organic carbon analysis

The organic carbon (C_{org}) content of the sediment samples was determined by the wet oxidation method (El Wakeel and Riley, 1957 and modified by Gaudette and Flight, 1974). The principle behind this method is based on the oxidation of organic carbon with chromic acid and titrimetric determination of the oxidant consumed.

About 0.2g of the powdered sample was accurately weighed out in a boiling tube and 10ml of chromic acid added, using a wide- tipped pipette. The tube was covered with aluminium foil wrapper and heated in a water bath for 15 minutes. It was allowed to cool and the contents of the tube were transferred into a 250ml conical flask containing 200ml distilled water. About 2-3 drops of ferrous phenanthroline indicator was added and titrated with 0.2 N ferrous ammonium sulphate solution until a pink colour just persists. A blank determination was also carried out in the same manner. Then, the concentration of the organic carbon available sediment was estimated as: 1 ml of 0.2N ferrous ammonium sulphate consumed = 1.15 x 0.6 mg of carbon. The percentage of organic carbon in the sample = 0.6 x {[(Blank reading- Sample reading)] / (Weight of the sample in mg)} x 1.15 x 100. The reproducibility of the organic carbon measurements was checked by running duplicates of sediment samples and it was found to be better than ±5%.

2.3.2.3 $CaCO_3$ determination

$CaCO_3$ content of the sediment sample was determined by the gasometric technique. Gasometer measures the $CaCO_3$ content of sediment by measuring the volume of CO_2 released by reaction of the $CaCO_3$ with dilute acid. The pressure generated in the reaction chamber is measured with a pressure gauge, which is proportional to the volume of CO_2 released. Initially acid pressure is determined by dispensing 7.5 ml of 1N HCl. Then 100g of the standard $CaCO_3$ is added in to the gasometer and pressure is adjusted to zero. Then 7.5 ml of 1N HCl is added and the gasometer was shaken till the pressure gauge showed highest constant pressure. Calibration is repeated till constant factor is obtained. Once the calibration is done by $CaCO_3$, sediment samples can be analysed. After every 10 samples, calibration procedure is repeated with $CaCO_3$.

Factor was calculated using the formula, F = (Total Pressure - Acid Pressure)/ wt.of $CaCO_3$. Then the percentage of the $CaCO_3$ was calculated using the formula

$$\%CaCO_3 = (\text{wt. of } CaCO_3 \times 100)/ \text{wt.of sample.}$$

Where wt. of $CaCO_3$ = (Actual pressure)/Factor. Replicate analysis of both the samples and carbonate standards showed that the analytical reproducibility was better than ±5%.

2.3.2.4 Analysis of REEs and trace elements

There is a series of instruments like Atomic Absorption Spectrometry (AAS), X-Ray Fluorescence Spectrometry (XRF), Thermal Ionization Mass Spectrometry (TIMS), Neutron Activation Analysis (NAA), and Inductively coupled Plasma- Atomic Emission Spectrometry (ICP-AES), with multi-elemental capabilities. All of these instruments are capable of carrying out rapid analysis of many elements at μg/ml, but each instrument has got its own limitations. In contrast to ICP-AES, which generally requires prior chromatographic separation from the matrix for REEs, ICP-MS offers very low detection levels and relatively fast turnaround.

2.4 ICP-MS System Outline

ICP-MS Instrument consists of 3 basic units and they are:-

1. Conventional argon ICP operating at temperature 6000-9000K with nebulizer, spray chamber, work coil and associated power supplies.

2. A conventional quadrupole mass spectrometer and data collection electronics, which permit rapid scanning of selected mass range between 0-300amu.
3. An interface unit consisting of two water coiled nickel cones, each containing a small orifice at the center, which allow sampling of plasma gases and transfer ion beam into the small spectrometer.

Samples in the form of solution are introduced through the peristaltic pump at a rate of about 1ml/min into the central region of the plasma at atmospheric pressure with the help of a nebulizer and water-cooled spray chamber system. The sample is heated to 9000K in plasma, resulting in a series of processes involving desolvation, vaporization, dissociation, atomization and ionization, in analytical zone of ICP (Fig 2.4). At this temperature chemical interference effects are insignificant.

54 elements are expected to ionize with an efficiency of 90% or more. A fraction of positively charged ions produced in plasma is transported through a narrow aperture of samples empanels at supersonic by skimmer cone.

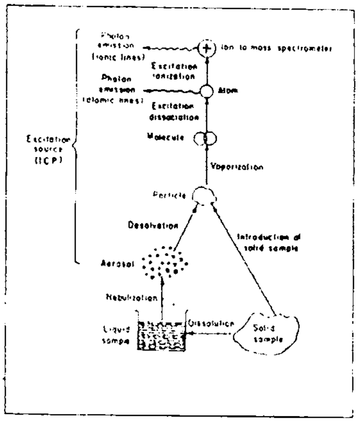

Figure 2.4. Sequence of sample introduction to the formation of ions (Balaram,1995).

2.4.1 Sample digestion and internal standard Rhodium

Standard and sediment samples were dissolved following acid dissolution procedure (Balaram and Rao, 2002). In this procedure 10ml of acid mixture containing 6 parts of HF, 3 parts of HNO_3 and 1 part of $HClO_4$ was added to a 50mg of samples and standards in the clean dry teflon beakers. These beakers were then evaporated to dryness in the fuming hood. After 30mts, 2ml of Conc. HCl was added to remove any black particles, if present in the sample. The addition of acid mixture was repeated to ensure the complete dissolution of samples, and was kept on sand bath till it was evaporated to dryness. Then 5ml of 1ppm Rh solution and 20ml 1:1 HNO_3 were added and made up to 250ml, when it was cooled. In all cases clear solutions were obtained. The solutions were then taken to ICP-MS for multi elemental analysis. A total of 67 sediment samples were analyzed along with repetitions, blank and MAG-1 standards. Among the samples, 29 were from the surface sediments of western continental shelf region, and the remaining were from 3 spade cores of Andaman's Backarc basin.

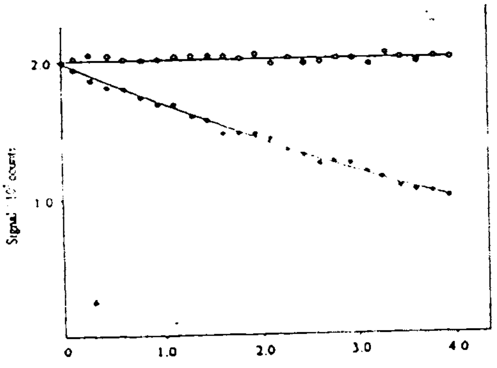

Figure 2.5. Matrix induced suppression effect on long term stability using La as an eg. Without internal standard intensity was suppressed sharply, up to about 50% within 4 hours. However, with internal standard changes in signal are very small. Zheng and Shan, (1997)

Internal standard Rh used here is considered to be almost absent in sediment samples. The results of Zhang and Shan (1997) in soil samples analysis show that internal standards improve the precision of analysis from 28.2-37.4 % (without internal standards) to less than 9.8% (with the internal standards) (Fig 2.5).

2.4.2 Accuracy and precision of elemental analysis

Marine sediment standard (MAG-1) prepared by US Geological Survey was used for determining the accuracy. Analysis of standard has yielded very good results in comparison with the certified values for MAG-1. The elements Al, Fe, Nb, Cs, Ba, La, Ce, Yb showed excellent results with accuracy better than 1% (Table2.1). All other elements showed accuracy better than 5%.

The precision of the analysis was calculated by repeated analysis of standard MAG 1.The results of duplicate analysis is given in the table 2.1. In this V, Cr, Fe, Co, Ni, Cu, Nb, Ba, La, Nd, Er showed good precision of 1%. All other elements showed precision better than 5% (Table 2.1).

2.5 Data analysis

Rare earth elements are normalized with PAAS (Post Archean Australian Shale, reference material for sediments) values for plotting shale normalized patterns and anomaly studies. Normalization means the concentration of each REE in the sample is divided by the concentration of the same REE in the reference material. Then the plot is usually given as logarithm of the normalized abundance versus atomic number.

Elements	Cert. MAG	MAG 1(Ana)	Accuracy	Elements	Analysis1	Analysis2	Precision
Al (%)	16.37	16.43	-0.35	Al (%)	16.4	15.9	-3.1
Sc	17.2	16.59	3.53	Sc	16.6	17.0	2.1
V	140	138.46	1.10	V	138.5	137.6	-0.7
Cr	97	94.81	2.26	Cr	94.8	94.9	0.1
Mn (%)	0.098	0.10	1.02	Mn (%)	0.1	0.1	3.0
Fe (%)	6.8	6.74	0.85	Fe (%)	6.7	6.7	-0.5
Co	20.4	19.99	2.02	Co	20.0	20.1	0.7
Ni	53	52.10	1.70	Ni	52.1	51.7	-0.8
Cu	30	29.34	2.20	Cu	29.3	29.4	0.1
Zn	130	127.77	1.71	Zn	127.8	125.8	-1.6
Ga	20.4	20.96	-2.75	Ga	21.0	20.1	-4.4
Rb	149	151.83	-1.90	Rb	151.8	147.5	-2.9
Sr	146	149.30	-2.26	Sr	149.3	143.9	-3.8
Y	28	28.77	-2.75	Y	28.8	27.8	-3.6
Zr	126	128.81	-2.23	Zr	128.8	124.4	-3.6
Nb	12	11.89	0.93	Nb	11.9	11.9	0.4
Cs	8.6	8.67	-0.83	Cs	8.7	8.5	-1.7
Ba	479	479.96	-0.20	Ba	480.0	479.3	-0.1
La	43	43.21	-0.49	La	43.2	43.0	-0.6
Ce	88	88.72	-0.82	Ce	88.7	87.5	-1.4
Pr	9.3	9.53	-2.47	Pr	9.5	9.3	-2.8
Nd	38	39.02	-2.69	Nd	39.0	38.8	-0.6
Sm	7.5	7.59	-1.21	Sm	7.6	7.8	2.1
Eu	1.55	1.63	-4.97	Eu	1.6	1.6	-3.0
Gd	5.8	6.04	-4.12	Gd	6.0	5.9	-1.7
Tb	0.96	0.99	-3.13	Tb	1.0	1.0	2.0
Dy	5.2	5.34	-2.63	Dy	5.3	5.2	-2.8
Ho	1.02	1.05	-3.24	Ho	1.1	1.0	-3.2
Er	3	2.93	2.23	Er	2.9	3.0	0.9
Tm	0.43	0.46	-6.51	Tm	0.5	0.4	-4.1
Yb	2.6	2.60	0.04	Yb	2.6	2.7	4.1
Lu	0.4	0.41	-3.00	Lu	0.4	0.4	-3.0
Hf	3.7	3.77	-1.84	Hf	3.8	3.9	2.1
Ta	1.1	1.13	-3.09	Ta	1.1	1.1	-2.2
Pb	24	24.71	-2.97	Pb	24.7	24.4	-1.4
Th	11.9	12.37	-3.92	Th	12.4	12.0	-2.9
U	2.7	2.83	-4.89	U	2.8	2.8	-1.1

Table 2.1. Accuracy and precision of the analysis done by ICP-MS

Plotting the abundance of REE against their atomic number, produces a zig-zag/ saw tooth pattern. This is because; the rare earths in natural geological materials follow the Oddo-Harkin's rule, which states that even atomic numbered elements (z) have a greater cosmic abundance than odd-numbered (z) elements (Henderson, 1984). This is due to the increased stability for nuclei with even numbers of protons and neutrons. The advantages of this normalization method are that the abundance variation between REE of odd and even atomic number is eliminated and it enables direct comparison both of relative patterns and concentration. This pattern will give the idea about REE fractionation ie, (La/Lu) normalized ratio gives a measure of the overall slope of the normalized plot and hence the extent of fractionation of LREE from the HREE can be estimated (Henderson, 1984). Eu and Ce anomaly if present can also be detected from this normalization plot. So, it is important in geochemical studies to normalize the REE patterns to either chondrite or average shale values. The chondrite values are taken to represent cosmic abundance of the rare earths, while shale values are taken to represent crustal abundances (Gromet et al, 1984).

Elements are normalized with UCC (Upper Continental Crust) values to compare with continental crust composition. Element excess and enrichment factors are other parameters calculated in the present study. Statistical analysis has been carried out for Arabian Sea samples separately for 30m, 100m and 200m depths. Correlation matrix and factor analysis were used for interpretation of data.

2.6 Hydrographic parameters

2.6.1 Arabian Sea

The hydrographic parameters of the bottom water samples of the eastern Arabian Sea are given in the table 2.2. For 30m samples, temperature showed an average value of 27.2°C and salinity showed 34.94 PSU. For 100m samples, temperature showed an average value of 23.5°C while salinity showed 35.77 PSU. For 200m samples, the average value of temperature is 14.8°C and for salinity is 35.45 PSU. Dissolved oxygen values of bottom water showed average values of 3.34ml/l for 30m samples, 1.49ml/l for 100m samples and 0.06ml/l for 200m samples.

St.No	Stations	Depth(m)	Lat °N	Long°E	Temp °C	Salinity (psu)	DO (ml/l)
1	Off Cape Comorin	30	8.07	77.37	28.35	33.71	3.25
2		100	7.35	77.34	22.27	34.80	0.86
3		200	7.17	77.33	13.92	35.06	0.14
4	Off Trivandrum	30	8.55	76.82	29.42	34.10	3.28
5		125	8.36	76.55	17.36	35.05	0.26
6	Off Quillon	30	9.01	76.40	29.42	34.01	3.33
7		50	8.97	76.31	29.13	34.19	3.08
8		100	8.91	76.03	22.45	35.33	1.45
9	Off Cochin	30	9.94	76.01	29.29	34.07	3.30
10		100	9.76	75.69	23.12	35.60	1.50
11		200	9.69	75.64	14.40	35.13	0.13
12	Off Calicut	30	11.35	75.57	29.24	34.60	3.20
13		100	11.30	74.95	27.43	37.31	1.70
14	Off Cannanore	30	11.99	75.08	29.07	34.70	3.17
15		200	11.72	74.56	14.31	35.21	0.06
16	Off Mangalore	30	12.88	74.68	29.13	35.03	3.70
17		200	12.73	74.11	13.75	35.27	0.04
18	Off Marmagao	30	15.42	73.65	27.50	35.36	2.99
19		200	15.43	72.88	14.32	35.42	0.03
20	Off Ratnagiri	30	16.73	73.20	26.67	35.42	3.20
21		200	16.62	72.18	15.06	35.49	0.04
22	Off Mumbai	30	18.00	72.78	25.75	35.55	3.39
23		100	18.00	71.84	26.26	35.96	2.07
24	Off Veraval	30	20.57	70.74	23.39	35.40	3.46
25		90	18.83	70.80	25.60	36.34	2.62
26	Off Porbandar	30	21.58	69.48	24.05	36.11	3.59
27		200	21.09	68.95	15.79	35.96	0.02
28	Off Dwaraka	30	22.24	68.89	22.64	36.12	3.56
29		200	21.95	67.96	16.93	36.06	0.03

Table 2.2. Hydrographic parameters of bottom waters of Arabian Sea

2.6.2 Seasonal studies (off Kerala)

Bottom water and surface sediment samples were collected from 7 transects along the Kerala coast to see the seasonal variations, and the hydrographic parameters are given in the table 2.3. The temperature showed high value in the range of 30°C for premonsoon samples, while post monsoon samples showed low temperature in the range 24-28°C.

				Temp °C		Sal (PSU)		DO (ml/l)	
Stn	Lat°N	Long°E	Depth (m)	pre mon	post mon	pre mon	post mon	pre mon	post mon
ALP	9.49	76.30	5	31.5	27.10	33.24	35.23	3.59	1.01
ALP	9.49	76.28	10	31.0	26.50	33.00	35.64	3.83	1.01
ALP	9.49	76.20	40	30.5	25.50	33.24	35.44	3.83	1.52
CHN	9.97	76.23	5	30.5	30.00	34.04	34.82	3.10	3.07
CHN	9.96	76.13	40	29.8	26.00	33.33	35.43	3.52	1.77
PON	10.78	75.89	5	31.0	27.50	34.02	34.53	4.07	3.03
PON	10.80	75.90	10	31.0	26.00	33.58	35.05	4.31	1.01
PON	10.78	75.82	40	29.0	25.00	33.84	35.39	3.83	1.26
CAL	11.16	75.79	5	32.0	27.25	34.17	34.52	4.31	1.83
CAL	11.16	75.76	10	31.0	26.50	33.96	35.10	4.07	0.76
CAL	11.16	75.71	40	30.0	25.00	33.82	35.30	3.49	0.51
CAN	11.83	75.38	5	30.5	28.25	33.93	34.81	4.07	2.78
CAN	11.81	75.38	10	31.0	28.25	33.81	34.79	3.30	2.51
CAN	11.77	75.38	40	30.5	24.50	33.92	35.20	4.07	3.54
KSG	12.48	74.97	5	30.5	25.00	34.29	33.18	3.59	3.03
KSG	12.48	74.93	10	30.5	27.00	34.27	34.75	3.83	3.54
MNG	12.97	74.80	5	30.0	28.75	34.12	34.35	5.50	2.02
MNG	12.94	74.78	10	30.5	28.25	34.12	35.07	4.79	1.77
MNG	12.94	74.74	40	30.5	24.50	34.16	35.30	4.55	0.51

Table 2.3 Hydrographic parameters of bottom waters of Kerala coast during pre monsoon and post monsoon season.

Salinity showed low value for pre monsoon samples (ranged between 33-34 PSU), while post monsoon samples showed high value (in the range 34-35 PSU). Dissolved oxygen showed low values for post monsoon samples in the range 0.5 ml/l for 40m samples. Low dissolved oxygen content and low temperature of water samples for post monsoon season may be due to the presence of upwelling during the sampling periods.

2.7 Textural characteristics

2.7.1 Arabian Sea

The main factors controlling the distribution of trace elements among the various phases in the aquatic system are the textural characteristics and organic carbon content (Balachandran et al, 2003). For 30m samples, the average values for sand (30.08%) silt (36.33%) and clay (33.59%). The distribution pattern of sand and clay along the west coast of India are given in the figure 2.6.

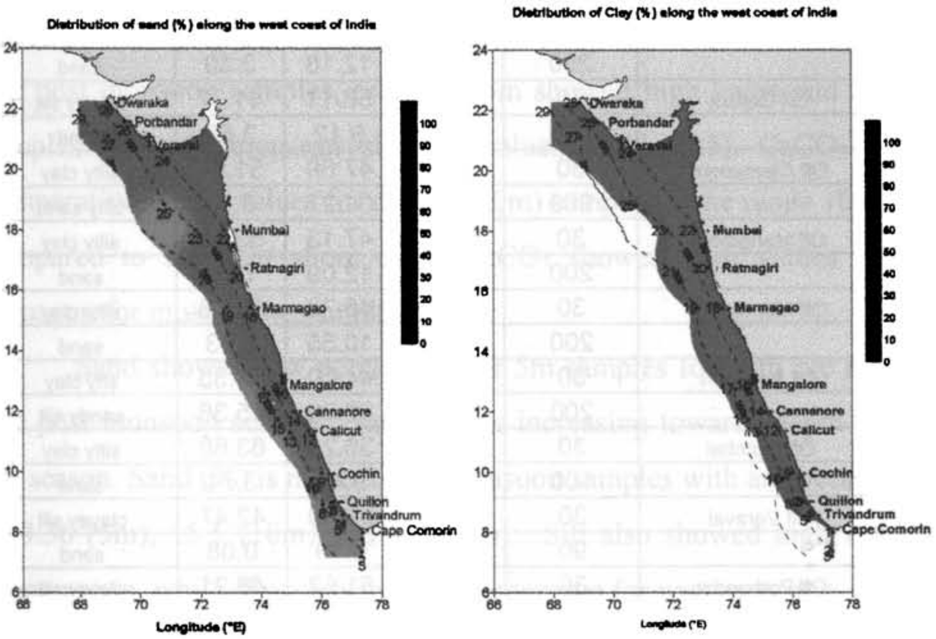

Figure 2.6. Distribution of sand (a) and clay (b) in the sediments of west coast of India.

For 100m samples, the average values for sand (89%) silt (8.43%) and clay (2.56%) and for 200m samples the average values for sand (53.7%) silt (29.5%) and clay (16.9%). For 100m samples, the percentage of sand is more, and this may be due to the presence of relict carbonate sand. The clay fraction is more for 30m and 200m samples. Most of the southern samples are characterized by major sand fraction (Table 2.4).

St.No	Stations	Depth(m)	sand %	silt %	clay %	Nomenclature
1	Off Cape Comorin	30	98.63	1.05	0.33	sand
2		100	96.37	2.97	0.66	sand
3		200	86.09	11.18	2.73	sand
4	Off Trivandrum	30	99.69	0.11	0.20	sand
5		125	98.46	0.81	0.76	sand
6	Off Quillon	30	9.53	72.56	18.55	clayey silt
7		50	96.89	1.83	1.28	sand
8		100	85.80	11.05	3.05	sand
9	Off Cochin	30	95.47	1.69	1.84	sand
10		100	68.69	25.34	5.97	silty sand
11		200	84.45	12.16	3.39	sand
12	Off Calicut	30	0.53	58.11	41.37	clayey silt
13		100	87.22	9.12	3.66	sand
14	Off Cannanore	30	0.40	47.69	51.91	silty clay
15		200	60.46	31.27	8.26	silty sand
16	Off Mangalore	30	0.29	47.13	52.59	silty clay
17		200	80.52	12.09	7.40	sand
18	Off Marmagao	30	0.72	48.73	50.56	silty clay
19		200	85.62	10.55	3.83	sand
20	Off Ratnagiri	30	0.38	44.69	53.35	slty clay
21		200	28.55	56.09	15.36	sandy silt
22	Off Mumbai	30	1.09	35.23	63.68	silty clay
23		100	86.79	9.47	3.74	sand
24	Off Veraval	30	4.03	53.49	42.47	clayey silt
25		90	99.74	0.19	0.08	sand
26	Off Porbandar	30	0.17	51.62	48.21	clayey silt
27		200	1.46	47.70	50.85	silty clay
28	Off Dwaraka	30	80.08	8.30	11.61	sand
29		200	2.29	54.64	43.08	clayey silt

Table 2.4. Textural characters of the Arabian Sea sediments.

But towards north, the coastal samples are either silty clay or clayey silt depending on the percentage of silt and clay. The continental shelf between Quilon and Cape Comorin does not contain clay zone unlike the rest of the inner shelf (between Saurashtra and Quilon). It consists of biogenic carbonate sands. The scarcity of estuaries in this region may be a reason for the absence of clay zone. The no- clay zone in the southwestern shelf may therefore be due to coastal rock formations and hydrodynamic factors influenced by coastal configurations (Rao and Wagle, 1997). In the present study also, the clay (%) in the region between Cape Comorin and off Quilon is very low (0.2 to 2.7%), which supports the earlier reports.

2.7.2 Seasonal studies (off Kerala coast)

Organic carbon showed high values for pre monsoon samples. The O.C content is high for 5m samples compared to 10m and 40m samples. For post monsoon samples, only Alp 5m showed high value and all other samples showed comparatively low values (Table 2.5). $CaCO_3$ showed comparatively high values for deeper (40m) samples in the range 10 to 32%, compared to the near shore ones. $CaCO_3$ showed high values for post monsoon for most of the samples.

Sand showed low percentage for 5m samples for both pre monsoon and post monsoon season. Sand (%) is increasing towards depth for both the season. Sand (%) is more for premonsoon samples with an average value of 4.36 (5m), 15.5 (10m) and 53 (40m). Silt also showed high value for premonsoon, while clay showed high percentage for post monsoon.

Stn	Depth (m)	O.C (%)		CaCO3 (%)		Sand (%)		Silt (%)		Clay (%)	
		pre mon	post mon	pre mon	post mon	pre mon	post mon	pre mon	post mon	pre mon	post mon
ALP	5	2.76	4.48	9.1	6.3	3.3	2.0	18.6	12.9	78.2	85.2
ALP	10	1.04	0.46	8.7	9.6	11.3	4.6	21.2	58.8	67.6	36.6
ALP	40	0.69	0.52	10.0	11.9	50.3	50.4	33.9	15.7	15.8	33.9
CHN	5	2.76	1.00	4.7	3.4	2.5	1.4	52.7	37.4	44.8	61.2
CHN	40	0.35	0.51	21.8	28.9	10.2	61.1	36.9	17.7	52.9	21.2
PON	5	3.45	1.28	3.4	2.6	3.8	4.2	78.1	40.7	18.1	55.2
PON	10	1.38	0.85	5.3	15.7	4.8	8.3	61.0	55.1	34.1	36.8
PON	40	1.04	0.71	32.2	28.7	59.1	1.2	38.5	52.0	2.4	46.8
CAL	5	2.07	1.85	6.9	7.6	4.2	2.0	55.5	63.1	40.3	34.9
CAL	10	1.38	0.47	3.8	6.4	53.5	68.0	41.6	3.8	4.9	28.3
CAL	40	1.04	1.48	18.7	16.2	61.0	1.8	21.2	20.8	17.8	76.5
CAN	5	2.42	0.94	7.9	5.5	8.4	5.3	30.7	56.0	66.9	38.7
CAN	10	2.07	1.18	4.8	5.4	4.1	2.2	54.9	15.8	41.0	82.0
CAN	40	0.35	0.51	19.6	29.6	69.6	27.6	17.8	49.4	12.6	23.1
KSG	5	2.07	0.86	6.5	7.0	3.7	6.1	82.0	43.9	14.2	50.0
KSG	10	1.73	0.39	4.1	4.9	8.3	0.9	36.4	15.0	55.3	84.1
MNG	5	3.11	0.68	6.1	1.4	4.6	3.5	36.5	18.0	58.9	78.6
MNG	10	1.73	1.89	7.7	6.5	11.1	38.1	54.1	24.9	34.9	37.0
MNG	40	0.69	1.85	16.1	16.4	67.8	40.9	28.2	28.9	4.0	30.2

Table 2.5. Textural characters of Kerala coast sediments during pre monsoon and post monsoon season.

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Chapter 3

RARE EARTH ELEMENTS, URANIUM AND THORIUM IN THE SEDIMENTS OF WESTERN CONTINENTAL SHELF OF INDIA

3.1 Results
  3.1.1 Distribution of REES
  3.1.2 Normalization and Anomaly
  3.1.3 Sector wise REE patterns
  3.1.4 Depth wise features of REEs
3.2 Discussion
  3.2.1 Provenance studies
  3.2.2 Relationship between Ce and bottom water oxygen concentration
  3.2.3 Eu anomaly:
  3.2.4 Fractionation indices:
  3.2.5 Uranium
  3.2.6 Thorium
  3.2.7 Element excess
  3.2.8 U/Th ratio
  3.2.9 Authigenic Uranium
3.3 Conclusions

Rare Earth Elements (REEs) have occupied an important role in marine geochemical research, particularly the pattern of abundance of REE to describe the geochemical pathways in marine sedimentation and authigenesis (Piper, 1974). REE in sedimentary phases are increasingly being used as indicators of several geological and oceanographic processes, the paleo-redox conditions (eg., Liu et al, 1988, German and Elderfield, 1990, Nath et.al, 1992), depositional environment and also to assess the crustal source (Taylor and McLennan, 1985). Such patterns in different marine phases have led to the recognition that some fractionation of the REE does take place in the oceans despite the chemical similarities of this group of elements. In this study, surface sediment samples from the eastern Arabian Sea have been taken for analysis, to discuss the provenance, compare with sediment texture, major constituents and dissolved oxygen in bottom waters and also to ascertain whether the redox changes observed in the water column are imparted to the underlying sediments. Additionally, this is the first study where the REEs and trace elements are compared with dissolved oxygen content of bottom water for seasonal studies, where surface sediment samples along the Kerala coast have been analyzed for pre monsoon and post monsoon seasons.

3.1 Results

Rare earth elements, major elements (Al, Fe, Mn etc.) and trace elements (Cr, Ni, Co, Zn. etc) were analyzed along with texture (sand, silt & clay), $CaCO_3$ and organic carbon. Dissolved oxygen, salinity and temperature of bottom water were also measured along with the sedimental analysis. In this chapter, an attempt is made to examine the distribution of

REEs in the study region, cerium and europium anomalies, fractionation indices, along with uranium and thorium distribution.

3.1.1 Distribution of REEs

The concentration obtained for REEs are given in the table A-1 in the appendix. The distribution of rare earth elements in the sediments along the western continental shelf of India can be easily understood from the figures. Most of the rare earths showed higher concentration at 30m samples especially in transects off Quilon, off Cochin, off Calicut, off Cannanore, off Mangalore, off Marmagao and off Veraval. The samples from the transect, off Cochin and off Dwaraka showed different patterns. The abundance of the rare earths for these stations is high for samples from deeper depths(200m).

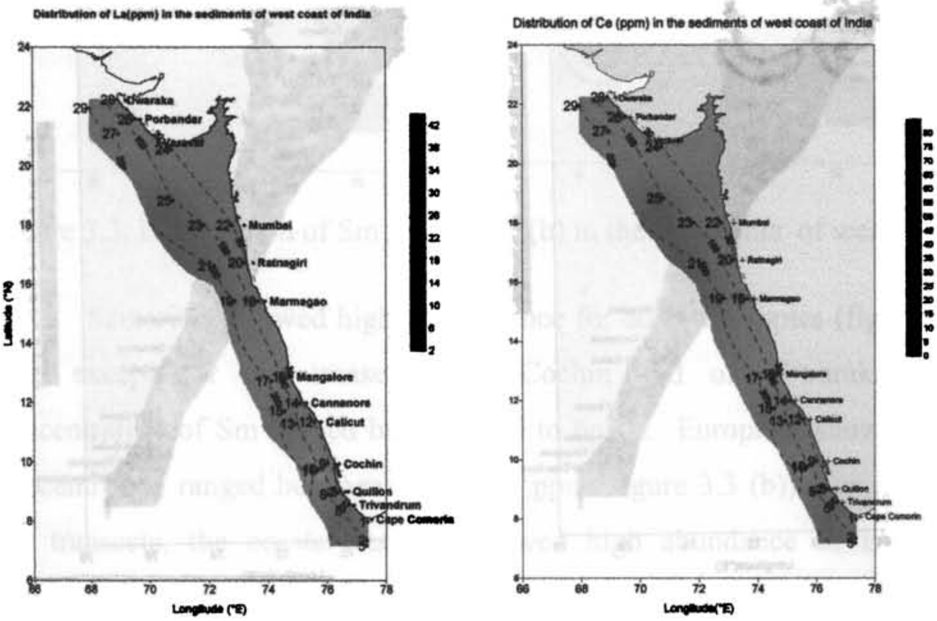


Figure 3.1. Distribution of La(a) and Ce (b) in the sediments of west coast

Lanthanam showed higher abundance off Quilon (44ppm), Cochin(50ppm) and of Mangalore (31ppm) (figure 3.1 (a)). Towards northern side, La concentration seems to be low compared to Kerala coast. Cerium is the most abundant element among the rare earths and showed similar distribution pattern like La along the west coast of India (figure 3.1.(b)). The highest values observed for Ce is 85ppm (off Quilon) and the concentration ranged between 4.39 to 85ppm. Ce showed higher values for most of the coastal samples compared to deeper ones. Praseodymium showed higher abundance off Quilon, Cochin, Cannanore and off Mangalore (figure 3.2 (a)). The concentration ranged between 0.65 to 7.7ppm.

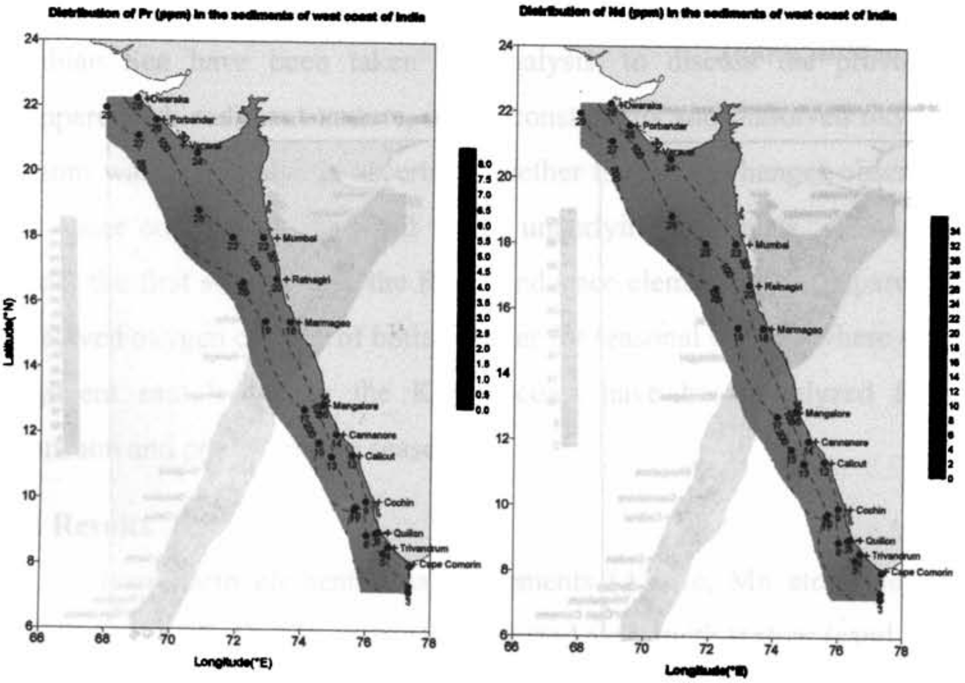


Figure 3.2. Distribution of Pr (a) and Nd (b) in the sediments of west coast

Neodymium also showed similar distribution trend like other REEs, with the highest values observed off Quilon (coastal sample). The distribution pattern is given in the figure 3.2. (b) and the concentration of Nd ranged between 3.86 to 32 ppm.

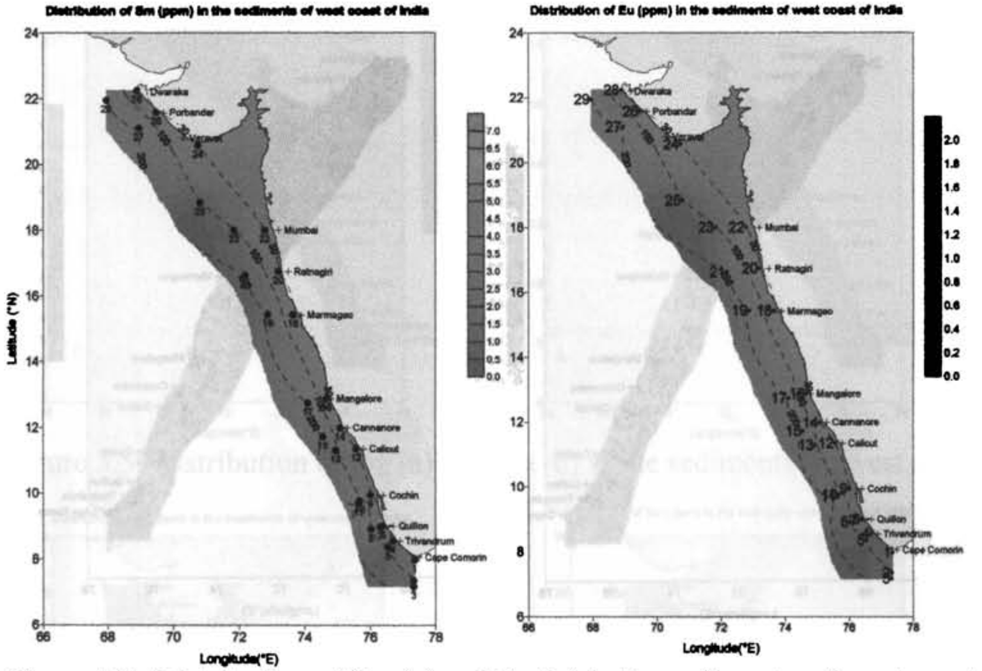


Figure 3.3. Distribution of Sm (a) and Eu (b) in the sediments of west coast

Samarium showed higher abundance for coastal samples (figure 3.3 (a)), except for the transects, off Cochin and off Dwaraka. The concentration of Sm ranged between 0.5 to 6ppm. Europium showed low concentration ranged between 0.3 to 1.4 ppm (figure 3.3 (b)). For most of the transects, the coastal stations showed high abundance of Eu. The distribution of gadolinium is given in the figure 3.4 (a), which showed the concentration between 0.5 to 4.7ppm. The higher concentration is observed along the transects off Cannanore, Mangalore and off Goa. Terbium also showed similar distribution pattern like Gd, but the concentration ranged between 0.1 to 0.85ppm (figure3.4 (b)). The concentration showed higher values for coastal samples.

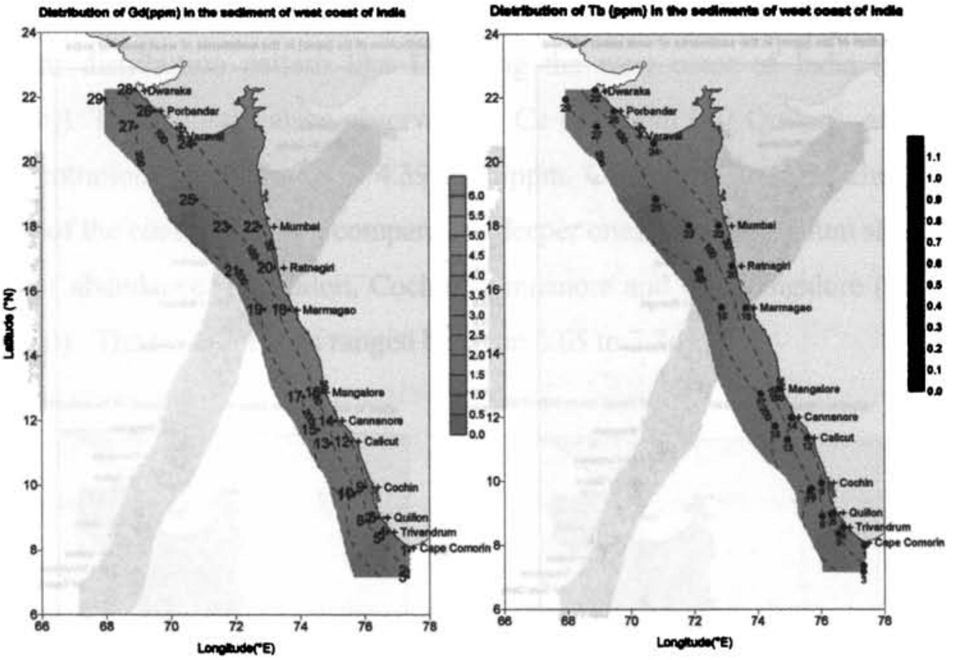
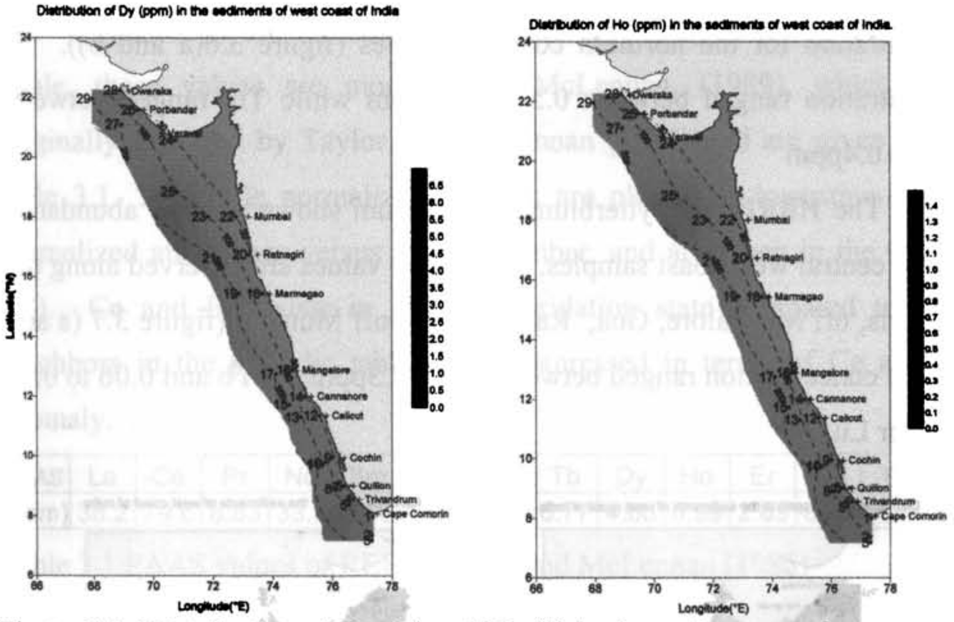


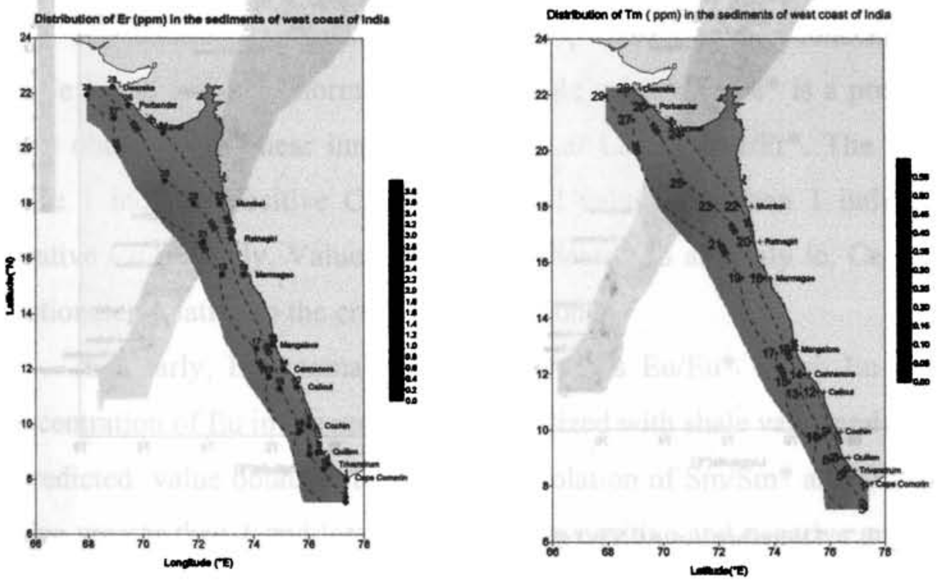
Figure 3.4. Distribution of Gd (a) and Tb (b) in the sediments of west coast

Dysprosium showed higher concentration for most of the coastal samples and the values increased towards the northern side of the west coast (figure 3.5(a)). The concentration ranged between 0.6 to 5ppm. Holmium also showed higher concentration for the coastal stations viz, off Ratnagiri, Mumbai, and off Veraval (figure 3.5 (b)). The concentration of Ho ranged between 0.2- 1 ppm.


Distribution of Dy (ppm) in the sediments of west coast of India

Distribution of Ho (ppm) in the sediments of west coast of India

Figure 3.5. Distribution of Dy (a) and Ho (b) in the sediments of west coast


Distribution of Er (ppm) in the sediments of west coast of India

Distribution of Tm (ppm) in the sediments of west coast of India

Figure 3.6. Distribution of Er (a) and Tm (b) in the sediments of west coast

Erbium and thulium showed similar distribution pattern with high concentration for the northern coastal samples (figure 3.6(a and b)). Er concentration ranged between 0.5 to 2.6 ppm while Tm ranged between 0.07 to 0.4ppm

The HRREs like ytterbium and lutetium showed higher abundance for the central west coast samples. The higher values are observed along the transects, off Mangalore, Goa, Ratangiri and off Mumbai (figure 3.7 (a and b). The concentration ranged between 0.3 to 2.3ppm for Yb and 0.06 to 0.36 ppm for Lu.

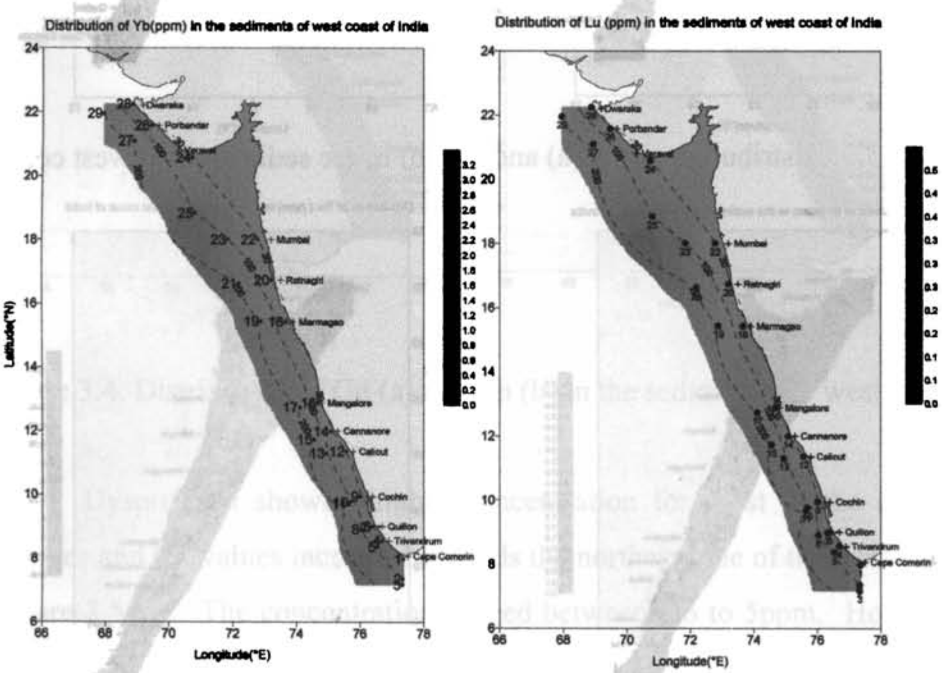


Figure 3.7. Distribution of Yb (a) and Lu (b) in the sediments of west coast

3.1.2 Normalization and Anomaly

The REEs are normalized with PAAS (Post Archaean Australian Shale, these values are modified by McLennan, (1989), which were originally prepared by Taylor and McLennan (1985) and are given in the table 3.1. The shale normalized patterns are plotted as logarithm of the normalized abundance versus atomic number, and are given in the (figure 3.8). Ce and Eu exists in different oxidation state compared to their neighbors in the periodic table and is expressed in terms of Ce and Eu anomaly.

PAAS	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
(ppm)	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.4

Table 3.1 PAAS values of REEs (Taylor and McLennan (1985)

3.1.2.1. Ce and Eu anomaly

Ce anomaly is represented as Ce/Ce*, where Ce is the concentration of Ce in the sediment normalized with shale value and Ce* is a predicted value obtained by linear interpolation of La/ La* and Pr/Pr*. The values above 1 indicate positive Ce anomaly and values less than 1 indicate a negative Ce anomaly. Value close to 1 indicates no anomaly ie, Ce is not fractionated relative to the crustal composition.

Similarly, Eu anomaly is represented as Eu/Eu* where Eu is the concentration of Eu in the sediments normalized with shale value and Eu* is a predicted value obtained by linear interpolation of Sm/Sm* and Gd/Gd*. Value greater than 1 and less than 1 indicate positive and negative anomaly respectively. A value of 1 indicates no anomaly.

Ce anomaly, Eu anomaly, fractionantion indices, sum REEs, U/Th and authigenic U are given in the table 3.2.

St.No	Ce Ano	Eu Ano	(La)n/(Yb)n	(Sm)n/(Yb)n	Sum REEs	U/Th	Authigenic U
1	1.03	0.76	1.61	1.97	105.08	0.12	
2	0.78	1.24	0.74	0.94	34.39	1.77	2.31
3	0.78	1.20	0.86	0.98	39.23	1.66	3.01
4	1.00	1.08	0.93	1.07	24.72	0.18	
5	0.82	1.29	0.77	0.95	21.23	1.84	1.48
6	1.02	1.23	1.68	1.57	193.56	0.17	
7	1.00	1.07	2.22	1.91	57.53	0.13	
8	0.95	0.90	2.40	1.94	97.26	0.29	
9	0.96	1.65	2.78	1.77	78.74	0.07	
10	0.98	0.97	3.58	2.08	186.01	0.15	
11	1.01	1.03	2.53	2.15	168.32	0.14	
12	1.09	1.33	0.95	1.11	141.37	0.33	
13	1.01	1.36	1.11	1.46	61.86	0.45	0.28
14	1.14	1.32	0.95	1.17	150.64	0.31	
15	1.00	1.30	0.93	1.31	69.38	0.52	0.70
16	1.11	1.30	0.95	1.16	141.89	0.29	
17	0.98	1.01	1.82	1.62	135.38	0.24	
18	1.12	1.38	0.85	1.08	139.51	0.34	0.05
19	0.75	1.29	0.58	0.75	46.98	3.31	4.50
20	1.08	1.52	0.63	1.07	110.18	0.38	0.24
21	0.81	1.30	0.69	0.83	35.57	3.66	4.13
22	1.04	1.45	0.66	1.08	114.13	0.29	
23	0.92	1.37	0.77	0.96	38.45	2.25	2.84
24	1.02	1.40	0.86	1.24	132.63	0.18	
25	0.70	1.36	0.68	0.76	14.01	10.87	3.57
26	1.02	1.36	0.92	1.21	120.21	0.18	
27	1.01	1.32	0.87	1.19	98.41	0.66	1.81
28	0.98	1.17	0.90	1.11	43.45	0.88	1.46
29	0.99	1.37	0.87	1.18	91.84	0.45	0.62

Table 3.2. Anomalies, fractionation indices, sum REEs and authigenic U in the sediments.

3.1.2.2 Transect wise Shale normalized REE patterns

Shale normalized patterns for REE are presented transect wise in this section and depth wise in the next section. In some transects, especially the southern ones showed, different pattern for coastal and offshore samples.

off Cape Comorin: The samples off Cape Comorin (30m) showed different pattern, with negative Eu anomaly (0.76), while for the other two samples Eu showed positive anomaly. 100m and 200m samples followed the same pattern with LREE depletion (0.74) and slight negative Ce anomaly, while 30m sample showed LREE enrichment (1.61) (figure 3.8 (a)). The total abundance of REE is higher for coastal sample (105ppm) compared to offshore samples (35ppm)

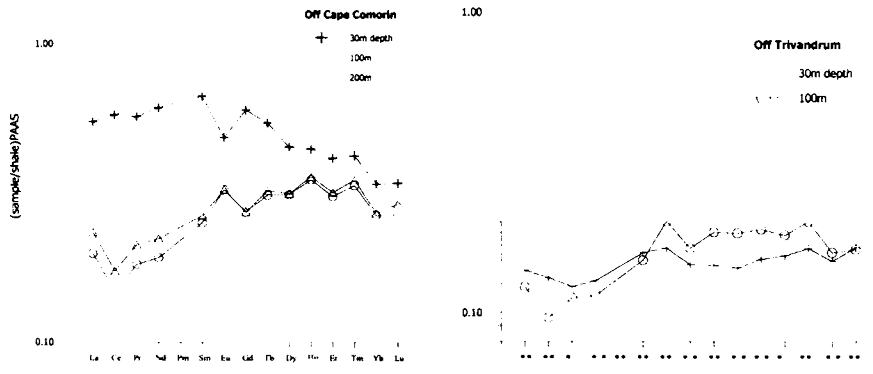


Figure 3.8. PAAS normalised pattern of REEs (a) Off Cape Comorin and (b) Off Trivandrum

off Trivandrum: For this transect 30m sample showed flat shale normalized pattern while 100m sample showed negative Ce anomaly (0.82) and positive Eu anomaly (1.29) (figure 3.8. (b)) LREE is depleted compared to HREE within this transect too. REEs showed lowest abundance (24ppm) for these samples.

off Quilon: Along this transect, 30 m sample showed flat shale normalized pattern, with slight positive Eu anomaly (1.23) (figure 3.8 (c). Other two samples showed pattern with LREE enrichment {(La)n/(Yb)n = 2.2}. The ΣREE showed highest value for the 30 m sample (193 ppm), while that of offshore samples are low (57ppm and 97ppm).

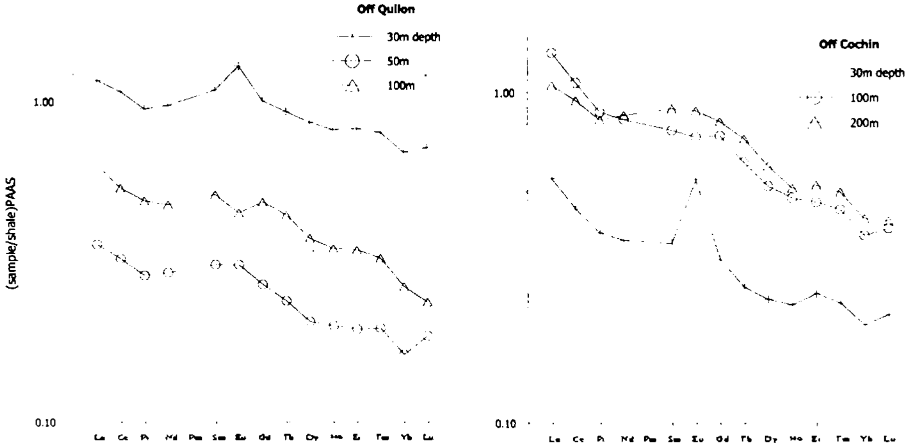


Figure 3.8 PAAS normalised pattern of REEs (c) Off Quilon and (d) Off Cochin

off Cochin: Along this transect, 30m sample showed highest positive Eu anomaly of 1.65 (figure 3.8 (d)). 100m and 200m samples showed different trend with high LREE enrichment with a value of 3.58 for (La)n/(Yb)n. But total REE content showed higher values for these two offshore sediment samples (186 ppm and 168ppm).

off Calicut: Along this transect, both the samples, (30m and 100m) showed flat pattern with positive Eu anomaly (1.3), while ΣREE content is higher for coastal sample (141ppm) compared to the offshore one (62ppm) (figure 3.8 (e)).

off Cannanore : In this transect also, similar shale normalized patterns are seen for both the samples (figure 3.8 (f). Here also coastal sample showed high REE content (150 ppm) compared to offshore one (69 ppm).

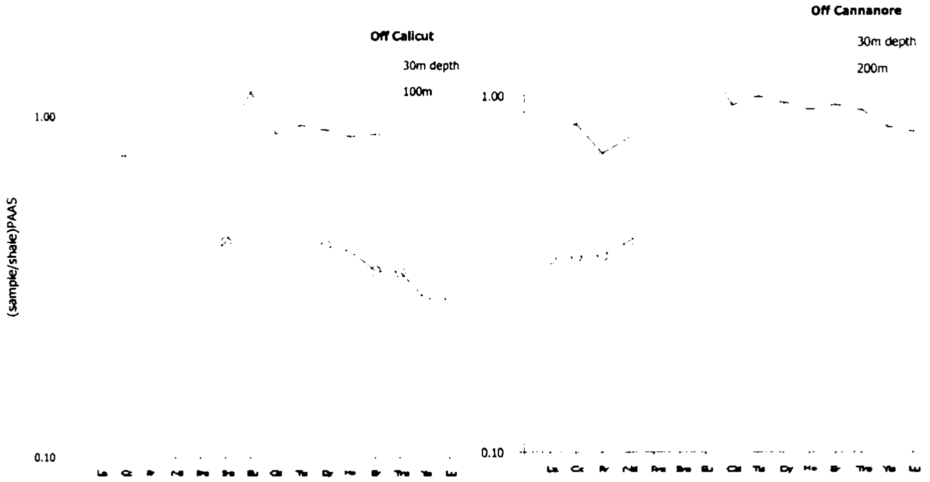


Figure3.8 PAAS normalised pattern of REEs (e) Off Calicut and (f) Off Cannanore

off Mangalore: Along this transect, 30m sample showed flat shale normalized pattern with positive Eu anomaly (1.3), while 200m sample showed flat pattern with HREE depletion {(La)n/(Yb)n = 1.82.(figure 3.8 (g)). These samples showed total REE content in the range of 140 ppm.

off Marmagao: Towards north of Goa, variation in shale normalized pattern are found with HREE enrichment {(La)n/(Yb)n= 0.58 for 200m sample} and positive Eu anomalies. Ce anomaly showed different trend for the two samples ie., 30m sample showed a Ce anomaly of 1.12, while 200m sample showed negative Ce anomaly of 0.75 (figure 3.8 h)). In this transect, response of Ce to bottom water oxygen is apparently significant. Coastal sample showed high value for total REE (139 ppm), while offshore sample showed low value (35 ppm).

off Ratnagiri: Along this transect also, Ce showed negative anomaly values for deeper one (0.8). Total REE also showed much difference for the coastal (110ppm) and deeper sample (35ppm) (figure 3.8 (i)). In this transect also HREE enrichment is observed.

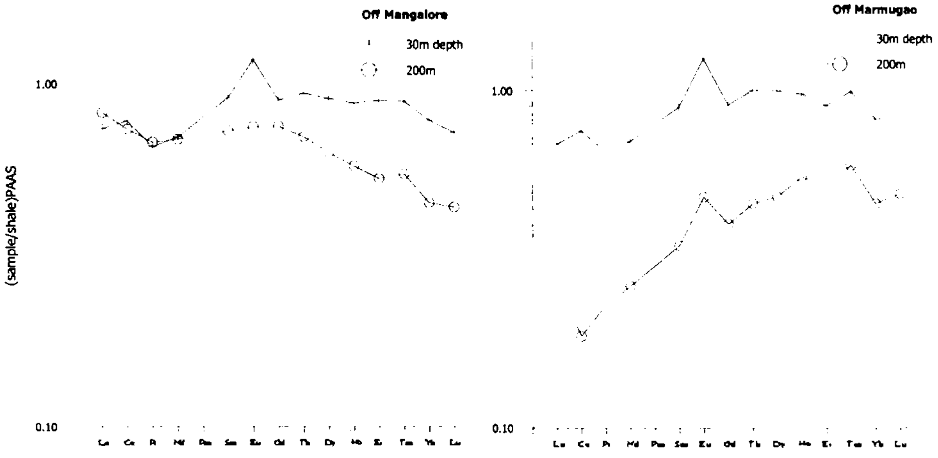


Figure 3.8 PAAS normalised pattern of REEs (g) Off Mangalore and (h) Off Marmagao

off Mumbai: Along this transect both the samples showed same pattern with positive Eu anomaly (1.4) (figure 3.8 (j)). Here also LREEs are depleted with (La)n/(Yb)n= 0.66. Total REE content showed much difference for coastal and offshore samples (114 ppm and 38 ppm).

off Veraval: For this transect, Ce anomaly showed much difference between both the samples. For 30m sample it showed 1.02, while 100m sample showed 0.7 (figure 3.8 (k)). Eu showed positive anomaly for both the samples (1.4). These samples showed flat shale normalized pattern, but the total REE content showed much variation.

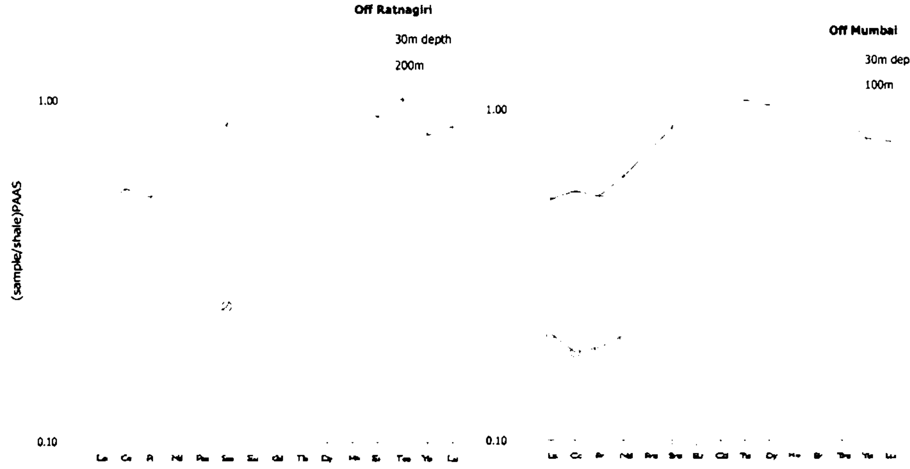


Figure 3.8 PAAS normalised pattern of REEs (i) Off Ratnagairi and (j) Off Mumbai

off Porbandar: The samples along this transect showed similar pattern for 30m and 200m samples with positive Eu anomaly (1.36). This showed slight HREE enrichment and total REE content also showed almost similar values around 100ppm (figure 3.8 (l)).

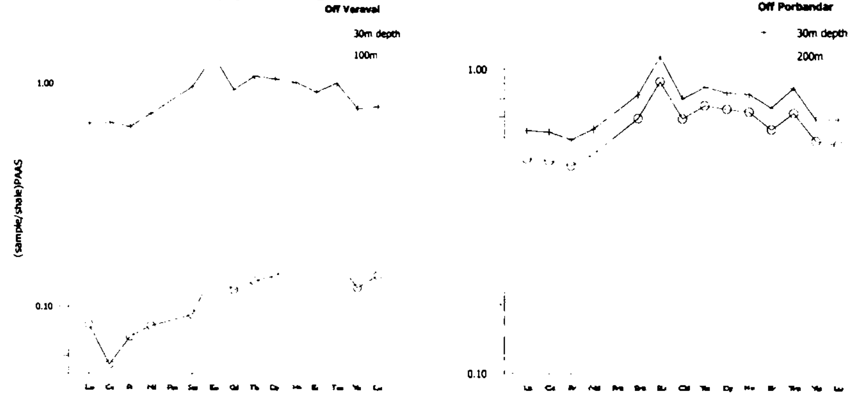


Figure3.8 PAAS normalised pattern of REEs (k) Off Veraval and (l) Off Porbandar

off Dwaraka: Along this transect, both coastal and offshore samples showed same pattern with positive Eu anomaly and slight HREE enrichment. For this transect, the total REE content is more for 200m sample (figure 3.8 (m)).

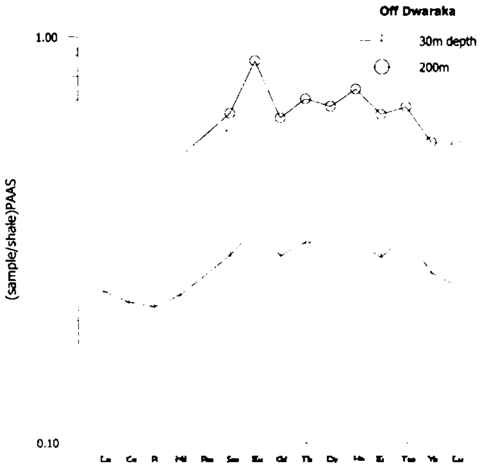


Figure3.8 PAAS normalised pattern of REEs (m) Off Dwaraka

3.1.3 Sector wise REE patterns

The thirteen transects along the western continental margin can be divided into 3 offshore sectors viz, 1) Cape Comorin to Goa, 2) Goa to Mumbai and 3) Mumbai to Dwaraka.

3.1.3.1 Cape Comorin to Goa

Distribution of REEs and shale normalized patterns

The sedimental ΣREE showed higher concentrations for Kerala coast samples, especially off Quilon and off Cochin. Thorium also showed higher values in these samples. The maximum value observed is from the station off Quilon. For this sector the LREES are very much enriched compared with HREEs, which can be seen from the LREE/HREE ratio of about 2.5. The shale normalized pattern is different for southern most samples such as, off Cape Comorin and off Trivandrum with HREE enrichment. Off Quilon and off Cochin samples showed same trend with HREE depletion and positive Eu anomaly for the coastal stations. The transects off Calicut and Cannanore showed similar patterns with MREE enrichment and positive Eu anomaly. These sediments are characterized by gneissic provenance (Rao and Rao, 1995). One of the reason for Th enrichment and very large Eu anomaly may be due to the presence of heavy minerals in these sediments.

The Kerala coast contains placer deposits of economic importance and are being mined at several places. The heavy minerals occur in layers and patches along the beaches and their weight percentage varies from 0.2-96% (Rao and Wagle (1997). Ilmenite, monazite, zircon, sillimanite and garnet are the important minerals. Highest concentration of heavy minerals occur along the beaches of south Kerala (Chavara- Manavalakurichi) which also contain high amounts of radioactive elements.

3.1.3.2 Goa to Mumbai

Distribution of REEs and shale normalized patterns

The shale normalized pattern showed HREE enrichment with positive Eu anomaly. The abundance of REE is more for coastal stations. These sediments are characterized by Deccan trap (basaltic provenance) (Rao and Rao, 1995). For this sector, REE showed low abundance for the offshore samples (figures 3.1 to 3.7)

The most important heavy minerals along Karnataka and Goa are hornblende, muscovite, tremolite, actinolite, garnet etc. Next to Kerala, placers of Maharashtra are important and are mostly derived from the Deccan Trap province ((Rao and Wagle, 1997).

3.1.3.3 Mumbai to Dwaraka

Distribution of REEs and shale normalized patterns

The abundance of REE is similar for both samples off Porbandar, but off Dwaraka, the offshore sample showed high abundance of REE. The total REE content is 92ppm for offshore sample, while coastal sample showed only 43 ppm. Positive Eu anomaly is reported for these samples.

The mouth of Indus is located in this region and brings sediments mainly from the glacial Himalayas and semi-arid to arid soils (Rao and Rao, 1995). Several workers reported illite, smectite, chlorite and minor kaolinite in the shelf sediments of the Indus and northern part of the gulf of Kachchh, which was attributed to the influence of the Indus discharge (Nair et. al, 1982, Rao, 1991). Stewart et al (1965) reported 20% quartz and 20% mica in the shelf sediments off the Indus.

3.1.4 Depth wise features of REEs

Shale normalized pattern for 30m stations, 100m stations and 200m stations are also given in separate figures (Figures 3.9 a, b and c). Among 30m samples, only the sediments off Cape Comorin showed negative Eu anomaly, all others showed positive Eu anomaly. Samples from some of the off shore stations showed different pattern such as Cape Comorin, Cochin, Dwaraka and Trivandrum. Sample off Trivandrum showed low values for all the REEs. Among the 30m stations, off Cochin sample showed highest HREE depletion. (Figure 3.9(a)), which is consistent with the observation of

Nath et.al (2000) who found a significant LREE enrichment related to gneissic provenance.

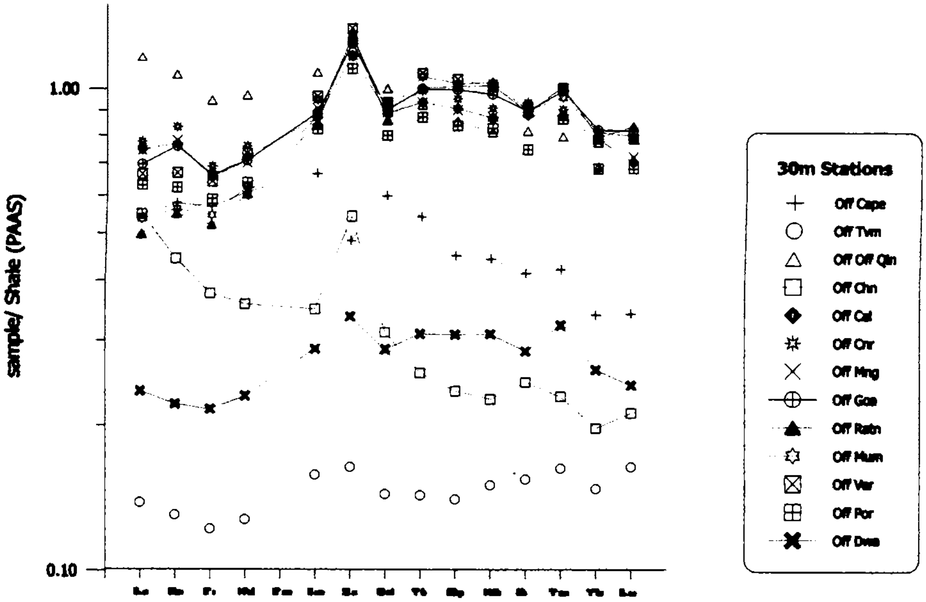


Figure 3.9 (a) PAAS normalized pattern for all 30m samples.

100m samples showed flat shale normalized pattern with slight positive Eu anomaly for some of the samples. Slight negative Ce anomaly is also observed in some stations off Cape Comorin and off Veraval. (Figure 3.9(b)).

Samples from 200m showed different trend where some samples with negative Ce anomaly and positive Eu anomaly. Among these samples, most of them showed HREE enrichment (figure 3.9(c).

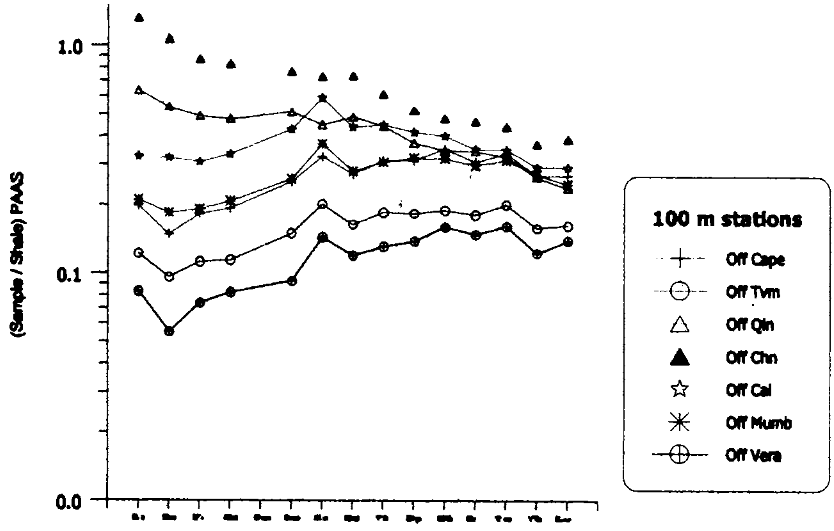


Figure 3.9 (b) PAAS normalized pattern for all 100m samples

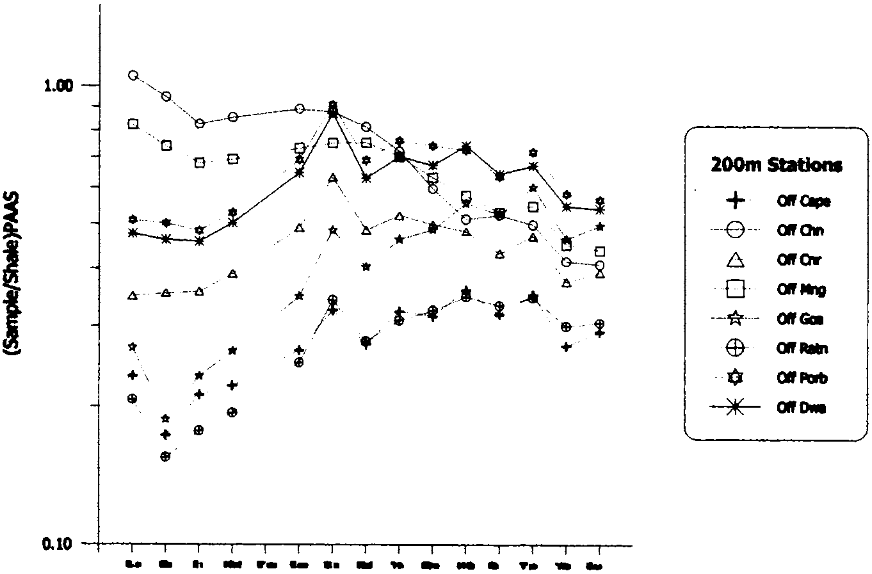


Figure 3.9 (c) PAAS normalized pattern for all 200m samples

In the present study, the total REE showed higher values along Kerala coast, especially off Quilon (193.5ppm) and off Cochin (186ppm). Most of the 30m stations showed higher values, >100ppm for total REEs, except Trivandrum and Dwaraka. While 100m stations showed high values only for two transects, off Quilon and off Cochin. 200m samples showed high values (>100ppm) for total REE especially for the transects off Cochin, Mangalore, Porbandar and off Dwaraka (figures 3.10, 3.11and 3.12(c)).

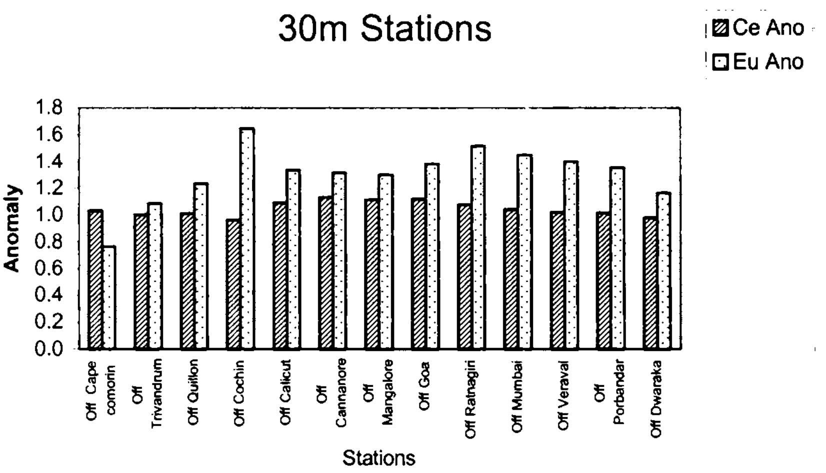


Figure 3.10 (a) Eu and Ce anomalies of 30m Samples

Ce anomaly helps to focus on the redox- controlled reactions of Ce by comparing its concentration to those of near neighbors, which undergo no redox transformation. For 30 samples, no significant Ce anomaly is observed from south to north. The Ce/Ce* values varied between 0.96-1.14 (Figure 3.10(a)). In this case all the values are either positive or close to one. For 100m stations, some of the samples showed negative values, especially off Cape Comorin (0.78) and off Veraval (0.7). (Figure 3.11(a)). For 200m stations, some of the samples showed negative Ce anomaly particularly, off Cape Comorin, Marmagao and off Ratnagiri (Figure 3.12(a)).

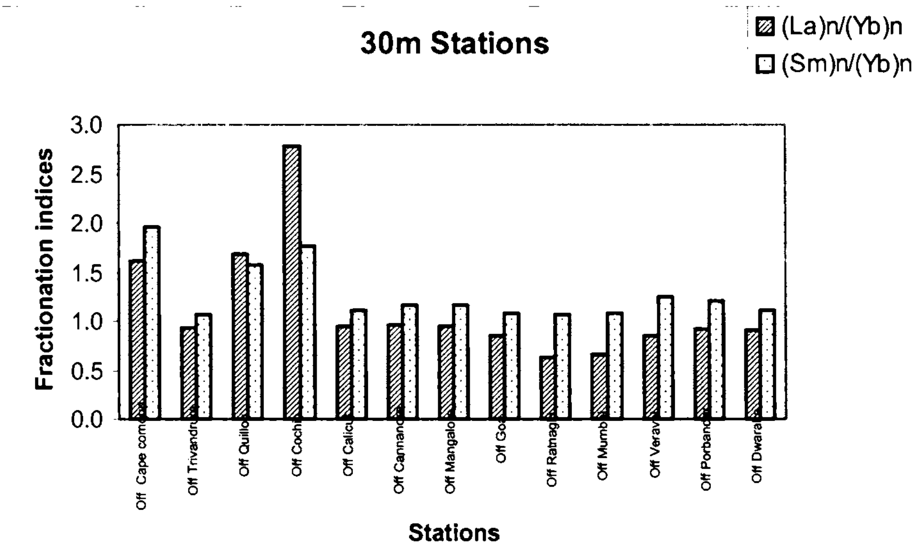


Figure 3.10 (b) Fractionation indices for 30m samples.

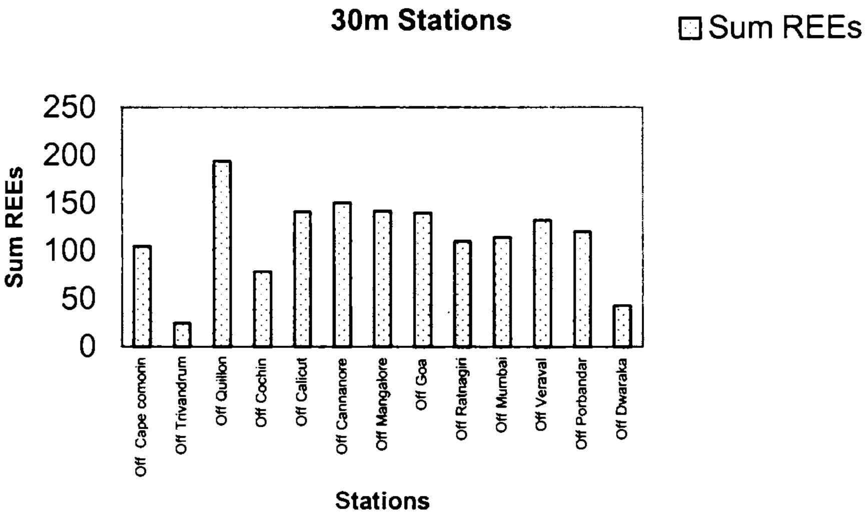


Figure 3.10 (c). Sum REE of 30m samples.

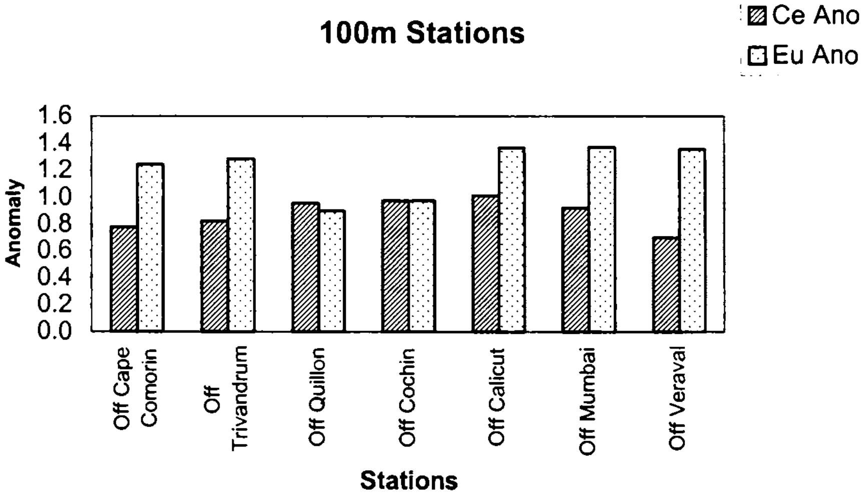


Figure 3.11 (a) Eu and Ce anomalies of 100m Samples

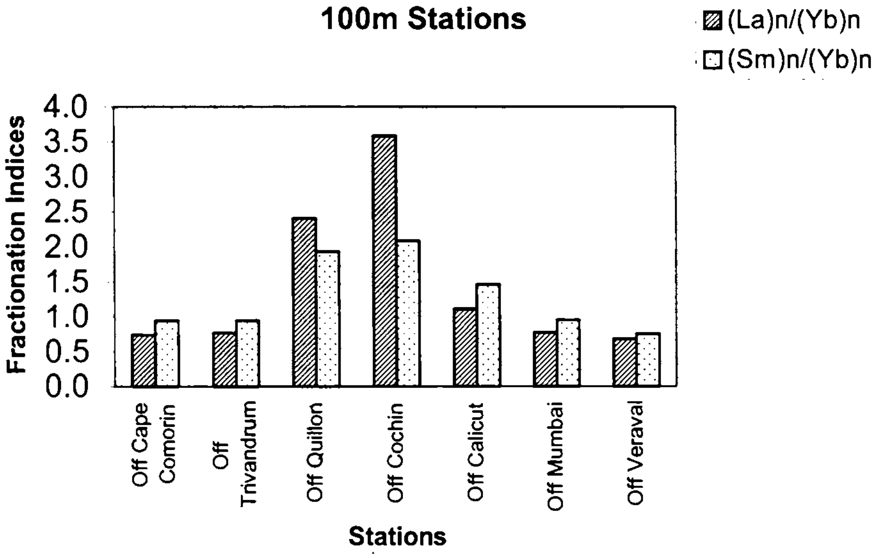


Figure 3.11(b) Fractionation indices for 100m samples.

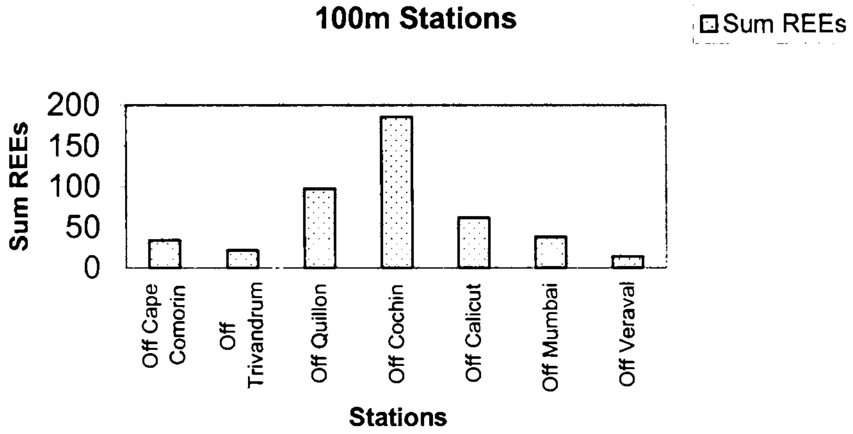


Figure 3.11 (c). Sum REE of 100m samples.

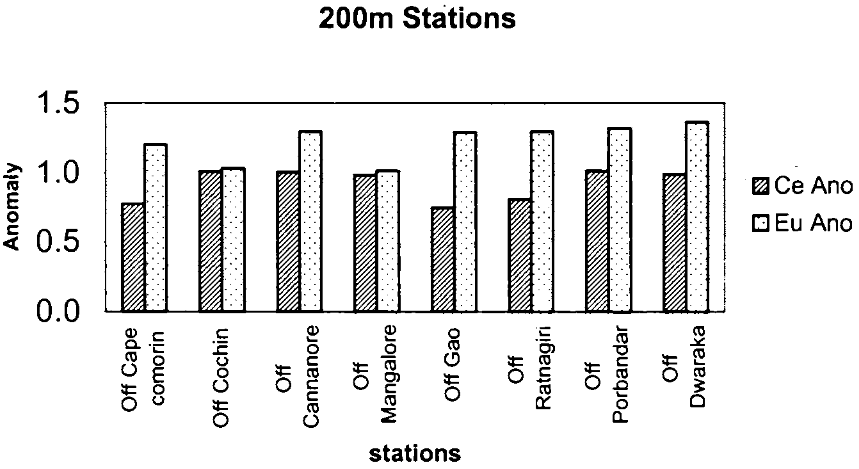


Figure 3.12 (a) Eu and Ce anomalies of 200m Samples

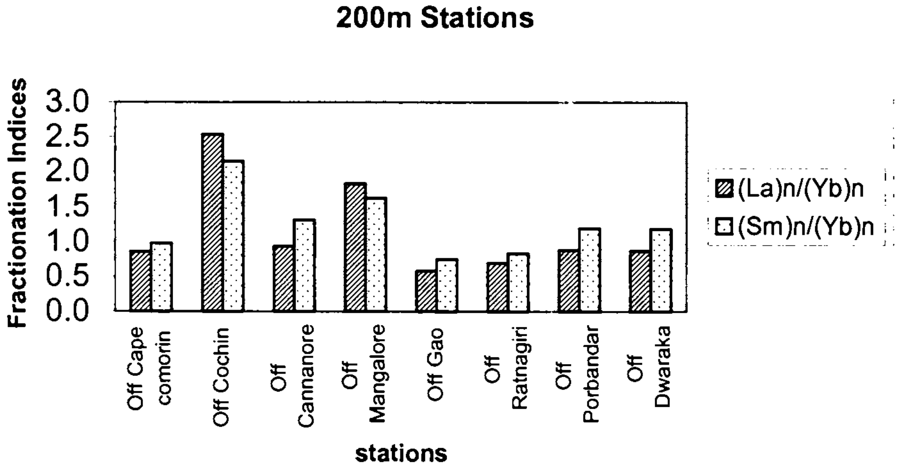


Figure 3.12 (b) Fractionation indices for 200m samples.

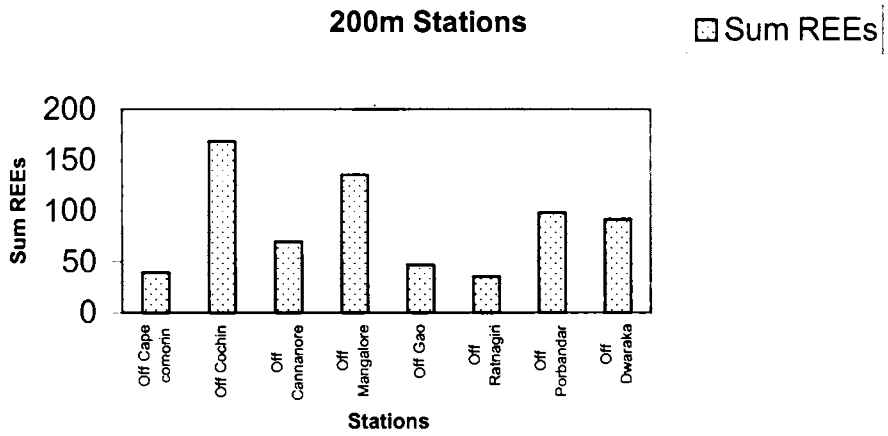


Figure 3.12 (c). Sum REE of 200m samples.

3.2 Discussion

3.2.1. Provenance studies

The chemical coherence and relatively predictable behavior of the rare earth elements have made these as one of the most extensively used geochemical tracers. The relative abundance of rare earth elements in sediments has been suggested as a tool for determining the source of rocks. (Morey and Setterholm, 1997).

By studying the distribution of clay minerals, Rao and Rao (1995) reported that there are three principal sources for sediments of the western continental shelf. They are a) the Indus province- rich in illite and chlorite along the northern side of Gulf of Kachchh. b)The Deccan Trap province – rich in smectite (basaltic) off Saurashtra- Goa and c) gneissic province- rich in smectite and Kaolinite. Between Goa and Kochi the shelf and slope sediments represent mostly the influence of gneissic-province indicating cross shelf transport in this region. The effect of the Indus decreases from north to south and is insignificant on the south west continental margin (Rao and Rao, 1995).

Trace element ratios such as Th/Sc, La/Sc and La/Th are particularly sensitive to average provenance composition because Th is highly incompatible where as Sc is relatively compatible. Wronkievics and Condie (1987) and Gu (1994) reported that in the absence of recycling, these ratios should distinguish between mafic/ultramafic and felsic source components and even if recycling is important, the ratios may exhibit only modest changes. Higher La/Th ratios and lower La/Sc and Th/Sc ratios are characteristics of felsic sources (eg. McLennan, et al. 1990).

Co has been widely used in determining the provenance/source area characteristics of sedimentary rocks, because it has been considered to belong to immobile trace elements along with Ta, La, Yb and Sc. Enrichment in Co and Sc in sedimentary rocks are assumed to be derived from mafic sources (Nath et al, 2000).LREE enrichment and steep HREE patterns are attributed to felsic source characteristics (Nath et al, 2000).

off Cape Comorin: The higher total REE abundance for 30m samples and different shale normalized pattern for coastal and deeper samples suggest that the sediments of 30m may have different source compared to 100m and 200m samples. The carbonate content is almost the same for three samples. Therefore, the dilution effect either from varying $CaCO_3$ contents or due to the distance from the shore could not be a reason for the different patterns. Wherever necessary ratios of trace elements involving REES, U and Th are used in the text to decipher the provenance. Ratios such as Th/Sc, La/Sc and

Co/Th are particularly sensitive to average provenance composition because all these three elements are said to be transferred quantitatively into terrigenous sediments from source through sedimentation (Taylor and McLennan, 1985, Nath et.al, 2000). La/Th ratio showed low value (2.21) compared to UCC (La/Th =2.8) for 30m sample, while La/Sc and Th/Sc ratio showed high values indicate some different source for the coastal sediment. For UCC, La/Sc ratio is 2.73 and Th/Sc ratio is 0.97. (Table 3.3)

off Trivandrum: The total REE abundance is almost same for these samples, even though the carbonate content is varying much. The dilution effect from the carbonate is not visible for these samples. La/Sc and Th/Sc ratios are low for the 30m samples compared to offshore one (Table 3.3).

off Quilon: The total REE content showed highest value for this coastal station. The carbonate content is more for the deeper sample. The dilution effect from the shore may be other reason for the low abundance of REE for the offshore samples. Co/Th ratio showed low values for these samples showed felsic characteristics for this sediment (Table 3.3)

off Cochin: The higher concentration of total REE observed along the coastal stations off Quilon has moved towards the offshore depth off Cochin and this might be due to the impact of coastal current which leads to the cross shelf transport of sediments. Presence of positive Eu anomaly for 30m sample is characteristically different from other two patterns. Barring Eu, the pattern is sloping downward towards HREE. Presence of strong Eu anomaly is consistent with the gneissic/ granulitic source for these sediments (Nath et. al, 2000 and Allen et al.1985). This LREE enrichment and steep HREE pattern for the sediments supports the finding of Nath et al. (2000). Shale normalized REE patterns of gneisses and charnockites formed by retrograde metamorphism showed similar pattern with positive Eu anomaly (Allen et al.1985). Rao and Rao (1995) also reported the influence of gneissic province for the shelf and slope sediments between Goa and Cochin. The REE abundance is more for offshore samples compared to coastal ones indicating different source.

off Calicut and off Cannanore: These two transects showed similar pattern for coastal and deeper samples. $CaCO_3$ content showed high value for the deeper sample, which may be a reason for low abundance of REEs for the deeper sample. Dilution effect due to the distance from the shore may be another reason for similar pattern and low REE abundance for deeper sample. La/Th ratio is high and La/Sc and Th/Sc ratio are low for these samples indicate similar source for these sediments (Table 3.3).

off Mangalore: 30m sample of this transect showed similar trend off Calicut and off Cannanore. But the offshore sample showed LREE enrichment sloping towards HREE shows gneissic provenance for the samples. The carbonate content showed different values for coastal and offshore samples, but carbonate dilution is not significant from the shale normalized pattern. By studying Sr and Nd isotopes, Kesarkar et. al (2003) also supported gneissic provenance for the sediments between Cape Comorin and Marmagao.

off Marmagao and off Mumbai: Shale normalized patterns showed different trend towards north of Goa, with HREE enrichment, positive Eu anomaly showed different source for these sediments. From clay mineral studies, Rao and Rao (1995) reported Deccan trap provenance (rich in basalt) for the sediment north of Goa to Saurashtra. The carbonate content showed much variation for the coastal sample and offshore sample and may be the reason for low abundance of REE for the offshore sample. The shale normalized pattern off Ratnagiri and off Mumbai showed similar trend with difference in carbonate content for coastal and offshore samples. The carbonate dilution and distance from the shore may be the reason for similar pattern with low abundance for offshore sample.

off Veraval and off Porbandar: The shale normalized pattern showed flat with positive Eu anomaly. The carbonate content is very high for the offshore sample off Veraval, may be the reason for the different REE abundance. Rivers are good source of REEs to the marine environment. Narmada and Tapti rivers bring lot of sediment flux into this area and may be the reason for high REE abundance for the coastal sample. The shale normalized pattern are similar off Veraval, indicates same source for the coastal and offshore sample. REE abundance and carbonate content also showed similar trend for these samples.

off Dwaraka: The shale normalized patterns are similar for both the sample, but the abundance is reverse in this transect. The offshore sample showed high abundance of REE compared to the coastal one. The carbonate content is high for the coastal sample. Al and Fe concentration showed high value for the offshore sample. Indus provenance for this sediment may be a reason for this anomalous behavior (Rao and Rao, 1995, Kessarkar et. al, 2003).

St.No	Depth(m)	La/Sc	Th/Sc	La/Th	Co/Th	Cr/Th	Th/U	Zr/Hf	Rb/Cs
1	30	8.56	3.87	2.21	0.32	7.15	8.33	35.11	30.05
2	100	6.52	1.39	4.70	0.92	23.34	0.57	34.96	18.06
3	200	3.65	0.93	3.92	1.06	22.63	0.60	33.69	20.86
4	30	0.84	0.41	2.02	1.14	20.04	5.45	35.57	45.73
5	100	5.00	1.06	4.73	1.23	27.65	0.54	35.66	9.90
6	30	3.68	1.13	3.26	0.67	12.11	5.86	37.43	28.77
7	50	2.16	0.99	2.17	0.53	11.41	7.55	39.54	48.78
8	100	4.48	1.59	2.82	0.33	10.00	3.47	39.96	30.34
9	30	3.24	1.33	2.42	0.47	8.05	14.63	40.61	144.72
10	100	7.27	2.12	3.42	0.35	7.90	6.63	41.91	32.87
11	200	4.68	1.81	2.59	0.48	9.46	6.98	35.53	34.23
12	30	1.70	0.47	3.64	1.59	31.52	3.00	35.77	16.46
13	100	3.41	0.66	5.18	2.22	19.65	2.23	39.63	18.17
14	30	1.63	0.48	3.41	1.52	32.35	3.24	35.78	15.91
15	200	2.35	0.65	3.62	2.24	20.55	1.91	36.39	14.73
16	30	1.58	0.50	3.18	1.63	28.69	3.40	35.55	15.97
17	200	7.84	1.52	5.17	0.81	9.59	4.19	36.27	20.39
18	30	1.32	0.36	3.63	3.04	22.81	2.93	38.61	14.84
19	200	3.01	0.44	6.80	2.87	74.66	0.30	35.91	13.88
20	30	0.74	0.20	3.79	5.51	26.77	2.62	38.96	15.06
21	200	2.16	0.34	6.36	3.41	29.53	0.27	38.16	13.88
22	30	0.77	0.20	3.89	5.82	21.08	3.46	39.70	15.95
23	100	1.57	0.29	5.41	4.19	30.78	0.44	39.71	14.87
24	30	1.18	0.32	3.67	4.46	13.34	5.66	41.17	17.58
25	90	4.11	0.44	9.36	6.35	81.84	0.09	42.27	10.15
26	30	1.22	0.39	3.11	3.06	12.93	5.53	39.15	15.15
27	200	1.15	0.33	3.49	3.84	14.77	1.52	40.69	15.72
28	30	2.49	0.74	3.35	2.58	10.45	1.14	42.75	13.91
29	200	1.28	0.38	3.34	3.46	17.07	2.24	38.05	15.76

Table 3.3. Inter elemental ratios for Arabian Sea sediments.

The presence of Indus sediments on the slope off Saurashtra and to some extent on the outer shelf indicate the influence of strong tidal current which is more on the inner shelf and decreases towards offshore and insignificant on the continental slopes. (Rao and Wagle, 1997).

The ratios such as Th/Sc, La/Th, Co/Th and REE patterns are useful for identifying the provenance of sediments, but in the case of some samples it is found to be difficult to identify the felsic or mafic source. This may be because of the complexity of the system, which is contributed by the different circulation patterns, variations in mixing, and bottom topography of the study area.

3.2.2 Relationship between Ce and bottom water oxygen concentration

Redox reactions lead to the preferential removal of Ce under oxidizing conditions and its preferential enrichment under reducing conditions (De Baar et.al 1988, German et al. 1991). Hence the distribution of Ce can be compared with that of other lanthanides to distinguish redox from nonredox transport processes (Moffett, 1994). Ce anomalies are well known in the marine environment. Negative Ce anomaly is characteristic of seawater and positive Ce anomaly is associated with manganese nodules. Elderfield (1988), Piepgras and Jacobsen (1992). Nath et al (1994) reported that most oceanic water samples resulting from the oxidation-reduction reactions are associated with Ce depletion. Variations in Ce fractionation has been found across the redox boundaries in Cariaco Trench (De Baar et al, 1988), oxygen deficient Chesapeake bay (Sholkovitz et al 1992), the OMZ of northwestern Indian Ocean, (German and Elderfield, 1990). Howmuch of this is reflected in the sediments impinged by low oxygenated waters is not known. Liu et.al (1988), Wang et.al (1986) and others have suggested that Ce anomaly in ancient sedimentary sequences can be used as a paleoredox proxy. But many factors control Ce distribution, and the magnitude of Ce anomaly may depend on: 1) influence of depositional environment (Murray et.al, 1990), 2) proximity to the source areas (Murray et.al, 1991a), 3) Redox conditions within the sediments (Murray et.al, 1991b), 4) lithological and diagenetic control (Nath et.al, 1992), and 5) carbonate content (Nath et.al, 1992). However, Nath et al (1997) reported REE along the Arabian Sea sediments beneath the intense OMZ (<0.2ml/l) and away from the OMZ (1-2ml/l) showed no dramatic variations in Ce anomalies.

In the present study also, Ce anomaly responded to the bottom water oxygen condition for some of the transects only. For most of the transects, 30m coastal stations showed higher values for Ce compared to deeper stations except off Cochin and off Dwaraka. Drastic change in Ce concentration is observed in certain transects for example- off Cape Comorin where a reduction from 46 ppm (30m) to 13.7ppm (200m) is noticed. At certain transects, Ce anomaly in the sediment also showed drastic change with depth. These transects are off Cape Comorin, off Goa and off Ratnagiri. At Cape Comorin (30m) sample, showed no Ce anomaly (1.03) while bottom water D.O. showed 3.25ml/l, while 200m samples showed Ce anomaly of 0.78 where bottom water D.O is very low (0.14ml/l). Off Goa (30m) showed no Ce anomaly (1.12) with bottom water D.O. content of 2.99ml/l/, while 200m sample showed Ce anomaly 0.75 with bottom water D.O. again falling to 0.03ml/l. At Ratnagiri and Veraval also, distinct difference in Ce anomaly is observed within a transect. This may be due to the response of Ce to the redox condition of the overlying water column.

St.No	Depth(m)	DO (ml/l)	Ce (ppm)	U(ppm)	Mn %	Ce Ano	Eu Ano
1	30	3.25	46.00	1.14	0.033	1.03	0.76
2	100	0.86	11.76	2.84	0.005	0.78	1.24
3	200	0.14	13.78	3.77	0.006	0.78	1.20
4	30	3.28	10.39	0.48	0.017	1.00	1.08
5	125	0.26	7.63	1.81	0.004	0.82	1.29
6	30	3.33	85.38	2.32	0.036	1.02	1.23
7	50	3.08	25.67	0.83	0.020	1.00	1.07
8	100	1.45	42.64	2.47	0.012	0.95	0.90
9	30	3.30	35.38	0.59	0.032	0.96	1.65
10	100	1.50	85.19	2.22	0.024	0.98	0.97
11	200	0.13	75.31	2.23	0.025	1.01	1.03
12	30	3.20	61.07	2.61	0.032	1.09	1.33
13	100	1.70	25.56	1.08	0.037	1.01	1.36
14	30	3.17	66.32	2.68	0.033	1.14	1.32
15	200	0.06	28.15	1.93	0.030	1.00	1.30
16	30	3.70	62.16	2.63	0.043	1.11	1.30
17	200	0.04	58.85	1.45	0.043	0.98	1.01
18	30	2.99	60.46	2.50	0.132	1.12	1.38
19	200	0.03	14.91	5.00	0.012	0.75	1.29
20	30	3.20	43.77	1.92	0.080	1.08	1.52
21	200	0.04	12.32	4.55	0.014	0.81	1.30
22	30	3.39	44.87	1.52	0.101	1.04	1.45
23	100	2.07	14.67	3.34	0.022	0.92	1.37
24	30	3.46	53.23	1.22	0.131	1.02	1.40
25	90	2.62	4.39	3.69	0.010	0.70	1.36
26	30	3.59	49.62	1.40	0.092	1.02	1.36
27	200	0.02	39.94	3.67	0.074	1.01	1.32
28	30	3.56	17.64	2.35	0.097	0.98	1.17
29	200	0.03	36.78	2.44	0.072	0.99	1.37

Table 3.4. D.O (ml/l) of bottom water and Ce, Eu anomalies, Mn and U conc. of sediments.

Ce anomalies in most of the 30m stations are close to unity suggesting the influence of terrigenous sedimentation in these stations close to the coast. As the sedimentation in these areas are influenced by shore currents and transportation from adjacent land masses, expectedly no relation is observed between D.O. levels and Ce anomalies. Incidentally all these areas have well oxygenated bottom waters (D.O>3 ml/l). It is usually assumed that the general depth range of suboxic waters in the Arabain Sea is between 100 and 1000m (Qasim, 1982). Among the 100m stations, bottom waters are gradually more oxic towards north, ie, D.O values showed <1ml/l off Cape Comorin, Trivandrum and found to increase to off Mumbai (~2ml/l). Both the stations with low D.O. showed negative Ce anomalies, while others showed no Ce anomaly (Table.3.4). Among the stations of 200m depth, D.O. values are very low with relatively higher values in the southernmost two stations (>0.1ml.l) over the northern stations (much less than 0.1ml/l). Inconsistent relation between D.O. and Ce anomalies is observed here. Among all, only three stations have negative Ce anomaly and all others have no Ce anomaly with their values close to 1 (Table 3.4).

3.2.3 Eu anomaly

Eu anomaly Eu/Eu* values varied from 0.76 to 1.65. Only station 1 (of Cape Comorin) showed negative Eu anomaly (0.76). All other values are close to one or greater than one. For 30m stations, no significant Eu anomaly is observed for southern stations till off Cochin, but towards north, positive Eu anomalies (1.3 to 1.4) was reported. Shale normalized positive

Eu anomalies are found either in waters affected by eolian input (Elderfield, 1988) or in hydrothermal solutions and the sediments resulting from high T-basalt alteration along the mid-ocean ridges and back-arc spreading centers (Michard et al 1983, Nath et.al, 1997). The present samples are not affected by these potential inputs and so terrestrial influence may be a reason for positive Eu anomaly. This terrestrial influence is supported by the good correlation of Eu with Al (0.95), Zr (0.88), and Y (0.97). High field strength elements like Hf (0.91) and Nb (0.93) also showed good correlation with Eu. Compared to coastal stations, 100m and 200m samples did not show significant positive Eu anomaly. For example, along the transect off Cochin, Eu/Eu* showed prominent decrease from 1.6 (30m) to 1.0 (100m).

3.2.4 Fractionation indices

Fractionation indices is represented by (La)n/(Yb)n ie, $\{(La_{sample}/La_{PAAS})/(Yb_{sample}/Yb_{PAAS})\}$ratio, defines relative behaviour of LREE to the HREEs. This ratio had been calculated for all the samples and the plots were given separately for 30m, 100m and 200m samples. In the present study, this ratio ranges from 0.63 to 2.78 for 30m samples. The values are plotted in figures 3.10, 3.11 and 3.12 (b). For the transect off Cochin, LREE/HREE showed higher values, for all the three sets. This indicates HREE are very much depleted for this station. But total REE showed highest values for the deeper samples off Cochin. La and Ce showed high values compared to PAAS for the 100 and 200m samples. This supports the studies of Nath et.al, (2000), who have found significant LREE enrichment in the sediments from the Vembanad lake and the inner shelf sediments off Cochin.

(Sm)n/(Yb)n ratio indicates the behaviour of MREEs to HREEs. The plots are made separately for three sets and are given in the figures 3.10, 3.11 and 3.12 (b). For 30m samples, this ratio varied from 1.06 to 1.96. Southern stations (along Kerala coast) showed MREE enrichment compared to HREEs. But towards north, almost all the stations showed value in the range 1 to 1.2. For 100m stations, the MREE/HREE ratio varied from 0.76 to 2.08. The highest values are observed for the transect off Cochin. Total REE is also highest for this transect. These fractionation indices indicate different provenance for these sediment. Along 200m stations, MREE/HREE ratio varied between 0.75 and 2.15. The higher values are reported off Cochin and off Mangalore. This suggests some local input for REEs for the off Cochin transect.

3.2.5 Uranium

The distributions of certain minor and trace elements in marine sediments should potentially provide forensic tools for determining the redox conditions of the bottom waters at the time of deposition (Calvert and Pedersen, 1993). The enrichment of trace elements like Cr, Mn, Mo, Re, U, V relative to their crustal abundances indicates that the host sediments accumulated under anoxic conditions, although not necessarily under anoxic bottom waters. The stable form of U in oxygenated waters is U (VI). Carbonate ions complex with dissolved U in seawater, creating $[UO_2(CO_3)_3]^{4-}$, which dominates the speciation in most natural waters

(Barnes and Cochran, 1990). Klinkhammer and Palmer (1991) and Barnes and Cochran (1993) reported that anoxic basins, organic-rich shelves and hemipelagic sediments are sites for authigenic U deposition. Occurrence of U enrichment in sediments can be used as a reliable guide for inferring suboxic to anoxic bottom water conditions (Wignall & Myers, 1988, Calvert and Pedersen, 1993).

Uranium behaves as a nearly conservative element in oxygenated seawater, but it is precipitated under chemically reducing conditions that occur in sediments underlying low-oxygen bottom water or in sediments receiving high fluxes of particulate organic carbon. (Zheng et al.2002). The Arabian Sea, because of its characteristic chemical and biological properties, is an interesting basin to study the geochemical behavior of uranium. One of the peculiar properties of the Arabian Sea is the semi-annual reversal of wind regimes caused by the monsoon. These reversals have significant impact on the upper ocean circulation and biological productivity of the region (Qasim, 1982 and Madhupratap et al., 1996).

The occurrence of primary uranium minerals in igneous rocks is partially controlled by the oxidation state of U in the melt. U (IV) compound are insoluble in water and crystallizes as primary minerals from wet granitic magmas. Under oxidizing conditions, as in near surface environments, U exists in the (VI) state. The U concentration of sediments is controlled by provenance of the source materials and the geochemical properties of the depositional environments. Terrigenous sand contains an average of 3ppm of U. The oxidation of organic matter in clays creates a reducing environment, which precipitates U (IV). As a result, black, carbonaceous- rich shales usually contain more U than red, gray or green shales (Huglund, 1972).

Oceanic waters contain a relatively uniform amount of U and are usually saturated in U with respect to local geochemical environments. U concentration in continental waters shows wide ranges due to the nature of the rocks forming the drainage basin. The important minerals of U are: Uranite -UO_2 , Pitchblende (variety of UO_2), Uranothorite- (Th,U) SiO_4 etc. (Huglund, 1972)

In the present study, uranium concentration increases towards offshore samples along the transects. The higher values are observed along the offshore transects of Marmagao, Ratnagiri, Mumbai and Veraval (Figure 3.13 (a)).

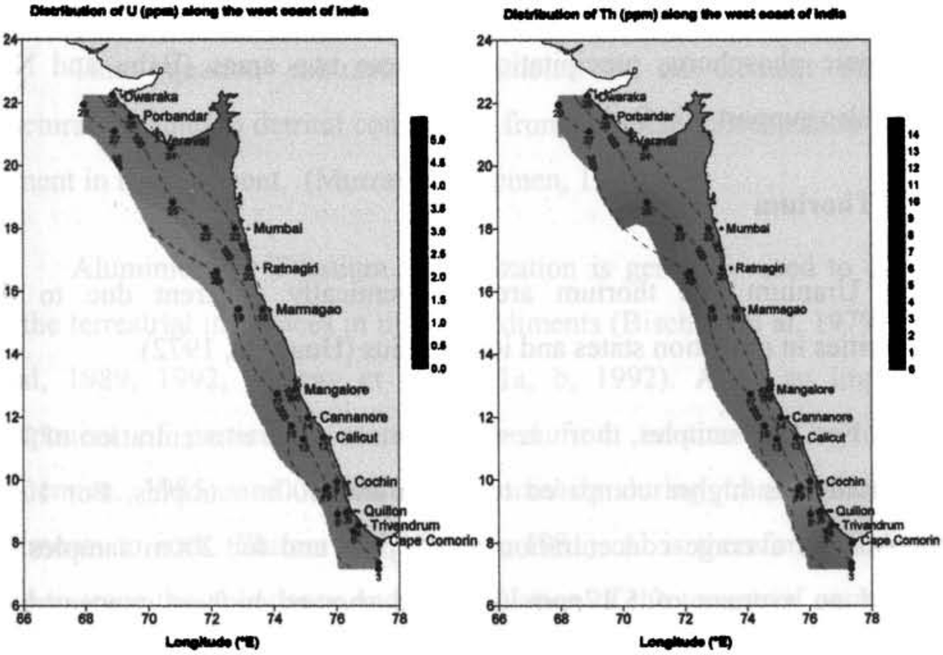


Figure 3.13. Distribution of U (a) and Th (b) in the sediments of west coast.

The average concentration showed 1.8 ppm for 30m samples with a D.O of 3.34ml/l for bottom water. For 100m samples U showed 2.49 ppm as an average, with D.O 1.49ml/l and for 200m samples, U average was 3.13 ppm with D.O value of 0.06ml/l (Table 3.4). The 200m samples were from the oxygen minimum zone with very low bottom water oxygen concentration indicates, the response of U to the bottom water redox conditions for most of the transects, with some exceptions as observed off Calicut, Cannanore and off Mangalore. For these samples, coastal stations showed high values of Uranium. The offshore sediments off Ratnagiri to Veraval showed significant enrichment than those off Kerala coast, although, both the areas are impinged by OMZ suggesting the influence of dentrification processes occurring in the northeastern Arabian Sea (Naqvi et.al, 2000). Sedimentary signatures of regeneration evidenced by varying authigenic phosphorus precipitation in these two areas (Babu and Nath, 2003) also support this finding.

3.2.6 Thorium

Uranium and thorium are geochemically coherent due to the similarities in oxidation states and ionic radius (Huglund, 1972).

For 30m samples, thorium showed an average concentration of 7.29 ppm, which is higher compared to 100m and 200m samples. For 100m samples, Th average concentration is 4.3 ppm and for 200m samples Th showed an average of 5.17ppm. Thorium showed highest concentration along the Kerala coast, (figure 3.13 (b)) especially off Cochin (15ppm) and off Quilon (13.6ppm), which may be due to the impact of monazite sand present along the southern coast of Kerala. Incidentally, largest Eu anomaly (Eu/Eu*= 1.65) is found for the sediments off Cochin (Table 3.2). For most of the stations, the coastal samples (30m) showed higher concentration compared to offshore ones. Towards north, Th concentrations decreased considerably. Th/U ratio showed high values for the transects off Cochin, and off Quilon coastal stations (Table. 3.3) reflecting the high Th values in these sediments.

3.2.7. Element excess

Elemental concentration in excess (El_{ex}) of that which can be supplied through shale like terrigenous particles are determined using the formula (Murray et. al, 1991a, Nath et.al, 1992, 1997)

$$El_{ex} = El_{total} - [\, Al_{sample} \times (El/Al)_{PAAS} \,]$$

This equation subtracts the amount of an element that has structurally bound to detrital component from the total concentration of that element in the sediment. (Murray and Leinen, 1993).

Aluminium or Titanium normalization is generally used to correct for the terrestrial influences in marine sediments (Bischoff et al, 1979, Nath et al, 1989, 1992, Murray et al, 1991a, b, 1992). Al is an important component of particulate matter derived from continents (Taylor and McLennan, 1985) and is relatively immobile during transformation of sediments to rock (Stumm and Morgan, 1981). Al is therefore frequently used to trace the abundance and accumulation of the terrestrial component (Murray et al. 1991b, 1992). However, a small portion of Al in the deep sea sediments is also attributed to submarine weathering of ridge rocks and hydrothermal activity (McMurty and Yeh, 1981)

Most of the rare earths showed excess values towards southern stations (Table 3.5).

St.No	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	78.5	79.7	79.4	80.8	82.4	75.7	80.4	78.3	73.9	73.5	71.6	72.2	65.4	65.6	81.9	67.9
2	61.7	48.6	58.2	60.4	69.8	76.6	72.2	75.6	75.7	78.4	75.4	77.4	71.5	71.7	31.1	91.7
3	29.2	4.5	22.0	25.7	37.8	49.1	39.6	48.8	47.6	54.0	48.0	52.9	39.1	43.2		86.4
4	13.5	8.5	2.0	6.4	24.4	27.1	17.1	16.7	14.9	20.5	22.6	26.7	19.2	27.1	33.3	22.8
5	47.0	32.8	42.4	43.4	56.8	67.9	60.5	65.1	64.8	65.8	64.3	67.8	59.2	60.1	4.2	88.9
6						6.4										
7	34.4	27.2	17.8	19.4	23.9	23.8	12.3	1.2							45.5	12.6
8	62.3	55.4	51.1	49.7	53.2	46.6	50.7	45.9	36.0	31.1	30.3	26.1	9.2		59.3	70.0
9	19.9	1.1				19.3									25.8	
10	64.6	56.4	46.4	43.6	39.1	36.1	36.7	23.7	10.2	2.3					53.7	34.9
11	46.7	40.8	32.1	34.3	37.2	36.3	31.3	22.4	6.3						47.3	21.9
12																
13	3.3	1.9		5.5	26.4	46.7	28.2	29.8	24.7	21.6	10.4	9.6				9.3
14																
15					10.3	30.3	9.2	15.7	11.7	8.5		6.5				29.0
16																
17	62.1	57.8	54.0	54.9	57.3	58.5	58.6	55.6	50.7	46.0	41.3	43.1	30.9	28.9	25.1	33.4
18																
19	16.0		3.2	14.7	35.3	53.5	44.2	51.4	53.7	59.5	57.1	62.6	51.5	54.6		86.0
20																
21					4.9	30.5	14.5	23.1	26.9	31.6	28.6	31.3	20.8	22.2		83.8
22																
23						14.8			2.0	0.7						70.7
24																
25	44.4	16.3	37.2	43.7	50.0	67.8	61.2	64.6	66.5	71.0	68.7	71.2	62.2	66.7		96.1
26																
27																3.1
28						3.1										56.9
29																

Table3.5.Element excess calculated w.r.to Al for the Arabian Sea sediments.

Towards north, excess values are absent, that means no elemental excess over the material which can be brought by the continental material. Nath et.al (1997) reported La_{ex} in the range 18 to 41% and Ce_{ex} in the range 2 to 34% along a transect off Karwar in the Arabian Sea. In the present study La_{ex} varied from 3.3 to 78.5% and Ce_{ex} varied from 1.1 to 79.6%. Excess values for REEs are not found for the transects off Cannanore, Mangalore, Ratnagiri, Mumbai, Porbandar and off Dwaraka.

U_{ex} values varied from 3.09 to 96.12% (Table 3.5). Towards north, the offshore samples (beneath the oxygen minimum zone) showed high excess values compared to coastal samples which is consistent with the observation of Nath et al. (1997), who have reported high U_{ex} contents (82-91%) for the samples falling in OMZ. Uranium is mobilized as U^{+6} under oxic conditions and precipitated as U^{+4} in reducing environments, whereas Th is relatively immobile in aqueous solution (Anderson et al, 1983, Wright et al, 1984). Yang et al (1995) have suggested that an increase in productivity-driven carbon flux raises the redox boundary closer to the sediment–water interface leading to an increased flux of U into subsurface anoxic sediments where it is precipitated. High U concentrations in these suboxic sediments are consistent with the estimate of Klinkhammer and Palmer (1991) that 75% of U supplied to the oceans is removed by diffusion into suboxic sediments (Nath et.al, 1997).

Th showed excess values for southern samples only especially for transects, off Cape Comorin, Trivandrum, Quillon and Kochi. A portion of this must be due to the presence of products from the heavy minerals, which are dominantly present in these areas. Th_{ex} values ranged from 4.18 to 81.9% and no excess were reported for northern continental shelf area.

3.2.8 U/Th ratio

U/Th ratio is used as a redox indicator by many geochemists (Wright et al, 1984, Jones and Manning, 1994). Since Th is immobile in low temperature environment, the ratio is sensitive to changes in U supplied from seawater. In turn, U variation depends on the redox state of seawater with fixation of low valency U under reducing conditions. U/Th ratio above 1.25 have been used to infer suboxic and anoxic conditions in upper Jurassic mudstones from the Norwegian North Sea and onshore formations of UK such as the Draupus, Heather and Kimmeridge clay formations (Jones and Manning, 1994). Nath et al (1997) reported that U/Th ratio along the Arabian Sea sediment also followed the same manner. They observed lower value of U/Th in the sediments outside the OMZ and above 1.25 in those beneath OMZ. In the present study, six transects supported the use of U/Th as a redox indicator, which showed this ratio >1.25 for the sediments overlying by suboxic waters. But other transects did not respond to this significantly (Table 3.2) probably because of the dilution effects of calcium carbonate, which is supported by the significant negative correlation between $CaCO_3$ and concentration of elements.

3.2.9 Authigenic Uranium

Recent studies suggested that redox sensitive elements (such as uranium) accumulate into suboxic/anoxic sediments during times of low oxygen concentration in bottom water and/or high surface water productivity (Wallace et al., 1988; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Anderson et al., 1993). Such tracers, independent of major biogenic phases, may provide useful information on export production changes. Authigenic uranium, a parameter based on U and Th concentrations has been suggested as an index of bottom water anoxia and ancient sedimentary sequences (Nath et al, 1997 and Wignall and Myers, 1988). It is calculated using the formula, authigenic U= [Total (U)- Th/3]. Nath et al, (1997) and Wignal and Myers, (1988) placed the boundary between oxic and dysoxic environments at 2 ppm authigenic U.

Moderate to high concentrations of authigenic uranium in the continental margin sediments makes Arabian Sea basin one of the potential sites for removal of U from seawater .[Borole et al., 1982, Sarkar et al., 1993, Somayajulu et al, 1994, Nath et al., 1997 and Pailler et al., 2002]. Based on the study of uranium distribution in a sediment core in the southeastern Arabian Sea, Sarkar et al. (1993) had inferred that anoxic conditions prevailed in this region during the last glacial period. From the elevated concentration of authigenic uranium in sediments from various regions of the Arabian Sea, Borole et al., (1982), Sarkar et al., (1993), and Balakrishna et al., (2001), reported that this oceanic region is a sink for seawater uranium. However, processes contributing to the supply of authigenic uranium to sediments of the Arabian Sea are not well understood.

In the present study, authigenic U is absent for some transects such as off Quilon, Cochin, Calicut and Off Mangalore (Table 3.2) part of which may reflect the influence of heavy mineral sands rich in Th in these areas. Authigenic U is greater than 2 ppm for those stations where U/Th ratio also reported above 1.25. Some samples are not responding to the redox condition of water column. Nath et. al (1997) calculated authigenic U and suggested that the boundary proposed by Wignall and Myers (1988) is reasonable for the sediments within the OMZ of Arabian Sea. As the present study samples are only up to 200m water depth, the use of authigenic U to determine the boundary between oxic and anoxic environment is not well understood.

3.3 Conclusions

1) ΣREE abundance is more for the coastal (30m) stations compared to offshore ones indicating REEs input through river run-off and terrigenous influence. Two exceptions for this are those off Cochin and off Dwaraka transects, which showed higher abundance for the offshore samples. The highest ΣREE observed (190ppm) is off Quilon, which may be due to the presence of monazite sand. The anomalous behavior showed in the sediment samples off Dwaraka may be due to the Indus provenance.

2) Ce is the most abundant element among the REEs and Tm and Lu are the least abundant.

3) Th enrichment and high Eu anomaly for the Kerala coast (especially in the transects off Quilon and Cochin) may be due to the presence of heavy minerals in these sediments.

4) Shale normalized pattern with positive Eu anomaly, LREE enrichment and HREE depletion in the samples off Cochin supports the gneissic provenance of this sediment.

5) Inconsistent relation between dissolved oxygen and Ce anomaly is observed for some of the transects, may be due to the influence of high terrigenous sedimentation and along shore currents over the coastal regions.

6) The enriched U concentration in the sediments impinged by oxygen minimum zone showed the response of U to the oxygen concentration of the bottom water, but the concept of authigenic U is not well understood because of inadequate sampling in the OMZ.

7) Most of the rare earths showed excess values towards the southern stations, while no elemental excess is reported from the northern transects. This indicates that, other than detrital sources, southern transects are influenced by heavy mineral sources also.

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Chapter 4

MAJOR ELEMENTS AND TRACE METALS IN THE SEDIMENTS OF WESTERN CONTINENTAL SHELF OF INDIA

Marine sediments represent the major sink for material that leaves the seawater reservoir. Nearshore or coastal sediments are deposited on the margins of the continents under a wide variety of conditions in chemical environments that range from oxic to fully anoxic in character. The sediments include gravels, sands, silt and muds and they are composed of mixtures of terrigenous, authigenic, biogenic components, and relatively high concentration of organic carbon are found in sediments deposited under reducing conditions (Chester, 1990). Elemental abundances and its relative distribution in sediments and sedimentary rocks are potential tools of various important geological processes. Major elements (like Al, Fe & Mn) and trace elements (eg, Cr, Ni, Co, Zn) were analyzed along with textural analysis (sand, silt & clay), $CaCO_3$ and organic carbon of the sediments of western continental shelf of India in order to understand the geological and oceanographic processes controlling the sedimentation and post depositional changes.

4.1. Results and Discussion

Sample location and methodology of analysis are given in 2nd chapter. The textural characteristics of sediments are given in the table 2.4. in the 2nd chapter. The concentration of major elements and trace metals for the samples are given in the table A-2 in the appendix. The average concentration of elements for 30m, 100m and 200m samples are given in the table 4.1. Statistical techniques such as linear correlations are used to understand the geochemical variations among the samples. Correlation coefficients were determined separately for three sets of data viz. 30m samples, 2) 100m samples and 3) 200m samples. The correlation matrices are presented in the tables 4.2, 4.3 and 4.4. In addition, multivariate statistical analysis was carried out using R-mode factor analyses to understand the general association among various sediments.

Stations	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y
30m	15.2	100.5	136.3	15.5	59.7	43.8	97.1	12.3	46.2	447	21.5
100m	3.4	20.7	55.3	3.5	22.2	9.0	29.9	2.5	9.4	2899	11.3
200m	7.4	57.0	82.1	9.0	46.0	25.6	58.7	5.9	26.5	1253	17.4

Stations	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Mn %	Fe %	Al %	O.C %
30m	91.9	7.6	2.7	201.6	2.4	0.5	15.9	0.07	6.9	11.4	1.7
100m	23.8	2.1	0.5	96.3	0.6	0.1	8.4	0.02	2.2	2.2	1.4
200m	57.2	3.6	1.6	120.0	1.5	0.2	7.7	0.03	5.1	5.2	2.1

Stations	$CaCO_3$ %	sand %	silt %	clay %	D.O(ml/l)
30m	16.3	30.1	36.3	33.6	3.34
100m	73.1	89.0	8.4	2.6	1.49
200m	54.1	53.7	29.5	16.9	0.06

Table 4.1. Average concentration of elements in the sediments of west coast (ppm)

4.1.1 Aluminium

Aluminium in marine sediments is derived principally from alumino-silicate minerals, which are generally detrital. Certain of them, however could be derived from the alteration of oceanic volcanic rocks, hydrothermal exhalations and authigenic growth (Kolla et al., 1976; Cronan, 1980; McMurtry and Yeh, 1981). Hence Al has been widely used as one of the best indicator of terrigenous contribution to marine sediments.

In the present study average Al concentrations in the sediments were11.4%, 2.18% and 5.15% for depths of 30m, 100m and 200m respectively. Southern stations showed lower values compared to northern samples. Al showed higher concentration for the coastal samples, and may be due to the terrigenous input from the adjacent landmasses. Al showed high concentration (>16%) for the coastal stations namely, off Cannanore, Mangalore and Ratnagiri. But its concentration showed low values for southern transects off Cape Comorin, Trivandrum and Cochin. Along a transect, 30m samples showed high Al concentration compared to offshore ones except off Dwaraka, which showed high Al (%) for offshore sample, may be due to the Indus provenance of these sediments. The distribution of Al along the west coast of India is given in the figure 4.1 (a), which showed higher values for the coastal samples between off Calicut and off Veraval.

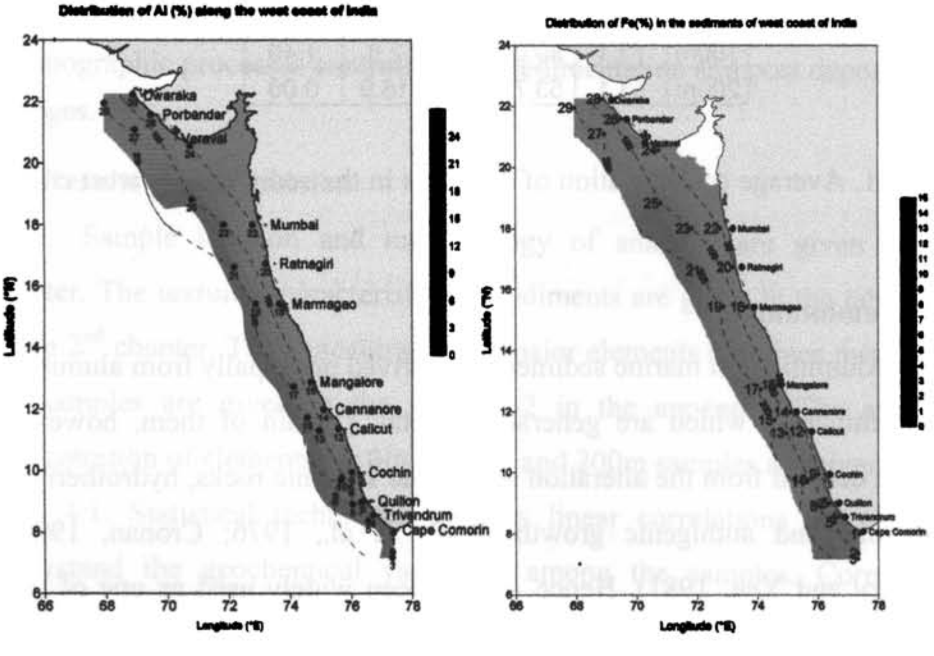

Figure 4.1. Distribution of Al (a) and Fe (b) in the sediments of west coast

For these transects, coastal samples showed very high values for Al compared to offshore samples and the highest concentration was observed along the transect off Marmagao (16.2%). The southernmost transects off Cape Comorin and off Trivandrum showed lowest concentration for Al in the sediment.

4.1.2 Iron

The concentration of iron showed high values for coastal samples compared to offshore ones. The average concentration for 30m, 100m and 200m samples were 6.9%, 2.2 % and 5.1% respectively. The distribution of Fe along the west coast of India is given in the figure 4.1(b). The highest concentration of Fe is observed for the 30m sample off Marmagao (10.3%), may be due to the river discharge from the mining sites of Goa. The concentration of Fe is found to be low along the southern transects, off Cape Comorin and off Trivandrum. The correlation matrix for Fe and Al also showed good correlation for three sets (Tables 4.2,4.3 and 4.4). The correlation co-efficient of Fe Vs. Al for 30m, 100m and 200m samples are 0.95, 0.97 and 0.63 respectively. Fe showed good positive correlation with other trace elements like Rb, Sc, Ni, Zn etc with correlation coefficient greater than 0.8. Percentage of clay in the sediments is one of the important factors in regulating the trace metal geochemistry of marine sediments. Clay is having maximum adsorption for elements compared to silt and sand fractions. 30m and 100m samples showed good positive correlation between Fe and clay ($r > 0.95$), but 200m samples showed not much correlation between them.

4.1.3 Manganese

The geochemistry of Mn and Ce are similar, both responding to oxidative precipitation and reductive dissolution (Mofett, 1990). Dickens and Owen (1994) have suggested that the redox-sensitive Mn oxyhydride particulates dissolve upon entering an OMZ. The resulting Mn^{2+} subsequently is redirected by advective or diffusive processes eventually to precipitate in distal, more oxygenated environments (Dickens and Owen, 1994; Nath et.al, 1997). This concept of oxygen minimum zone Mn redirection has been used by Dickens and Owen (1994).

The average concentration of Mn for 30m, 100m and 200m samples showed 0.07%, 0.02% and 0.03% respectively. The highest concentration was observed for 30m coastal sample of Marmagao transect (0.132%), which may be due to the impact from the onshore mining sites of Goa. Fe also showed highest value for this sample. The distribution of Mn along the west coast of India is given in the figure 4.2(a). The sample from off Veraval also showed high concentration compared to the southern ones. For most of the transects, the coastal samples showed high concentration of Mn compared to offshore ones. This is indicated in the present study also, Mn showing reduced concentration in the sediments impinged by oxygen minimum layer. For each transect, lower value is shown by 200m samples, which is having overlying suboxic waters. Ce also showed similar pattern like Mn.

Manganese concentrations of 0.0044-0.0318% have been reported along Kerala coast and 0.0123-.028% in Cochin backwaters (Rajamani

Amma, 1994). In the present study also, the Mn concentration along the Kerala coast varied in the range 0.004-.037%.

In the present study, Mn concentration is found to be higher for the coastal samples and for the northern transects compared to the southern ones. More than 50% of Mn in the sediments was found to be in the non-lithogenous fraction indicating the high chemical reactivity of manganese in marine environments (Balachandran et al, 2003).

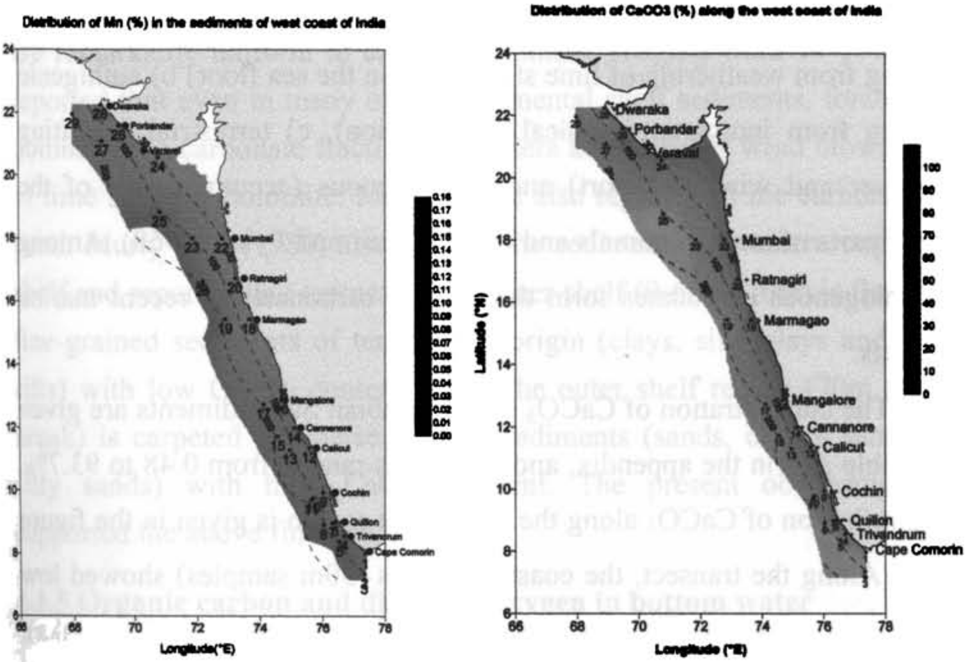

Figure 4.2 Distribution of Mn (a) and $CaCO_3$ (b) in the sediments of west coast.

4.1.4 $CaCO_3$

The pioneer work on sediment traps study in the Arabian Sea by Nair et.al. (1989) suggests that higher wind speeds during SW and NE monsoon leads to a deepening of the mixed layer and the introduction of nutrient rich surface waters into the euphotic zone results in high productivity in the area. They also reported that carbonate is the main component in the total flux (~65%). This supports the fact that productivity is the main factor which controls the observed $CaCO_3$ fluctuations in the Arabian Sea. By studying the $CaCO_3$ content in the sediment cores from the Arabian Sea, Divakar (1991) also emphasized that $CaCO_3$ content in the sediment is directly related to the productivity of overlying waters. The principal sources of carbonate in marine sediments are:- a) residual (resulting from weathering of lime stone rock on the sea floor) b) authigenic (resulting from inorganic chemical precipitation), c) terrestrial (resulting from river and wind transport) and d) biogenous (accumulations of the skeletal parts of marine animals and plants) (Nair and Pylee (1968). Among these, biogenous carbonates form the bulk of carbonates in recent marine sediments.

The concentration of $CaCO_3$ in the Arabian Sae sediments are given in the table A-2 in the appendix, and the values ranged from 0.48 to 93.7%. The distribution of $CaCO_3$ along the west coast region is given in the figure 4.2 (b). Along the transect, the coastal stations (30m samples) showed low values compared to the deeper stations except for one station (off Dwaraka). The average concentration of $CaCO_3$ for 30m, 100m, and 200m samples are 16.3%, 73% and 54% respectively. The high values for $CaCO_3$ for coastal stations off Cape Comorin and Dwaraka may be due to the molluscan shells in the sediments. Most of the coastal stations showed low value for $CaCO_3$ in the range 0.48-12.42%. The lowest value is reported from the sediment, off Cannanore (0.48%).

Nair and Pylee (1968) studied $CaCO_3$ content and size distribution of the western continental shelf sediments. In their observation, $CaCO_3$ ranges between 10% (near shore) and 45% (offshore). In our study also, the carbonate content of the sediment increases offshore. The maximum values are reported for 100m stations. The sand percentage is also higher for 100m stations. This observation may be due to the presence of relict carbonate sand along the margins. Stewart et al (1965) studied the sediments of northern Arabian Sea and they observed a band of $CaCO_3$ rich sediment (up to 86%) on the outer shelf. The Indian and eastern Pakistan shelf sediments are remarkably uniform in carbonate content, ranging from 14-19%. They reported that even in many of the continental shelf sediments, foraminifera dominate the carbonate fraction and others are probably wind blown grains of lime stone or dolomite. Molluscs are also reported in the carbonate-rich band. Murty et.al (1980) also studied the sediments of western continental shelf and reported that texturally, the inner shelf (0-60 to 70m) is floored by fine-grained sediments of terrigenous origin (clays, silty clays and clayey silts) with low $CaCO_3$ content, while the outer shelf region (70m to shelf break) is carpeted by coarse grained sediments (sands, clayey sands sand silty sands) with high $CaCO_3$ content. The present observation also supported the above findings.

4.1.5 Organic carbon and dissolved oxygen in bottom water

Many authors have reported the variation in organic carbon content of sediments along the western continental shelf, Arabian Peninsula, Pakistan slope and along the Indian margin (Paropkari et al, 1992, 1993, Calvert et al, 1995). Comparing the values of organic carbon of these regions, the maximum values were reported along the western continental shelf of India especially from Bombay to Cochin (>4%) (Paropkari et al.1992). A debate on productivity or anoxia of bottom water, which is the controlling factor for preservation of organic carbon, is going on (Paropkari et al, 1992, 1993, Calvert et al, 1995, Prakash Babu et al, 1999). Paropkari et al. (1992) emphasized that the productivity is not an ultimate control for the organic carbon enrichment of bottom sediments, but it is the bottom water anoxia in conjunction with various depositional parameters, which determine the degree of preservation. Calvert et al. (1995) suggested that the distribution of organic matter on the western continental margin is controlled by variation in supply, dilution by other sedimentary components and the texture of sediments. Cowie et al (1995) reported that along with productivity and anoxia, sundry factors such as sedimentation rates, local productivity, water depth, sediment mineralogy, texture, particle winnowing, biological mixing and irrigation also contribute for the preservation of organic carbon.

The average value of organic carbon for 30m samples showed 1.66% (bottom water D.O- 3.34 ml/l) and for 100m samples 1.37% (D.O 1.49 ml/l) and for 200m samples 2.13% (D.O. 0.06ml/l) (Table 4.1). The distribution of organic carbon along the west coast of India is given in the figure 4.3 (a). Organic carbon showed higher values (~3%) for the transects, off Calicut, Cannanore, Marmagao and off Ratnagiri, but the dissolved oxygen of bottom water showed almost constant values of 2.98 to 3.69ml/l for these stations.

From the plot between organic carbon and D.O (figure 4.3 (b), it is observed that for 30m samples, the range of variability is high. Organic carbon values varied from 0.1 to 4%, indicating dissolved oxygen in bottom water has not much control on organic carbon at this depth. The organic carbon at this depth may in turn be related to the provenance control such as land run-off, derived plankton material or sewage supply and upwelling. Correlation coefficient between D.O. and O.C. also showed low values (Tables 4.2, 4.3 and 4.4).

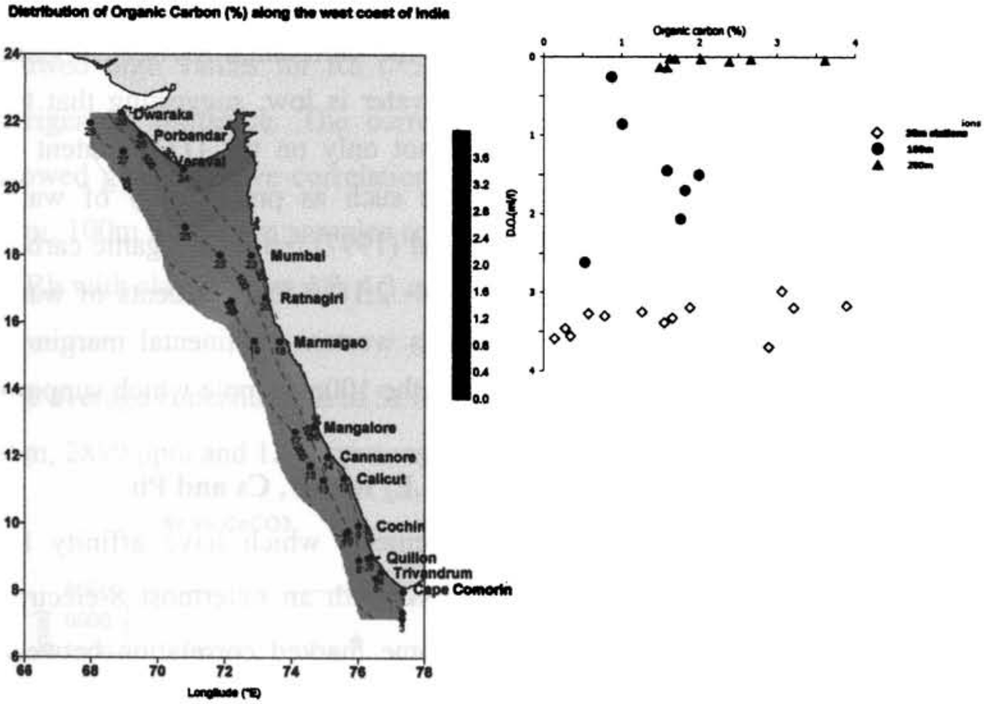

Figure 4.3. Distribution of organic carbon (a) in the sediments of west coast and correlation of organic carbon and dissolved oxygen in bottom water(b)

For 100m samples, organic carbon showed lower values compared to 30m samples. Here organic carbon varied between 0.5 to 2% and the variability in the values may be due to the variation in sediment exposure time to oxygen because of cross shelf transport. Surficial sediments between 60m and 100m usually are of relict nature and are of olden age (Rao and

Wagle, 1997). Because of their nature, they must have been exposed for longer time to ambient O_2 than the sediments on either side of this relict sediment band.

The average organic carbon content for 200m samples showed higher value compared to other two sets (Table 4.1). The dissolved oxygen content of overlying water showed suboxic values with an average of 0.06ml/l/. But among the 200m samples, the correlation between organic carbon and dissolved oxygen in bottom water is low, suggesting that the preservation of organic matter depends not only on the D.O. content of bottom waters but also on other factors such as productivity of water column, sedimentation rates etc. Nath et al (1997) reported organic carbon content of the sediments varied from 0.44- 2.18% for sediments of water depth 23m to 218m in a transect across western continental margin of India. They also reported lowest value for the 100m sample which supports the present observation.

4.1.6 Large-Ion Lithophile elements (LILE) Rb, Sr, Cs and Pb

Lithophile elements are those elements which have affinity for silicates. These elements readily form ions with an outermost 8-electron shell. Goldschmidt (1954) pointed out some marked correlation between geochemical character and atomic volume. If the atomic volume of the elements is plotted against atomic number, the resulting curve shows maxima and minima and the lithophile elements are near the maxima and on the declining sections of the curve. The lithophile elements analyzed in the present study are Rb, Sr, Cs and Pb and their concentration are given in the table A-2 in the appendix.

Rubedium:

Rubedium showed good positive correlation with clay and similar trends are observed for all the three sets of samples. Rb showed average value of 46 ppm (clay 33.6%), 9.4 ppm (clay 2.6%) and 26.5ppm (clay 16.9 %) for 30m, 100m and 200m samples respectively. Rb showed higher values for the transects, north of Calicut. For these transects, coastal samples showed high values for Rb (>55ppm), and clay (>40%) may be due to terrigenous influence. The correlation coefficient for Rb and clay also showed good positive correlation with r-values of 0.88, 0.97 and 0.94 for 30m, 100m and 200m samples respectively, which supports the association of Rb with clay (Tables 4.2, 4.3 and 4.4).

Strontium:

The average concentration of Sr for 30m, 100m and 200m samples are 447 ppm, 2899 ppm and 1253 ppm respectively.

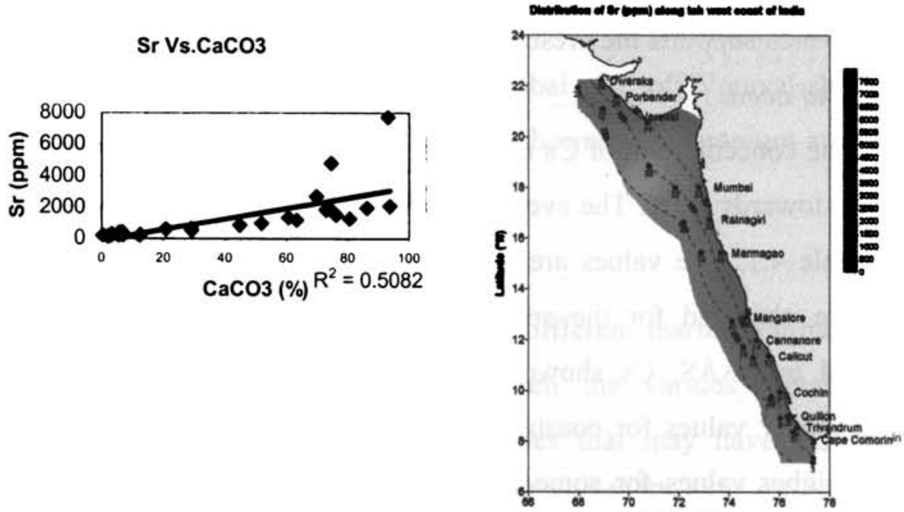

Figure 4.4 Correlation of Sr Vs $CaCO_3$ (a) and distribution of Sr (b) in the sediments of west coast.

Sr followed the same pattern of $CaCO_3$, the highest value for 100m samples, and the lowest for 30m samples. Sr showed strong positive correlation with $CaCO_3$ (Tables 4.2, 4.3 and 4.4) reflecting its well known association with calcite in the carbonate phase.

It is thought that Sr is present mainly in the calcareous tests of organisms. Foraminifers and coccoliths are known to contain upto 1750ppm Sr, part of which may have diagenetically added (Turekian, 1964). Acantharid skeletons made up of celestite ($SrSO_4$) are also important contributors of Sr to marine sediments (Turekian, 1977). The X-Y plots of $CaCO_3$ versus Sr also showed positive correlation (Figure 4. 4 (a)).

The Sr value showed highest concentration for 100m sample off Veraval which is associated with highest $CaCO_3$ content (93%) (Figure 4.4 (b)). Nath et al (1997) analysed $CaCO_3$ and Sr of Arabian sea sediments and observed high $CaCO_3$ (80%) and high Sr (4894ppm) for 100m offshore samples which supports the present observation.

Cesium and Lead:

The concentration of Cs is low for southern samples, and the values increased towards north. The average concentrations of Cs and Pb are given in the table 4.1. The values are high for coastal samples and the highest values are observed for the sediments off Veraval and off Marmagao. Compared to PAAS, Cs showed low values for all the samples. Lead showed higher values for coastal samples with an average of 15ppm. Pb showed higher values for some of the coastal stations of Kerala (Table). Rajamani Amma (1994) reported Pb concentration in the range 17.9 to 80.9

ppm along the Kerala coast, but its concentration is comparatively low in the present study.

4.1.7. High Field Strength Elements (HFSEs) Zr, Hf, Y, Th and U

Zirconium, hafnium, yttrium, thorium and uranium are generally resistant to weathering and alteration processes (eg. Taylor and McLennan 1985, Bhatia and Crook 1986 and Nath et al, 1997) and are classified as HFSEs. The average values for these elements are given in the table 4.1. Zr, Y and Hf showed good correlation among themselves, with correlation coefficient greater than 0.8 (tables 4.2, 4.3 and 4.4).

Zirconium showed high value for coastal samples compared to deeper ones. Zr showed low values for southern transects, but 30m samples off Quilon, Marmagao and off Mumbai showed higher values (>100ppm). Hafnium also showed low values for southern stations especially off Cape Comorin and off Trivandrum. Yttrium showed high values for coastal samples with an average 21ppm. Some of the northern stations off Cannannore, Marmagao, Ratnagiri, Mumbai and off Veraval showed Y concentration greater than PAAS values. Thorium and uranium are already discussed in the chapter 3 along with REEs.

4.1.8 Trace elements: Cr, Co, Ni, Cu, Zn

The study of metal distribution in different marine sediments is an important tool for distinguishing between the various metal bearing components and to delineate the processes that may have led to their enrichment in the sediments. The studies of metals like, Cr, Co, Ni, Cu, Zn and Fe, which have an affinity for biota, and have nutrient-like distribution in the oceans are important. Some metals like Fe and Mn are enriched in marine sediments due to their direct precipitation from seawater as hydroxides (Landing and Bruland, 1987) and elements like Zn, Cu, Ni, and Co are scavenged by their incorporation and/or adsorption to authigenic mineral phases (Altschuler, 1980).

The elements like Cr, Co, Ni, Cu and Zn showed high concentrations for coastal stations (table A-2 in the appendix). Cr showed enriched values (>250ppm) for some of the coastal stations, especially off Calicut, Cannanore and Mangalore. Co showed high values (30ppm) for some of the northern coastal stations off Mumbai, Veraval and off Porbandar. Ni also showed high values (>70ppm) compared to PAAS (55ppm) for some of the coastal stations such as off Calicut, Cannanore, Mangalore, Marmagao, Ratnagiri and off Mumbai. Cu showed higher values (>80 ppm) for the coastal stations viz. off Ratnagiri, Mumbai and off Veraval. Zn also showed enriched values for these coastal stations.

Murty et al (1970) reported that the fine-grained sediments in the inner shelf and the sediments in the slope region contain relatively high Ni content than the sediments in the outer shelf. In the present study, Ni concentration is low for the southern coastal stations (off Cape Comorin to Cochin), while other coastal samples (Calicut to Porbandar) showed high Ni concentration compared to offshore ones. Mn, Cu and Ni are present in terrigenous material in small quantities, and this detrital fraction is important for coastal stations. But for deep-sea sediments, these elements are associated with authigenic formation of manganese nodules. Cu responds to the redox condition of overlying water column, and in reducing environment Cu may be precipitated as copper sulphides. Percentage of clay in the sediment is one of the important factors in regulating the trace metal geochemistry of marine sediments. The samples with high trace metal concentration showed higher clay percentage. The correlation coefficient of Co, Cu, Ni, and Zn with clay showed good positive correlation with r > 0.8 (tables 4.2, 4.3 and 4.4).

4.1.10 Barium and its significance for paleoproductivity studies

Sedimentary barium has been recognized as an important proxy for the reconstruction of past variation in oceanic productivity (eg. Dehairs et al 1980, Bishop 1988, Dymond et al, 1992, Francois et al, 1995). In view of the significance of Ba as a productivity indicator, Ba has been analyzed here.

The average concentration of Ba is 201ppm, 96 ppm and 120ppm for 30m, 100m and 200m samples respectively. Its concentration is very low compared to PAAS (650ppm) and UCC values (550ppm). Ba concentration of ~550ppm was observed only for two samples, off Quilon (30m) and off Kochi (30m). No excess values are seen for other samples. This is consistent with the Ba deficiency noted in the near shore sediments off Namibia, in sediments from Baja California upwelling system, at ODP site 680 off Peru and ODP site 724 off Oman margin (Nath, 2001). Sediments from all these locations contain higher organic matter including the data presented here and yet depleted in Ba. This is probably because the high sedimentation rates in the areas such as the above have shallow sulphate reduction zones which may induce the diagenetic changes in Ba content and hence the productivity signal is obliterated. This is in contrast to the result obtained by Babu et. al (2002) from the Arabian Sea sediments.

	Rb	Sr	Y	Zr	Ba	La	Ce	Eu	Yb	Ta	Hf	Nb	Sc	Cr	Co
Rb	1.00														
Sr	-0.55	1.00													
Y	0.86	-0.41	1.00												
Zr	0.81	-0.64	0.84	1.00											
Ba	0.10	-0.25	-0.06	0.10	1.00										
La	0.55	-0.32	0.64	0.42	0.58	1.00									
Ce	0.62	-0.34	0.74	0.48	0.42	0.98	1.00								
Eu	0.88	-0.55	0.97	0.88	0.15	0.73	0.80	1.00							
Yb	0.87	-0.49	0.99	0.83	-0.07	0.63	0.75	0.97	1.00						
Ta	0.80	-0.71	0.75	0.65	0.12	0.57	0.64	0.81	0.81	1.00					
Hf	0.83	-0.67	0.86	1.00	0.10	0.47	0.53	0.91	0.86	0.70	1.00				
Nb	0.86	-0.72	0.85	0.86	0.28	0.73	0.77	0.93	0.86	0.80	0.88	1.00			
Sc	0.84	-0.64	0.87	0.95	-0.13	0.32	0.43	0.87	0.88	0.74	0.96	0.82	1.00		
Cr	0.55	-0.49	0.63	0.33	0.06	0.64	0.73	0.65	0.71	0.84	0.41	0.59	0.46	1.00	
Co	0.78	-0.42	0.79	0.92	-0.21	0.17	0.26	0.76	0.76	0.51	0.89	0.70	0.92	0.14	1.00
Ni	0.79	-0.53	0.87	0.75	-0.34	0.31	0.46	0.81	0.91	0.78	0.79	0.70	0.90	0.67	0.76
Cu	0.70	-0.52	0.77	0.93	-0.22	0.13	0.23	0.75	0.75	0.57	0.91	0.69	0.95	0.22	0.96
Zn	0.85	-0.64	0.88	0.96	-0.01	0.45	0.52	0.90	0.88	0.72	0.96	0.90	0.96	0.41	0.92
Pb	0.11	-0.42	0.10	-0.01	0.53	0.60	0.55	0.23	0.18	0.43	0.06	0.29	-0.04	0.68	-0.36
Th	0.25	-0.14	0.32	0.11	0.66	0.91	0.85	0.43	0.31	0.33	0.14	0.51	-0.01	0.46	-0.14
U	0.49	0.01	0.61	0.22	-0.08	0.51	0.60	0.54	0.64	0.50	0.28	0.30	0.32	0.74	0.15
Fe	0.86	-0.47	0.96	0.88	-0.17	0.45	0.57	0.92	0.96	0.74	0.90	0.79	0.94	0.57	0.86
Mn	0.52	0.02	0.47	0.57	-0.24	-0.07	-0.01	0.39	0.40	0.04	0.51	0.28	0.52	-0.24	0.76
Al	0.93	-0.61	0.94	0.85	0.01	0.58	0.68	0.95	0.97	0.88	0.89	0.87	0.92	0.73	0.76
OC	0.32	-0.33	0.51	0.19	-0.07	0.48	0.59	0.50	0.59	0.65	0.27	0.35	0.35	0.90	0.04
CaCO3	-0.54	0.98	-0.40	-0.63	-0.35	-0.36	-0.36	-0.55	-0.48	-0.71	-0.67	-0.70	-0.62	-0.52	-0.37
Sand	-0.93	0.55	-0.96	-0.85	0.00	-0.62	-0.71	-0.96	-0.98	-0.82	-0.88	-0.88	-0.89	-0.68	-0.76
Silt	0.84	-0.51	0.87	0.73	0.23	0.80	0.84	0.91	0.88	0.73	0.77	0.87	0.70	0.67	0.57
Clay	0.88	-0.51	0.89	0.83	-0.24	0.34	0.47	0.86	0.92	0.79	0.85	0.74	0.94	0.60	0.84
DO	0.18	0.21	-0.08	-0.05	0.00	-0.10	-0.15	-0.09	-0.10	-0.02	-0.06	-0.03	-0.06	-0.18	0.06

	Ni	Cu	Zn	Pb	Th	U	Fe	Mn	Al	OC	CaCO3	Sand	Silt	Clay	DO
Ni	1.00														
Cu	0.80	1.00													
Zn	0.81	0.92	1.00												
Pb	0.03	-0.27	-0.04	1.00											
Th	-0.02	-0.18	0.16	0.57	1.00										
U	0.57	0.14	0.22	0.39	0.26	1.00									
Fe	0.95	0.87	0.90	-0.02	0.11	0.57	1.00								
Mn	0.42	0.61	0.50	-0.63	-0.30	0.11	0.55	1.00							
Al	0.92	0.77	0.88	0.23	0.25	0.61	0.95	0.39	1.00						
OC	0.62	0.14	0.23	0.57	0.33	0.74	0.49	-0.22	0.57	1.00					
CaCO3	-0.50	-0.47	-0.60	-0.53	-0.17	-0.06	-0.46	0.05	-0.61	-0.38	1.00				
Sand	-0.88	-0.75	-0.88	-0.22	-0.28	-0.63	-0.95	-0.41	-0.98	-0.51	0.55	1.00			
Silt	0.67	0.53	0.76	0.40	0.50	0.63	0.79	0.27	0.86	0.44	-0.52	-0.92	1.00		
Clay	0.96	0.85	0.87	0.01	0.01	0.53	0.96	0.50	0.95	0.49	-0.49	-0.92	0.70	1.00	
DO	-0.17	-0.04	-0.03	-0.14	-0.07	-0.07	-0.11	0.08	-0.04	-0.47	0.23	0.00	-0.02	0.03	1.00

Table 4.2. Correlation matrix for 30m samples of Arabian Sea sediments n =13, r values >0.51 are significant at 95% level (Fisher and Yates,1967)

	Rb	Sr	Y	Zr	Ba	La	Ce	Eu	Yb	Ta	Hf	Nb	Sc	Cr	Co
Rb	1.00														
Sr	-0.28	1.00													
Y	0.78	-0.54	1.00												
Zr	0.93	-0.48	0.81	1.00											
Ba	0.81	-0.44	0.76	0.92	1.00										
La	0.79	-0.45	0.76	0.89	1.00	1.00									
Ce	0.80	-0.48	0.77	0.91	1.00	1.00	1.00								
Eu	0.83	-0.66	0.84	0.96	0.86	0.83	0.87	1.00							
Yb	0.84	-0.65	0.97	0.89	0.77	0.76	0.78	0.93	1.00						
Ta	0.86	-0.43	0.77	0.96	0.98	0.96	0.97	0.90	0.81	1.00					
Hf	0.93	-0.50	0.82	1.00	0.91	0.88	0.90	0.97	0.90	0.95	1.00				
Nb	0.88	-0.51	0.77	0.97	0.95	0.92	0.94	0.94	0.84	0.94	0.97	1.00			
Sc	0.96	-0.35	0.77	0.91	0.83	0.81	0.83	0.83	0.82	0.83	0.91	0.93	1.00		
Cr	0.81	-0.44	0.78	0.88	0.98	0.98	0.98	0.82	0.77	0.92	0.87	0.94	0.88	1.00	
Co	0.85	-0.11	0.54	0.75	0.46	0.40	0.44	0.68	0.66	0.58	0.76	0.64	0.76	0.43	1.00
Ni	0.13	0.03	-0.05	-0.11	-0.43	-0.44	-0.42	-0.14	0.04	-0.30	-0.10	-0.25	0.04	-0.39	0.41
Cu	0.96	-0.20	0.78	0.81	0.70	0.68	0.69	0.70	0.79	0.72	0.81	0.78	0.95	0.75	0.79
Zn	0.86	-0.61	0.79	0.98	0.91	0.89	0.91	0.98	0.88	0.93	0.98	0.98	0.89	0.89	0.67
Pb	0.57	-0.60	0.62	0.67	0.75	0.74	0.77	0.71	0.65	0.63	0.68	0.83	0.75	0.84	0.26
Th	0.75	-0.44	0.73	0.84	0.98	0.99	0.98	0.78	0.72	0.92	0.83	0.91	0.81	0.99	0.33
U	-0.12	0.86	-0.16	-0.36	-0.26	-0.24	-0.29	-0.53	-0.37	-0.30	-0.37	-0.36	-0.15	-0.19	-0.13
Fe	0.93	-0.37	0.69	0.92	0.69	0.64	0.68	0.87	0.82	0.79	0.92	0.84	0.88	0.66	0.94
Mn	0.65	-0.31	0.43	0.72	0.42	0.35	0.41	0.74	0.60	0.55	0.73	0.63	0.58	0.35	0.88
Al	0.97	-0.42	0.78	0.98	0.82	0.79	0.82	0.92	0.87	0.89	0.98	0.92	0.94	0.80	0.87
OC	0.91	-0.57	0.79	0.91	0.71	0.68	0.72	0.91	0.90	0.77	0.92	0.87	0.91	0.72	0.84
CaCO3	-0.55	0.56	-0.48	-0.70	-0.44	-0.38	-0.44	-0.80	-0.66	-0.53	-0.72	-0.65	-0.53	-0.38	-0.71
Sand	-0.95	0.45	-0.83	-0.99	-0.95	-0.93	-0.95	-0.92	-0.88	-0.97	-0.98	-0.96	-0.93	-0.93	-0.69
Silt	0.93	-0.44	0.83	0.98	0.96	0.95	0.96	0.91	0.87	0.98	0.97	0.96	0.92	0.94	0.66
Clay	0.97	-0.46	0.78	0.98	0.85	0.82	0.84	0.92	0.88	0.90	0.98	0.94	0.95	0.83	0.83
DO	0.27	0.67	-0.03	0.16	0.05	-0.01	0.00	0.03	-0.06	0.09	0.15	0.14	0.22	0.04	0.49

	Ni	Cu	Zn	Pb	Th	U	Fe	Mn	Al	OC	CaCO3	Sand	Silt	Clay	DO
Ni	1.00														
Cu	0.24	1.00													
Zn	-0.19	0.73	1.00												
Pb	-0.36	0.56	0.79	1.00											
Th	-0.47	0.67	0.85	0.80	1.00										
U	0.01	0.06	-0.49	-0.37	-0.21	1.00									
Fe	0.23	0.83	0.87	0.50	0.58	-0.34	1.00								
Mn	0.19	0.49	0.70	0.29	0.27	-0.46	0.87	1.00							
Al	0.09	0.87	0.93	0.60	0.74	-0.32	0.98	0.78	1.00						
OC	0.23	0.86	0.90	0.66	0.64	-0.43	0.95	0.77	0.96	1.00					
CaCO3	-0.06	-0.38	-0.75	-0.45	-0.31	0.66	-0.79	-0.94	-0.72	-0.77	1.00				
Sand	0.14	-0.85	-0.95	-0.69	-0.90	0.27	-0.87	-0.60	-0.95	-0.88	0.57	1.00			
Silt	-0.18	0.84	0.94	0.69	0.92	-0.25	0.84	0.56	0.93	0.85	-0.53	-1.00	1.00		
Clay	0.07	0.88	0.94	0.64	0.77	-0.34	0.96	0.74	1.00	0.96	-0.69	-0.97	0.95	1.00	
DO	-0.07	0.26	0.06	-0.10	-0.03	0.54	0.30	0.42	0.22	0.08	-0.19	-0.12	0.11	0.16	1.00

Table 4.3. Correlation matrix for 100m samples of Arabian Sea sediments n =7, r values >0.66 are significant at 95% level (Fisher and Yates,1967)

	Rb	Sr	Y	Zr	Ba	La	Ce	Eu	Yb	Ta	Hf	Nb	Sc	Cr	Co
Rb	1.00														
Sr	-0.63	1.00													
Y	0.51	-0.20	1.00												
Zr	0.72	-0.75	0.37	1.00											
Ba	0.48	-0.50	0.11	0.54	1.00										
La	0.18	-0.56	0.03	0.68	0.79	1.00									
Ce	0.28	-0.62	0.04	0.74	0.80	0.99	1.00								
Eu	0.76	-0.80	0.43	0.90	0.75	0.73	0.79	1.00							
Yb	0.81	-0.62	0.84	0.76	0.40	0.33	0.39	0.82	1.00						
Ta	0.84	-0.64	0.37	0.75	0.80	0.54	0.61	0.87	0.71	1.00					
Hf	0.67	-0.75	0.33	1.00	0.56	0.73	0.79	0.90	0.73	0.72	1.00				
Nb	0.97	-0.68	0.48	0.81	0.65	0.39	0.48	0.87	0.82	0.94	0.77	1.00			
Sc	0.98	-0.63	0.51	0.73	0.57	0.27	0.36	0.81	0.81	0.93	0.68	0.99	1.00		
Cr	0.22	-0.35	0.41	0.21	0.75	0.57	0.56	0.56	0.44	0.53	0.23	0.36	0.33	1.00	
Co	0.99	-0.61	0.53	0.70	0.42	0.13	0.23	0.75	0.83	0.84	0.64	0.96	0.98	0.22	1.00
Ni	0.91	-0.45	0.54	0.43	0.31	-0.12	-0.02	0.56	0.73	0.73	0.36	0.85	0.91	0.24	0.94
Cu	0.96	-0.46	0.61	0.60	0.35	0.01	0.09	0.62	0.80	0.78	0.53	0.91	0.95	0.16	0.97
Zn	0.95	-0.71	0.47	0.83	0.66	0.45	0.53	0.91	0.84	0.95	0.80	1.00	0.98	0.40	0.94
Pb	0.55	-0.32	0.22	0.43	0.84	0.52	0.57	0.71	0.46	0.85	0.42	0.70	0.68	0.72	0.57
Th	0.24	-0.51	-0.05	0.53	0.93	0.92	0.92	0.70	0.25	0.66	0.57	0.45	0.35	0.71	0.19
U	-0.21	0.66	0.30	-0.60	-0.42	-0.67	-0.72	-0.60	-0.17	-0.29	-0.65	-0.30	-0.18	-0.15	-0.17
Fe	0.52	-0.53	0.26	0.47	0.79	0.57	0.62	0.79	0.55	0.79	0.47	0.67	0.64	0.81	0.56
Mn	0.94	-0.70	0.51	0.87	0.38	0.29	0.39	0.82	0.86	0.76	0.83	0.92	0.90	0.11	0.93
Al	0.99	-0.65	0.50	0.74	0.55	0.26	0.35	0.81	0.82	0.90	0.69	0.99	1.00	0.30	0.99
OC	-0.27	0.61	-0.31	-0.13	-0.43	-0.26	-0.26	-0.37	-0.36	-0.43	-0.12	-0.33	-0.34	-0.67	-0.28
CaCO3	-0.91	0.70	-0.51	-0.94	-0.52	-0.47	-0.55	-0.90	-0.87	-0.84	-0.91	-0.94	-0.91	-0.23	-0.90
Sand	-0.83	0.15	-0.35	-0.44	-0.13	0.21	0.12	-0.38	-0.53	-0.56	-0.37	-0.73	-0.78	0.20	-0.83
Silt	0.63	0.12	0.15	0.23	0.01	-0.33	-0.25	0.16	0.28	0.36	0.17	0.52	0.57	-0.32	0.63
Clay	0.94	-0.42	0.52	0.62	0.23	-0.06	0.03	0.56	0.74	0.70	0.55	0.87	0.91	-0.04	0.95
DO	-0.40	-0.06	-0.69	-0.34	0.31	0.23	0.19	-0.22	-0.62	-0.08	-0.30	-0.31	-0.34	0.19	-0.45

	Ni	Cu	Zn	Pb	Th	U	Fe	Mn	Al	Corg	CaCO3	Sand	Silt	Clay	DO
Ni	1.00														
Cu	0.95	1.00													
Zn	0.82	0.88	1.00												
Pb	0.55	0.50	0.72	1.00											
Th	0.03	0.07	0.50	0.73	1.00										
U	0.05	0.06	-0.34	-0.23	-0.57	1.00									
Fe	0.53	0.43	0.71	0.93	0.73	-0.41	1.00								
Mn	0.78	0.87	0.92	0.42	0.23	-0.39	0.45	1.00							
Al	0.91	0.95	0.98	0.65	0.33	-0.23	0.63	0.93	1.00						
OC	-0.33	-0.25	-0.35	-0.32	-0.40	0.01	-0.49	-0.15	-0.32	1.00					
CaCO3	-0.71	-0.83	-0.95	-0.53	-0.40	0.41	-0.53	-0.97	-0.92	0.17	1.00				
Sand	-0.82	-0.88	-0.68	-0.35	0.15	-0.08	-0.18	-0.75	-0.79	-0.21	0.68	1.00			
Silt	0.65	0.68	0.47	0.28	-0.25	0.12	0.06	0.54	0.58	0.46	-0.47	-0.95	1.00		
Clay	0.90	0.98	0.83	0.38	-0.03	0.02	0.29	0.89	0.91	-0.08	-0.83	-0.94	0.77	1.00	
DO	-0.42	-0.50	-0.30	0.05	0.43	-0.15	0.05	-0.53	-0.36	-0.38	0.47	0.58	-0.53	-0.56	1.00

Table 4.4. Correlation matrix for 200m samples of Arabian Sea sediments n =8, r values >0.63 are significant at 95% level (Fisher and Yates,1967)

Their results indicate that although Ba tends to be partially lost during suboxic diagenesis, the productivity trend along the western continental margin of India still appears to be reflected by this element.

4.2 Enrichment factor

Enrichment factor is used for the determination of level of contamination of sediments. Several methods for normalization are possible, ranging from the use of simple metal/normalizer ratios to more complex methods based on regression analysis. (Rowlatt and Lovell, 1994). We have chosen to normalize metal concentration as ratios to another constituent of the sediment. The constituent chosen for normalization should be associated with finer particles (related to grain size) and its concentration should not be anthropogenically altered (Ackerman, 1980). Al is a conservative element and a major constituent of clay minerals (Rubio et. al, 2000). Fe is the next most consistent element and has been used as a grain size proxy by number of authors working on marine and estuarine sediments. (Ackerman, 1980, Lee et al, 1998, in Rubio et al, 2000). The enrichment factor is calculated using the formula

$$EF = \frac{[\text{Concentration of metal/Aluminium}]\text{ in sediments}}{[\text{Concentration of metal/Aluminium}]\text{ in background}} \quad \text{and}$$

$$EF = \frac{[\text{Concentration of metal/iron}]\text{ in sediments}}{[\text{Concentration of metal/iron}]\text{ in background}}$$

4.2.1. Metal to Aluminium EF:

The enrichment factor calculated with respect to Al and Fe are given in the tables A-3 and A-4 in the appendix. Southern most stations especially off Cape Comorin showed higher values of EF for all the elements. This showed different source for this sediment samples. Off Quilon, Cochin, Mangalore, Marmagao and off Veraval also showed high values for most of the elements. All the rare earths showed similar pattern for a sample, and showed high values for southernmost stations. Th showed comparatively higher values for south Kerala samples. U showed high values for southern stations and off Veraval also. Fe showed values greater than 1 for all the samples.

4.2.2. Metal to Iron EF:

Enrichment factor with respect to iron showed low values compared to Al (Table). Lanthanides showed values greater than 1 for stations off Cochin and off Mangalore. Cr showed EF>1 off Cochin samples. Ni showed high values off Cape Comorin. U showed enrichment for southern samples and off Veraval also.

4.2.3.Comparison of Enrichment Factors w.r.to Al and Fe:

Enrichment factors w.r.to Al and Fe are compared for some of the elements and are given in the figures 4.5, 4.6 and 4.7. EF of lanthanides w.r.to. Al showed higher values (~4) for the transect off Cape Comorin, but EF w.r.to. Fe showed comparatively higher values (~1) for the transects off Cochin, Quilon, Mangalore and off Ratnagiri (figure, 4.5 a and b).

EF of Cr w.r.to Al showed high values (~4) for the transects off Cape Comorin, Marmagao and off Veraval, while EF of Cr w.r.to Fe showed high values (~1) for the coastal samples off Cape Comorin, Trivandrum, Quilon and off Cochin (Figure 4.6 a and b).

EF of Ni w.r.to Al and Fe showed high values for the transects off Cape Comorin and off Veraval, but the value for the latter is comparatively low (figure 4.7 a and b).

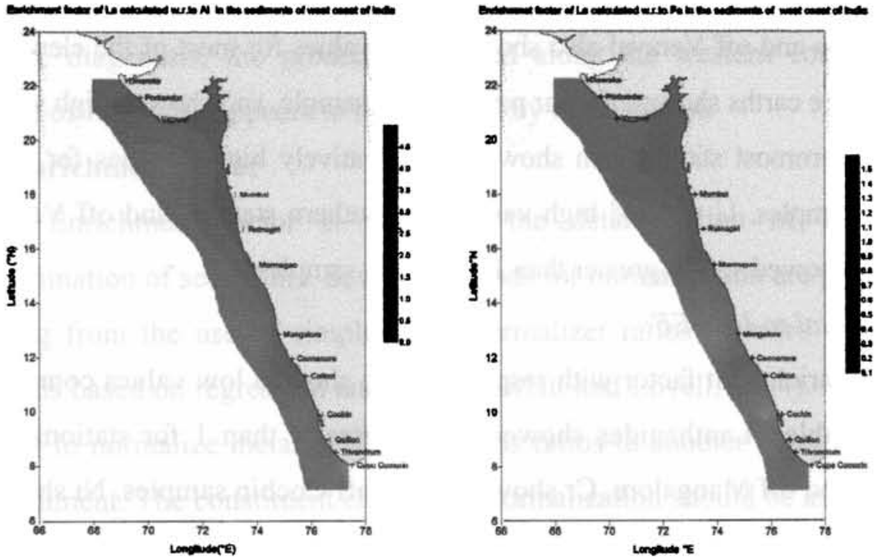

Figure 4.5. Enrichment factor of La calculated w.r.to. Al (a) and Fe (b)

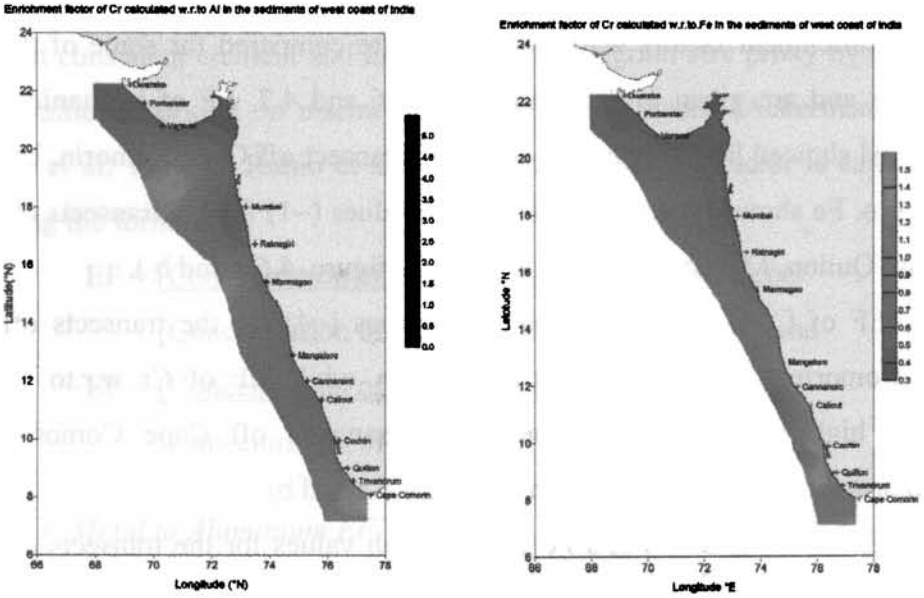

Figure 4.6. Enrichment factor of Cr calculated w.r.to. Al (a) and Fe (b)

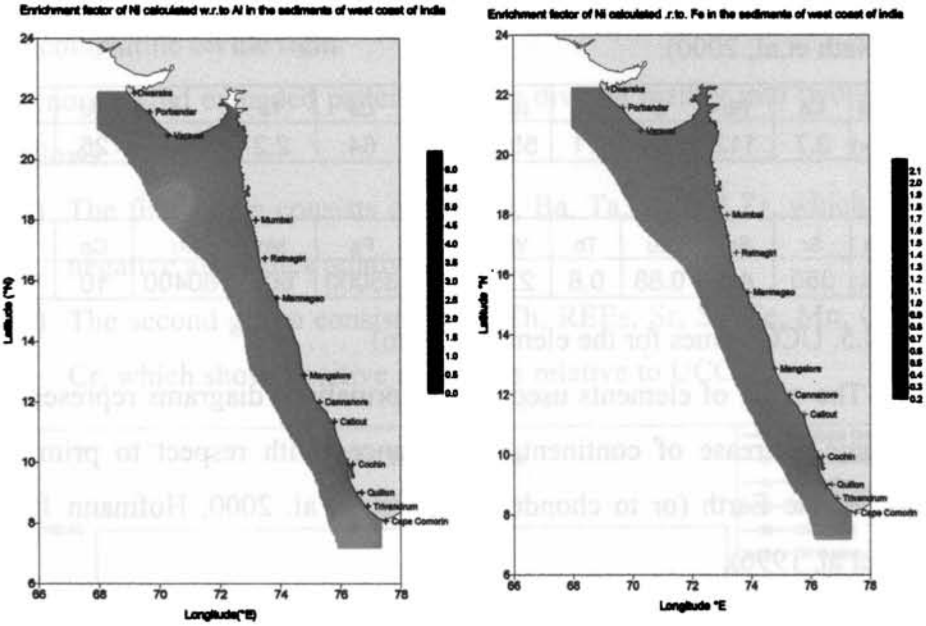

Figure 4.7. Enrichment factor of Ni calculated w.r.to. Al (a) and Fe (b)

The difference in the enrichment factors calculated with respect to Al and Fe and the spatial difference in the enrichment showed different geochemical reactivity of Al and Fe in the marine environment.

4.3 Upper Crust Normalized extended Patterns

The elemental patterns normalized to upper crust (UCC) values (Taylor and McLennan 1985) are plotted separately for three sets, 30m, 100m and 200m samples. The UCC values are given in the table 4.5. The significance of this normalization is to check the similarity of pattern for many elements, which support the observation that the sedimentary mass is quite homogenous in its composition (Taylor and McLennan, 1985) which is thought to be caused by efficient mixing of material derived from different provenance areas, with differing ages, and differing rock types during weathering transport, and deposition (McLennan 1989, Dupre et. al, 1996, Nath et.al, 2000).

Elements	Cs	Rb	U	Th	Ba	La	Ce	Ta	Hf	Nd	Zr
UCC (ppm)	3.7	112	2.8	11	550	30	64	2.2	5.8	26	190

Elements	Sr	Sm	Eu	Tb	Yb	Sc	Fe	Mn	Al	Co	Cr
UCC (ppm)	350	4.5	0.88	0.6	2.2	11	35000	600	80400	10	35

Table 4.5. UCC values for the elements (ppm)

The order of elements used in the normalized diagrams represents a monotonic decrease of continental abundances with respect to primitive mantle of the Earth (or to chondrites), (Nath et al. 2000, Hofmann 1988, Dupre et al. 1996).

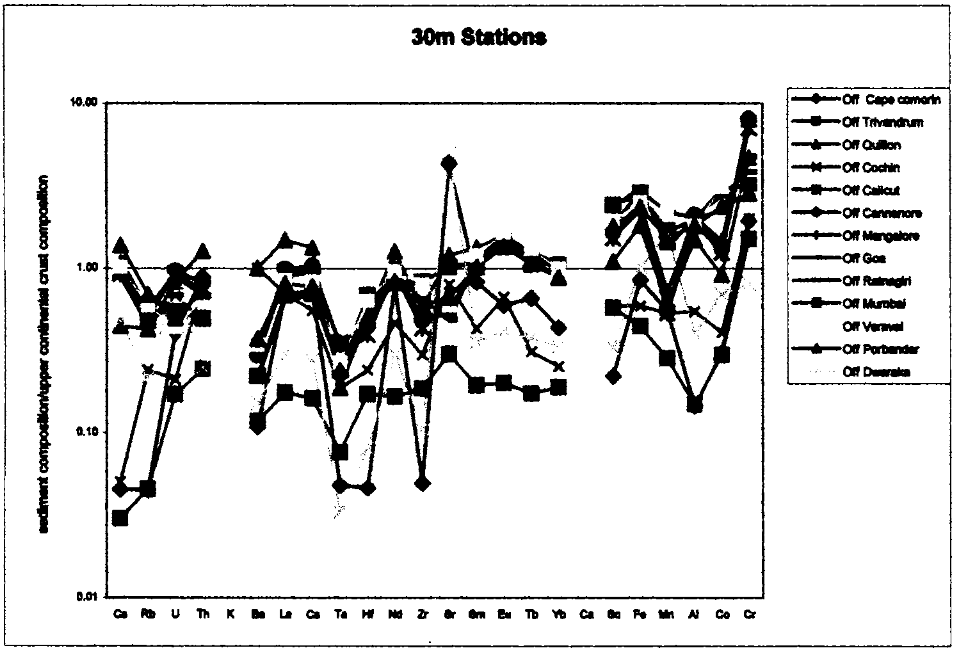

Figure 4.8. UCC normalized pattern for 30m samples

The diagram has the most incompatible elements on the left and the most compatible on the right.

UCC normalized extended patterns can be divided mainly into two groups, as follows:

1) The first group consists of Cs, Rb, Ba, Ta, Hf and Zr, which show, negative anomalies relative to UCC.
2) The second group consists of U, Th, REEs, Sr, Sc, Fe, Mn, Co and Cr, which show, positive anomalies relative to UCC.

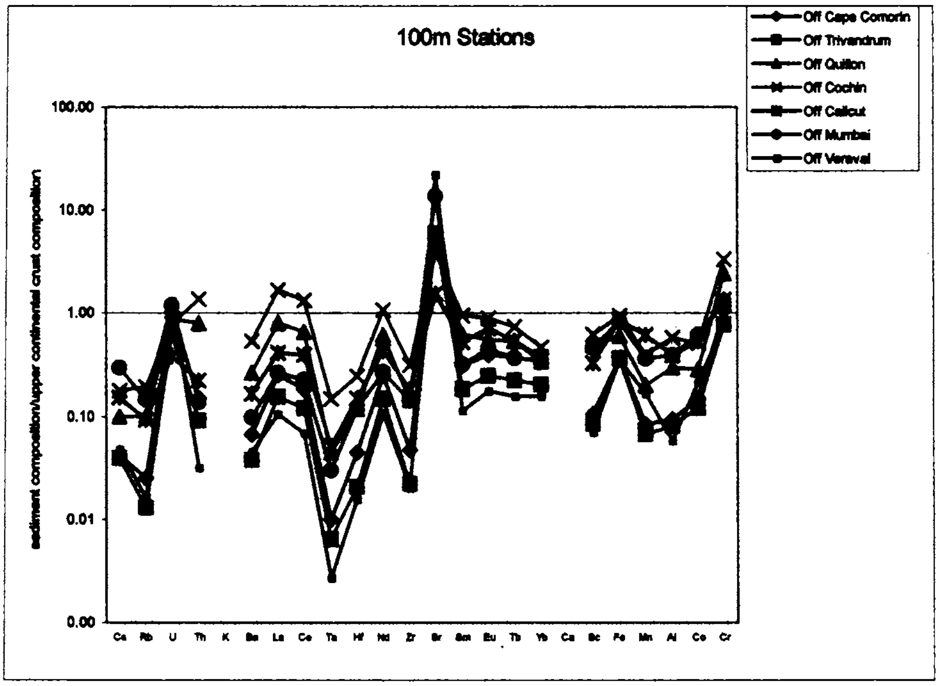

Figure 4.9 UCC normalised pattern for 100m samples

30m samples: Samples from some of the coastal stations viz. off Cape Comorin, Trivandrum and off Dwaraka showed low values for the elements like, Cs, Rb, Ta, Hf and Zr compared to UCC values. All other UCC patterns behave similarly (Figure 4.8).

100m samples: All the 100m samples showed similar UCC pattern with depletion of group 1 elements and enrichment of group 2 elements (Figure 4.9).

200 samples: All the 200m samples also showed similar pattern for the UCC extended patterns (Figure 4.10). Sr showed enriched value for all the samples because of high carbonate content. For 200m samples, U showed positive values compared to the UCC values.

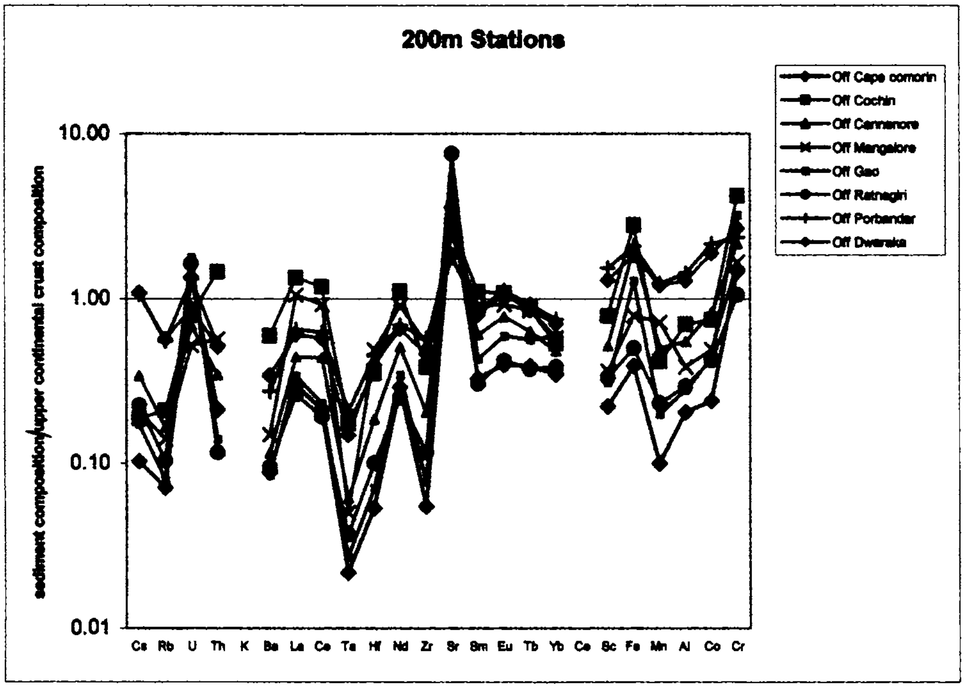

Figure 4.10. UCC normalised pattern for 200m samples

U enrichment in these offshore samples indicate its response to the influence of OMZ on these sediments. Cr showed enriched values compared to UCC for all the samples. The UCC value for Cr is 35ppm, while the average value of Cr for the coastal (30m) samples is 136ppm (four times enriched than UCC), while for 100m samples 55ppm and for 200m samples

82ppm. All the samples, except the one off Dwaraka from 30m and 200m show chromium enrichment, a feature indicating that coastal western margin could be a sink for Cr. Similar results were also reported from the Kerala coast by Nath et. al. (2000). Enriched Cr contents may also indicate the intense chemical weathering conditions, (eg. Wronkiewitcz and Condie, 1989). Most of the coastal areas in India have lateritic formations. Narayanaswami and Ghosh (1987) have documented four to six fold Cr enrichment in modern lateritic profiles of India (Nath et.al, 2000). The similarity of UCC normalized patterns in the present study for most of the samples showed that; the sedimentary mass seems to be homogenous through different geochemical processes.

4.4. Factor Analysis

Inter element relations, correlation coefficients, factor analysis, and discrimination plots are used for interpretation of geochemical data. Factor analysis was carried out using the programme developed by Fernandez and Mahadevan (1982). Columns were standardized before the data matrix presentation. The initial four factors were rotated using the varimax criterion.

Factor analysis is a statistical treatment applied to the data of elemental concentrations to group those parameters that have identical attributes. The probable properties controlling the grouping of elements are detrital sources, weathering products, association with clay, carbonate bound fractions etc. Factor analysis was done separately for 3 sets of samples, viz, 30m, 100m and 200m. The various isolated factor loading of first four factors are considered.

a) Factor analysis of 30m samples.

R-mode factor analysis of the elemental data indicates that four major factors accounts for a total of 95% variance (Figure 4.11)

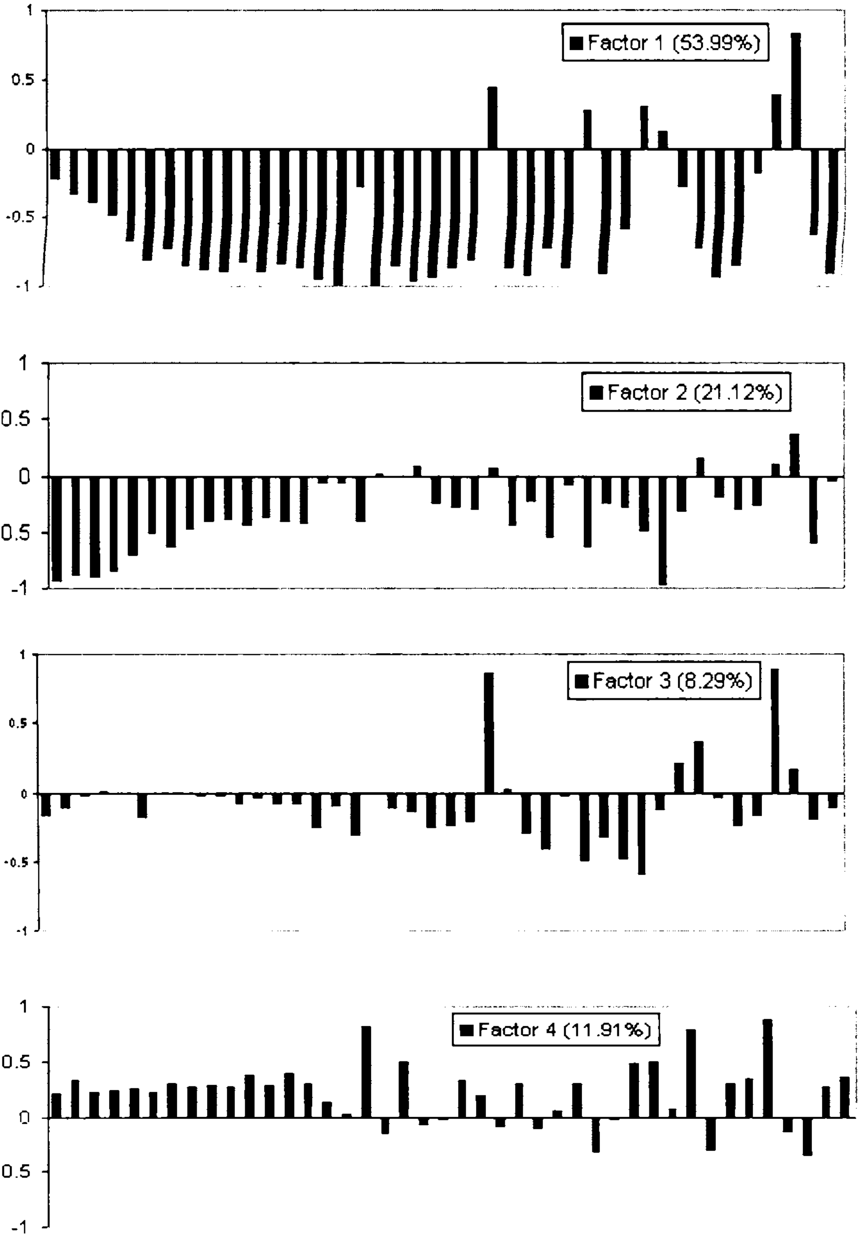

Figure 4.11 R-mode factor analysis for 30m stations

The sequence of elements are La,Ce,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu,Sc,V,Cr,Co, Ni,Cu,Zn,Ga,Rb,Sr,Y,Zr,Nb, Cs,Ba,Hf,Ta,Pb,Th,U,Mn,Fe,Al,C_{org},$CaCO_3$, sand, silt and clay

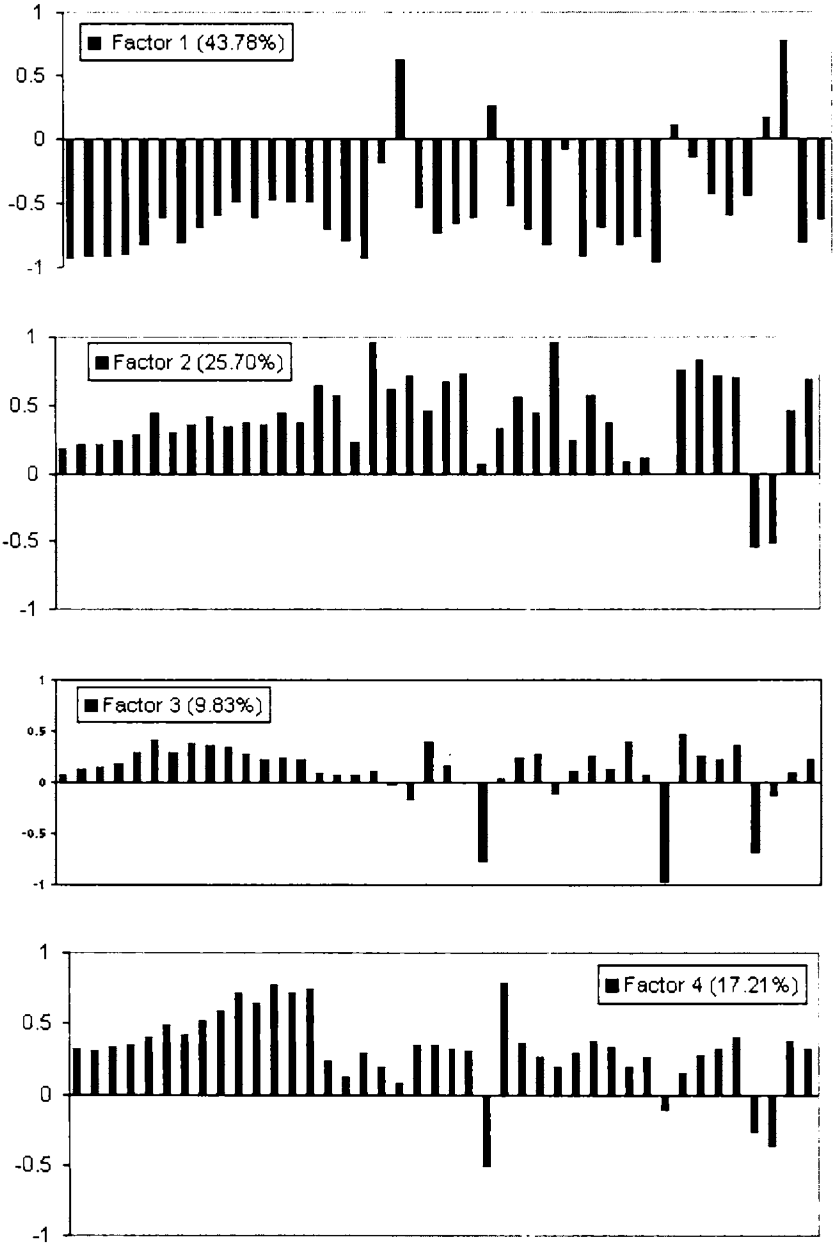

Figure 4. 12. R-mode factor analysis for 100m stations

The sequence of elements are La,Ce,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu,Sc,V,Cr,Co, Ni,Cu,Zn,Ga,Rb,Sr,Y,Zr,Nb, Cs,Ba,Hf,Ta,Pb,Th,U,Mn,Fe.Al,C_{org},$CaCO_3$, sand, silt and clay

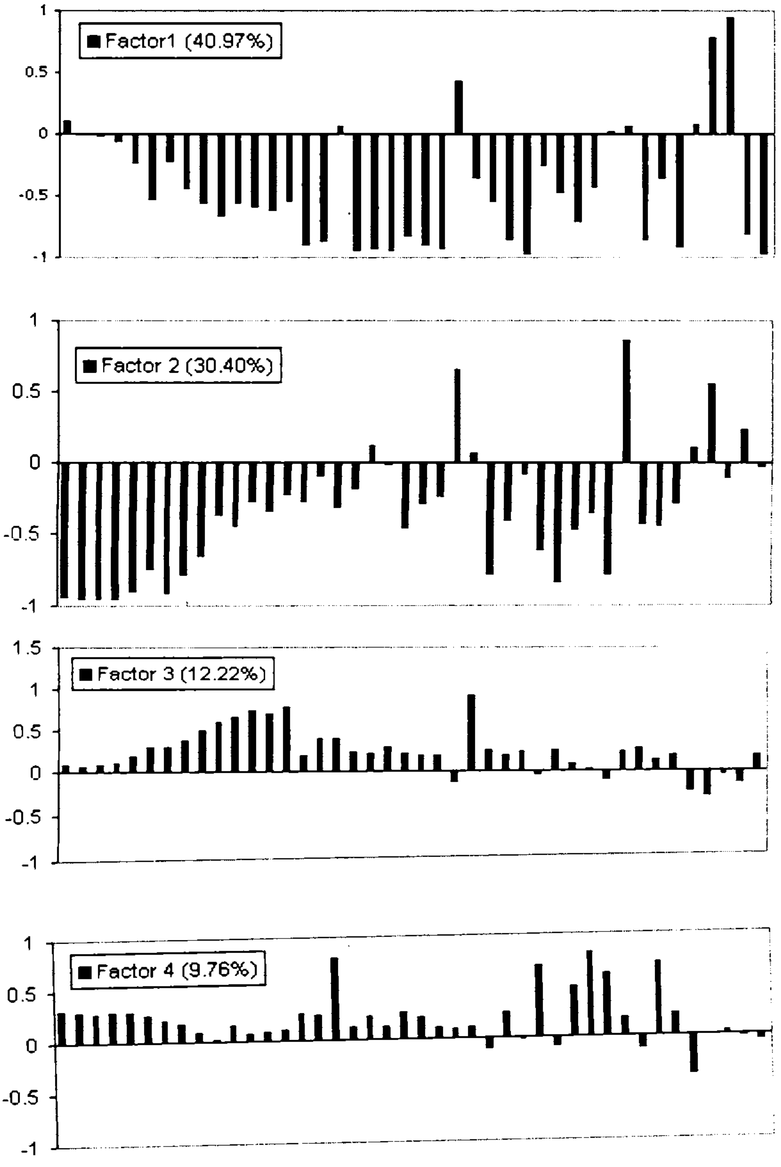

Figure 4. 13. R-mode factor analysis for 200m samples.
The sequence of elements are La,Ce,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu,Sc,V,Cr,Co, Ni,Cu,Zn,Ga,Rb,Sr,Y,Zr,Nb, Cs,Ba,Hf,Ta,Pb,Th,U,Mn,Fe,Al,C_{org},$CaCO_3$, sand, silt and clay

Factor 1 is the major factor (53.9% variance) and showed positive loading (>0.5) for sand which can be explained in the coastal area. For this factor 1, Fe, Al, clay, HREEs, V, Sc, Cu, Co and Zn showed high negative loading (>0.5). This means detrital or terrestrial inputs are controlling this factor. Fe and Al must have derived from the land. Rb also showed high negative loading indicates its association with clay.

Factor 2 (21.2%) showed high negative loadings for LREEs, Th, Y, Nb, Ba, and silt (>0.5) (figure 4.11). This factor grouped those elements, which are derived by weathering processes.

Factor 3 (8.29% variance) showed high positive loading for Sr and $CaCO_3$ a and this reflects the carbonate fraction is mainly controlling this factor.

Factor 4 (11.9%) showed high positive loading for organic carbon, U, Cr, Ni and moderate positive loading for LREEs, Ga, Rb, Y, Cs, Ta, Pb, Fe, Al , silt and clay. The figure shows organic carbon and U controls this factor.

b) Factor analysis for 100m samples.

For 100m samples, four major factors account for 96.52% variance. Factor 1 (43.78% variance) showed positive loading for Ni and sand. LREEs, Cr, Ba and Th showed very high negative loading (>0.5) for this factor indicates scavenged materials controls this factor (figure 4.12).

Factor 2 (25.7% variance) – Most of the elements like Co, Cs, Fe, Mn, Al, $C_{org,}$ clay, Rb, showed high positive loading while other elements like Sc, V, Ni, Cu, Zn, Ga, Zr, Ta showed moderate positive loading for this factor. Here also Rb is associated with clay fraction.

Factor 3 (9.83% variance) showed moderate positive loading for REEs, Zn, Pb, Zr, Nb, Mn, Fe, Al and $C_{org.}$ For this factor U, Sr and $CaCO_3$ showed high negative loading. This showed carbonate fraction is dominating in this group.

Factor 4 (17.2% variance) showed high positive loading for HREEs and Y (figure 4.12). Other elements LREE, Cu, Zn, Ga, Rb, Zr, Hf, Ta, Mn, Fe, Al, $C_{org,}$ silt and clay showed moderate positive loadings. This indicates detrital inputs controls this factor.

c) Factor analysis for 200m samples.

Four major factors together account for 98.32 % variance. Factor 1 (40.97% variance) showed positive loading for elements Sr, $CaCO_{3,}$ and sand (figure 4.13). This indicates the association of Sr and $CaCO_3$ with sand. Elements like Sc, V, Co, Ni, Cu, Ga, Rb, Cs, Mn, Al and clay showed very high negative loadings for this factor while other HREEs, Zr, Hf, Fe showed moderate negative loading. In this Al, Mn and Rb associated with fine grained detrital materials.

Factor 2 (30.4% variance) showed high positive loading for U, Sr and $CaCO_{3,}$ while all LREEs, Zr, Hf, Ba, Th showed high negative loading for this factor (figure 4.13).

Factor 3 (12.2% variance) showed high positive loading for HREEs and Y with values >0.5. This reveals the association of HREEs with Y.

Factor 4 (9.76% variance) showed high positive loading for Cr, Ba, Ta, Pb, Th and Fe while most of the REEs, Ni, Cu and Zn showed low positive loading. Organic carbon showed negative loading for this factor.

4.5 Conclusions

1) The concentration of Al is observed to be higher in the coastal samples compared to offshore ones. The higher values about 16% is reported along the transects between Calicut and Veraval. This indicates the terrigenous source of Al in the sediments.
2) The concentration of Fe and Mn also found to be higher for the coastal stations than the offshore ones. The highest value is observed for the coastal station off Marmagao, which may be due to the impact from the onshore mining sites of Goa.
3) $CaCO_3$ (%) of sediments varied from 0.48 to 93% and the higher values are observed for 100m stations which is correlated with the relict carbonate band present in the western continental shelf. Sr showed strong positive correlation with $CaCO_3$ with higher values for the 100m samples.
4) Organic carbon (%) is found to be higher for the 200m samples which is overlying by suboxic waters, but the present study indicates that the preservation of organic matter depend not only on D.O. of bottom water, but also on other factors such as productivity of water column and sedimentation rates.
5) In the present study also, Rb and clay are positively correlated with $r > 0.8$ for all the samples, as reported by other investigations. Pb showed higher values for the coastal stations, especially from the transects off Kerala.

6) High field strength elements like, Zr, Hf and Y showed higher values for the coastal stations of northern Arabian Sea, while Th showed higher concentration for the southern stations.
7) Clay fraction of the sediments has good adsorption for metals compared to silt and sand fractions.
8) The Ba content in the sediments are depleted compared to PAAS and UCC values, which may be due to high sedimentation rate of the coastal stations.
9) Enrichment factor calculated w.r.to Al showed higher values compared to E.F calculated w.r.to Fe and this may be due to the different geochemical reactivity of Al and Fe.
10) UCC normalized patterns showed U enrichment in the sediments under OMZ. Cr also showed enriched pattern, which indicates coastal western margin could be a sink for Cr and its enrichment can be due to intense chemical weathering.
11) Factor analysis is useful to group the parameters that have identical attributes and accordingly used for that purpose.

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Chapter 5

SEASONAL VARIABILITY OF SEDIMENT GEOCHEMISTRY ALONG THE KERALA COAST DURING PRE MONSOON AND POST MONSOON

The southwest coast of India is under the influence of changing wind patterns associated with the summer and winter monsoons. The coastal currents are southerly from April to September and reverse their direction to northerly from November to February (Shetye et al, 1991, 1994, Shankar, 2000). The coastal zone of western India experiences upwelling from June to October (Banse, 1959, 1968, Naqvi et al, 2000). Surface sediment samples were collected from 7 transects along the Kerala coast (off Alleppey to off Mangalore) during pre monsoon and post monsoon periods. The main objective of this study is to examine whether seasonal variations are reflected in the REEs and trace elements of bottom sediments. These samples have been collected from the coastal areas of water depths 5m, 10m and 40m. The other objective of this study is to see the coastal effect of REEs and trace elements and to compare with the offshore samples of the western continental margin, which is already discussed in the 3rd and 4th chapters.

5.1 Results and Discussion

The methodology of analysis, hydrographic parameters and textural characteristics of the samples are given in the Chapter II.

5.1.2 Seasonal variability of Rare Earth Elements

The Concentration of REEs for both the seasons are given in the table A-5 in the appendix and shale normalized patterns are presented in the figures 5.1 to 5.7.

Off Alleppey: The 5m samples showed higher LREE concentration for premonsoon, while HREE concentration is higher for post monsoon. REE showed high value (192ppm) for pre monsoon compared to post monsoon (184ppm). Ce did not show any significant anomaly for both the seasons, but positive Eu anomaly was observed for pre monsoon sample (1.3) (table 5.1). Fractionation indices showed HREEs are depleted compared to PAAS values for both the seasons. The 10m samples showed high REE values for post monsoon (175ppm) compared to pre monsoon (158ppm). This may be due to the terrigenous influence of materials during monsoon. No significant Ce anomaly is observed for both the seasons, but positive Eu anomaly (1.45) for pre monsoon and HREE depletion (compared to PAAS) is reported for this season. 40m samples also showed similar trend like 10m samples, with high values of REE for post monsoon (129ppm) compared to pre monsoon (119 ppm). For this station, LREE/HREE ratio showed highest value among all the samples for both the seasons (2.53 and 2.14).

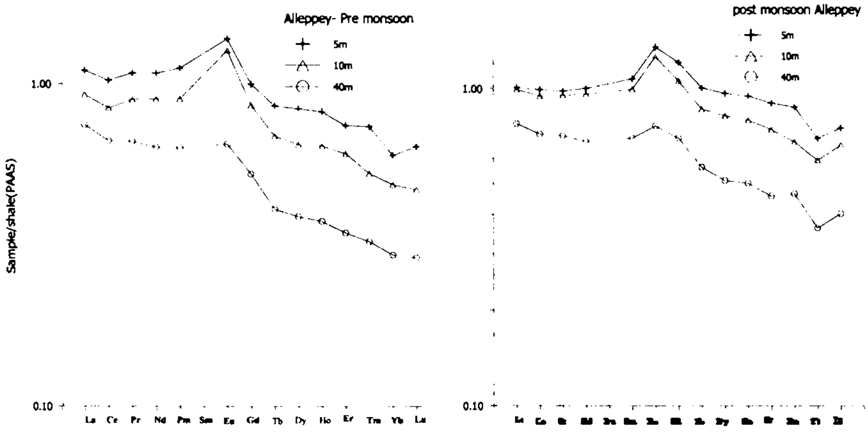

Figure 5.1. PAAS Normalised pattern for pre monsoon and post monsoon –off Alleppey

For Alleppey, shale normalized pattern were similar for both the seasons (Figure 5.1), but with stronger HREE depletion for pre-monsoon sediments. The patterns showed similar trend with low abundance for 40m samples. The abundance of total REE decreases towards depth for a season may be because of the distance from the shore. The same normalized pattern indicates same source for these REEs. The percentage of $CaCO_3$ also showed similar values for both the season. Ten meter and 40m depth samples showed high abundance of REE for post monsoon may be due to influence of river discharge during monsoon. The pattern showed similar trend reported by Nath et al, (2000). Nath et.al (2000) have plotted shale normalized patterns of charnockites and gneisses based on data presented in Allen et. al, (1985) and the shale normalized pattern of present study is similar to those pattern indicating gneissic source for these sediments.

Off Cochin: Samples from 5m showed high values of REE for post monsoon season compared to pre monsoon. Positive Eu anomaly is reported for these samples. In the present study, REEs showed lowest abundance (33ppm) for the 40m sample of pre monsoon season. The highest positive Eu anomaly is reported for this station (1.5), and HREE depletion is more for post monsoon sample. This sample showed flat shale normalized pattern for pre monsoon with positive Eu anomaly, while HREE depletion is significant for post monsoon season.

The abundance of total REE for 40m sample is very low for both the season. The abundance of total REE decreases towards offshore viz, 144ppm (5m), 75 ppm (30m- Stn.9 off Cochin), 33ppm (40m) and then increases to 190ppm (100m- Stn.10) and 170ppm (200m- Stn.10). This trend shows some that varying coastal current may be acting along this transect, at a depth of 30m.

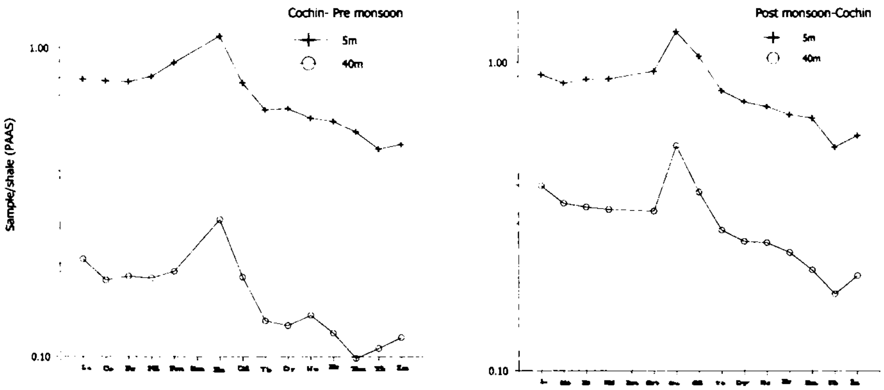

Figure 5.2. PAAS Normalised pattern for pre monsoon and post monsoon –off Cochin

Off Ponnani: Pre monsoon samples showed high values for REE compared to post monsoon for all 5m, 10m and 40m samples. Positive Eu anomaly is reported for these stations and shale normalized patterns are similar for both the seasons. This showed similar source for these sediments. $CaCO_3$ showed high value for the 40m samples.

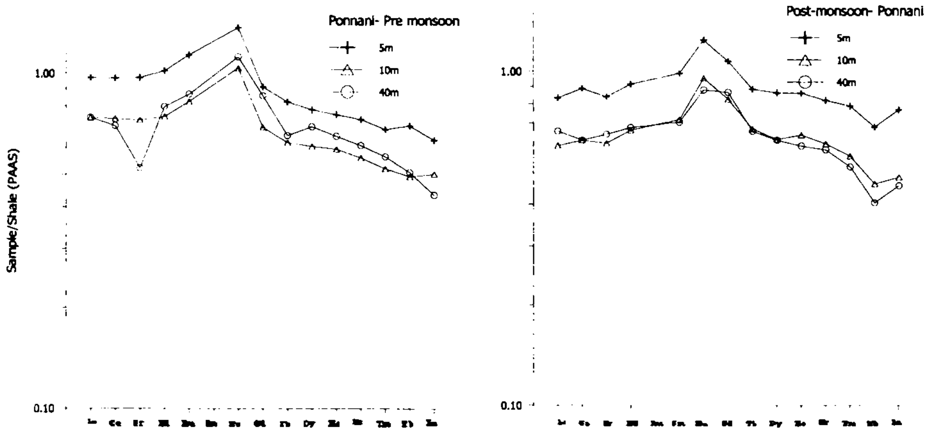

Figure 5.3. PAAS Normalised pattern for pre monsoon and post monsoon –off Ponnani

off Calicut: Post monsoon sample showed high values for total REE (102ppm) compared to pre monsoon (89.5ppm) may be due to river discharge during monsoon.

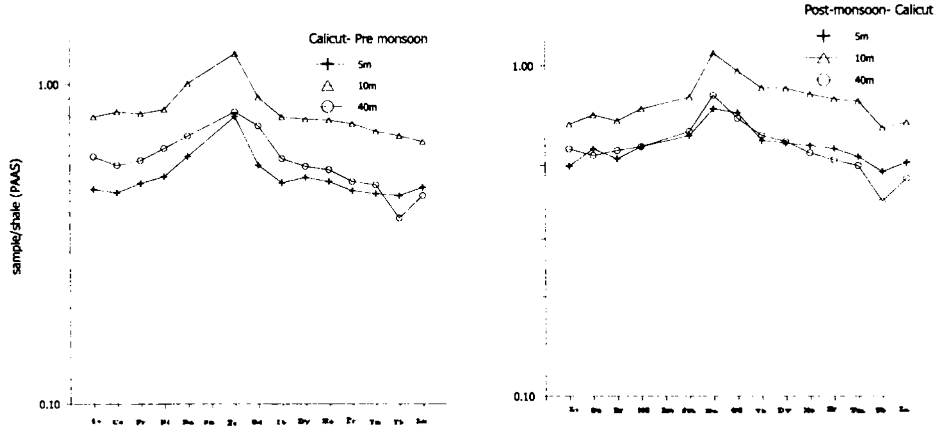

Figure 5.4. PAAS Normalised pattern for pre monsoon and post monsoon –off Calicut

Positive Eu anomaly is observed for pre monsoon sample. For 10m and 40m stations, pre monsoon samples showed high values compared to post monsoon. Ce anomaly is not significant, but Eu showed positive anomaly for these samples (figure 5.4). Shale normalized patterns are similar for these two seasons with positive Eu anomaly, and slight negative anomaly for terbium especially for 40m samples.

off Cannanore: For these three stations, pre monsoon samples showed high values for total REE. Shale normalized patterns are similar for both the seasons, with low values for 40m samples compared to coastal ones may be due to the dilution effect as the distance from the source is more for these sediment.

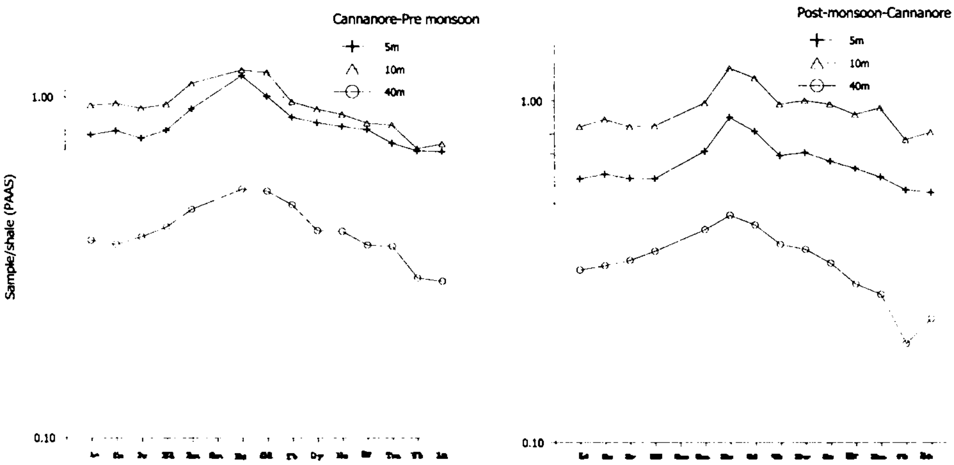

Figure 5.5. PAAS Normalised pattern for pre monsoon and post monsoon –off Cannanore

off Kasargode: For these stations, post monsoon samples showed slight higher values for total REE compared to pre monsoon. Shale normalized patterns are similar for both the seasons (flat) which indicate seasonal variation is not significant for REEs. $CaCO_3$ also showed similar values for these samples for both the seasons.

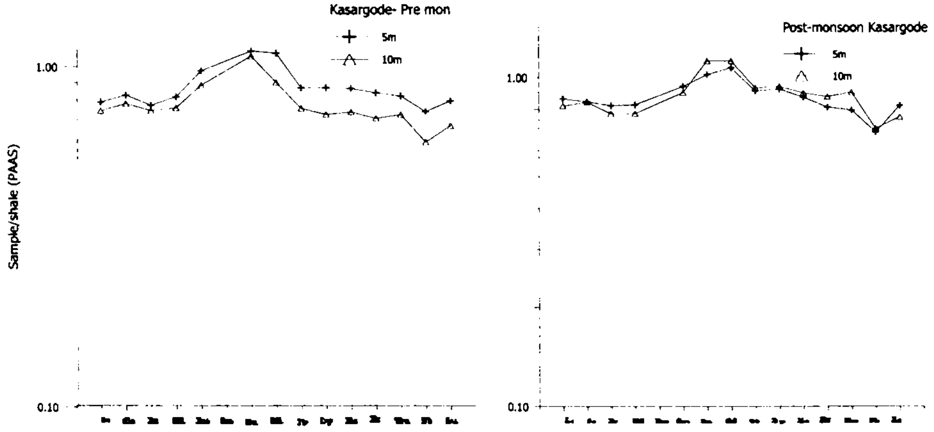

Figure 5.6. PAAS Normalised pattern for pre monsoon and post monsoon –off Kasargode

off Mangalore; For 5m station, Pre monsoon sample showed high total REE (180ppm) value compared to post monsoon (164ppm). For 10m and 40m stations, post monsoon samples showed high values for total REE compared to Pre monsoon.

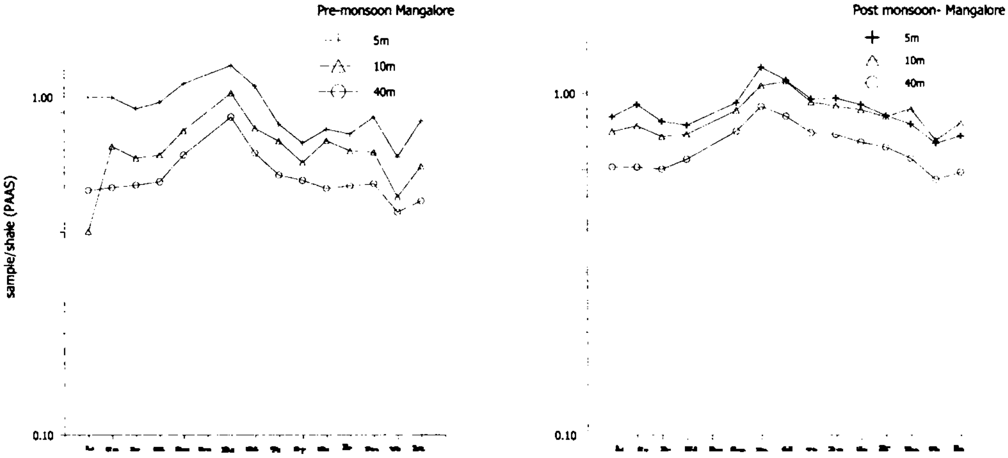

Figure 5.7. PAAS Normalised pattern for pre monsoon and post monsoon –off Mangalore

Eu showed positive anomaly for pre monsoon samples. For 10m samples, LREE are depleted compared to HREEs. Shale normalized patterns are similar, except La showed low value for pre monsoon 10m sample compared to others.

In the present study, seasonal variations are not significant for some of the stations, which are supported by the similar shale normalized patterns (figures 5.1 to 5.7). Certain transect such as off Alleppey, Cochin, Calicut, Kasargode and off Mangalore showed high abundance of total REE during post monsoon season.

	Ce Ano		Eu Ano		LREE/HREE		MREE/HREE		Sum REE (ppm)	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
Alleppey 5m	0.94	1.00	1.30	1.19	1.84	1.45	1.87	1.54	192	185
Alleppey 10m	0.92	0.97	1.45	1.23	1.91	1.68	1.85	1.68	159	176
Alleppey 40m	0.94	0.97	1.12	1.09	2.53	2.14	2.15	1.92	120	130
Cochin 5m	1.00	0.95	1.31	1.27	1.68	1.72	1.90	1.76	144	161
Cochin 40m	0.91	0.95	1.50	1.51	1.95	2.24	1.78	1.86	33	65
Ponnani 5m	1.00	1.06	1.34	1.21	1.39	1.22	1.63	1.45	179	163
Ponnani 10m	1.00	1.03	1.37	1.24	1.50	1.30	1.67	1.56	134	102
Ponnani 40m	1.11	0.95	1.30	1.12	1.46	1.64	1.71	1.74	133	120
Calicut 5m	0.96	1.10	1.37	1.11	1.05	1.04	1.32	1.28	89	102
Calicut 10m	1.03	1.06	1.30	1.24	1.14	1.02	1.46	1.24	152	133
Calicut 40m	0.95	0.96	1.15	1.23	1.55	1.44	1.80	1.62	108	103
Cannanore5m	1.04	1.03	1.20	1.17	1.11	1.08	1.32	1.30	148	114
Cannanore10m	1.02	1.05	1.05	1.16	1.33	1.09	1.55	1.28	177	163
Cannanore40m	0.96	1.00	1.08	1.09	1.29	1.64	1.59	2.15	72	62
Kasargode 5m	1.06	1.00	1.07	1.01	1.07	1.26	1.32	1.38	153	157
Kasargode 10m	1.05	1.06	1.21	1.11	1.24	1.17	1.47	1.29	142	154
Mangalore 5m	1.04	1.10	1.14	1.17	1.50	1.20	1.64	1.31	181	164
Mangalore 10m	1.35	1.06	1.28	1.07	0.79	1.06	1.57	1.22	119	148
Mangalore 40m	1.00	1.01	1.29	1.12	1.16	1.09	1.48	1.39	102	117

Table 5.1. Anomalies, fractionation indices and Sum REE of samples during pre monsoon and post monsoon.

Sholkovitz et. al (1992) studied geochemistry of REEs in the seasonally anoxic water column and porewaters of Chesapeake Bay. Their time series results indicate that REEs have large seasonal cycles in both the water column and porewaters in response to the development of anoxia in the spring and reoxygenation in the fall. The transitions from oxic to suboxic to anoxic conditions results in the release of REEs into the upper pore waters and bottom waters and are accompanied by 1) fractionation across the trivalent REE series and 2) the preferential input of Ce relative to its neighbors. During reoxygenation, removal of dissolved REEs occur from the water column and upper pore waters and follows the same relative rates LREE> MREE> HREE. But in the present study, the response of REEs to the bottom water oxygen is less significant as the depth of water column is only 40m and dissolved oxygen is found to be similar for pre monsoon season. But, post monsoon season showed variation in bottom water D.O for some of the stations. The low D.O and low temperature of water indicates the presence of upwelled water in this season. The shale normalized patterns for most of the transects showed similar trend for both the seasons. The correlation between DO and REEs are given in the correlation matrices (tables 5.2 to 5.7) and showing no relation for 5m samples of pre monsoon season, while strong negative correlation (LREEs showed $r > -0.9$, while MREEs and HREEs showed $r > -0.6$) for 10m samples (tables 5.3 and 5.6). 40m samples did not show significant correlation for D.O and REEs for this season. For post monsoon season, 5m samples have shown no correlation between D.O and REEs, while 40m samples showed significant negative correlation ($r > -0.6$) (tables 5.5 and 5.7).

5.1.2 Seasonal variation of major elements and trace metals

Two major factors controlling the distribution of trace elements among the various phases in the aquatic system are the textural characteristic and organic matter content (Balachandran et. al, 2003). The seasonal variation of elements are given transect wise.

off Alleppey: Elements like Y, Th and U showed high value for all the stations except off Cannanore for post monsoon. Sediments of Alleppey showed increased values for elements Cr, Co, Ni, Cu, Zn, Pb and Zr in post monsoon. This can be explained by the river input or terrigenous influence during monsoon. The metal concentration decreased from the shallow to deeper stations. Rb, Sr and Ba showed higher concentration for pre monsoon samples, while Zr showed high value for the 40m sample of pre monsoon season. Sr values are correlated with $CaCO_3$ which also showed high value for the 5m sample. Clay percentage is higher for the shallow samples compared to 40m, which showed high sand percentage (50%). Fe was found to be the most abundant element present in the sediment and did not show much variation during both the observations. Mn showed high values for the pre monsoon samples. Th and U showed higher values for the post monsoon season.

off Cochin: Most of the elements showed high values for coastal station (5m) compared to 40m sample. Y, Th, U, Zn, Ga, Ba and Pb showed high value for post monsoon season. But trace metals like Cr, Co, Ni, Cu, Rb and ln showed high values for pre monsoon sample. Fe and Mn also showed igh value for pre monsoon. Rajamani Amma (1994) reported 123-280ppm or Mn concentration in Cochin back waters. The textural characteristics howed clay and silt fractions dominate the sediment. For pre monsoon eason, Mn showed high concentration for the 5m sample (432ppm) ompared to 40m sample (94ppm). Sr showed high value for 40m sample, hich is correlated with high $CaCO_3$ and sand percentage. Most of the lements showed low concentration for sample at 40m at Cochin, which can explained by high sand content (61%) and low silt and clay percentage. lachandran et al (2003) studied the seasonal variability of trace metals along the Cochin estuary and reported that the fall inter-monsoon period (October) along the south west coast of India is characterized by weakening of coastal currents, inducing greater amount of Cochin backwater derived material to be transported onto the coastal zone. Th and U showed higher concentration for the post monsoon season. For 40m sample, both showed comparatively low concentration compared to other samples. Zr also showed very low values for the 40m samples. The low concentration observed for all the elements for the 40m samples may indicate the presence of the coastal current, which results in sediment churning, and transport towards deeper areas. The hydrographic parameters suggest the signature of upwelling for the southern transects for post monsoon season.

off Ponnani: Fe and Mn concentration increased towards depth for both the seasons. Mn and Fe showed high values for pre monsoon season. For Ponnani 5m sample, most of the trace elements also showed high value for the pre moonsoon season. Organic carbon content showed high value for the premonsoon season (3.5%) and the enriched trace metals for this season may be due to the organic association of elements. Zr showed almost similar values for both the seasons.

off Calicut: Trace metals showed low concentration for the coastal station (5m depth) compared to offshore one. Most of the elements showed high value for post monsoon season. Sand percentage is high for 10m samples (68%) for post monsoon, which may be the reason for low Mn concentration. Ba showed high concentration for premonsoon sample for all the three depths. Organic carbon also showed high values for premonsoon season. Fe did not show wide variation with respect to the season. Clay showed low value for 10m samples.

off Cannanore: The coastal sample (5m) showed high value for most of the trace metals for pre monsoon season. The sample at 40m showed decreased concentration for all the elements for both the season may be due to the high percentage of sand (69%) and low clay content. Organic carbon and Fe also showed low value for this sample. Fe showed highest value (9.43%) for the post monsoon (10m) sample, which is correlated with high clay percentage (82%).

off Kasargode: Most of the elements showed high concentration for post monsoon season, while Rb and Ba showed high value for pre monsoon (table A-6 in the appendix). For this transect, the sediments are characterized by silt and clay fractions. Mn showed high value for post monsoon season, but Fe did not show much variation with season. Organic carbon showed low value for post monsoon season, while percentage of $CaCO_3$ is low for both the seasons.

off Mangalore: The concentration of elements decreases gradually with the distance from the shore. The coastal sample showed high value for all the elements compared to offshore ones. Most of the elements showed enriched value for the post monsoon season, except Sr, Zr and Ba. For pre monsoon season organic carbon decreased with depth, while its percentage increased gradually for post monsoon season. Zn showed enhanced value for the coastal sample of post monsoon season. It increased from 91ppm (pre monsoon) to 490ppm (post monsoon), but for other two depths Zn concentration is more for pre monsoon season. The highest concentration of

Zr is observed for the 5m sample of pre monsoon season (1136ppm). Th and U also showed high values for this sample (12.9 and 3.2ppm) and post monsoon sample showed low concentration compared to premonsoon season (table A-6 in the appendix).

5.1.3. Correlation Matrix:

The Correlation matrix has been made separately for pre monsoon and post monsoon samples and separately for different depths, to know the actual relation of elements with respect to depth and season. Some of the elements showed distinct relation with depth and season. $CaCO_3$ showed positive correlation with Sr, but showed very low value for 5m samples, but r value increased towards offshore samples. For 40m samples, it showed good correlation (r =0.96) for both season. For pre monsoon, clay showed low r-values for most of the elements, while post monsoon, (5m sample) showed good correlation with elements like Rb, Y, REEs, Pb, Fe, Th, U etc. This showed the influence of river discharge during monsoon season, as clay is a good carrier of trace metals. Lanthanides showed good correlation among themselves for both the season. Lanthanides showed high correlation coefficient with Rb and clay for post monsoon season (especially for coastal 5m samples), which indicates REEs enter the system through river runoff during monsoon. But the correlation coefficient decreases towards deeper samples (tables 5.2 to 5.7). Fe also showed good correlation with REEs for post monsoon coastal samples. Most of the trace metals like, Ga, Cr, Co, Ni, Cu showed good correlation with lanthanides.

For pre monsoon season (10m samples), elements like Ta, Nb, Cr, Co, Ni, Cu, Zn, Th and U showed good correlation with organic carbon. Fe also showed good correlation with Cr, Co, Ni etc. indicates that organic carbon and Fe may act as the carrier of metals to the sediment for this season. Pb showed good correlation with Rb for all the pre monsoon samples. The correlation matrix showed that each of the metals Co, Cr and Ni are strongly related with Cu with $r > 0.7$. For coastal samples, Mn did not show any association with clay and organic carbon. While Mn showed positive good correlation with metals and organic carbon for deeper samples. Boyle (1981) and Palmer (1985) reported that Mn-oxide coating on settling biogenic particles carrying several scavenged metals and Mn-micronodule in the sediments are ubiquitous in the marine environment (Balachandran et al, 2003). For deeper samples (40m) Fe and Mn showed very good relation with r value > 0.96.

From the correlation matrix, it is understood that, clay acts as a carrier for most of the elements during post monsoon season especially for coastal sample, while in the case of offshore samples, Fe and organic carbon act as carriers for the pre monsoon season. Th and U showed good correlation with most of the trace metals for post monsoon season.

	Rb	Sr	Y	Ba	La	Ce	Sm	Eu	Nd	Yb	Ta	Nb	V	Ga
Rb	1													
Sr	0.49	1												
Y	0.06	-0.20	1											
Ba	0.86	0.81	0.08	1										
La	0.61	0.35	0.78	0.69	1									
Ce	0.55	0.20	0.85	0.58	0.99	1								
Sm	0.56	0.16	0.84	0.55	0.96	0.99	1							
Eu	0.67	0.25	0.76	0.63	0.96	0.96	0.97	1						
Nd	0.65	0.33	0.76	0.69	0.99	0.98	0.98	0.99	1					
Yb	-0.08	-0.43	0.84	-0.20	0.49	0.61	0.67	0.59	0.53	1				
Ta	-0.19	-0.36	0.72	-0.23	0.41	0.53	0.57	0.43	0.41	0.80	1			
Nb	0.18	-0.30	0.71	0.05	0.59	0.70	0.74	0.61	0.61	0.74	0.90	1		
V	0.02	-0.51	0.67	-0.18	0.42	0.56	0.62	0.48	0.45	0.80	0.91	0.97	1	
Ga	0.51	-0.08	0.67	0.36	0.75	0.83	0.87	0.80	0.79	0.65	0.72	0.93	0.85	1
Cr	-0.08	-0.55	0.71	-0.26	0.40	0.53	0.57	0.43	0.41	0.78	0.94	0.94	0.98	0.79
Co	0.34	-0.33	0.56	0.08	0.51	0.62	0.68	0.60	0.55	0.65	0.79	0.95	0.93	0.94
Ni	0.27	-0.54	0.65	-0.06	0.47	0.60	0.67	0.60	0.53	0.78	0.71	0.87	0.92	0.87
Cu	0.12	-0.54	0.64	-0.16	0.41	0.55	0.62	0.52	0.46	0.81	0.84	0.93	0.98	0.86
Zn	0.39	-0.41	0.29	0.04	0.28	0.39	0.49	0.42	0.36	0.52	0.51	0.77	0.80	0.81
Pb	0.87	0.17	0.48	0.69	0.81	0.81	0.84	0.87	0.85	0.36	0.19	0.55	0.43	0.81
Fe	0.46	-0.36	0.41	0.21	0.44	0.50	0.49	0.44	0.45	0.20	0.11	0.45	0.43	0.55
Mn	-0.26	-0.08	-0.27	-0.16	-0.27	-0.25	-0.29	-0.44	-0.34	-0.42	0.14	0.16	0.11	-0.01
Th	0.03	-0.17	0.94	0.10	0.76	0.83	0.81	0.69	0.72	0.75	0.82	0.83	0.76	0.74
U	0.37	-0.23	0.90	0.24	0.83	0.91	0.92	0.85	0.84	0.76	0.68	0.85	0.79	0.89
OC	0.77	0.35	0.35	0.67	0.72	0.71	0.73	0.75	0.74	0.22	0.41	0.64	0.48	0.82
CaCO3	-0.39	0.15	0.21	-0.12	0.02	-0.04	-0.13	-0.07	-0.05	-0.02	-0.24	-0.51	-0.49	-0.55
Sand	-0.40	-0.56	0.28	-0.62	-0.17	-0.11	-0.10	-0.06	-0.17	0.41	0.33	0.05	0.22	-0.09
Silt	-0.09	-0.33	-0.25	-0.25	-0.31	-0.22	-0.11	-0.20	-0.23	0.19	0.17	0.28	0.37	0.22
Clay	0.10	0.31	0.24	0.25	0.31	0.22	0.11	0.21	0.23	-0.19	-0.18	-0.29	-0.37	-0.22
DO	-0.36	0.03	0.26	-0.21	0.09	0.12	0.10	0.01	0.04	0.23	0.70	0.42	0.39	0.22

	Cr	Co	Ni	Cu	Zn	Pb	Fe	Mn	Th	U	OC	CaCO3	Sand	Silt	Clay	DO
Cr	1															
Co	0.89	1														
Ni	0.86	0.92	1													
Cu	0.94	0.95	0.97	1												
Zn	0.69	0.88	0.89	0.86	1											
Pb	0.33	0.63	0.65	0.51	0.64	1										
Fe	0.41	0.51	0.63	0.48	0.56	0.69	1									
n	0.18	0.11	-0.14	-0.02	0.01	-0.29	0.10	1								
h	0.81	0.65	0.64	0.68	0.35	0.45	0.42	0.04	1							
J	0.78	0.79	0.85	0.80	0.61	0.76	0.68	-0.16	0.89	1						
C	0.43	0.73	0.52	0.51	0.55	0.78	0.36	0.06	0.44	0.60	1					
03	-0.38	-0.65	-0.51	-0.53	-0.83	-0.41	-0.32	-0.37	0.03	-0.18	-0.53	1				
nd	0.33	0.12	0.25	0.28	-0.07	-0.29	-0.12	-0.28	0.12	0.10	-0.19	0.35	1			
t	0.23	0.31	0.33	0.38	0.64	0.04	-0.01	0.09	-0.15	-0.05	-0.06	-0.72	-0.32	1		
y	-0.23	-0.32	-0.32	-0.38	-0.64	-0.03	0.03	-0.10	0.14	0.05	0.05	0.71	0.33	-1.00	1	
)	0.50	0.33	0.07	0.27	-0.07	-0.30	-0.39	0.44	0.43	0.11	0.27	0.01	0.33	-0.19	0.16	1

le 5.2. Correlation matrix for 5m samples of Kerala coast during pre monsoon season

l, r values >0.67 are significant at 95% level (Fisher and Yates, 1967)

	Rb	Sr	Y	Ba	La	Ce	Sm	Eu	Nd	Yb	Ta	Nb	V	Ga	Cr
Rb	1														
Sr	0.60	1													
Y	-0.65	-0.47	1												
Ba	0.63	0.98	-0.50	1											
La	0.71	0.41	0.05	0.44	1										
Ce	0.18	0.09	0.55	0.13	0.80	1									
Sm	0.08	-0.14	0.63	-0.14	0.70	0.93	1								
Eu	0.38	0.56	0.21	0.51	0.75	0.73	0.70	1							
Nd	0.43	0.35	0.31	0.38	0.91	0.95	0.85	0.85	1						
Yb	-0.22	-0.47	0.78	-0.52	0.40	0.68	0.89	0.44	0.53	1					
Ta	-0.72	-0.94	0.67	-0.94	-0.40	-0.02	0.16	-0.51	-0.31	0.51	1				
Nb	-0.54	-0.81	0.76	-0.75	-0.03	0.40	0.46	-0.26	0.11	0.63	0.88	1			
V	-0.44	-0.91	0.50	-0.86	-0.17	0.09	0.21	-0.54	-0.17	0.46	0.92	0.92	1		
Ga	0.67	0.87	-0.50	0.93	0.48	0.15	-0.18	0.32	0.36	-0.56	-0.81	-0.56	-0.62	1	
Cr	-0.66	-0.95	0.67	-0.92	-0.30	0.11	0.26	-0.46	-0.18	0.56	0.98	0.94	0.95	-0.77	1
Co	-0.29	-0.90	0.16	-0.82	-0.28	-0.11	0.01	-0.68	-0.32	0.23	0.77	0.73	0.92	-0.60	0.83
Ni	-0.60	-0.98	0.51	-0.94	-0.36	-0.01	0.15	-0.59	-0.28	0.44	0.95	0.89	0.96	-0.77	0.98
Cu	-0.56	-0.97	0.47	-0.94	-0.37	-0.07	0.09	-0.63	-0.34	0.41	0.96	0.86	0.97	-0.75	0.97
Zn	-0.56	-0.62	0.55	-0.54	-0.16	0.39	0.40	-0.15	0.16	0.41	0.58	0.76	0.60	-0.47	0.70
Pb	0.91	0.74	-0.64	0.81	0.67	0.25	0.03	0.40	0.49	-0.39	-0.83	-0.55	-0.54	0.86	-0.74
Fe	-0.27	-0.92	0.26	-0.86	-0.16	0.04	0.21	-0.51	-0.17	0.42	0.78	0.76	0.91	-0.68	0.85
Mn	-0.65	-0.25	-0.08	-0.23	-0.85	-0.53	-0.53	-0.52	-0.62	-0.42	0.18	-0.01	0.01	-0.31	0.16
Th	-0.58	-0.57	0.89	-0.53	0.05	0.51	0.50	-0.07	0.24	0.61	0.76	0.93	0.73	-0.37	0.80
U	-0.64	-0.78	0.84	-0.75	-0.09	0.36	0.44	-0.24	0.07	0.65	0.90	0.98	0.87	-0.59	0.94
OC	-0.65	-0.82	0.75	-0.77	-0.16	0.31	0.37	-0.33	0.02	0.55	0.90	0.99	0.90	-0.59	0.95
CaCO3	0.01	0.64	-0.39	0.69	-0.22	-0.20	-0.49	0.02	-0.09	-0.75	-0.60	-0.52	-0.63	0.64	-0.59
Sand	-0.06	0.03	0.15	-0.13	0.02	0.00	0.30	0.48	0.07	0.45	-0.08	-0.29	-0.33	-0.44	-0.15
Silt	-0.31	-0.81	0.01	-0.73	-0.40	-0.18	-0.04	-0.61	-0.34	0.12	0.59	0.54	0.70	-0.62	0.67
Clay	0.26	0.53	-0.14	0.62	0.26	0.12	-0.24	-0.01	0.18	-0.48	-0.34	-0.11	-0.20	0.82	-0.33
DO	-0.37	-0.12	-0.44	-0.16	-0.90	-0.91	-0.82	-0.61	-0.88	-0.61	0.01	-0.38	-0.17	-0.27	-0.09

	Co	Ni	Cu	Zn	Pb	Fe	Mn	Th	U	OC	CaCO3	Sand	Silt	Clay	DO
Co	1														
Ni	0.92	1													
Cu	0.92	0.99	1												
Zn	0.57	0.69	0.59	1											
Pb	-0.40	-0.68	-0.68	-0.39	1										
Fe	0.97	0.92	0.91	0.62	-0.41	1									
Mn	0.17	0.24	0.17	0.43	-0.44	0.08	1								
Th	0.44	0.68	0.66	0.66	-0.52	0.46	-0.07	1							
U	0.64	0.85	0.84	0.70	-0.65	0.67	0.01	0.96	1						
OC	0.73	0.90	0.87	0.81	-0.62	0.74	0.15	0.92	0.98	1					
CaCO3	-0.53	-0.56	-0.61	-0.07	0.37	-0.65	0.51	-0.34	-0.50	-0.42	1				
Sand	-0.35	-0.21	-0.21	-0.25	-0.28	-0.18	-0.11	-0.29	-0.21	-0.31	-0.37	1			
Silt	0.90	0.80	0.75	0.68	-0.34	0.89	0.45	0.21	0.42	0.57	-0.32	-0.21	1		
Clay	-0.31	-0.36	-0.33	-0.24	0.48	-0.46	-0.21	0.12	-0.10	-0.12	0.54	-0.74	-0.51	1	
DO	0.06	0.03	0.03	-0.12	-0.35	-0.05	0.80	-0.49	-0.34	-0.25	0.35	0.12	0.28	-0.30	1

Table 5.3 Correlation matrix for 10m samples of Kerala coast during pre monsoon season n= 6, r values >0.7 are significant at 95% level (Fisher and Yates,1967)

	Rb	Sr	Y	Ba	La	Ce	Sm	Eu	Nd	Yb	Ta	Nb	V	Ga
Rb	1													
Sr	-0.02	1												
Y	0.17	0.08	1											
Ba	0.57	0.46	-0.40	1										
La	0.36	-0.05	0.66	0.08	1									
Ce	0.34	-0.05	0.75	-0.02	0.99	1								
Sm	0.20	0.11	0.90	-0.16	0.90	0.95	1							
Eu	0.23	0.27	0.94	-0.14	0.80	0.86	0.97	1						
Nd	0.22	0.10	0.82	-0.05	0.96	0.98	0.99	0.93	1					
Yb	0.14	0.14	0.99	-0.34	0.73	0.81	0.95	0.98	0.88	1				
Ta	0.10	-0.67	0.59	-0.46	0.62	0.66	0.62	0.49	0.60	0.57	1			
Nb	0.47	-0.70	0.20	0.01	0.67	0.64	0.40	0.22	0.47	0.22	0.76	1		
V	0.16	-0.25	0.87	-0.42	0.61	0.70	0.79	0.78	0.72	0.84	0.85	0.43	1	
Ga	0.76	0.20	0.42	0.54	0.54	0.53	0.51	0.55	0.52	0.43	0.30	0.34	0.52	1
Cr	0.06	-0.07	0.94	-0.56	0.45	0.56	0.75	0.81	0.63	0.90	0.66	0.14	0.92	0.35
Co	-0.16	0.21	0.75	-0.30	0.39	0.47	0.68	0.74	0.60	0.75	0.50	-0.08	0.82	0.44
Ni	0.16	-0.27	0.83	-0.60	0.29	0.41	0.56	0.62	0.44	0.75	0.68	0.21	0.88	0.32
Cu	0.10	-0.40	0.71	-0.67	0.13	0.25	0.40	0.45	0.26	0.60	0.66	0.19	0.80	0.19
Zn	-0.04	-0.36	0.78	-0.69	0.28	0.39	0.55	0.57	0.43	0.71	0.77	0.22	0.91	0.22
Pb	0.75	0.02	0.60	0.35	0.81	0.81	0.74	0.72	0.76	0.63	0.53	0.60	0.65	0.91
Fe	-0.16	0.42	0.84	-0.25	0.57	0.64	0.84	0.90	0.78	0.88	0.35	-0.11	0.70	0.35
Mn	-0.27	0.41	0.81	-0.33	0.49	0.56	0.78	0.84	0.72	0.85	0.33	-0.18	0.67	0.25
Th	0.31	-0.60	0.31	-0.03	0.80	0.76	0.56	0.36	0.63	0.35	0.81	0.96	0.52	0.35
U	0.23	-0.57	0.73	-0.49	0.72	0.78	0.73	0.63	0.70	0.71	0.92	0.76	0.82	0.26
OC	0.26	0.30	0.70	0.19	0.79	0.81	0.86	0.86	0.87	0.76	0.47	0.27	0.72	0.76
CaCO3	-0.11	0.96	0.26	0.22	-0.03	0.00	0.21	0.39	0.18	0.30	-0.58	-0.74	-0.12	0.10
Sand	-0.32	-0.28	0.79	-0.78	0.54	0.62	0.73	0.67	0.67	0.79	0.72	0.29	0.75	-0.10
Silt	0.80	0.46	-0.09	0.82	0.19	0.13	0.02	0.09	0.08	-0.07	-0.44	0.05	-0.31	0.53
Clay	0.02	0.12	-0.90	0.55	-0.74	-0.81	-0.89	-0.85	-0.84	-0.92	-0.66	-0.37	-0.76	-0.13
DO	0.14	-0.42	0.56	-0.70	0.10	0.20	0.27	0.30	0.16	0.47	0.42	0.23	0.44	-0.15

	Cr	Co	Ni	Cu	Zn	Pb	Fe	Mn	Th	U	OC	$CaCO_3$	Sand	Silt	Clay	DO
Cr	1															
Co	0.82	1														
Ni	0.95	0.67	1													
Cu	0.88	0.56	0.98	1												
Zn	0.93	0.74	0.96	0.95	1											
Pb	0.47	0.41	0.42	0.27	0.32	1										
Fe	0.77	0.89	0.53	0.37	0.56	0.43	1									
Mn	0.76	0.90	0.53	0.38	0.58	0.32	0.99	1								
Th	0.22	0.11	0.21	0.16	0.27	0.62	0.10	0.04	1							
U	0.71	0.38	0.72	0.68	0.73	0.58	0.38	0.35	0.79	1						
OC	0.58	0.78	0.39	0.20	0.40	0.81	0.82	0.75	0.45	0.44	1					
$CaCO_3$	0.13	0.31	-0.08	-0.20	-0.17	-0.02	0.55	0.55	-0.62	-0.44	0.30	1				
Sand	0.79	0.61	0.69	0.64	0.77	0.20	0.68	0.70	0.43	0.79	0.41	-0.06	1			
Silt	-0.31	-0.37	-0.31	-0.40	-0.53	0.47	-0.18	-0.28	-0.06	-0.24	0.13	0.32	-0.59	1		
Clay	-0.81	-0.56	-0.68	-0.58	-0.68	-0.45	-0.73	-0.71	-0.49	-0.84	-0.55	-0.07	-0.93	0.24	1	
DO	0.62	0.07	0.74	0.79	0.64	0.07	0.10	0.11	0.12	0.65	-0.16	-0.20	0.58	-0.19	-0.61	1

Table 5.4. Correlation matrix for 40m samples of Kerala coast during pre monsoon season n= 6 r values >0.7 are significant at 95% level (Fisher and Yates,1967)

	Rb	Sr	Y	Ba	La	Ce	Sm	Eu	Nd	Yb	Ta	Nb	V	Ga	Cr
Rb	1														
Sr	0.24	1													
Y	0.55	-0.35	1												
Ba	0.60	0.83	0.02	1											
La	0.66	0.02	0.88	0.44	1										
Ce	0.69	-0.16	0.95	0.27	0.97	1									
Sm	0.63	-0.10	0.95	0.31	0.98	0.98	1								
Eu	0.84	0.09	0.86	0.50	0.94	0.94	0.94	1							
Nd	0.65	0.07	0.90	0.42	0.96	0.95	0.98	0.95	1						
Yb	0.34	-0.65	0.93	-0.30	0.71	0.83	0.80	0.65	0.69	1					
Ta	-0.06	-0.93	0.64	-0.63	0.34	0.48	0.45	0.23	0.28	0.86	1				
Nb	0.03	-0.70	0.73	-0.35	0.60	0.67	0.63	0.39	0.51	0.87	0.90	1			
V	0.05	-0.91	0.56	-0.54	0.29	0.45	0.39	0.23	0.23	0.77	0.95	0.81	1		
Ga	0.76	-0.01	0.62	0.55	0.78	0.77	0.74	0.82	0.71	0.47	0.25	0.37	0.40	1	
Cr	0.10	-0.89	0.46	-0.52	0.24	0.39	0.29	0.17	0.11	0.70	0.89	0.78	0.95	0.35	1
Co	0.31	-0.75	0.48	-0.30	0.28	0.44	0.35	0.32	0.21	0.62	0.75	0.60	0.92	0.59	0.89
Ni	0.39	-0.75	0.51	-0.34	0.29	0.48	0.34	0.33	0.20	0.67	0.74	0.61	0.87	0.50	0.93
Cu	0.28	-0.82	0.59	-0.37	0.36	0.52	0.44	0.37	0.28	0.75	0.86	0.70	0.96	0.56	0.93
Zn	0.45	-0.51	0.27	-0.12	0.20	0.35	0.18	0.24	0.07	0.39	0.48	0.43	0.66	0.51	0.80
Pb	0.85	0.21	0.75	0.64	0.91	0.88	0.89	0.97	0.92	0.51	0.10	0.30	0.16	0.89	0.08
Fe	0.41	-0.61	0.83	-0.11	0.75	0.82	0.77	0.65	0.63	0.90	0.83	0.88	0.82	0.69	0.81
Mn	-0.91	-0.16	-0.75	-0.45	-0.75	-0.79	-0.79	-0.93	-0.81	-0.53	-0.07	-0.13	-0.09	-0.67	-0.04
Th	0.41	-0.43	0.88	0.02	0.86	0.91	0.86	0.72	0.78	0.88	0.72	0.91	0.68	0.67	0.64
U	0.55	-0.26	0.99	0.11	0.93	0.97	0.98	0.88	0.94	0.90	0.58	0.74	0.50	0.64	0.40
OC	0.27	0.39	0.33	0.18	0.33	0.31	0.33	0.34	0.42	0.17	-0.24	-0.04	-0.45	-0.21	-0.41
CaCO3	-0.71	0.27	-0.44	-0.19	-0.38	-0.49	-0.42	-0.58	-0.37	-0.39	-0.31	-0.17	-0.54	-0.79	-0.50
Sand	-0.56	-0.72	0.07	-0.67	-0.15	-0.13	-0.05	-0.28	-0.21	0.34	0.66	0.44	0.57	-0.16	0.49
Silt	-0.78	0.14	-0.86	-0.23	-0.86	-0.92	-0.85	-0.86	-0.80	-0.76	-0.41	-0.59	-0.37	-0.65	-0.43
Clay	0.81	-0.07	0.82	0.29	0.85	0.90	0.83	0.87	0.80	0.71	0.33	0.53	0.31	0.65	0.37
DO	-0.25	-0.10	-0.17	0.10	-0.09	-0.17	-0.08	-0.11	-0.11	-0.15	0.09	-0.04	0.22	0.30	0.05

	Co	Ni	Cu	Zn	Pb	Fe	Mn	Th	U	OC	CaCO3	Sand	Silt	Clay	DO
Co	1														
Ni	0.94	1													
Cu	0.98	0.94	1												
Zn	0.83	0.92	0.76	1											
Pb	0.30	0.26	0.31	0.23	1										
Fe	0.76	0.77	0.85	0.60	0.57	1									
Mn	-0.23	-0.29	-0.27	-0.19	-0.88	-0.45	1								
Th	0.59	0.61	0.67	0.48	0.66	0.93	-0.47	1							
U	0.41	0.44	0.52	0.24	0.79	0.81	-0.73	0.91	1						
OC	-0.56	-0.34	-0.46	-0.38	0.22	-0.12	-0.44	0.09	0.35	1					
CaCO3	-0.80	-0.74	-0.73	-0.70	-0.61	-0.54	0.60	-0.39	-0.38	0.40	1				
Sand	0.33	0.20	0.45	-0.06	-0.36	0.34	0.39	0.12	0.02	-0.48	0.09	1			
Silt	-0.40	-0.56	-0.47	-0.50	-0.77	-0.76	0.79	-0.82	-0.86	-0.44	0.46	0.26	1		
Clay	0.36	0.52	0.42	0.49	0.78	0.71	-0.80	0.78	0.84	0.47	-0.46	-0.35	-1.00	1	
DO	0.27	-0.05	0.23	-0.10	0.03	0.06	0.24	-0.08	-0.17	-0.81	-0.27	0.50	0.46	-0.49	1

Table 5.5. Correlation matrix for 5m samples of Kerala coast during post monsoon season n= 7, r values >0.67 are significant at 95% level (Fisher and Yates,1967)

	Rb	Sr	Y	Ba	La	Ce	Sm	Eu	Nd	Yb	Ta	Nb	V	Ga	Cr
Rb	1														
Sr	0.31	1													
Y	0.27	-0.82	1												
Ba	0.64	0.66	-0.22	1											
La	0.60	-0.29	0.72	0.49	1										
Ce	0.58	-0.41	0.81	0.37	0.99	1									
Sm	0.54	-0.52	0.88	0.25	0.95	0.99	1								
Eu	0.50	-0.54	0.88	0.24	0.91	0.94	0.97	1							
Nd	0.64	-0.27	0.70	0.53	0.97	0.96	0.94	0.95	1						
Yb	0.01	-0.92	0.92	-0.47	0.51	0.62	0.73	0.68	0.47	1					
Ta	-0.30	-0.96	0.78	-0.62	0.33	0.44	0.54	0.49	0.27	0.94	1				
Nb	0.01	-0.88	0.91	-0.32	0.64	0.73	0.80	0.74	0.59	0.97	0.94	1			
V	-0.28	-0.88	0.70	-0.82	0.08	0.22	0.32	0.27	0.00	0.86	0.89	0.76	1		
Ga	0.52	-0.49	0.84	0.27	0.96	0.99	0.99	0.94	0.93	0.72	0.55	0.81	0.31	1	
Cr	-0.18	-0.81	0.64	-0.84	-0.04	0.11	0.25	0.23	-0.06	0.81	0.79	0.65	0.94	0.22	1
Co	-0.24	-0.66	0.45	-0.89	-0.23	-0.08	0.04	-0.02	-0.29	0.65	0.67	0.47	0.91	0.02	0.95
Ni	-0.30	-0.86	0.64	-0.86	-0.08	0.06	0.19	0.25	-0.07	0.74	0.74	0.58	0.90	0.14	0.94
Cu	-0.31	-0.90	0.69	-0.84	0.05	0.19	0.30	0.27	-0.01	0.85	0.89	0.75	1.00	0.28	0.95
Zn	-0.55	-0.93	0.64	-0.73	0.12	0.21	0.29	0.30	0.04	0.75	0.89	0.74	0.86	0.27	0.70
Pb	0.66	0.44	0.01	0.97	0.66	0.55	0.46	0.47	0.71	-0.26	-0.43	-0.10	-0.69	0.47	-0.71
Fe	0.55	-0.37	0.61	-0.25	0.24	0.35	0.45	0.46	0.30	0.56	0.31	0.39	0.48	0.40	0.68
Mn	-0.41	-0.51	0.20	-0.65	-0.19	-0.09	0.02	-0.13	-0.25	0.56	0.68	0.51	0.66	0.07	0.67
Th	0.17	-0.74	0.88	-0.03	0.81	0.86	0.91	0.86	0.78	0.87	0.80	0.95	0.53	0.92	0.41
U	0.06	-0.84	0.91	-0.17	0.74	0.81	0.87	0.83	0.71	0.91	0.87	0.98	0.63	0.87	0.51
OC	-0.10	-0.22	0.08	-0.33	-0.08	-0.02	0.06	-0.12	-0.13	0.40	0.44	0.37	0.39	0.13	0.45
CaCO3	0.11	0.95	-0.92	0.40	-0.56	-0.65	-0.73	-0.75	-0.54	-0.93	-0.91	-0.94	-0.76	-0.71	-0.65
Sand	-0.68	-0.32	-0.10	-0.33	-0.32	-0.32	-0.23	-0.10	-0.21	0.08	0.25	0.09	0.03	-0.23	0.10
Silt	0.50	0.92	-0.62	0.79	0.03	-0.09	-0.21	-0.30	0.01	-0.73	-0.80	-0.64	-0.81	-0.16	-0.80
Clay	0.28	-0.49	0.66	-0.36	0.32	0.42	0.43	0.37	0.22	0.57	0.45	0.48	0.69	0.39	0.61
DO	0.02	-0.58	0.63	-0.44	0.31	0.40	0.40	0.30	0.15	0.61	0.61	0.58	0.77	0.39	0.58

	Co	Ni	Cu	Zn	Pb	Fe	Mn	Th	U	OC	CaCO3	Sand	Silt	Clay	DO
Co	1														
Ni	0.87	1													
Cu	0.91	0.93	1												
Zn	0.63	0.79	0.87	1											
Pb	-0.84	-0.72	-0.71	-0.58	1										
Fe	0.59	0.58	0.49	0.09	-0.15	1									
Mn	0.69	0.46	0.65	0.46	-0.61	0.19	1								
Th	0.20	0.35	0.51	0.56	0.20	0.30	0.33	1							
U	0.30	0.48	0.62	0.68	0.07	0.31	0.36	0.99	1						
OC	0.47	0.15	0.36	0.09	-0.32	0.23	0.91	0.27	0.23	1					
CaCO3	-0.46	-0.71	-0.77	-0.85	0.16	-0.35	-0.32	-0.88	-0.94	-0.09	1				
Sand	-0.03	0.23	0.10	0.30	-0.24	-0.28	0.29	0.07	0.12	0.12	-0.20	1			
Silt	-0.67	-0.92	-0.85	-0.89	0.62	-0.31	-0.42	-0.46	-0.58	-0.06	0.80	-0.50	1		
Clay	0.64	0.59	0.66	0.49	-0.30	0.59	0.07	0.33	0.40	-0.07	-0.50	-0.63	-0.36	1	
DO	0.64	0.55	0.73	0.67	-0.38	0.31	0.24	0.43	0.50	0.04	-0.58	-0.51	-0.42	0.93	1

Table 5.6 Correlation matrix for 10m samples of Kerala coast during post monsoon season

n= 6, r values >0.7 are significant at 95% level (Fisher and Yates,1967)

	Rb	Sr	Y	Ba	La	Ce	Sm	Eu	Nd	Yb	Ta	Nb	V	Ga	Cr
Rb	1														
Sr	-0.82	1													
Y	0.70	-0.54	1												
Ba	-0.17	0.44	-0.33	1											
La	0.63	-0.59	0.72	0.16	1										
Ce	0.69	-0.66	0.79	0.02	0.99	1									
Sm	0.76	-0.70	0.96	-0.30	0.85	0.91	1								
Eu	0.73	-0.52	0.96	-0.08	0.80	0.84	0.93	1							
Nd	0.66	-0.61	0.89	-0.10	0.94	0.97	0.97	0.91	1						
Yb	0.85	-0.66	0.97	-0.32	0.69	0.77	0.94	0.94	0.84	1					
Ta	0.85	-0.97	0.62	-0.31	0.75	0.80	0.79	0.61	0.74	0.72	1				
Nb	0.65	-0.87	0.39	-0.09	0.77	0.78	0.62	0.43	0.66	0.46	0.93	1			
V	0.75	-0.81	0.89	-0.58	0.64	0.73	0.92	0.82	0.81	0.91	0.80	0.59	1		
Ga	0.64	-0.35	0.46	0.58	0.75	0.69	0.51	0.68	0.60	0.53	0.48	0.49	0.31	1	
Cr	0.54	-0.51	0.93	-0.64	0.47	0.58	0.86	0.80	0.74	0.87	0.52	0.24	0.90	0.11	1
Co	0.25	-0.34	0.73	-0.76	0.19	0.31	0.63	0.57	0.50	0.64	0.28	0.03	0.78	-0.18	0.92
Ni	0.73	-0.71	0.87	-0.71	0.44	0.57	0.84	0.73	0.68	0.90	0.69	0.40	0.94	0.13	0.94
Cu	0.81	-0.81	0.77	-0.60	0.41	0.52	0.76	0.71	0.59	0.86	0.74	0.47	0.93	0.29	0.81
Zn	0.83	-0.88	0.75	-0.45	0.57	0.64	0.79	0.74	0.67	0.84	0.82	0.63	0.93	0.45	0.72
Pb	0.59	-0.41	0.24	0.61	0.75	0.68	0.40	0.45	0.52	0.34	0.56	0.67	0.17	0.91	-0.11
Fe	-0.12	-0.03	0.55	-0.64	0.13	0.21	0.46	0.36	0.41	0.36	0.02	-0.12	0.51	-0.39	0.76
Mn	-0.05	-0.01	0.59	-0.65	0.03	0.13	0.44	0.42	0.34	0.43	-0.03	-0.24	0.54	-0.33	0.80
Th	0.67	-0.60	0.59	0.27	0.97	0.95	0.75	0.70	0.86	0.61	0.77	0.82	0.52	0.80	0.31
U	0.48	-0.72	0.67	-0.49	0.73	0.80	0.82	0.57	0.81	0.62	0.79	0.75	0.78	0.12	0.69
OC	0.74	-0.56	0.70	-0.44	0.21	0.30	0.59	0.67	0.40	0.80	0.47	0.15	0.76	0.33	0.71
CaCO3	-0.81	0.94	-0.49	0.14	-0.70	-0.72	-0.66	-0.56	-0.64	-0.62	-0.93	-0.90	-0.72	-0.60	-0.35
Sand	0.20	-0.05	-0.47	0.40	-0.12	-0.17	-0.36	-0.40	-0.35	-0.29	0.10	0.19	-0.45	0.17	-0.63
Silt	-0.45	0.42	0.15	-0.46	-0.26	-0.19	0.02	-0.06	-0.02	-0.04	-0.40	-0.50	0.00	-0.66	0.39
Clay	0.11	-0.26	0.45	-0.12	0.34	0.35	0.42	0.53	0.44	0.37	0.18	0.16	0.53	0.30	0.45
DO	-0.72	0.44	-0.71	-0.19	-0.64	-0.64	-0.68	-0.86	-0.66	-0.78	-0.48	-0.33	-0.61	-0.86	-0.49

	Co	Ni	Cu	Zn	Pb	Fe	Mn	Th	U	OC	CaCO3	Sand	Silt	Clay	DO
Co	1														
Ni	0.82	1													
Cu	0.70	0.92	1												
Zn	0.59	0.83	0.96	1											
Pb	-0.43	-0.02	0.12	0.31	1										
Fe	0.88	0.55	0.31	0.20	-0.55	1									
Mn	0.94	0.60	0.42	0.30	-0.59	0.96	1								
Th	-0.01	0.34	0.34	0.50	0.87	-0.09	-0.19	1							
U	0.55	0.70	0.54	0.59	0.20	0.54	0.38	0.64	1						
OC	0.63	0.80	0.92	0.84	0.05	0.20	0.40	0.14	0.20	1					
CaCO3	-0.16	-0.53	-0.71	-0.86	-0.65	0.16	0.16	-0.73	-0.60	-0.50	1				
Sand	-0.81	-0.37	-0.29	-0.26	0.44	-0.85	-0.90	0.11	-0.30	-0.27	-0.10	1			
Silt	0.53	0.18	-0.15	-0.33	-0.74	0.82	0.74	-0.41	0.17	-0.17	0.65	-0.55	1		
Clay	0.57	0.30	0.46	0.57	0.05	0.39	0.50	0.19	0.23	0.45	-0.38	-0.77	-0.11	1	
DO	-0.28	-0.48	-0.64	-0.72	-0.60	0.05	-0.11	-0.60	-0.18	-0.73	0.60	0.20	0.45	-0.59	1

Table 5.7. Correlation matrix for 40m samples of Kerala coast during post monsoon season n= 6, r values >0.7 are significant at 95% level (Fisher and Yates,1967)

5.1.4 Comparison of REEs and trace elements in the coastal and offshore samples

The sediment samples of western continental margin were collected at water depths of 30m, 100m and 200m as discussed in the previous chapters. In the present study, sediment samples were collected from 5m, 10m and 40m water depths. These samples were collected in different season and analysed using different ICP-MS instruments. Hence the comparison of concentration value is not effective, but the trend of elements towards offshore can be compared. The 40m samples of this study were collected to compare with 30m samples of previous study. 5m and 10m samples belong to geochemically very active area, as land contribution during monsoon influence the processes like dissolution and precipitation of elements in the system. Four transects of both the study are common, they are off Cochin, Calicut, Cannanore and off Mangalore. The Arabian Sea samples of previous study were collected during pre monsoon season and hence the pre monsoon samples of this study are compared with the previous study.

In general, the concentration of REEs and trace elements showed high value for the 5m sample compared to 10m and 40m samples in the present study. In the previous study, 30m samples showed high concentration of REEs compared to 100m and 200m samples. This indicates the concentration of elements decrease as the distance from the shore increases. For the transect off Cochin, the ΣREE concentration showed the order 100m> 200m> 5m> 30m> 40m. This indicates, the presence of coastal current which results in cross shelf transport of elements, which is prevalent at water depth of 30meters. For the transect off Calicut, the ΣREE and trace elements concentration decreased towards offshore, as the distance from the coast increase. The transect off Cannanore, also showed similar trend towards offshore. For the transect off Mangalore, the coastal samples showed higher concentration, but the offshore 200m sample showed higher concentration compared to 40m sample. In general, the major elements and trace metals of sediments from entire west coast region showed higher values for 30m samples compared to offshore ones. The coastal samples of present study also supports the fact that concentration of these elements decreases offshore, except for two transects off Cochin and Dwaraka.

5.2 Conclusions

1. In general, total REE concentrations are higher in the shallower stations compared to the offshore samples indicating a reduced supply of REEs and other trace elements to the offshore areas. The previous study of sediments from the entire western continental margin of India also supports the decrease in concentration towards offshore. Despite the varition of ΣREE contents with depth, shale-normalized patterns are similar for all the depths in nearly all the transects suggesting a similar source for the depth ranges considered here (5 to 40 m).
2. Inter-elemental/parameter correlation data reveal that the clays are responsible for most of the variation in trace and REE systematics in the post monsoon season probably due to the increased run-off during monsoons.

. In contrast to the water column characteristics, which have shown distinct seasonal variation, REEs and other trace elements including the redox-sensitive elements in the sediments have not significantly responded to the changing bottom water chemistry. This is also different to findings on water column and particles from seasonally anoxic basins such in Chesapeake Bay where redox sensitive elements such as Mn and Ce show a quick response to changing water column oxygenation. In addition, sedimentary organic carbon also shows variation. This may suggest that the time scales necessary for imparting changes in trace elements and cerium are much longer than studied here.

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Chapter 6

RARE EARTH ELEMENT GEOCHEMISTRY OF ANDAMAN BACKARC BASIN

The Andaman Basin extends from Myanmar in the north to Sumatra in the south and from the Malay Peninsula in the east to the Andaman and Nicobar Island in the west. Subduction of the Indian plate along the Andaman arc, formation of the Andaman Nicobar ridge and initiation of the spreading in the Andaman Sea are some of the important tectonic events that shaped the Andaman Backarc basin (Kamesh Raju et.al, 2004). The oceanographic and geomorphologic settings and sediment characteristics of the Andaman Sea are given in Chapter 1. The core locations are given in the figure 6.1 with topographic features associated with the Andaman Backarc basin.

The southwestern part of the basin is dominated by N-S- trending fault systems. The backarc basin is bisected by a prominent valley- like feature with a trough of about 500m in the eastern part that continues toward the west. This feature corresponds to the Andaman Backarc-spreading center. The Western part is dominated by volcanic constructs that are related to arc volcanism and backarc spreading activity, whereas the eastern part represents distinctly smooth topography probably resulting from the sediment fill of the Irrawadi river system situated further north of the study area (Kamesh Raju et. al, 2004). SPC –1 was taken from the northern side of the rift valley, while SPC-2 and SPC 5 were taken from the southern side of the rift valley. All the three cores were taken from the sediment filled smooth topographic zone, even though SPC 5 location is near to the southwestern area of Andaman basin, which is related to arc volcanism and spreading activity.

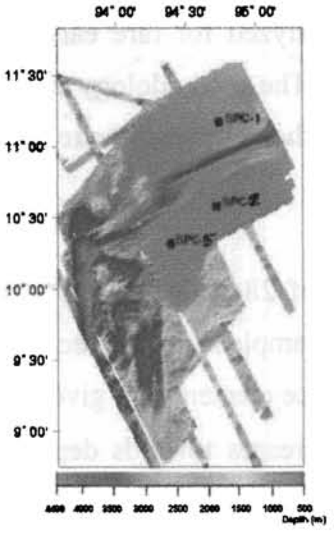


Figure. 6.1 Core locations are inserted on the topographic features of Andaman Backarc basin (Ref. Kamesh Raju et.al, 2004).

6.1 Results and Discussion

In the present study, three spade cores collected from the Andaman Backarc basin were used to study the downcore variation of REEs and other trace elements in the sediment cores, and to study their accumulation with respect to other major elements such as Mn. One of the main objectives is to decipher the hydrothermal signatures from the REE fractionation indices and to compare the behavior of Ce with that of Mn in view of their similar geochemical properties in order to understand the mechanism of Mn enrichment in sediments. The other objective is to estimate the proportion of

REEs and other trace elements contributed by hydrothermal processes vis-a vis the terrigenous source such as Irrawadi river.

The samples were analyzed for rare earth elements, trace metals, organic carbon and $CaCO_3$. The methodology of analysis is given in the second chapter. REEs and other elements were measured using ICP-MS after acid digestion.

6.1.1 SPC-1

The core taken was of 28cm length from the Andaman basin of water depth 3040m and sub sampled into 14 sections at 2cm interval. The concentration of REEs and trace elements are given in the tables A-7 and A-9 in the appendix. ΣREE increases towards depth and the values ranged between 103- 165ppm (Table. 6.1). The lowest value is observed in the 2-4cm section and the highest value for the deepest section 26-28cm (figure 6.3 (c)). The sediments are normalized with PAAS and the shale normalized patterns are given in the figures 6.4 (a and b).

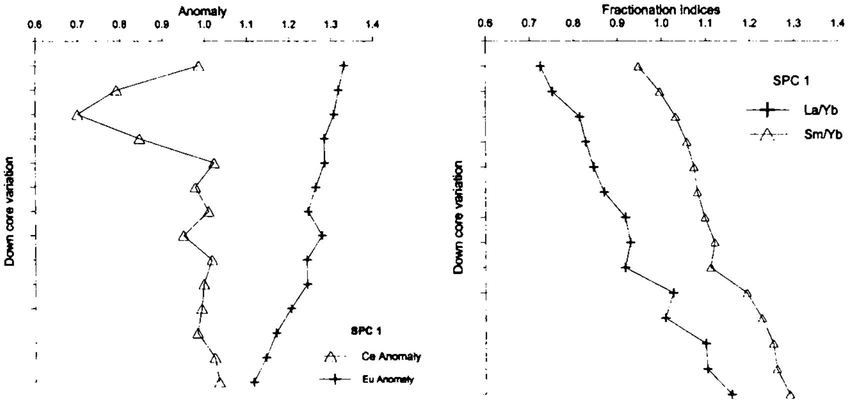


Figure 6.2 Down core variation of anomalies (a) and fractionation indices (b) of the core SPC 1

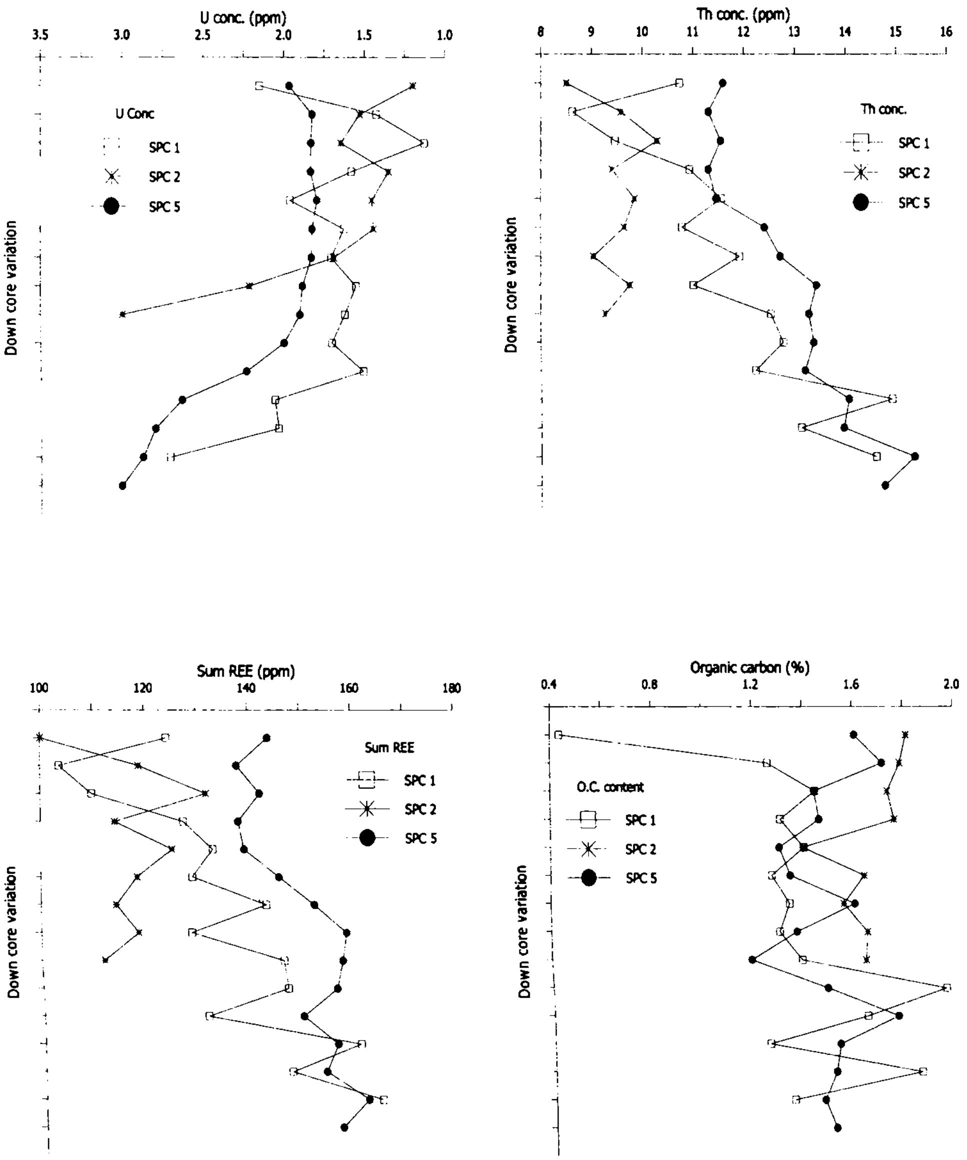


Figure 6.3. Down core variation of U (a), Th (b), Sum REE (c) and Organic carbon of the cores SPC 1, SPC 2 and SPC 5.

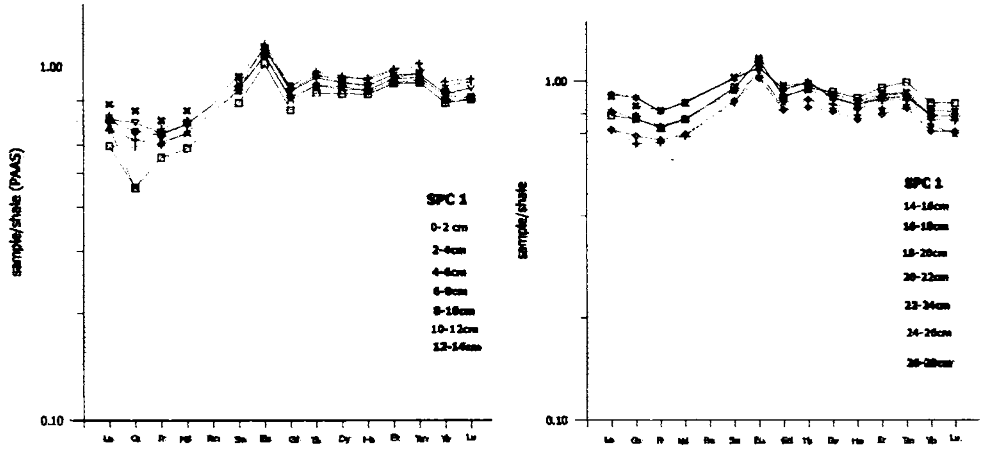


Figure 6.4 (a & b) Shale normalized (PAAS) patterns of the sediment samples of the core SPC 1.

Fractionation indices and anomalies of sediment cores from the Andaman Backarc basin

SPC-1						
S.No	core sample	Ce Ano	Eu Ano	(La)n/(Yb)n	(Sm)n/(Yb)n	Sum REEs (ppm)
1	0-2 cm	0.986	1.331	0.725	0.947	124.311
2	2-4cm	0.791	1.318	0.752	0.996	103.631
3	4-6cm	0.699	1.307	0.814	1.032	109.859
4	6-8cm	0.845	1.284	0.828	1.057	127.490
5	8-10cm	1.022	1.285	0.846	1.074	133.172
6	10-12cm	0.978	1.264	0.870	1.081	129.158
7	12-14cm	1.009	1.245	0.918	1.098	143.468
8	14-16cm	0.949	1.278	0.929	1.121	128.944
9	16-18cm	1.017	1.242	0.917	1.111	146.697
10	18-20cm	0.998	1.243	1.026	1.193	147.300
11	20-22cm	0.992	1.205	1.009	1.227	131.595
12	22-24cm	0.983	1.169	1.100	1.253	161.034
13	24-26cm	1.023	1.145	1.104	1.261	147.579
14	26-28cm	1.034	1.116	1.159	1.290	165.075

SPC 2						
S.No	core sample	Ce Ano	Eu Ano	(La)n/(Yb)n	(Sm)n/(Yb)n	Sum REEs (ppm)
1	0-2cm	0.95	1.32	1.08	0.83	100.07
2	2-4cm	1.06	1.32	0.76	0.59	118.92
3	4-6cm	1.07	1.27	1.13	0.90	131.95
4	6-8cm	1.05	1.32	1.09	0.85	114.23
5	8-10cm	1.06	1.27	1.14	0.92	125.31
6	10-12cm	1.05	1.29	1.14	0.92	118.50
7	12-14cm	1.06	1.27	1.19	0.96	114.44
8	14-16cm	1.05	1.29	1.14	0.94	118.72
9	16-18cm	1.06	1.25	1.15	0.94	112.06

SPC 5						
S.no	Core sample	Ce Ano	Eu Ano	(La)n/(Yb)n	(Sm)n/(Yb)n	Sum REEs (ppm)
1	0-2	1.06	1.30	0.81	1.09	143.96
2	2-4'	1.05	1.28	0.81	1.07	137.97
3	4-6'	1.05	1.29	0.82	1.08	142.38
4	6-8'	1.05	1.25	0.81	1.08	138.15
5	8-10'	1.06	1.30	0.80	1.06	139.27
6	10-12'	1.05	1.25	0.83	1.10	145.94
7	12-14'	1.05	1.31	0.83	1.08	152.80
8	14-16'	1.05	1.26	0.84	1.10	158.99
9	16-18'	1.05	1.26	0.86	1.12	158.14
10	18-20	1.04	1.26	0.87	1.13	156.80
11	20-22	1.04	1.21	0.89	1.15	150.02
12	22-24	1.04	1.26	0.95	1.17	156.56
13	24-26	1.04	1.19	0.94	1.20	154.24
14	26-28	1.05	1.17	1.03	1.30	162.35
15	28-30	1.04	1.17	1.13	1.40	157.28

ble 6.1. Anomalies, fractionation indices and sumREEs of the cores SPC
SPC 2 and SPC 5.

All the samples showed similar pattern except for 2 samples, which showed negative Ce anomaly. Flat shale normalized pattern with significant positive Eu anomaly is observed for the sediment sections. Ce anomaly values ranged from 0.7 to 1.03. Two samples (2-4cm and 4-6 cm) showed negative Ce anomaly. All other sections showed no Ce anomaly with Ce/Ce* value close to 1. Eu showed positive anomaly with values between 1.12 to 1.33. The surface samples showed higher values and anomaly decreased gradually towards depth. The down core variation of Ce and Eu anomalies are given in the figure 6.2 (a).

Fractionation indices {(La/Yb)n and (Sm/Yb)n} showed low values for surface samples and gradually increased towards depth. (La/Yb)n values ranged between 0.72 to 1.16 while (Sm/Yb)n showed values between 0.95 and 1.29. The down core variation of fractionation indices are shown in figure 6.2 (b).

$CaCO_3$ and organic carbon of these sediment sections were also analyzed following the procedure given in the 2nd chapter. $CaCO_3$ (%) is very low for this core sample in the range of 0.47 to 7.7(%) (table A-9 in the appendix). The surface 1-2 cm section showed lowest value and increased towards deeper sections. Organic carbon ranged between 0.44 to 1.96 (%) and the lowest value is observed at surface (0-2 cm section) and increased towards bottom and remain steady for the deeper sections (figure 6.3 (d)).

Thorium concentration ranged between 8-14 ppm and value increased towards depth (figure 6.3 (b)). While, U concentration ranged between 1.1 to 2.7ppm with only the surface (0-2cm) and bottom sections showing values greater than 2ppm (figure 6.3 (a)).

While the elements Cr, Ni, Cu and Pb showed highest concentration for the surface section of this core and the values decreased towards bottom sections of the core, elements like Rb, Sr, Nb, Cs and Ta increased towards the deeper section of the core. Ba concentration ranged between 430-677ppm and its value decreased towards the deeper sections (table. A-9 in the appendix).

6.1.2 SPC-2

The core was of 18cm length collected from the Andaman basin (water depth 3150m) and sub sampled at 2 cm interval.

The REE abundance of this core was found to be less compared to SPC 1. For this core ΣREE varied in the range 100-132ppm (Table, 6.1). The lowest concentration observed at the surface 0-2cm section, while the highest concentration is noted at 4-6 cm section (figure 6.3 (c)).

Ce anomaly is not observed for this core sample, while Eu showed positive anomaly with value of 1.32 (figure 6.5 (a)). Eu/Eu* values decreased towards depth and the highest value obtained is 1.32 for the surface section. The REE concentration is normalized with PAAS and these patterns showed similar flat pattern with positive Eu anomaly (figures 6.6(a and b)). (La/Yb)n ranged between 0.76 to 1.19, and the lowest values observed for 2-4cm section and for other sections, it is close to 1. (Sm/Yb)n ranged between 0.59 and 0.96, and for this also the highest value observed for 2-4 cm section (figure 6.5 (b)). For the deeper sections, these ratios are close to 1, which means that there is no significant LREE or HREE fractionation.

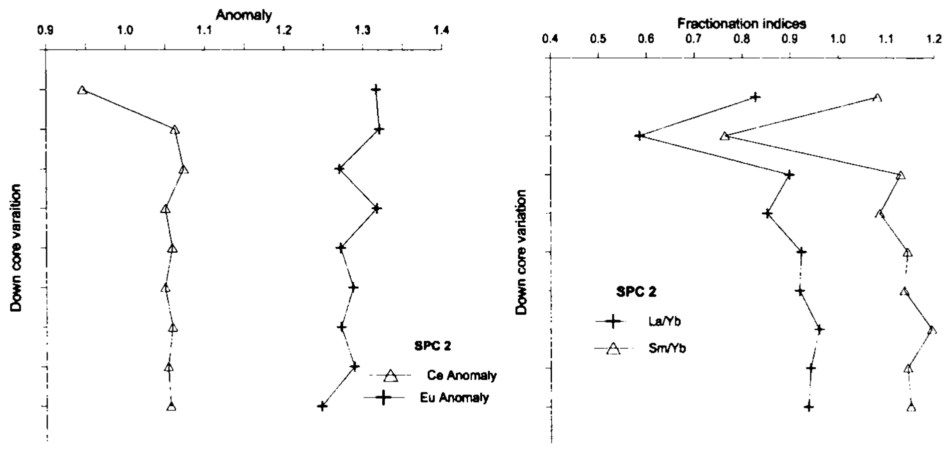


Figure 6.5 Down core variation of anomalies
(a) and fractionation indices (b) of the core SPC 2

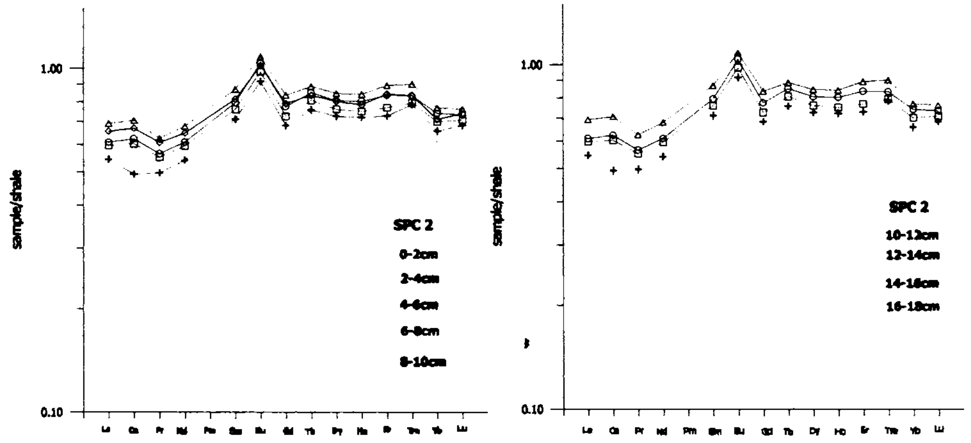


Figure 6.6 (a & b) Shale normalized (PAAS) patterns for the sediment samples of the core SPC 2.

$CaCO_3$ (%) values varied between 3 and 19.6(%). For this core, the value increased towards deeper sections and the lowest value is observed for surface section (table A-9 in the appnedix). On the other hand, organic carbon varied narrowly between a range of 1.4 and 1.8 (%) (Figure 6.3 (d)).

Thorium values ranged between 8.5 and 10.3ppm, where the highest value observed for the 4-6 cm section (figure 6.3(b)). U concentration varied between 1.32 to 3ppm and the values increased gradually for the deeper section of the core (figure 6.3(a)).

Cr and Ni showed higher values for this core compared to that of SPC-1. Sr and $CaCO_3$, which showed good positive correlation for this core and increased towards depth. While Ba concentration decreased towards depth like SPC 1 samples. Pb concentration also decreased towards deeper sections of the core and varied from 19 to 47ppm (table A-9 in the appendix).

6.1.3 SPC-5

This core is of 30cm length and was taken from the Andaman Backarc basin at a water depth of 3124m. The core is sub sampled to 15 sections of 2cm interval.

ΣREE of these samples ranged between 138 to 162ppm and the abundance increased towards depth of the core (figure 6.3 (c)). Ce/Ce* values close to 1 indicated that no Ce anomaly is observed for this core samples. But Eu/Eu* showed positive anomaly with values 1.3 at the surface and decreased to 1.17 for the deeper sections (figure 6.7 (a)). (La/Yb)n and (Sm/Yb)n showed values close to 1, but slightly increased towards deeper sections (figure 6.7. (b)). Shale normalized pattern showed flat pattern with positive Eu anomaly and found to be similar for all the 15 sub samples (figure 6.8 (a and b)).

Thorium concentration ranged between 11.6 and 15ppm, and the value increased towards the deeper sections (Figure 6.3 (b)). U also followed similar trend with higher concentration up to 3ppm for the deeper section (figure 6.3 (a)). Organic carbon content varied between 1.2 and 1.7(%) with the highest values for the 20-22 cm section (figure 6.3 (d)). Ramamurty et. al (1979) studied organic matter in the surficial sediments of north eastern Andaman and reported that slope sediments showed high value compared to near shore ones (0.2 to 2%).

Mn concentration varied between 0.1 and 2.3(%) with the highest concentration for 8-10cm and 10-12cm sections and again decreased to 0.1(%) for the deeper sections. Co (32ppm) and Ni (170ppm) also showed higher values for these two sections. Mo also showed higher values for surface and 10-12 cm section (10ppm) (table A-10 in the appendix). Ba showed similar trend like other two cores where the concentration decreased depthwise and the values ranged between 486 to 690ppm.

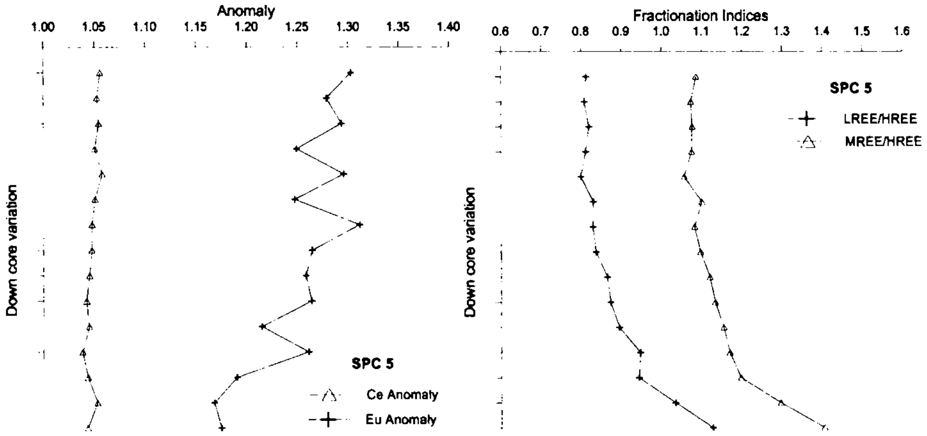


Figure 6.7 Down core variation of anomaly
(a) and fractionation indices (b) of the core SPC 5.

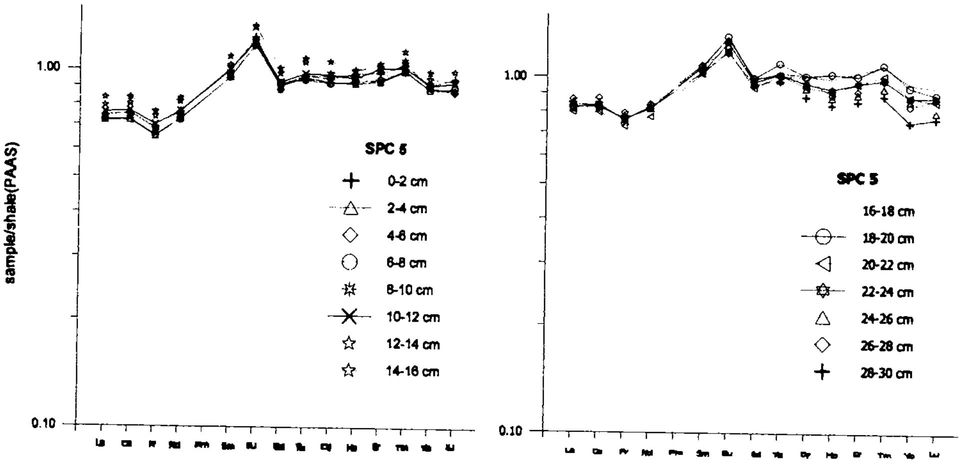


Figure 6.8. (a & b) Shale normalized (PAAS) patterns for the sediment samples of the core SPC 5.

6.2. The components of marine sediments

According to Goldberg (1954), the components of marine sediments are classified as lithogenous, biogenous, hydrogenous and cosmogenous components. Lithogenous components are defined as those, which arise from land erosion, from submarine volcanoes or from underwater weathering where the solid phase undergoes no major change during its residence in seawater. The most important of the land derived components found in marine sediments are the clay minerals and quartz, together with generally smaller amounts of feldspar. The most common varieties of clay minerals belong to the kaolinite, chlorite, illite and montmorillonite groups. Biogenous components are defined as those produced in the biosphere and as such include both organic matter and inorganic shell materials. The organic matter includes hydrocarbons, fatty acids, steroids, pigments, amino acids, carbohydrates, natural polymers, PAHs etc. Other biogenic components include phosphates (skeletal apatites), sulphates (barites), carbonates and opaline silica shell material. Goldberg (1954) defined hydrogenous components as those which results from the formation of solid material in the Sea by inorganic reactions, i.e., by non-biological processes. According to Goldberg (1954), hydrothermal components would include in the general hydrogenous category since they are also formed from seawater by inorganic reactions. Cosmogenous components have been formed in outer space and have reached the surface of the earth via atmosphere. The extra terrestrial materials identified in the deep-sea sediments are cosmic spherules and microtectites, together with cosmic-ray produced radioactive and stable nuclides.

6.3 Hydrogenous or hydrothermal sources of sediments

6.3.1. Hydrogenous component

Elderfield (1976) subdivided hydrogenous components into two basic categories, termed precipitates (primary inorganic components formed directly from seawater) and halmyrolysates (secondary components formed as a result of reaction between sediment components and seawater subsequent to *in situ* weathering but prior to diagenesis). Elderfield (1976) identified four main groups of hydrogenous material in marine sediments. They are:-

a) Volcanic precipitates, which result from the introduction of elements into seawater from volcanic processes.

b) Supergene precipitates, which are precipitated from sea water, or interstitial water, but are non-volcanogenic in origin.

c) Lithogenous halmyrolysates, which are formed from the reaction of lithogenous components with seawater.

d) Volcanic halmyrolysates, which are usually formed as a result of seawater–basalt interactions.

Direct seawater-derived elements are further subdivided into hydrogenous elements, i.e, those originating from the general background of elements dissolved in seawater and hydrothermal elements i.e., those originating from the debouching of hydrothermal solutions at the ridge crest spreading centers.

6.3.2 *Hydrothermal activity*

The convection of seawater through freshly generated oceanic crust at the centers of sea-floor spreading plays an important role in controlling the chemical mass balance of the oceans. Cold seawater penetrates through the pre existing crust around the spreading centers, where it undergoes heat-driven circulation and comes into contact with the zones of active magma intrusion. During this process the seawater undergoes drastic changes in composition to form high temperature hydrothermal solutions, which emerge through the sea-floor venting system as hot springs that mix with the overlying seawater. Hydrothermal solutions are involved with both thermal and chemical transfer between circulating water and the heat source.

In the present study, an attempt has been made to identify the hydrogenous or hydrothermal source for the Andaman Backarc basin sediments. A plot of Cu+Ni+Co versus Co/Zn was used by Toth (1980) to indicate the relative contribution of hydrothermal deposition in ferromanganese deposits. This plot is also useful to classify the hydrothermal or hydrogenetic sources of the sediments. In this plot, the low contents for hydrothermal crusts indicate low hydrothermal input of Co, Ni and Cu, but relatively high hydrothermally derived Zn contents. These plots are given for all the three cores and all the sediment samples are fallen exactly in the hydrothermal area (figures 6.9 (b, c and d)).

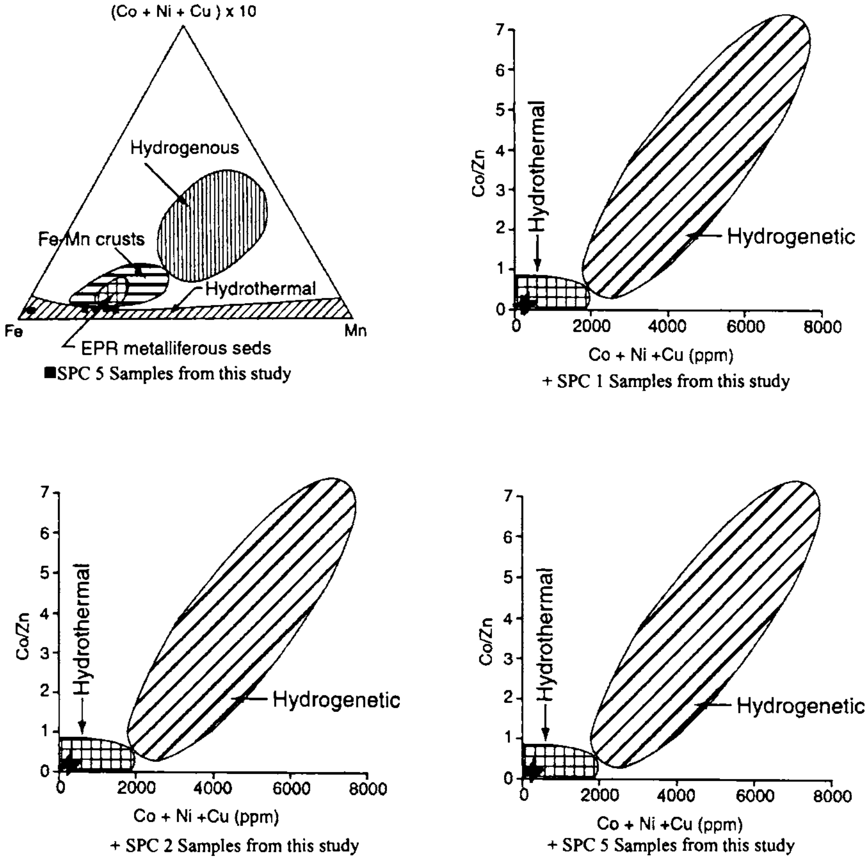
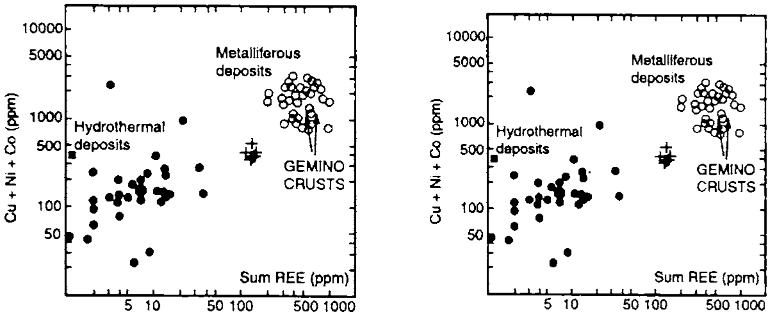


Figure 6.9. (a) Ternary diagram of Fe-Mn- (Cu+Ni+Co) x 10 (All field interpretations are from Bonatti et.al, 1972 and by Toth, 1980).

Figure 6.9 (b), (c) and (d). Co/Zn versus Co+Ni+Cu contents (Toth , 1980) for the cores SPC 1, SPC 2 and SPC 5. All the sediment core samples fall exactly in the hydrothermal field.

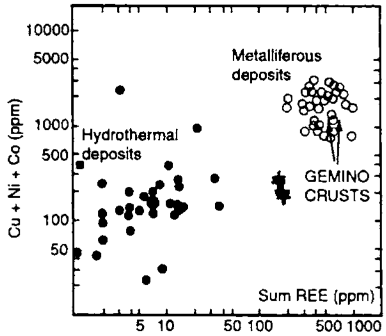
Co/Zn ratios were used by Toth (1980) as an indicator of hydrothermal mineralization, with a mean value for hydrothermal deposits being 0.15, and that for hydrogenous deposits being 2.5. Experimental work has shown that, after Mn and Fe, Zn is the trace metal that is most enriched in seawater having undergone reaction with hot basalt (Seyfried & Mottl, 1982). Zn has been found to be enriched in proximal hydrothermal deposits (Rona, 1984). Co/Zn ratios have been calculated for these cores and are given in the table 6.2. For SPC-1, SPC2 and SPC5 the average value of Co/Zn are 0.12, 0.11 and 0.17 respectively. This ratio indicates the possible source of hydrothermal signatures for these sediment cores. The mean Zn/Fe ratios for the core SPC-5 is 0.002 (table 6.2) and are close to the hydrothermal end member ratios (0.0022) suggested by Graybeal & Heath, 1984). Nath et. al (1997) studied the origin of ferromanganese encrustations from Indian Ocean Triple Junctions and they also observed Zn/Fe ratio of 0.0024 and those are mostly of hydrothermal origin.

The ternary diagram of Fe-Mn-Co+Ni+Cu shows interpreted hydrothermal and hydrogenetic fields (Bonatti et.al, 1972). A third field based on the studies of Fe-Mn crusts was included by Toth (1980). This field lies midway between the Fe end member and the nodule field demonstrating the enrichment and depletion of Fe and trace elements respectively. The ternary plot of Fe-Mn-Co+Ni+Cu of the core SPC-5 is given in the figure 6.9 (a). Most of the sediment samples of this core fallen in the hydrothermal field and some of the samples fall just at the base of EPR metalliferous data in the hydrothermal field.



+ SPC1 samples from this study

+ SPC2 samples from this study



+ SPC5 samples from this study

Figure 6.10. Correlation between Sum REE and Cu+Ni+Co concentrations in hydrothermal deposits and metalliferous sedimentary deposits (adopted from Clauer et. al, 1984) for the cores SPC 1, SPC 2 and SPC 5 (a, b, and c)).

Discrimination plot including concentration of Cu+Ni+Co and ΣREE concentration provides a means of characterizing the hydrothermal and hydrogenous Fe-Mn deposits (Clauer et. al., 1984). Hydrothermal deposits have REE and Cu, Ni and Co concentrations that are distinctly lower than those of hydrogenous deposits. The discrimination plots for three spade cores are given in the figures 6.10 (a, b and c) and in these plots, the present sediment samples fall in the field closer to metalliferous deposits.

This accounts for the possible Fe-Mn mineralization, which is revealed by the inclination of samples more towards the Fe axis in the ternary plot (figure 6.9(a)).

The positive Eu anomaly observed in all the sediment sections can be due to the influence of hydrothermal inputs. For SPC1 core, the surface two sections are characterized by negative Ce anomaly also. Many studies have reported the occurrence of positive Eu anomalies in the marine environments. Shale normalized positive Eu anomalies are found either in waters affected by eolian input (Elderfield, 1988) or in hydrothermal solutions and the sediments resulting from high T-basalt alteration along the mid-ocean ridges and back-arc spreading centers (eg. Michard et al 1983, German et al, 1993). The discrimination plots of these cores support the hydrothermal sources for these sediments in addition to the influence of metalliferous deposits. But, Eu anomaly is decreasing towards the deeper sections of the core and the absence of significant negative Ce anomaly suggests the influence of the detrital sources too for these sediments. These detrital (lithogenous) components include crust derived weathering products, continental and submarine volcanic debris and clays (which include the oxides of aluminium and silicon). From these discrimination plots, it is understood that hydrothermal (or metalliferous) influence is superimposed with detrital inputs for these sediments. Rao et.al (1996) also reported the evidence of hydrothermal activity in the Andaman Backarc basin through geophysical and geological studies. They recovered pyrite clusters in the form of rods and irregular lumps in the sediments. These are interpreted as evidence for hydrothermal activity in the region, related to backarc spreading and associated volcanism.

U/Fe ratios: Though U contents are lower than the known hydrothermal sites, U/Fe ratios in the Mn rich layer range between 2.8 and 3.4 x 10^{-5} (Table, 6.2), which are comparable to the ratios of 2×10^{-5} found for other metalliferous sediments (Mills et.al.1993). But this ratio is about an order of magnitude higher than that obtained for plume particulates (U/Fe= 1-5 x $^{10-6}$) [German et, al 1991]. Thus, the plume derived sediment contains excess U as compared with plume particulates. The sediments containing sulfides contain even higher U concentrations and U/Fe ratios up to 5×10^{-5} (Mills et. al, 1993). Incidentally the deeper sections with lower Mn and Mo contents contain higher ratios. Higher ratios and high Th contents indicate the influence of detrital sources to the deeper sediments.

Mills et.al (1993) studied the dual origin for the hydrothermal component in a metalliferous sediment core from the Mid –Atlantic Ridge and they used a three component model to explain the distribution of major and trace elements down the core. They are biogenic, detrital and hydrothermal components.

Larger detrital component in the lower section is also supported by (La/Yb)n ratios. The deeper sediments have higher ratios (close to 1) typical of continental material reaching the Oceans (Piper 1974, Sholkovitz, 1990, and Nath et.al, 1997). Presence of hydrothermal component in the top layer is also supported by enrichment of Mo and stronger Eu anomalies. The core section interpreted to have higher hydrothermal component has stronger Eu anomaly and in the deeper layer with more detrital component has smaller

Eu anomaly. The positive Eu anomaly is due to the large hydrothermal component in these sediments as hydrothermal fluids show a large positive Eu anomaly. Metalliferous sediments show shale normalized pattern with HREE enrichment, positive Eu anomaly and negative Ce anomaly which are similar to seawater (Bender et. al, 1971, Dymond et. al, 1973, Mills et. al, 1993.) Throughout the core, negative Ce anomaly is less pronounced than that seen in plume particulates. This is due to the significant detrital component mixed with the hydrothermal material which acts to flatten the REE patterns and reduce the values of Ce anomaly. Mo enrichment can result either during 1) lower oxygenation levels in bottom water/sediments or 2) hydrothermal processes. If bottom water were oxygen poor, the environment could not have allowed Mn enrichment, which rules out the probability of suboxic/anoxic diagenesis influencing Mo enrichment. Mo enrichment as high as 200ppm is seen in TAG metalliferous sediments. (Mills, et.al, 1993).

Shale normalized Eu/Sm ratio is calculated for the SPC-5 core and the average value is 1.21 (Table, 6.2). Eu/Sm ratio for average plume particulates are 1.23 (Barrett et. al, 1990). For this core, (Eu/Sm)n ratio is decreasing towards bottom of core, which is supported by the down core decrease in Eu anomaly. The surface sediments showing the ratio more close to 1.23, while the bottom sections showed low value, may be due to the detrital input. REE/Fe ratios are also calculated for this core and are given in the table 6.2.

SPC-5								
Depth (cm)	Zn/Fe	Co/Zn	La/Fe*10-6	Ce/Fe*10-6	Nd/Fe*10-6	Eu/Fe*10-6	U/Fe *10-5	(Eu/Sm)n
0-2	0.0022	0.2008	488.6	1033.7	444.7	23.0	3.38	1.25
2-4'	0.0020	0.2158	475.6	993.1	426.5	22.2	3.16	1.24
4-6'	0.0021	0.2095	475.2	1002.9	425.4	22.2	3.08	1.25
6-8'	0.0020	0.2384	478.5	998.4	427.5	22.0	3.19	1.23
8-10'	0.0021	0.2687	481.1	1023.5	426.4	22.4	3.13	1.25
10-12'	0.0021	0.2587	479.4	1009.5	429.4	21.5	3.02	1.20
12-14'	0.0018	0.1379	470.0	990.8	428.4	22.2	2.84	1.28
14-16'	0.0017	0.1422	471.0	983.2	417.4	21.3	2.79	1.22
16-18'	0.0021	0.1260	516.7	1074.3	453.4	22.8	3.08	1.21
18-20	0.0022	0.1321	490.6	1026.0	431.3	22.0	3.11	1.22
20-22	0.0020	0.1365	513.7	1070.7	443.4	21.8	3.77	1.16
22-24	0.0021	0.1259	525.0	1085.7	456.6	22.5	4.33	1.23
24-26	0.0020	0.1336	521.6	1095.9	463.5	21.5	4.69	1.15
26-28	0.0020	0.1349	548.5	1153.9	472.8	21.8	4.77	1.12
28-30	0.0020	0.1367	574.1	1197.2	498.6	22.6	5.33	1.12
Mean	**0.0020**	**0.1732**	**500.6**	**1049.2**	**443.0**	**22.1**	**3.6**	**1.21**

Table 6.2. Elemental ratios calculated for the core SPC 5.

Average plume particulate ratios are : La/Fe = 66.2 x 10^{-6}, Ce/Fe = 47.7 x 10^{-6}, Nd/Fe = 70.2 x 10^{-6} and Eu/Fe= 4.6 x 10^{-6} (German et. al, 1990). But in the present study, the ratios are very high compared to the plume ratio. The average ratio for the present study are La/Fe = 500 x 10^{-6}, Ce/Fe = 1050 x 10^{-6}, Nd/Fe= 440 x 10^{-6}, and Eu/Fe= 22 x 10^{-6}. The deviations from plume average ratio for this core indicates, apart from hydrothermal input other sources (detrital) are also present. The REE/Fe ratio increasing towards bottom, further supports the presence of detrital component is more significant for the deeper sediment sections.

Nature of hydrothermal component:

Hydrothermal component in this core is likely of Mn –oxide type, although the data points fall close to the Fe-member in the Bonatti triangular plot. If it were of sulphide- sulphate type deposit, Nd concentration would be very low. For example, Barrett et. al (1990) measured Nd concentration of 2.4 and 0.74ppm in the massive sulphide sulphate deposits of the Southern Explorer Ridge. Presence of Mn –oxde type mineralization would in turn indicate either a distal hydrothermal source or oxidation of sulphide rich material during seawater dilution (Mills et al. 1993).

6.4 Mass accumulation rates or Burial rates

The sediment accumulation rate were calculated using the formula

$$S_{acc} = S \times \rho$$

Where S is the linear sedimentation rate (cm/kyr) which is about 10cm/kyr for the Andaman sediments (Colin et.al, 1998) and ρ is the dry bulk density calculated from wet bulk density and porosity (Φ) values.

The mass accumulation rate or burial rate of an element is calculated using the formula

$$\text{Burial rate of an element} = (\text{Conc. of the element}) * (S_{acc})$$

The accumulation rate of the elements like La, Sm, ΣREE, Co, Cr, Ni, Cu, Mn and organic carbon are calculated for these cores and given in the table 6.3. Some of the elements showed spatial variation in the accumulation rate. Organic carbon showed low value for the surface section of SPC-1 core compared to other 2 cores. For SPC-5, organic carbon accumulation rate increased downward and the highest accumulation rate is noted for the section 22-24 cm (94 mg C/cm^2/kyr). The core SPC 2 showed low accumulation rate for the lanthanides compared to SPC 1 and SPC 5, while Cr and Ni showed high accumulation rate for this core (Table. 6.3)

For SPC- 5, the down core variation of the accumulation rate for some of the elements is given in the figures 6.11 and 6.12. The accumulation rates for lanthanides and other elements are given in mg/cm^2/kyr.

Mass accumulation rate (Burial rate) in mg/cm2/kyr

SPC 1									
S.No	Depth	O.C bur	La Burial	Sm burial	Cr burial	Co burial	Ni burial	Cu burial	ΣREE burial
1	0-2 cm	19.038	0.110	0.021	0.550	0.133	0.915	0.514	0.542
2	2-4'	45.558	0.082	0.016	0.405	0.102	0.651	0.382	0.374
3	4-6'	53.267	0.095	0.017	0.429	0.108	0.603	0.377	0.403
4	6-8'	42.537	0.090	0.017	0.397	0.099	0.535	0.330	0.413
5	8-10'	80.730	0.156	0.029	0.580	0.181	0.915	0.580	0.765
6	10-12'	66.527	0.139	0.025	0.549	0.182	0.810	0.499	0.672
7	12-14'	62.409	0.138	0.024	0.499	0.100	0.527	0.357	0.664
8	14-16'	74.155	0.155	0.027	0.566	0.094	0.575	0.415	0.731
9	16-18'	46.586	0.101	0.018	0.368	0.057	0.377	0.262	0.490
10	18-20'	92.143	0.146	0.025	0.520	0.081	0.552	0.583	0.692
11	20-22'	97.794	0.163	0.029	0.619	0.096	0.596	0.384	0.783
12	22-24'	54.402	0.149	0.025	0.501	0.080	0.488	0.284	0.698
13	24-26'	94.380	0.159	0.026	0.508	0.080	0.480	0.272	0.750
14	26-28'	39.235	0.102	0.016	0.315	0.052	0.287	0.143	0.480
SPC 2									
S.No	Depth	O.c bur	La burial	Sm burial	Cr burial	Co burial	Ni burial	Cu burial	ΣREE burial
1	0-2cm	74.362	0.085	0.016	1.045	0.114	1.083	0.384	0.410
2	2-4'	72.551	0.094	0.018	1.069	0.119	1.049	0.392	0.482
3	4-6'	64.850	0.098	0.018	0.992	0.115	0.984	0.342	0.492
4	6-8'	73.053	0.094	0.017	1.050	0.099	1.026	0.319	0.473
5	8-10'	59.488	0.106	0.019	1.088	0.099	1.068	0.312	0.531
6	10-12'	67.484	0.098	0.018	1.051	0.089	1.011	0.901	0.486
7	12-14'	59.509	0.088	0.016	1.008	0.085	0.946	0.263	0.435
8	14-16'	52.381	0.076	0.013	0.789	0.078	0.811	0.196	0.376
9	16-18'	57.895	0.080	0.014	0.790	0.082	0.838	0.202	0.394

SPC 5									
S.No	Depth	O.C burial	La burial	Sm burial	Mn burial	Co burial	Ni burial	Mo burial	ΣREE bur
1	0-2 cm	51.114	0.090	0.018	72.06	0.081	0.469	0.032	0.457
2	2-4'	66.306	0.106	0.020	62.40	0.096	0.541	0.022	0.532
3	4-6'	59.031	0.115	0.022	55.08	0.104	0.565	0.017	0.580
4	6-8'	67.490	0.127	0.024	74.18	0.126	0.668	0.020	0.635
5	8-10'	68.638	0.144	0.028	105.88	0.171	0.877	0.033	0.730
6	10-12'	64.133	0.137	0.026	95.01	0.155	0.807	0.039	0.692
7	12-14'	58.611	0.110	0.021	5.29	0.059	0.390	0.004	0.557
8	14-16'	64.489	0.149	0.028	5.34	0.077	0.524	0.004	0.745
9	16-18'	49.773	0.133	0.025	4.33	0.067	0.451	0.003	0.659
10	18-20’	57.976	0.122	0.023	4.51	0.071	0.447	0.003	0.610
11	20-22’	77.184	0.125	0.023	4.14	0.067	0.479	0.003	0.615
12	22-24’	94.737	0.171	0.031	5.42	0.088	0.574	0.003	0.839
13	24-26’	45.346	0.092	0.017	2.93	0.047	0.312	0.002	0.456
14	26-28’	33.101	0.072	0.013	2.14	0.035	0.224	0.001	0.355
15	28-30’	40.740	0.090	0.016	2.78	0.043	0.287	0.002	0.436

Table 6.3 Mass Accumulation rate (Burial rate) calculated for the sediment cores of SPC 1, SPC2 and SPC 5

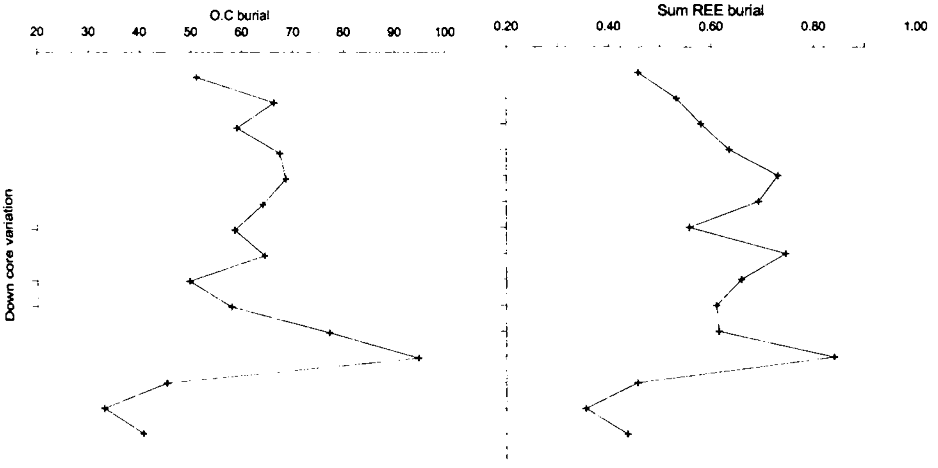


Figure 6.11. Down core variation of burial rates of organic carbon (a), ΣREE (b)

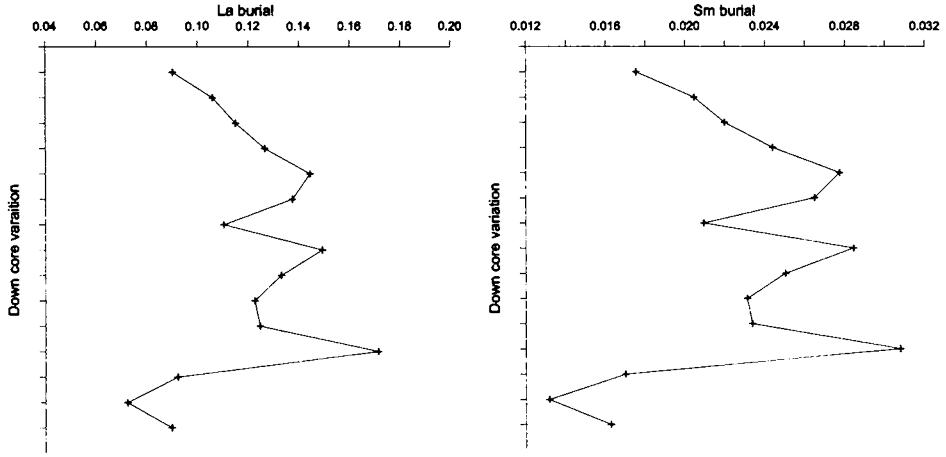


Figure 6.11. Down core variation of burial rates of La (c) and Sm (d) for the core SPC 5

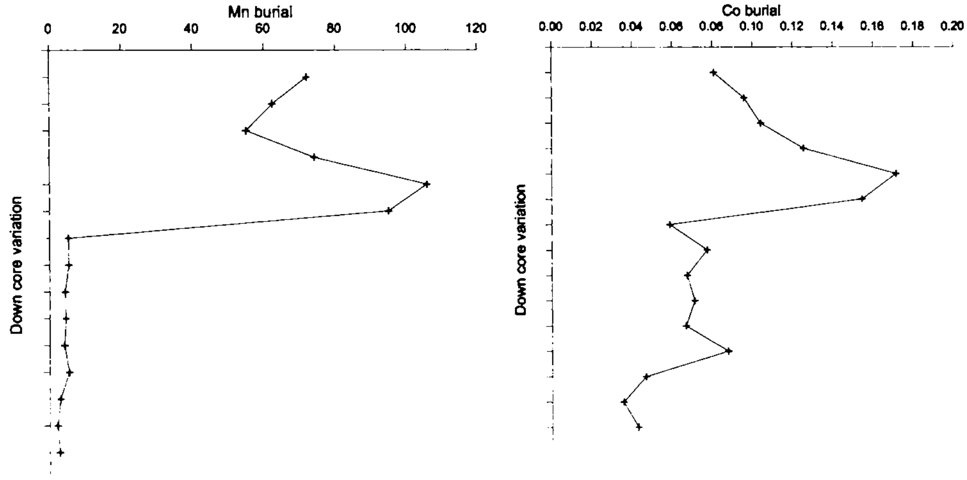


Figure 6.12. Down core variation of burial rates of Mn (a), Co (b) of the core SPC 5

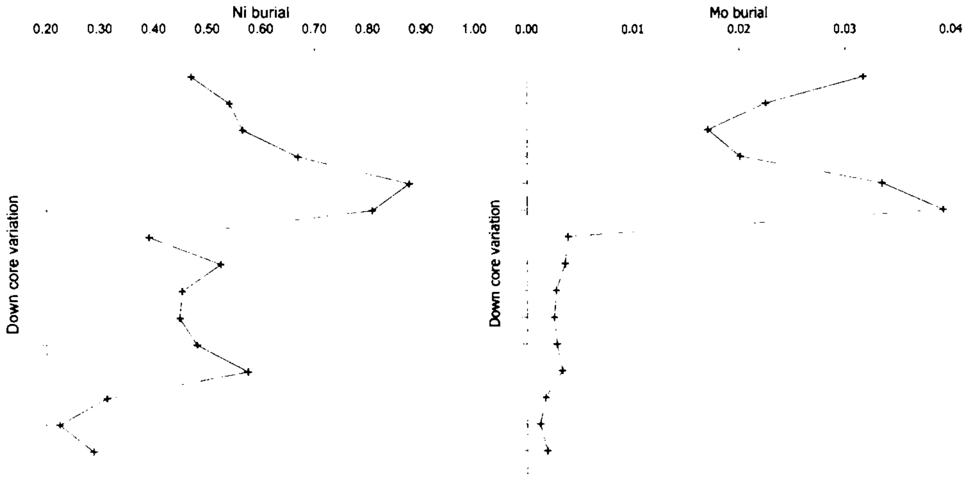


Figure 6.12. Down core variation of burial rates of Ni (c) and Mo (d) of the core SPC 5

Lanthanides showed highest accumulation rate for the sediment section 22-24cm and followed similar down core variation like organic carbon (figure 6.11). Lanthanides showed highest accumulation rate for 22-24cm section and small peaks for 8-10cm and 14-16cm sections. Mn showed highest accumulation rate or burial rate for the sediment sections 8-10cm and 10-12cm (100mg Mn/cm^2/kyr) and this value is decreasing towards deeper sections (figure 6.12 (a)). Co and Ni also showed enriched accumulation rate for the sediment section 8-10cm (figure 6.12 (b and c)). Co and Ni showed slightly enriched value for the section 22-24cm, where all the lanthanides and organic carbon showed highest value. The accumulation rate of Mn, Co and Ni showed different trend as compared to lanthanides. Lack of correlation between the mass accumulation rate (MAR) of Mn and REEs indicate a predominant hydrothermal source for Mn and a mixed detrital- hydrothermal signature for REEs.

6.5. Conclusions

Three spade cores have been collected from the Andaman Backarc basin, and studied for REEs, and other trace elements.

1) REE studies, discrimination plots and trace metal ratios suggest hydrothermal source along with some detrital input for these sediments. Shale like flat REE patterns and (La/Yb)n ratios on one hand suggest a significant detrital component in the sediment (La= 20 to 30ppm in the sediment compared to 35- 40ppm in shale), while the positive Eu anomaly, Mn and Mo enrichment and negative Ce anomalies in few samples, U/Fe ratios close to plume ratios collectively indicate an unquantifiable metalliferous/ hydrothermal component in these sediments. This is consistent with the earlier studies comprising multibeam bathymetric geophysical studies, disseminated sulphides and pyritic lumps, vent like structures in rocks, which have indicated the occurrence of hydrothermal activity.
2) Detrital component in the sediments could possibly be due to the delivery from Himalayan River such as Irrawadi or Sawleen. The seismic studies have revealed sediment infilling in the northeastern part of neotectonic spreading ridge indicating large continental detrital supplies into the basin. In fact, the high sedimentation may be masking the hydrothermal signatures.
3) Bulk accumulation rate or burial rate is also calculated for the cores studied here. Organic carbon and lanthanides showed similar accumulation, while Mn, Co, and Ni showed different trend for these sediments indicate a predominant hydrothermal source for Mn and a mixed detrital-hydrothermal signature for REEs.

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Summary

The Rare Earth Elements (REEs) from lanthanum to lutetium are members of Group IIIA in the periodic table and all have very similar chemical and physical properties.

REEs along with certain other trace metals give information about the various mechanisms, by which they have been incorporated into the sediments such as scavenging onto the particles, co-precipitation, ion pairing and redox reactions. Many trace elements can be disassociated or get associated during their transport from the source to the depositional sites due to biogeochemical processes in seawater. But in case of REEs, only subtle variations may take place across the series, and this coherence makes them useful geochemical tracers. To use the REEs as natural tracers we need to understand the extent to which these processes are dominant in different geochemical environments. The REEs in sediments are likely to be influenced by (1) particulate supply from the adjacent landmasses 2) biogenic sedimentation from overlying seawater 3) oxygenation conditions in the water column. In view of the importance of REE studies reported earlier, an attempt has been made to address the behaviour and processes of REEs and trace elements in the Arabian Sea sediments and Andaman Backarc basin sediments.

In the present study, surface sediment samples were collected from the western Indian continental shelf to estimate the distribution pattern and geochemical behaviour of REEs, major elements and trace metals. Bottom water samples were also taken at each station, and analysed for temperature, salinity and dissolved oxygen, hence the response of redox sensitive elements to varying oxygenation conditions can be addressed. Sediments collected from the Kerala coast were analysed to examine the seasonal variations of REEs and trace elements. In addition, three sediment cores were studied from the Andaman Backarc basin to understand the downcore variation of REEs and other trace elements and also to study their accumulation with respect to other major elements such as Mn, so as to see the signatures of hydrothermal influences through REE fractionation indices.

Rare earth elements were normalized with PAAS (Post Archean Australian Shale) values for plotting shale normalized patterns and determining the anomalies if any. Eu and Ce anomalies and fractionation indices were used for explaining REE behaviour in the system. Additionally, elements were normalized with UCC (Upper Continental Crust) values to compare with continental crust composition. Element excess and enrichment factors are other parameters calculated in the present study. Correlation matrix and factor analysis were used for interpretation of data.

The results and conclusions of the study can be summarised as follows.

1) 1) ΣREE abundance is more for the coastal stations compared to offshore ones indicating REE input through river run-off and terrigenous influence. The study of REEs in the sediments of Kerala coast also supports this observation. Ce is the most abundant element among the REEs and the inconsistent relation between dissolved

oxygen and Ce anomaly is observed for some of the transects, may be due to the influence of high terrigenous sedimentation and along shore currents over the coastal regions.

2) Thorium enrichment and high Eu anomaly for the Kerala coast (especially for the transects Quilon and Cochin) may be due to the presence of heavy minerals in these sediments. U showed enriched concentration in the sediments impinged by oxygen minimum zone.

3) The concentration of Al is observed to be higher in the coastal samples compared to offshore ones and this indicates the terrigenous source of Al in the sediments. The concentration of Fe and Mn are also found to be higher for the coastal stations than the deeper ones. The highest value is observed for the coastal station off Goa, which may be due to the impact from the onshore mining sites of Goa.

4) $CaCO_3$ and sand (%) showed higher values for 100m stations which is correlated with the relict carbonate band present in the western continental shelf. Organic carbon (%) is found to be higher for the 200m samples which is overlying by suboxic waters, but the present study indicates that the preservation of organic matter depend not only on D.O. of bottom water, but also on other factors such as productivity of water column and sedimentation rates. Clay rich sediments were found to have higher trace metal contents compared to silty and sandy fractions of sediments probably because of stronger adsorption capacity of clay sized fraction for metals.

5) UCC normalized patterns showed U enrichment in the sediments under OMZ. Cr also showed enriched pattern, which indicates coastal western margin could be a sink for Cr and its enrichment can be due to intense chemical weathering.

6) In contrast to the water column characteristics, which have shown distinct seasonal variation, REEs and other trace elements including the redox-sensitive elements in the coastal sediments have not significantly responded to the changing bottom water chemistry and seasonal variations, indicating slower response time of sediments vis-à-vis the overlying waters.

7) REE studies, discrimination plots and trace metal ratios of Andaman Backarc sediments suggest hydrothermal source along with some detrital input for these sediments. Shale like flat REE patterns and (La/Yb)n ratios on one hand suggest a significant detrital component in the sediment, while the positive Eu anomaly, Mn and Mo enrichment and negative Ce anomalies in few samples and U/Fe ratios close to plume ratios collectively indicate an unquantifiable metalliferous/ hydrothermal component in these sediments. Detrital component in the Andaman sediments could possibly be due to the delivery from Himalayan River such as Irrawadi or Sawleen. The accumulation studies of elements indicate a predominant hydrothermal source for Mn and a mixed detrital-hydrothermal signature for REEs.

The major objectives of the study were 1) the assessment of distribution of REEs in the western continental margin 2) seasonal variation of REEs in the coastal environment and 3) behaviour and depositional characters of REEs in a different geochemical environment such as Andaman Backarc basin. The present study could generate sufficient data to analyse the distributional character of the REEs in the EEZ of west coast of India, but to establish geochemical character and reactivity of these elements and to use these as provenance indicator further detailed and comprehensive investigations are essential. This is not attempted here, as it is beyond the scope and dimensions of this work.

List of Abbreviations

REE	-	Rare Earth Elements
LREE	-	Light REE
HREE	-	Heavy REE
MREE	-	Middle REE
OMZ	-	Oxygen Minimum Zone
EEZ	-	Exclusive Economic Zone
SW	-	Southwest
NW	-	Northwest
NE	-	Northeast
CAB	-	Central Andaman Basin
PAAS	-	Post Archean Australian Shale
UCC	-	Upper Crustal Composition
PSU	-	Practical Salinity Unit
ppm	-	Parts per million
HFSE	-	High Field Strength Elements
LILE	-	Large Ion Lithophile Elements
DO	-	Dissolved Oxygen
O.C	-	Organic Carbon
EF	-	Enrichment Factor
ΣREE	-	Sum REEs /total REEs
El_{ex}	-	Elemental concentration in excess
MAR	-	Mass Accumulation Rate

Appendix

St.No	Stations	Depth(m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	Off Cape Comorin	30	20.92	46.00	5.03	20.70	3.70	0.52	2.80	0.42	2.11	0.44	1.18	0.17	0.96	0.15	9.47	1.14
2		100	7.57	11.76	1.61	6.50	1.39	0.35	1.27	0.24	1.46	0.35	0.88	0.14	0.75	0.12	1.61	2.84
3		200	8.92	13.78	1.87	7.54	1.48	0.35	1.28	0.25	1.48	0.36	0.91	0.14	0.77	0.13	2.27	3.77
4	Off Trivandrum	30	5.28	10.39	1.08	4.33	0.88	0.18	0.67	0.11	0.66	0.15	0.44	0.07	0.42	0.07	2.61	0.48
5		100	4.65	7.63	0.99	3.86	0.83	0.22	0.76	0.14	0.86	0.19	0.51	0.08	0.45	0.07	0.98	1.81
6	Off Quillon	30	44.41	85.38	8.36	32.88	6.02	1.39	4.67	0.72	4.02	0.81	2.33	0.32	1.95	0.31	13.60	2.32
7		50	13.67	25.67	2.52	9.88	1.71	0.33	1.25	0.18	0.96	0.20	0.55	0.08	0.46	0.08	6.29	0.83
8		100	24.20	42.64	4.32	16.12	2.84	0.48	2.26	0.34	1.75	0.34	0.98	0.13	0.74	0.10	8.57	2.47
9	Off Cochin	30	20.97	35.38	3.32	12.12	1.94	0.59	1.46	0.20	1.10	0.23	0.70	0.09	0.56	0.09	8.65	0.59
10		100	50.47	85.19	7.70	28.07	4.26	0.79	3.44	0.47	2.43	0.47	1.33	0.18	1.04	0.17	14.74	2.22
11		200	40.18	75.31	7.29	28.93	4.95	0.95	3.80	0.56	2.80	0.51	1.49	0.20	1.17	0.18	15.54	2.23
12	Off Calicut	30	28.52	61.07	5.80	24.48	4.84	1.27	4.14	0.73	4.26	0.86	2.52	0.36	2.22	0.31	7.83	2.61
13		100	12.44	25.56	2.72	11.29	2.38	0.64	2.04	0.35	1.96	0.40	1.00	0.14	0.82	0.13	2.40	1.08
14	Off Cannanore	30	29.64	66.32	6.09	25.76	5.27	1.34	4.39	0.77	4.47	0.91	2.68	0.37	2.30	0.34	8.69	2.68
15		200	13.32	28.15	3.14	13.23	2.73	0.68	2.26	0.41	2.34	0.48	1.23	0.19	1.06	0.17	3.68	1.93
16	Off Mangalore	30	28.38	62.16	5.81	23.78	5.06	1.27	4.18	0.73	4.23	0.87	2.54	0.36	2.21	0.31	8.94	2.63
17		200	31.45	58.85	5.99	23.43	4.06	0.81	3.52	0.54	2.96	0.57	1.51	0.22	1.27	0.19	6.08	1.45
18	Off Marmagao	30	26.60	60.46	5.84	24.05	4.95	1.34	4.22	0.78	4.67	0.97	2.57	0.40	2.32	0.36	7.32	2.50
19		200	10.26	14.91	2.06	8.96	1.93	0.52	1.88	0.36	2.28	0.55	1.50	0.24	1.31	0.22	1.51	5.00
20	Off Ratnagiri	30	19.08	43.77	4.61	20.51	4.71	1.40	4.01	0.78	4.74	1.01	2.55	0.41	2.24	0.36	5.03	1.92
21		200	7.91	12.32	1.56	6.57	1.39	0.37	1.29	0.24	1.52	0.34	0.95	0.14	0.85	0.13	1.24	4.55
22	Off Mumbai	30	20.47	44.87	4.83	21.26	4.87	1.39	4.18	0.82	4.81	1.02	2.57	0.39	2.30	0.35	5.27	1.52
23		100	8.02	14.67	1.68	7.02	1.44	0.40	1.31	0.24	1.51	0.32	0.85	0.13	0.77	0.11	1.48	3.34
24	Off Veraval	30	25.38	53.23	5.67	24.88	5.37	1.44	4.37	0.84	4.91	1.00	2.62	0.41	2.19	0.34	6.92	1.22
25		100	3.17	4.39	0.65	2.78	0.51	0.16	0.56	0.10	0.64	0.16	0.42	0.07	0.34	0.06	0.34	3.69
26	Off Porbandar	30	24.09	49.62	5.21	21.65	4.58	1.19	3.73	0.68	3.93	0.82	2.14	0.35	1.93	0.30	7.75	1.40
27		200	19.47	39.94	4.27	17.93	3.84	0.99	3.21	0.59	3.47	0.72	1.81	0.29	1.64	0.25	5.58	3.67
28	Off Dwaraka	30	9.00	17.64	1.91	7.81	1.60	0.36	1.34	0.24	1.45	0.31	0.81	0.13	0.74	0.11	2.69	2.35
29		200	18.19	36.78	4.05	17.04	3.59	0.94	2.94	0.54	3.15	0.74	1.83	0.27	1.55	0.23	5.45	2.44

Table A-1 Concentration of Rare earth elements, Th and U (ppm) in the sediments of west coast of India

St.No	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Mn %	Fe %	Al %	O.C%	Carb%
1	2.44	37.1	67.7	3.1	23.2	3.7	45.1	1.68	5.05	1503	14.05	9.4	4.68	0.17	60	0.27	0.11	7.98	0.033	2.98	1.18	1.26	76.30
2	1.16	8.1	37.6	1.5	21.6	5.3	14.9	0.87	2.82	1957	12.97	9.0	0.71	0.16	37	0.26	0.02	6.31	0.005	1.30	0.76	1.01	86.20
3	2.44	10.2	51.4	2.4	36.2	10.4	23.9	1.99	7.97	1246	12.73	10.5	1.05	0.38	48	0.31	0.05	3.00	0.006	1.37	1.65	1.58	80.56
4	6.32	35.1	52.4	3.0	23.9	14.7	46.4	1.93	5.12	105	4.22	35.4	4.52	0.11	65	1.00	0.17	18.14	0.017	1.56	1.20	0.57	2.10
5	0.93	11.7	27.2	1.2	24.8	2.1	10.9	0.66	1.44	2056	7.53	4.2	0.47	0.15	21	0.12	0.01	4.91	0.004	1.27	0.65	0.87	93.70
6	12.07	73.5	164.8	9.1	32.4	22.1	98.5	12.66	47.67	420	25.44	108.7	9.55	1.66	551	2.90	0.41	30.07	0.036	6.35	12.06	1.65	6.58
7	6.34	37.6	71.8	3.3	16.1	13.0	50.3	2.98	11.32	223	5.81	36.6	6.40	0.23	204	0.93	0.20	15.42	0.02	1.85	2.35	0.69	6.79
8	5.40	30.8	85.7	2.9	18.4	12.2	40.6	2.89	11.14	1893	11.97	27.5	3.36	0.37	147	0.69	0.10	16.69	0.012	2.15	2.39	1.58	74.19
9	6.48	38.2	69.6	4.1	9.8	13.4	54.9	4.66	27.06	279	6.87	56.9	6.12	0.19	553	1.40	0.41	18.13	0.032	2.06	4.40	0.78	3.30
10	6.95	38.1	116.4	5.1	16.7	16.7	65.4	5.60	21.69	1340	15.71	60.1	5.05	0.66	300	1.44	0.32	12.81	0.024	3.30	4.68	2.00	60.66
11	8.59	51.9	146.9	7.4	40.4	18.3	74.9	6.66	23.65	970	15.80	72.7	4.66	0.69	326	2.05	0.38	13.65	0.025	9.77	5.61	1.49	51.80
12	16.73	101.2	246.7	12.5	79.3	38.2	103.6	15.72	56.21	209	26.00	81.8	8.06	3.42	177	2.29	0.78	22.70	0.032	7.96	15.24	3.21	3.13
13	3.65	19.8	47.2	5.3	23.7	7.3	45.8	3.31	10.30	539	11.51	34.8	2.90	0.57	91	0.88	0.11	9.44	0.037	3.00	3.15	1.82	29.20
14	18.21	110.3	281.2	13.2	89.9	43.5	104.6	17.58	56.48	187	27.38	92.1	8.78	3.55	163	2.58	0.76	25.85	0.033	8.63	16.91	3.89	0.48
15	5.67	57.3	75.6	8.2	47.3	15.5	50.3	5.03	18.56	1192	13.93	39.1	2.68	1.26	64	1.07	0.14	8.45	0.03	7.15	4.42	2.38	63.24
16	17.91	108.0	256.3	14.6	83.1	43.3	102.1	17.55	63.44	201	25.51	94.5	8.84	3.97	174	2.66	0.76	22.78	0.043	8.47	16.58	2.89	5.44
17	4.01	25.3	58.3	4.9	28.2	11.2	49.8	3.53	15.74	846	17.19	102.6	2.70	0.77	82	2.83	0.11	3.84	0.043	2.77	3.12	2.66	44.73
18	20.13	130.6	167.0	22.2	95.3	56.7	113.7	16.74	62.28	170	28.24	122.3	8.55	4.20	161	3.17	0.49	13.48	0.132	10.30	16.18	3.06	2.13
19	3.41	53.8	112.7	4.3	42.8	18.4	31.5	2.49	8.91	1842	22.95	14.8	1.43	0.64	47	0.41	0.06	6.04	0.012	4.46	2.26	1.69	72.96
20	25.80	175.7	134.7	27.7	93.9	98.9	147.6	18.04	49.46	203	28.47	152.5	8.62	3.28	117	3.91	0.55	9.14	0.08	10.84	16.33	1.88	6.83
21	3.67	25.5	36.7	4.2	37.9	19.1	30.7	2.62	11.65	2660	14.87	22.2	1.71	0.84	52	0.58	0.08	6.48	0.014	1.75	2.38	3.61	69.69
22	26.55	154.6	111.0	30.6	85.6	90.8	142.9	17.83	59.35	356	29.21	157.5	8.58	3.72	122	3.97	0.53	12.66	0.101	9.88	15.79	1.55	5.66
23	5.11	26.3	45.6	6.2	34.1	16.7	26.3	3.49	16.38	4803	12.09	27.1	1.92	1.10	54	0.68	0.07	5.45	0.022	2.93	3.16	1.76	74.64
24	21.44	166.7	92.3	30.9	66.2	80.8	146.7	16.72	66.17	207	28.91	150.9	10.24	3.76	188	3.67	0.59	8.72	0.131	8.80	14.60	0.28	12.28
25	0.77	10.3	27.7	2.2	16.5	2.5	5.3	0.50	1.81	7705	7.32	3.8	0.48	0.18	25	0.09	0.01	2.99	0.01	1.25	0.46	0.53	93.07
26	19.72	134.4	100.2	23.8	71.1	55.4	133.9	15.47	77.41	233	24.28	113.1	9.46	5.11	206	2.89	0.53	9.53	0.092	8.18	14.54	0.14	12.42
27	16.87	119.2	82.4	21.4	69.0	60.1	111.3	13.14	61.95	626	21.38	108.6	7.78	3.94	151	2.67	0.46	10.79	0.074	7.29	11.48	1.62	20.78
28	3.62	41.4	28.1	6.9	22.9	8.2	22.6	3.49	24.43	1743	10.79	19.9	2.26	1.76	84	0.47	0.07	8.06	0.097	3.58	3.27	0.34	75.04
29	14.18	113.0	93.1	18.9	66.4	51.3	97.2	11.89	63.70	644	20.23	87.5	6.97	4.04	190	2.30	0.33	9.06	0.072	6.42	10.30	2.02	29.02

Table A-2 Concentration of trace metals (ppm), major elements (%), $CaCO_3$, O.C (%) in the sediments of west coast of India

St.No	Stations	Depth(m)	La	Ce	Sm	Eu	Yb	Lu	Sc	Cr	Co	Ni	Cu	Zn	Pb	Th	U	Mn	Fe
1	Off Cape Comorin	30	4.66	4.92	5.68	4.12	2.89	2.91	1.30	5.23	1.13	3.59	0.63	4.52	3.40	5.52	3.12	3.30	5.57
2		100	2.61	1.95	3.31	4.28	3.51	3.53	0.96	4.50	0.85	5.16	1.41	2.31	4.15	1.45	12.08	0.77	3.78
3		200	1.41	1.05	1.61	1.97	1.64	1.76	0.92	2.83	0.63	3.98	1.26	1.70	0.91	0.94	7.36	0.43	1.82
4	Off Trivandrum	30	1.16	1.09	1.32	1.37	1.24	1.37	3.30	3.98	1.08	3.64	2.47	4.57	7.59	1.50	1.30	1.67	2.87
5		125	1.89	1.49	2.31	3.12	2.45	2.51	0.90	3.83	0.81	6.99	0.67	2.00	3.81	1.04	9.03	0.73	4.34
6	Off Quillon	30	0.96	0.89	0.90	1.07	0.57	0.59	0.63	1.24	0.33	0.49	0.37	0.96	1.25	0.77	0.62	0.35	1.16
7		50	1.52	1.37	1.31	1.31	0.69	0.79	1.69	2.78	0.62	1.25	1.11	2.52	3.28	1.83	1.14	1.00	1.73
8		100	2.65	2.24	2.14	1.87	1.10	0.99	1.41	3.26	0.52	1.40	1.02	2.00	3.49	2.46	3.34	0.59	1.98
9	Off Cochin	30	1.25	1.01	0.79	1.24	0.45	0.48	0.92	1.44	0.40	0.41	0.61	1.47	2.06	1.35	0.43	0.86	1.03
10		100	2.83	2.29	1.64	1.57	0.79	0.83	0.93	2.27	0.48	0.65	0.72	1.65	1.37	2.16	1.54	0.60	1.55
11		200	1.88	1.69	1.59	1.57	0.74	0.73	0.96	2.38	0.58	1.31	0.65	1.57	1.22	1.90	1.28	0.52	3.83
12	Off Calicut	30	0.49	0.50	0.57	0.77	0.52	0.46	0.69	1.47	0.36	0.95	0.50	0.80	0.75	0.35	0.55	0.25	1.15
13		100	1.03	1.02	1.36	1.88	0.93	0.92	0.72	1.36	0.74	1.37	0.46	1.71	1.50	0.52	1.10	1.38	2.10
14	Off Cannanore	30	0.46	0.49	0.56	0.74	0.48	0.47	0.67	1.51	0.34	0.97	0.51	0.73	0.77	0.35	0.51	0.23	1.12
15		200	0.79	0.80	1.11	1.44	0.85	0.89	0.80	1.56	0.81	1.95	0.70	1.34	0.96	0.57	1.41	0.80	3.57
16	Off Mangalore	30	0.45	0.47	0.55	0.71	0.47	0.44	0.68	1.41	0.38	0.91	0.52	0.73	0.69	0.37	0.51	0.31	1.13
17		200	2.64	2.37	2.34	2.41	1.45	1.41	0.80	1.70	0.69	1.64	0.72	1.88	0.62	1.34	1.50	1.62	1.96
18	Off Marmagao	30	0.43	0.47	0.55	0.77	0.51	0.51	0.78	0.94	0.60	1.07	0.70	0.83	0.42	0.31	0.50	0.96	1.40
19		200	1.19	0.83	1.55	2.15	2.06	2.20	0.94	4.54	0.83	3.45	1.64	1.64	1.34	0.46	7.16	0.63	4.36
20	Off Ratnagiri	30	0.31	0.34	0.52	0.80	0.49	0.51	0.99	0.75	0.74	1.05	1.21	1.06	0.28	0.21	0.38	0.58	1.46
21		200	0.87	0.65	1.05	1.44	1.26	1.28	0.97	1.41	0.78	2.90	1.61	1.52	1.36	0.36	6.18	0.69	1.62
22	Off Mumbai	30	0.34	0.36	0.56	0.81	0.52	0.51	1.05	0.64	0.84	0.99	1.15	1.07	0.40	0.23	0.31	0.75	1.38
23		100	0.66	0.58	0.82	1.17	0.86	0.78	1.01	1.31	0.85	1.96	1.06	0.98	0.86	0.32	3.41	0.82	2.04
24	Off Veraval	30	0.46	0.46	0.66	0.92	0.53	0.54	0.92	0.58	0.92	0.82	1.11	1.18	0.30	0.32	0.27	1.06	1.33
25		90	1.80	1.19	2.00	3.11	2.64	3.00	1.04	5.46	2.03	6.48	1.10	1.36	3.24	0.50	25.76	2.55	5.94
26	Off Porbandar	30	0.43	0.43	0.57	0.76	0.47	0.47	0.85	0.63	0.71	0.89	0.76	1.08	0.33	0.37	0.31	0.74	1.24
27		200	0.44	0.44	0.60	0.80	0.51	0.49	0.92	0.65	0.81	1.09	1.05	1.14	0.47	0.33	1.03	0.76	1.40
28	Off Dwaraka	30	0.72	0.68	0.88	1.03	0.80	0.74	0.69	0.78	0.92	1.27	0.50	0.81	1.23	0.56	2.32	3.49	2.41
29		200	0.46	0.45	0.63	0.85	0.53	0.53	0.86	0.82	0.80	1.17	1.00	1.11	0.44	0.36	0.76	0.82	1.37

Table A-3 Enrichment factor of elements calculated w.r.to. Al in the sediments of west coast of India

St.No	Stations	Depth(m)	La	Ce	Sm	Eu	Yb	Lu	Sc	Cr	Co	Ni	Cu	Zn	Pb	Th	U	Mn	Al
1	Off Cape Comorin	30	0.84	0.88	1.02	0.74	0.52	0.52	0.23	0.94	0.20	0.65	0.11	0.81	0.61	0.99	0.56	0.59	0.18
2		100	0.69	0.52	0.88	1.13	0.93	0.93	0.25	1.19	0.22	1.37	0.37	0.61	1.10	0.38	3.20	0.21	0.26
3		200	0.77	0.57	0.88	1.08	0.90	0.96	0.51	1.55	0.35	2.18	0.69	0.93	0.50	0.52	4.03	0.23	0.55
4	Off Trivandrum	30	0.40	0.38	0.46	0.48	0.43	0.48	1.15	1.39	0.38	1.27	0.86	1.59	2.65	0.52	0.45	0.58	0.35
5		125	0.43	0.34	0.53	0.72	0.56	0.58	0.21	0.88	0.19	1.61	0.15	0.46	0.88	0.24	2.08	0.17	0.23
6	Off Quillon	30	0.83	0.77	0.78	0.92	0.49	0.51	0.54	1.07	0.28	0.42	0.32	0.83	1.08	0.67	0.54	0.30	0.86
7		50	0.88	0.79	0.76	0.76	0.40	0.45	0.98	1.61	0.36	0.72	0.64	1.46	1.90	1.06	0.66	0.58	0.58
8		100	1.34	1.13	1.08	0.95	0.56	0.50	0.71	1.65	0.26	0.71	0.52	1.01	1.77	1.24	1.69	0.30	0.51
9	Off Cochin	30	1.21	0.98	0.77	1.20	0.44	0.47	0.89	1.39	0.39	0.39	0.59	1.42	2.00	1.30	0.42	0.83	0.97
10		100	1.82	1.47	1.06	1.01	0.51	0.53	0.60	1.46	0.31	0.42	0.46	1.06	0.88	1.39	0.99	0.39	0.64
11		200	0.49	0.44	0.42	0.41	0.19	0.19	0.25	0.62	0.15	0.34	0.17	0.41	0.32	0.50	0.33	0.14	0.26
12	Off Calicut	30	0.43	0.44	0.50	0.67	0.45	0.40	0.60	1.28	0.31	0.82	0.44	0.70	0.65	0.31	0.48	0.22	0.87
13		100	0.49	0.49	0.65	0.89	0.44	0.44	0.35	0.65	0.35	0.65	0.22	0.82	0.71	0.25	0.53	0.66	0.48
14	Off Cannanore	30	0.41	0.44	0.50	0.66	0.43	0.42	0.60	1.35	0.30	0.86	0.46	0.65	0.68	0.31	0.46	0.20	0.89
15		200	0.22	0.22	0.31	0.40	0.24	0.25	0.23	0.44	0.23	0.55	0.20	0.38	0.27	0.16	0.39	0.22	0.28
16	Off Mangalore	30	0.40	0.42	0.49	0.63	0.42	0.39	0.60	1.25	0.34	0.81	0.46	0.64	0.61	0.33	0.45	0.27	0.89
17		200	1.35	1.21	1.20	1.23	0.74	0.72	0.41	0.87	0.35	0.84	0.37	0.96	0.31	0.68	0.77	0.83	0.51
18	Off Marmagao	30	0.31	0.34	0.39	0.55	0.36	0.36	0.56	0.67	0.43	0.76	0.50	0.59	0.30	0.22	0.36	0.69	0.71
19		200	0.27	0.19	0.35	0.49	0.47	0.51	0.22	1.04	0.19	0.79	0.38	0.38	0.31	0.11	1.64	0.14	0.23
20	Off Ratnagiri	30	0.21	0.23	0.36	0.54	0.33	0.35	0.68	0.51	0.51	0.72	0.83	0.73	0.19	0.14	0.26	0.39	0.68
21		200	0.54	0.40	0.65	0.89	0.78	0.79	0.60	0.87	0.48	1.79	0.99	0.94	0.84	0.22	3.81	0.43	0.62
22	Off Mumbai	30	0.25	0.26	0.40	0.59	0.38	0.37	0.76	0.46	0.61	0.72	0.84	0.77	0.29	0.17	0.23	0.55	0.73
23		100	0.33	0.29	0.40	0.58	0.42	0.38	0.50	0.64	0.42	0.96	0.52	0.48	0.42	0.16	1.67	0.40	0.49
24	Off Veraval	30	0.34	0.35	0.50	0.69	0.40	0.41	0.69	0.43	0.69	0.62	0.83	0.89	0.23	0.24	0.20	0.80	0.75
25		90	0.30	0.20	0.34	0.52	0.45	0.51	0.18	0.92	0.34	1.09	0.19	0.23	0.55	0.08	4.34	0.43	0.17
26	Off Porbandar	30	0.35	0.35	0.46	0.61	0.38	0.38	0.68	0.51	0.57	0.72	0.62	0.88	0.26	0.30	0.25	0.60	0.81
27		200	0.32	0.31	0.43	0.57	0.36	0.35	0.66	0.47	0.58	0.78	0.75	0.82	0.34	0.24	0.74	0.54	0.71
28	Off Dwaraka	30	0.30	0.28	0.37	0.43	0.33	0.31	0.29	0.32	0.38	0.53	0.21	0.34	0.51	0.23	0.96	1.45	0.42
29		200	0.34	0.33	0.46	0.62	0.39	0.38	0.63	0.60	0.58	0.85	0.73	0.81	0.32	0.26	0.56	0.60	0.73

Table A-4 Enrichment factor of elements calculated w.r.to. Fe in the sediments of west coast of India

Elements	Alleeppey 5m		Alleppey 10m		Alleppey 40m		Cochin 5m		Cochin 40m		Ponnani 5m		Ponnani 10m	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
La	42.1	38.5	35.4	37.9	28.5	29.5	30.3	34.9	7.92	15.2	37.1	31.8	28.2	19
Ce	81.7	79	67	75.3	52.9	57.1	62.3	68.2	14.1	27.8	77.1	70.7	58.4	44.6
Pr	9.54	8.66	7.9	8.39	5.84	6.25	6.87	7.79	1.61	3	8.58	7.41	6.42	4.62
Nd	36.6	33.90	30.4	32.5	21.5	23	27.4	30	6.09	11.31	34.5	31	25.2	19.3
Sm	6.21	5.95	4.98	5.51	3.51	3.86	4.97	5.2	1.05	1.83	6.31	5.47	4.58	3.41
Eu	1.49	1.46	1.37	1.36	0.7	0.82	1.18	1.36	0.3	0.58	1.48	1.34	1.12	0.8
Gd	4.65	5.63	3.99	4.92	2.44	3.24	3.6	4.88	0.844	1.77	4.25	4.99	3.22	3.36
Tb	0.661	0.777	0.532	0.665	0.315	0.436	0.488	0.628	0.101	0.221	0.637	0.684	0.482	0.46
Dy	3.91	4.51	3.02	3.83	1.81	2.39	2.98	3.49	0.59	1.23	3.65	4.03	2.84	2.73
Ho	0.81	0.937	0.634	0.786	0.37	0.497	0.588	0.714	0.135	0.258	0.747	0.852	0.59	0.569
Er	2.11	2.56	1.73	2.11	0.98	1.3	1.65	1.93	0.34	0.69	2.08	2.33	1.6	1.6
Tm	0.298	0.353	0.213	0.274	0.131	0.188	0.217	0.268	0.04	0.086	0.276	0.319	0.211	0.215
Yb	1.69	1.96	1.37	1.67	0.83	1.02	1.33	1.5	0.3	0.5	1.97	1.92	1.39	1.35
Lu	0.276	0.324	0.203	0.286	0.125	0.174	0.211	0.251	0.05	0.088	0.274	0.332	0.217	0.221

Elements	Ponnani 40m		Calicut 5m		Calicut 10m		Calicut 40m		Cannanore 5m		Cannanore 10m		Cannanore 40m	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
La	28.2	25.3	18	19	30.2	25.4	22.7	21.4	29.6	22.6	36.1	32.1	14.5	12.2
Ce	55.6	49.6	36.6	44.6	65.3	56.5	44.5	42.6	63.4	48.6	76.3	70.4	29.4	26.2
Pr	4.62	5.72	4.34	4.62	7.15	6.01	5.11	4.89	6.69	5.24	8.19	7.44	3.43	3.01
Nd	27	23	17.5	19.3	28.3	25.1	21.4	19.3	27.1	20.1	32.3	28.7	14.1	12.3
Sm	4.81	3.91	3.31	3.41	5.59	4.46	3.83	3.51	5.13	3.96	6.1	5.49	2.6	2.33
Eu	1.21	0.95	0.858	0.8	1.35	1.18	0.887	0.88	1.25	0.97	1.3	1.35	0.58	0.5
Gd	4	4.03	2.61	3.36	4.25	4.49	3.46	3.23	4.7	3.81	5.52	5.45	2.47	2.02
Tb	0.506	0.512	0.382	0.46	0.612	0.663	0.454	0.476	0.677	0.537	0.752	0.76	0.374	0.294
Dy	3.25	2.91	2.4	2.73	3.65	4	2.6	2.76	3.95	3.31	4.33	4.71	1.9	1.72
Ho	0.645	0.592	0.494	0.569	0.768	0.813	0.537	0.54	0.816	0.662	0.885	0.973	0.4	0.332
Er	1.74	1.66	1.33	1.6	2.15	2.26	1.42	1.48	2.3	1.81	2.4	2.61	1.05	0.83
Tm	0.229	0.21	0.185	0.215	0.289	0.317	0.197	0.202	0.298	0.243	0.337	0.388	0.148	0.11
Yb	1.43	1.14	1.27	1.35	1.95	1.83	1.08	1.1	1.97	1.55	2	2.18	0.833	0.55
Lu	0.188	0.197	0.207	0.221	0.287	0.292	0.195	0.198	0.301	0.234	0.317	0.352	0.125	0.1

Elements	Kasargod 5m		Kasargod 10m		Mangalore 5m		Mangalore 10m		Mangalore 40m	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
La	30.1	32.9	28.4	31.3	38.1	32.7	15.3	29.6	20.3	23.3
Ce	65.8	67.2	62.1	67	79.4	74	57	64.1	43.1	48.6
Pr	6.82	7.25	6.57	6.85	8.17	7.32	5.84	6.62	4.86	5.31
Nd	27.7	28	25.7	26.3	32.7	27.4	22.9	25.8	19.1	21.8
Sm	5.4	5.21	4.9	4.99	6.08	5.22	4.42	4.95	3.75	4.31
Eu	1.2	1.1	1.16	1.21	1.34	1.29	1.11	1.14	0.944	0.99
Gd	5.11	4.98	4.19	5.22	5.02	5.1	3.77	5.06	3.19	4
Tb	0.671	0.703	0.584	0.718	0.644	0.746	0.575	0.731	0.456	0.595
Dy	4.06	4.31	3.39	4.39	3.43	4.54	3	4.31	2.66	3.56
Ho	0.855	0.861	0.729	0.888	0.797	0.921	0.738	0.888	0.533	0.715
Er	2.39	2.31	2.01	2.49	2.22	2.46	1.98	2.44	1.56	1.99
Tm	0.332	0.322	0.293	0.365	0.354	0.33	0.279	0.365	0.225	0.262
Yb	2.08	1.92	1.69	1.97	1.88	2.02	1.43	2.06	1.29	1.58
Lu	0.343	0.355	0.29	0.328	0.369	0.326	0.271	0.355	0.214	0.255

Table A-5 Concentration of REEs (ppm) in the sediments of Kerala coast during pre-monsoon and post-monsoon

	Alleeppey 5m		Alleppey 10m		Alleppey 40m		Cochin 5m		Cochin 40m		Ponnani 5m		Ponnani 10m	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
Y	20.4	23.1	16.6	20.4	9.59	12.9	15.6	18.4	3.45	6.65	18.5	22.1	14.4	16.8
V	76.7	91.00	64.4	77.2	42.8	55.9	97.3	84.7	20.6	19.7	141	124	102	87.8
Cr	160	198	127	163	78.9	110	202	166	40.3	45.8	277	242	201	199
Co	11.3	11.9	10.4	11.9	4.59	7.41	14.5	13.8	4.07	4.39	19.7	16.6	14.9	14.1
Ni	59.6	70.8	42.9	58.4	23.2	37.4	81	62.7	12.3	16.6	112	102	79.1	69.9
Cu	20.4	28	14	23.6	8.1	15.9	31.5	29.2	5.6	6.33	54.5	47.3	35	29
Zn	68.8	71	53.8	86	39	70.2	97.7	157	15.1	52.3	119	97.8	86	85.4
Ga	23.9	23.4	30.4	26.2	13.9	16.7	25.1	30.4	12.9	15.2	33.6	25.8	24.5	19.5
Rb	112	76.7	100	71.6	57.1	45.7	113	78.7	51.5	32.8	127	63.5	100	53.6
Sr	338	298	480	402	263	322	231	369	528	783	263	216	221	483
Zr	125	156	151	155	231	182	153	116	88	67	219	132	162	112
Nb	10.2	11.7	9.43	10.9	13.5	13.6	11.2	10.1	3.79	4.19	14.6	11.2	10.6	8.38
Cs	2.37	2.84	1.37	2.2	0.97	1.46	3.09	2.47	0.481	0.4	4.12	3.65	2.88	2.51
Ba	655	573	1220	875	552	599	509	1051	680	920	550	340	422	403
Ta	0.561	0.706	0.349	0.618	0.589	0.731	0.48	0.542	0.09	0.185	0.92	0.801	0.641	0.529
Pb	20.9	21.6	17.9	39	10.9	15.1	21	23.3	8.1	12.5	24.3	20.5	17.1	16.2
Th	9.21	10.5	6.69	9.97	9.97	9.42	6.93	8.93	1.68	4.69	8.68	9.29	6.4	6.09
U	2.72	3.28	1.84	2.84	2.54	3.21	2.53	2.38	0.86	1.06	3	2.93	2.11	2.58
Mn	238.9	190.0	316.7	223.5	158.0	157.4	432.7	259.0	94.4	95.4	288.5	226.2	332.5	270.3
Fe (%)	5.56	5.50	4.27	5.45	2.71	3.13	7.90	5.09	1.73	1.39	5.83	5.39	6.21	5.26

Elements	Ponnani 40m		Calicut 5m		Calicut 10m		Calicut 40m		Cannanore 5m		Cannanore 10m		Cannanore 40m	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
Y	17.4	16.6	11.9	14.5	19.5	20.3	13.2	14.1	20.3	16.2	21.8	22.9	10.2	8.47
V	48.3	52.2	64.4	81.8	88.6	106	60.4	63.6	119	96.6	117	130	36.4	40.3
Cr	144	161	137	164	204	237	145	146	267	225	260	296	107	113
Co	11.5	11.8	9.28	11.6	12.5	14.1	15.2	12.2	15.2	13.4	14.6	16.2	7.44	10.5
Ni	35.7	40	34.8	48.9	71.5	94	41.8	43.1	98	70	92	103	30.5	35.8
Cu	9.9	12.9	13	18.6	30.1	40	13.9	23	44.3	33	40	50	11.9	12.4
Zn	50.8	60.8	66.5	85	81.2	100	82.2	77.9	88.6	77.3	172	97	58.6	57.5
Ga	15.2	14.7	14.8	15.5	20.4	22.5	15.2	15.2	23.9	19.7	23.1	25.8	7.65	7.44
Rb	52.4	34.1	52.1	35.8	71.5	43.3	40.3	40.4	69.6	48	66.6	69	27.1	27.8
Sr	685	713	274	291	235	206	428	436	160	243	169	186	383	621
Zr	98	120	255	270	251	177	16	175	144	205	274	157	101	66
Nb	5.57	5.59	8.08	9.62	10.6	11.1	7.57	8.01	11.7	9.79	12.9	12.5	5.03	5.34
Cs	1.12	1.14	0.822	1.27	2.57	2.83	1.36	1.56	3.19	1.93	3.06	3.66	1.18	1.26
Ba	560	581	330	301	296	259	428	382	255	309	263	259	125	119
Ta	0.319	0.327	0.501	0.572	0.695	0.767	0.612	0.484	0.819	0.678	0.842	0.837	0.381	0.303
Pb	11.1	11.1	8.2	9.4	15.4	17.4	10.3	11.2	16.2	11.9	16.1	17.2	6.5	7.2
Th	4.67	6.86	3.77	5.93	7.24	9.15	6.54	5.67	8.77	6.1	10.2	10.3	3.9	2.83
U	1.99	2.66	1.1	1.43	2.3	2.83	2.09	2.33	2.8	1.67	3.02	2.9	1.91	2.35
Mn	543.8	493.8	394.3	422.5	318.6	270.8	492.8	412.5	270.3	349.8	318.0	303.3	347.0	392.0
Fe (%)	6.90	6.37	3.32	3.90	5.53	5.59	6.05	4.66	6.22	4.78	6.32	9.43	4.10	5.32

Elements	Kasargod 5m		Kasargod 10m		Mangalore 5m		Mangalore 10m		Mangalore 40m	
	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon	Pre mon	Post mon
Y	20.4	20.5	20.1	21.7	21.9	21.6	19.2	20.6	17.7	18.2
V	132	130	112	127	145	149	99.5	121	64.3	70.9
Cr	272	304	240	246	327	416	234	252	192	181
Co	14.7	15.1	13.8	15.1	18.1	20.2	13.7	15	11.1	11.9
Ni	94.2	84.4	84	93	91.7	194	85.4	83	70.6	59.7
Cu	45.1	43	39.6	48	48	64	36.9	45	25	27.6
Zn	98.8	96.6	64.3	106	90.8	490	136	99.9	109	78.9
Ga	25.6	23.1	23.6	24.4	30.7	28.2	21.6	24.8	14.7	15.7
Rb	50.4	31.2	65.2	49.6	70.1	76.5	29.8	46.9	57.2	56.4
Sr	178	185	205	186	245	148	188	208	309	343
Zr	367	520	351	231	1136	140	450	375	331	276
Nb	13.1	13.4	11.8	12.1	15.3	12.8	11.3	12.7	8.87	8.59
Cs	2.91	2.18	3.02	3.04	2.19	3.95	2.38	2.8	2.33	2.38
Ba	286	241	282	256	427	265	248	281	232	246
Ta	0.881	0.901	0.867	0.841	1.15	0.914	0.818	0.898	0.636	0.659
Pb	16.3	15.3	15.3	15.6	17.2	18.9	14.6	16.9	10.7	12.1
Th	10.1	11.1	9.16	9.9	12.8	11.4	8.3	10.7	5.79	6.91
U	2.83	2.77	2.77	2.89	3.16	2.84	2.56	2.92	2.76	2.69
Mn	320.5	399.8	301.5	270.3	478.8	268.7	397.4	362.8	352.6	364.9
Fe (%)	6.05	5.90	5.70	5.35	5.96	6.36	5.63	5.34	4.65	4.28

Table A-6 Concentration of trace elements (ppm) in the sediments of Kerala coast during pre monsoon and post monsoon season

SPC 1

Stations	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	0-2 cm	25.19	49.44	5.30	22.13	4.78	1.24	4.02	0.73	4.36	0.92	2.81	0.42	2.57	0.40
2	2-4cm	22.77	36.16	4.88	19.91	4.38	1.10	3.52	0.65	3.93	0.83	2.56	0.37	2.24	0.35
3	4-6cm	25.76	35.83	5.41	21.90	4.74	1.17	3.76	0.69	4.04	0.86	2.63	0.38	2.34	0.36
4	6-8cm	27.92	47.02	5.89	23.96	5.18	1.26	4.11	0.75	4.42	0.91	2.79	0.41	2.49	0.39
5	8-10cm	27.13	55.25	5.72	23.21	5.00	1.22	3.98	0.72	4.22	0.88	2.71	0.39	2.37	0.38
6	10-12cm	26.79	52.20	5.65	23.47	4.84	1.16	3.83	0.69	4.12	0.85	2.57	0.37	2.27	0.35
7	12-14cm	29.91	59.71	6.21	25.45	5.20	1.22	4.10	0.74	4.24	0.87	2.65	0.39	2.41	0.36
8	14-16cm	27.31	51.86	5.81	23.33	4.79	1.16	3.84	0.68	4.00	0.82	2.50	0.36	2.17	0.33
9	16-18cm	30.21	61.37	6.40	26.08	5.32	1.24	4.17	0.74	4.35	0.88	2.73	0.40	2.43	0.37
10	18-20cm	31.10	61.45	6.48	26.25	5.25	1.24	4.22	0.73	4.19	0.84	2.59	0.37	2.24	0.34
11	20-22cm	27.42	54.78	5.91	23.58	4.85	1.10	3.82	0.65	3.80	0.76	2.27	0.34	2.01	0.31
12	22-24cm	34.37	67.23	7.23	29.19	5.69	1.26	4.53	0.76	4.28	0.86	2.61	0.38	2.31	0.35
13	24-26cm	31.20	63.21	6.49	25.95	5.18	1.11	4.02	0.68	3.86	0.78	2.36	0.34	2.09	0.30
14	26-28cm	34.94	71.11	7.19	29.35	5.65	1.18	4.40	0.77	4.17	0.84	2.53	0.37	2.23	0.34

SPC 2

Stations	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	0-2cm	20.80	39.20	4.39	18.31	3.95	0.99	3.18	0.59	3.40	0.72	2.08	0.32	1.86	0.30
2	2-4cm	23.29	49.63	4.98	20.68	4.41	1.12	3.61	0.66	3.78	0.80	2.39	0.34	2.94	0.32
3	4-6cm	26.40	56.22	5.52	23.02	4.83	1.17	3.90	0.69	3.97	0.84	2.55	0.37	2.17	0.33
4	6-8cm	22.80	48.00	4.87	20.17	4.22	1.06	3.38	0.63	3.56	0.74	2.19	0.32	1.98	0.31
5	8-10cm	25.09	53.30	5.38	21.98	4.52	1.10	3.69	0.65	3.76	0.78	2.41	0.34	2.01	0.32
6	10-12cm	23.83	50.12	5.09	20.88	4.28	1.06	3.49	0.63	3.60	0.76	2.22	0.33	1.91	0.29
7	12-14cm	23.21	48.69	4.84	20.03	4.20	1.01	3.35	0.59	3.39	0.70	2.08	0.30	1.79	0.27
8	14-16cm	24.16	50.49	5.05	20.67	4.26	1.06	3.49	0.61	3.56	0.72	2.18	0.31	1.89	0.28
9	16-18cm	22.64	47.94	4.84	19.50	4.04	0.96	3.28	0.56	3.23	0.69	2.04	0.29	1.78	0.27

Table A-7 Concentration of Rare earth elements (ppm) in the sediment sections of cores SPC 1 and SPC 2 of Andaman Backarc basin

SPC 5

S.No	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	0-2	28.41	60.11	6.06	25.86	5.52	1.34	4.23	0.75	4.45	0.98	2.82	0.42	2.58	0.41
2	2-4'	27.47	57.36	5.74	24.63	5.30	1.28	4.21	0.74	4.35	0.91	2.67	0.41	2.51	0.39
3	4-6'	28.24	59.59	6.01	25.28	5.40	1.32	4.26	0.75	4.53	0.96	2.70	0.43	2.55	0.38
4	6-8'	27.53	57.43	5.77	24.59	5.31	1.27	4.30	0.73	4.31	0.93	2.70	0.41	2.51	0.39
5	8-10'	27.55	58.61	5.93	24.41	5.29	1.28	4.11	0.73	4.43	0.94	2.65	0.40	2.55	0.38
6	10-12'	28.98	61.03	6.19	25.96	5.59	1.30	4.32	0.76	4.56	0.95	2.90	0.42	2.58	0.40
7	12-14'	30.27	63.81	6.52	27.59	5.74	1.43	4.58	0.82	4.62	1.00	2.90	0.44	2.70	0.41
8	14-16'	31.84	66.46	6.72	28.22	6.07	1.44	4.73	0.84	4.98	1.00	2.99	0.46	2.81	0.43
9	16-18'	31.92	66.37	6.71	28.01	6.01	1.41	4.62	0.80	4.76	0.99	2.96	0.44	2.73	0.41
10	18-20	31.49	65.86	6.74	27.68	5.94	1.41	4.66	0.85	4.75	1.02	2.89	0.44	2.67	0.39
11	20-22	30.41	63.38	6.43	26.25	5.70	1.29	4.38	0.79	4.44	0.91	2.76	0.41	2.51	0.37
12	22-24	31.97	66.11	6.74	27.80	5.74	1.37	4.55	0.79	4.53	0.92	2.76	0.40	2.49	0.38
13	24-26	31.14	65.44	6.71	27.67	5.75	1.28	4.48	0.77	4.39	0.87	2.57	0.38	2.44	0.35
14	26-28	33.08	69.59	7.02	28.52	6.03	1.32	4.66	0.79	4.70	0.89	2.63	0.40	2.36	0.38
15	28-30	32.33	67.42	6.87	28.08	5.86	1.27	4.44	0.76	4.15	0.83	2.45	0.36	2.12	0.33

Table A-7 Concentration of Rare earth elements (ppm) in the sediment sections of core SPC 5 of Andaman Backarc basin

SPC 1

Stations	Depth	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Th	U	O.C.(%)	Carb%
1	0-2 cm	22.3	163	126	30.5	210	118	199	21.5	110	163	29.2	94.4	7.2	8.9	677	2.51	0.33	44.8	10.7	2.15	0.44	0.5
2	2-4cm	19.2	158	112	28.4	180	106	183	19.4	97	166	26.1	84.6	7.6	8.2	644	2.30	0.24	39.7	8.6	1.43	1.26	1.9
3	4-6cm	17.2	139	117	29.4	164	103	231	19.0	105	163	27.4	81.8	7.8	8.7	597	2.20	0.40	37.3	9.5	1.13	1.45	3.3
4	6-8cm	20.3	144	123	30.7	165	102	171	19.4	108	167	29.7	85.8	8.0	8.9	661	2.31	0.37	37.5	10.9	1.58	1.31	3.2
5	8-10cm	18.4	122	101	31.6	159	101	171	19.3	110	211	28.6	90.8	8.5	8.8	676	2.33	0.47	41.3	11.6	1.96	1.41	4.2
6	10-12cm	17.6	121	106	34.9	156	96	285	19.1	107	194	26.8	87.5	8.3	8.1	660	2.38	0.53	35.9	10.8	1.63	1.28	5.1
7	12-14cm	19.0	140	108	21.6	114	77	407	17.2	114	207	28.2	84.4	7.9	8.9	623	2.29	0.32	36.6	11.9	1.71	1.35	4.8
8	14-16cm	19.1	135	100	16.7	101	73	205	15.7	108	189	26.0	76.5	7.7	8.2	571	1.98	0.41	34.9	11.0	1.55	1.31	5.5
9	16-18cm	18.6	148	110	17.1	113	78	160	17.3	119	227	29.3	85.6	8.6	9.7	607	2.26	0.42	38.7	12.5	1.62	1.39	5.4
10	18-20cm	18.0	159	111	17.2	117	124	173	17.6	124	206	27.4	80.8	8.9	9.6	575	2.24	0.40	28.0	12.8	1.70	1.96	5.4
11	20-22cm	15.9	141	104	16.1	100	65	200	16.5	115	216	23.9	77.0	8.6	9.1	467	2.03	0.37	20.2	12.2	1.51	1.64	6.2
12	22-24cm	19.2	156	116	18.5	113	65	207	19.2	142	220	27.9	85.3	10.2	11.3	523	2.32	0.51	21.3	14.9	2.06	1.26	6.3
13	24-26cm	16.8	123	100	15.8	94	54	224	16.8	124	250	24.9	75.1	8.9	9.7	476	2.08	0.36	18.8	13.1	2.04	1.86	7.7
14	26-28cm	17.6	131	108	17.8	98	49	155	18.1	140	207	26.6	88.5	10.9	10.8	430	2.41	0.64	16.4	14.6	2.71	1.35	5.5

SPC 2

Stations	Depth	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Th	U	O.C.%	Carb %
1	0-2cm	16.4	98	255	27.9	264	94	166	17.6	94	206	23.5	68.7	6.4	7.4	618	1.80	0.38	47.9	8.5	1.20	1.82	3.1
2	2-4cm	17.5	104	264	29.3	259	97	743	17.6	99	263	25.9	74.9	6.8	8.1	667	1.93	0.37	47.3	9.6	1.53	1.79	5.5
3	4-6cm	16.6	97	266	30.8	264	92	218	17.4	106	343	27.3	69.0	6.8	8.2	679	1.86	0.34	46.1	10.3	1.65	1.74	11.2
4	6-8cm	15.9	93	254	23.9	248	77	186	15.3	96	374	24.7	69.2	6.1	7.7	591	1.75	0.25	37.0	9.4	1.35	1.77	11.8
5	8-10cm	16.5	96	257	23.4	252	74	751	15.9	103	409	25.6	65.7	6.7	8.1	590	1.83	0.38	33.8	9.9	1.45	1.40	15.3
6	10-12cm	16.9	99	256	21.8	247	220	163	14.9	99	426	24.1	71.5	6.4	7.7	543	1.86	0.40	29.4	9.6	1.44	1.65	16.0
7	12-14cm	14.3	117	265	22.4	249	69	198	14.5	96	490	22.8	58.6	6.1	7.7	525	1.63	0.23	19.8	9.0	1.69	1.56	18.4
8	14-16cm	16.0	108	250	24.6	256	62	213	15.2	100	494	23.9	70.4	6.2	8.1	548	1.84	0.20	22.6	9.8	2.21	1.66	19.6
9	16-18cm	17.3	85	225	23.5	239	58	150	14.4	97	481	22.6	67.9	6.0	7.7	498	1.77	0.20	19.6	9.3	3.00	1.65	19.0

Table A-9 Concentration of trace elements (ppm) in the sediment sections of cores SPC 1 and SPC 2 of Andaman Backarc basin

SPC 5

S.No	Depth	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Cs	Ba	Hf	Ta	Pb	Th	U	Mo	Al%	Mn%	Fe%	OC%
1	0-2	12.3	122	90	25	148	80	127	15.7	97	232	27.2	85	6.7	8.3	691	2.6	0.37	39	11.6	2.0	10.0	13.1	2.269	5.82	1.61
2	2-4'	12.1	109	85	25	140	76	115	15.1	96	261	27.0	84	6.7	7.7	635	2.4	0.35	28	11.3	1.8	5.8	12.8	1.618	5.78	1.72
3	4-6'	12.6	107	76	26	139	78	122	15.4	98	267	27.7	87	7.0	7.9	641	2.5	0.43	29	11.5	1.8	4.2	13.2	1.352	5.94	1.45
4	6-8'	11.9	102	73	27	145	72	115	14.8	95	270	26.7	85	6.8	7.6	624	2.4	0.42	28	11.3	1.8	4.4	12.6	1.613	5.75	1.47
5	8-10'	11.7	104	74	33	167	73	122	14.9	95	166	26.3	82	6.8	7.7	637	2.3	0.41	31	11.5	1.8	6.4	12.3	2.019	5.73	1.31
6	10-12'	12.1	111	93	33	170	73	126	15.6	101	120	27.7	85	7.1	8.2	658	2.4	0.37	32	12.4	1.8	8.2	13.0	2.003	6.05	1.35
7	12-14'	12.9	117	98	16	107	71	117	15.0	105	213	27.9	86	7.4	8.8	633	2.5	0.41	35	12.7	1.8	1.1	13.8	0.145	6.44	1.61
8	14-16'	12.5	118	96	16	112	75	116	14.9	105	229	27.5	85	7.1	9.9	664	2.7	0.36	49	13.4	1.9	0.8	13.7	0.114	6.76	1.38
9	16-18'	12.4	119	83	16	108	69	128	14.8	106	228	26.9	84	7.4	9.8	653	2.5	0.39	38	13.3	1.9	0.7	13.6	0.104	6.18	1.19
10	18-20	12.9	128	84	18	115	67	138	15.6	109	229	28.1	89	7.7	9.3	629	2.6	0.41	29	13.4	2.0	0.7	14.0	0.116	6.42	1.49
11	20-22	12.0	120	78	16	117	68	119	14.3	105	244	25.8	83	7.3	9.2	586	2.4	0.42	32	13.2	2.2	0.7	12.9	0.101	5.92	1.77
12	22-24	12.4	128	81	16	107	62	130	15.1	112	239	26.4	86	7.9	9.6	566	2.5	0.41	29	14.1	2.6	0.6	13.7	0.101	6.09	1.53
13	24-26	12.2	120	79	16	105	58	118	15.1	113	231	24.7	84	7.9	9.6	540	2.4	0.47	23	14.0	2.8	0.6	13.6	0.099	5.97	1.52
14	26-28	12.1	110	80	16	103	52	120	15.7	121	235	24.8	84	8.6	10.3	513	2.4	0.53	23	15.4	2.9	0.6	13.7	0.098	6.03	1.47
15	28-30	11.4	112	76	15	103	47	113	15.0	117	245	22.8	70	8.0	10.4	486	2.1	0.45	21	14.8	3.0	0.7	13.2	0.100	5.63	1.51

Table A-10 Concentration of elements (ppm) in the sediment sections of core SPC 5 of Andaman Backarc basin